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PLENARY LECTURES

DETECTION CAPABILITIES: SOME HISTORICAL FOOTNOTES & LESSER KNOWN CURRIE RESEARCH

Lloyd A. Currie

National Institute of Standards and Technology, Gaithersburg, MD 20899, USA, (retired), e-mail: lloyd.currie@alum.mit.edu

Keywords: detection capabilities, historical perspective (1939, 1989), international standards, false positive dilemma, exploratory (nuclear) data analysis, bivariate Poisson analysis

Part I: Summary of relevant topics from 1923 to present – including Currie (1968) detection concepts & capabilities; International detection & uncertainty standards; Failure of classical ^{14}C dating & birth of new scientific disciplines; Exploratory nuclear data analysis of ^{85}Kr monitors found coincident with the collapse of the Iron Curtain (1989); Faulty statistics proved responsible for mistaken assertions that Currie's L_C yields excessive false positives; Erroneous assumption that our low-level background is a Poisson Process linked to ~8% spurious anticoincidence events.

Part II: Exact treatment of bivariate Poisson data – solved in the 1930s by Przyborowski & Wilenski, University of Krakow, for detecting extreme trace amounts of a malicious contaminant (dodder) in high purity seed standards; we adapted their treatment to detection capabilities in ultra-low-level nuclear counting. Timing of their work had great historical significance, marking the start of World War II with the invasion of Poland (1939).

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RADIATION CHEMICAL ASPECTS OF THE ORIGINS OF LIFE

Franco Cataldo[1]*, Susana Iglesias-Groth*[2]*, Yaser Hafez*[3]

[1]Università della Tuscia, Viterbo, Italy
[2]Instituto de Astrofisica de Canarias, Tenerife, Spain
[3]National Center for Astronomy, Riyadh, Saudi Arabia

C_{60} was detected for the first time in space in 2010 in the circumstellar medium (in certain protoplanetary nebulae) but also in the interstellar medium (for example in reflection nebulae). Actually C_{60} is the largest molecule known in the space. C_{60} once ejected in the interstellar medium can condense together with water and other ices in dense molecular clouds. Under the action of high energy radiation C_{60} reacts with the free radicals generated from the matrix where it is embedded [1]. If C_{60} is trapped in water ices it is hydroxylated and oxidized by the radiolysis products of water. The oxidation of C_{60} makes this molecule hydrophilic and hence soluble in water, while before hydroxylation C_{60} is completely insoluble in water. The same phenomenon occurs in water/ammonia, in water/methanol and in water/ammonia/ methanol mixtures [1]. Thus, C_{60} which in the solid state displays a considerable radiation resistance [2], when embedded in radiolytic sensitive matrices like those just mentioned, it reacts swiftly, it is solubilized and consequently its carbon content becomes available for abiotic processes of synthesis of other molecules of astrobiological interest [1]. Once elemental carbon is transformed into a soluble form, then the irradiation of interstellar ices leads to the formation of amino acids [3–6] which could be in enantiomeric excess if the irradiation occurred with circularly polarized light [7, 8].

Our interest was focused on the radiolytic stability of amino acids once buried in comets or asteroids. First we have studied the radiolytic stability of all proteinogenic amino acids [9–13]. More recently, a series of non-proteinogenic amino acids, most of them found quite commonly in the meteorites known as carbonaceous chondrites, were subjected to solid state radiolysis in vacuum to a total radiation dose of 3.2 MGy corresponding to 23% of the total dose expected to be taken by organic molecules buried in asteroids and meteorites since the beginning of the solar system 4.6×10^9 years ago [14–16]. It is shown that an important fraction of each amino acid is able to "survive" the massive dose of radiation, while the enantiomeric excess is partially preserved [14–16]. Based on the results obtained, it is concluded that it is not a surprise to find amino acids even in enantiomeric excess in carbonaceous chondrites.

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NEW ADVANCES OF NUCLEAR ENERGY RADIOCHEMISTRY IN CHINA

Zhifang Chai

Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China, e-mail: chaizf@ihep.ac.cn

Nuclear energy radiochemistry should address the following 4 issues:

1. Is nuclear fuel amount enough for hundreds years consumption of nuclear energy?
2. Is nuclear fuel safe and effective in reactor running?
3. How to reprocess spent nuclear fuel in an economic and safe way?
4. How to safely dispose the high level radioactive waste in deep geological deposit?

For all the above questions of nuclear energy chemistry, the key is the actinide chemistry, which constitutes a true challenge due to the complexity of their 5f electron structures.

With advancement of nuclear energy industries, nuclear energy-related radiochemistry, particularly actinide chemistry, in China is at a renaissance period. In this review, the latest achievements in this field will be selectively described with the emphasis on the extraction chemistry of uranium from sea water, new nuclear fuel materials with nano-structures, and new type organic extraction systems with soft and hard coordination abilities for wet spent nuclear fuel reprocessing. In the meantime, dry procedure for actinide separation based on electro-refining will be briefly introduced. Finally, theoretical calculation for actinide chemistry will be dealt with as well.

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EIGHTY YEARS OF NEUTRON ACTIVATION ANALYSIS: 1936–2016

Amares Chatt

Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, 6274 Coburg Road, Room 212,
PO BOX 15000, Halifax, Nova Scotia, B3H 4R2, Canada, e-mail: chatt@dal.ca

Keywords: instrumental, radiochemical, preconcentration, neutron activation

Neutron activation analysis (NAA) is being continually developed as a sophisticated analytical technique since its discovery by Hevesy and Levi in 1936. With the availability of reactors giving neutron flux of about 10^{12} to 10^{14} cm^{-2} s^{-1}, NAA has become an extremely valuable analytical tool especially for simultaneous multielement determinations and for measuring concentrations of some elements down to parts per trillion levels. Isotopic sources and accelerator-produced neutrons can also be used. NAA can be performed in a variety of ways depending primarily on the nature of the background matrix in the sample and the elements of interest as well as their concentrations. The main types of NAA include instrumental NAA (INAA), preconcentration NAA (PNAA), and radiochemical NAA (RNAA), and prompt gamma NAA (PGNAA). Thermal, epithermal, fast and fission spectrum neutrons can be employed in NAA. It can be done using conventional one-step irradiation-decay-counting or in cyclic mode. Sample sizes can be varied between microgram and kilogram quantities. High-resolution, high-efficiency, large-volume, and well-type detectors can be employed for conventional, coincidence and anticoincidence gamma-ray spectrometry. Comparator and k_0 NAA methods can be applied to provide elemental concentrations of high accuracy and precision with excellent sensitivity. The uncertainty of measurement can be kept very low due to certain inherent properties of NAA. It can be applied to measure not only the total concentration of an element but also to various species of elements. Various developments in NAA over the last 80 years will be summarized.

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NOVEL NUCLEAR FUELS FOR A SUSTAINABLE FUEL CYCLE, PRODUCTION AND RECYCLABILITY

C. Ekberg[1], E. de Visser-Týnová[2], T. Retegan[1], M. Sarsfield[3], J. Wallenius[4]

[1]Chalmers University of Technolog, SE-412 96 Göteborg, Sweden
[2]Nuclear Research & consultancy Group (NRG), Research and Innovation, PO Box 25, 1755 ZG Petten, the Netherlands
[3]National Nuclear Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG, United Kingdom
[4]Division of Reactor Physics, KTH, AlbaNova University Centre, SE-106 91, Stockholm, Sweden

Today a considerable focus is put in sustainable energy production. One of the options that could potentially significantly increase the sustainability of nuclear powers is the employment of the so called Gen IV nuclear systems. These systems comprise fast reactors, recycling of parts of the used nuclear fuel as well as a fuel fabrication. Naturally the use of efficient and recyclable fuel is a main prerequisite for the Gen IV systems to work properly. However, there are several challenges in this area relating to the manufacture and recyclability of the selected fuels. Today the main industrial choice if so called mixed oxide fuel, MOX. This fuel made through the powder pressing route is rather well known for traditional uranium and plutonium containing MOX but for proper use in Gen IV systems also other elements such as neptunium and americium need to be incorporated. Then maybe other manufacturing techniques directly from the separated waste mat be more efficient and safer. There are also other types of fuels such as nitrides and carbides that have several advantages and some problems compared to traditional MOX fuel.

In this paper issues are addressed concerning the fabrication and recyclability of these novel fuels. The manufactured fuels are also investigated with respect to chemical and physical characterisation. When a suitable route for uniform production on lab scale was settled, the possibilities for recycling is addressed by investigating possible dissolution routes. Different fuels have different issues, e.g. in the nitride case the isotopically enriched nitrogen (15N) must be recycled and for the carbides the formation of different organic species produced upon dissolution is addressed.

The final aim is together with the separation community to find a convenient route to convert the separated product solutions (U, Pu, MAs) from reprocessing and convert them into materials suitable for fuel production.

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ANALYSIS OF THE GLOBAL RADIOCARBON RECORD FOR EVIDENCE OF NEAR-EARTH SUPERNOVAE

Richard B. Firestone

Department of Nuclear Engineering, University of California, Berkeley, CA 94720, USA; Lawrence Berkeley National Laboratory, MS-88R0192, Berkeley, CA 94730, USA

Keywords: ^{14}C, radiocarbon dating, supernovae, climate change

After development of radiocarbon dating by Libby et al. [1] it became apparent that the abundance of ^{14}C was much higher in the past than in modern times. This led to the development of database of radiocarbon abundance for the past 50,000 years based on measurements of ^{14}C in tree rings and ocean sediments [2]. The radiocarbon record shows that ^{14}C abundance suddenly increased to nearly double present levels ≈45,000 years ago and has been decreasing, albeit with many significant fluctuations, since then. The cause of the higher past radiocarbon abundance was previously ascribed to fluctuations in Earth's magnetic field. This theory is falsified by a sudden rate of ^{14}C increase that is inconsistent with plausible rates, even if the magnetic field to entirely disappear, radiocarbon pool effects which limit how fast the global abundance can change, and the requirement that Earth's magnetic field had disappeared during most of the past 50,000 years.

In this talk I will show that the entire radiocarbon record can be explained by cosmic γ-rays from four supernovae <250 pc from Earth plus a constant background of cosmic rays from more distant SNe. The first event, 45,000 years ago, doubled global radiocarbon while the fourth event 22,000 years ago is likely consistent with the Vela SN that explode 250 pc from Earth. These SNe follow nearly identical cosmic ray production patterns lasting ≈3500 years consisting of a sudden spike in ^{14}C production at the time of the explosion, followed with a hiatus of ≈1500 years, and concluding with ≈2500 of substantial ^{14}C production due to diffusive shock in the SN remnant as predicted by theory [3]. Each event was followed by the decay of excess radiocarbon with the expected 5700 year half-life. The last SN is followed by an 18,000 year decay curve with $t_{1/2} = 5700 \pm 700$, likely the longest half-life measurement ever observed. Small fluctuations in the decay curve can be shown to correlate directly with variations in Earth's magnetic field.

The SN induced fluctuations in the radiocarbon record are also observed to correlate with increases in global temperatures in the order of 3–5 °C. This result is inconsistent with previous predictions that cosmic rays would enhance cloud formation causing decreases in global temperatures [4]. An additional 19 SNe, occurring over the past 300,000 years, have been identified in the ^{10}Be record [5], consistent with the rate expected from historical SNe. For additional information see my paper published in the Astrophysical Journal [6].

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NUCLEAR FORENSICS: A MATURING DISCIPLINE

Stephen LaMont

Nuclear and Radiochemistry, Los Alamos National Laboratory, PO Box 1663 / MS J514, Los Alamos, NM 87545 USA, e-mail: lamont@lanl.gov

Keywords: nuclear forensics, national nuclear forensics libraries

The discipline of nuclear forensics was born out of necessity in the early 1990s due to a marked increase in the number of incidents involving smuggling or illicit trafficking of nuclear material. Despite the relatively low frequency of these events, the potential threat posed by nuclear and radioactive materials outside of regulatory control is now widely recognized. Nuclear forensics has been highlighted in major policy forums including the Nuclear Security Summit and Global Initiative to Combat Nuclear Terrorism as an important capability to investigate nuclear smuggling incidents, as well as serving as a deterrent to poor material security practices. Internationally accepted guidance for nuclear forensics best practices now exists from the International Atomic Energy Agency and the Nuclear Forensics International Technical Working Group. As a result, many countries have now incorporated nuclear forensics capabilities into their nuclear security framework.

The practice of nuclear forensics has also matured significantly since the early 1990s, and forensics examinations are now generally used for three purposes:

- Providing the technical evidence necessary for prosecuting individuals involved with illicit activity
- Determining material production history or associations with fuel cycle operations, provenance, and connections between cases
- Characterizing materials of known provenance to build national nuclear forensics libraries

As countries establish nuclear forensics programs to support these three applications, they must carefully consider the size and scope of those programs, how to leverage existing laboratory infrastructure and expertise, and when to rely on established forensics programs in other countries for assistance. Coordination and cooperation between law enforcement, forensic examiners, and the technical experts at laboratories responsible for characterizing materials is essential. Laboratories may also have to adopt more rigorous chain-of-custody and quality assurance procedures, and even be required to get accredited to a national or international standard to ensure nuclear forensic data is defensible.

Examples of nuclear forensic applications will be presented, as will milestones in the development of nuclear forensics as a unique sub discipline of nuclear science.

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BELIEVABLE STATEMENTS OF UNCERTAINTY

Richard M. Lindstrom

Scientist Emeritus, National Institute of Standards and Technology, Gaithersburg, Maryland, USA

Nearly fifty years ago, two landmark papers appeared that should have cured (but did not) the problem of ambiguous uncertainty statements in published data. Eisenhart's paper in *Science* called for statistically meaningful numbers, and Currie's *Analytical Chemistry* paper revealed the wide range in common definitions of detection limit.

A wise mentor said "Believe your data," but it is wrong to impose your preconceptions on them. The recent histories of cold fusion, variable radioactive decay, and piezonuclear reactions provide cautionary examples. Currie has pointed out that in any measurement campaign the number of degrees of freedom is in fact negative: there are more variables than we know, so scientific insight is essential. We show examples from our laboratory and others to illustrate that uncertainty depends on both science and statistics.

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THE THING THAT BECOMES CLEAR BY A RADIATION AND THE USE OF THE RADIOISOTOPES FOR PLANT PHYSIOLOGY – WITH THE FINDINGS OF FUKUSHIMA NUCLEAR ACCIDENT

Tomoko M. Nakanishi

Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1, Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan,
e-mail: atomoko@mail.ecc.u-tokyo.ac.jp

Keywords: neutron imaging, water imaging and measurement, radioisotope, real-time radioisotope imaging system, plant physiology, Fukushima nuclear accident, agricultural impact of contamination

Plants live on water and inorganic elements. Then, how we can study the dynamics of water and elements in a plant? Only the application of radiation and radioisotopes, which allows non-destructive analysis, revealed the living plant activity.

In the case of water, first, the neutron beam was applied and water distribution and uptake manner was visualized. Neutron beam enabled to image water specific image of the living plants as well as the morphological development of the roots imbedded in soil. Since there was a space in the vicinity of the root surface in soil, the roots were suggested to absorb water vapor, not water solution.

Then, water uptake manner was studied using both ^{18}F labeled and ^{15}O labeled water. In the case of ^{15}O labeled water the trace amount of water taken up by the soybean was measured, though the half-life of ^{15}O is extremely short, 2 min. To our great surprise, the tremendous amount of water was horizontally leaking out from the xylem and suggesting the replacement of the water already existed in the stem. Through simulation, half of the water already existed was replaced within 20 min. This water circulating activity was confirmed also by using ^{3}H labeled water.

Since the elements are moving as ions in water, the real-time radioisotope imaging systems, macroscopic and microscopic one, for the plants were developed, using as many radionuclides as possible. In the case of Mg and K, ^{28}Mg and ^{42}K were prepared and used as tracers for imaging.

Applying radioactive tracers and the imaging system, behavior of ^{137}Cs in Fukushima after the nuclear plant accident was investigated. The fallout was hardly moved from the place where it originally touched and adsorbed firmly on the fine particle of the soil. Therefore plants were hardly absorbing ^{137}Cs from the soil. Behaviors of ^{137}Cs in agricultural fields, mountains, rivers, etc. were investigated.

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GEORGE DE HEVESY (1885–1966) – DISCOVERER OF HAFNIUM, FOUNDER OF RADIO ANALYTICAL CHEMISTRY AND X-RAY FLUORESCENCE ANALYSIS AND FATHER OF NUCLEAR MEDICINE

Siegfried Niese

Wilsdruff, Germany, e-mail: siegfried@niese-mohorn.de

Keywords: George de Hevesy, radioanalytical chemistry, nuclear medicine

George de Hevesy has founded radioanalytical chemistry and nuclear medicine, discovered the element hafnium and first separated stable isotopes. In this paper I present his life and work, which he has done mostly under extremely complicated conditions, caused by the political situation in Europe in the 20th century.

Hevesy was born on August 1, 1885 in Budapest as the fifth child of a wealthy aristocratic Hungarian Jewish family. The most important invention of Hevesy is the indicator method. Some of the discovered radioactive elements seemed to be chemically similar and inseparable. The term "isotope" had not yet been coined. 1913 he defended his habilitation in Budapest where after World War I in 1919 he obtained a chair for physical chemistry. After Admiral Horthy became to power he lost his chair and in1920 he immigrated to Denmark where his friend Niels Bohr had invited him. In 1922 together with Coster Hevesy found the until unknown element number 72 which they named hafnium.

After the discovery of hafnium he received offers from German universities and he take from 1926 to 1934 a chair at the University in Freiburg and became citizen of the German state Baden. There he applied the X-ray spectroscopy for the determination of trace elements in minerals and rocks and developed together with his assistant und students the X-ray fluorescence analysis. He loved Freiburg very much, and after 1931, when his mother has been died, he saw in Freiburg his homeland.

Because of his Jewish ancestors in 1934 after establishment of the Nazi regime he decided to immigrate again to Copenhagen for working in the institute of Bohr. After the discovery of the artificial radioactivity he was soon able to use P-32 and other radioactive isotopes as indicators in life sciences. But before he produced P-32 he studied the reactions of neutrons with r. e. e. Together with Hilde Levi, he developed the neutron activation analysis. In 1943 he must flee to Stockholm where he continued his work with radioactive tracers in biology, physiology and medicine. In 1944 he got the Nobel Prize for Chemistry for the year 1943 for founding the indicator method and its application in biology and medicine.

Going along his way through physical, inorganic, analytical, radio- and biochemistry, geology, physics, physiology and nuclear medicine Hevesy invented such important radio-analytical methods like indicator method, isotope dilution and activation analysis, which encompass the topic of this conference. Most of its time he was working as a guest in laboratories in different countries, he must adapt himself at the interest of the head of the laboratory and the experimental possibilities. When he must flee from a country he must change his colleagues, his equipments, and the topic of his work. It is extremely surprising that he could receive important results under such circumstances even at an advanced age. We admire his important discoveries and developments and are surprised that he could receive such results under complicated circumstances even at an advanced age.

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LOW BACKGROUND GAMMA-SPECTROMETRY: LIMITS AND APPLICATIONS

Pavel P. Povinec

Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University,
84248 Bratislava, Slovakia, e-mail: povinec@fmph.uniba.sk

Keywords: HPGe gamma-spectrometry, underground laboratory, Monte Carlo simulation

New developments in low-level gamma-spectrometry have had great impact on nuclear sciences and applications in environmental and space sciences. Many of the applications were not possible to carry out before either because of a lack of suitable samples (as too large samples were required for radionuclide analyses), or because of limited analytical sensitivities of existing instruments. Large volume HPGe spectrometers operating underground represent the most important recent achievements in the radiometric sector mainly because of better sensitivity, which helped to decrease a sample size at least by about a factor of ten, and improve the detection limits down to nBq/g, by about three orders of magnitude. Specific attention has been given to Monte Carlo simulations of background characteristics of HPGe detectors, which if carried out in advance of the construction of a low-level spectrometry system, they could predict its characteristics and parameters. Together with developments of mass spectrometry systems such as ICPMS (Inductively Coupled Plasma Mass Spectrometry) and AMS (Accelerator Mass Spectrometry), which have been dominating in analyses of long-lived radionuclides, we have at disposal analytical technologies, which have opened new applications in natural and life sciences.

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NEW DEVELOPMENTS IN ACCELERATOR PRODUCTION OF RADIONUCLIDES FOR MEDICAL APPLICATIONS

Syed M. Qaim

Institut für Neurowissenschaften und Medizin, INM-5: Nuklearchemie, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany,
e-mail: s.m.qaim@fz-juelich.de

Keywords: accelerator/cyclotron, nuclear reaction, high-current targetry, chemical separation, radionuclide, medical application

The “tracer principle” developed by Georg v. Hevesy has revolutionised medicine and today radionuclides and radiopharmaceuticals are extensively used in diagnostic organ imaging at the molecular level via emission tomography, i.e. SPECT and PET, as well as in internal radiotherapy. The demands on their quality, especially the purity and specific activity, are constantly increasing. Continuous research and development work is therefore underway to improve the presently used radionuclides as well as to develop novel radionuclides for new applications. Both research reactors and accelerators are extensively used. This presentation describes some recent developments in the accelerator/cyclotron production of radionuclides. In recent years the main thrust has been towards novel non-standard positron emitters and therapeutic radionuclides. To the first group belong radionuclides like ^{52}Mn, ^{55}Co, ^{64}Cu, ^{76}Br, ^{86}Y, ^{94m}Tc, ^{124}I, etc. and to the second radionuclides like ^{67}Cu, ^{103}Pd, ^{117m}Sn, ^{193m}Pt, ^{225}Ac, etc. which emit low-range highly-ionising radiation. A brief review of some of the production routes is given and the major applications of the recently developed novel radionuclides are outlined. The development work involved nuclear data measurement, high-current targetry, radiochemical separation and quality assurance of the product. Nuclear reaction cross sections were generally measured using γ-ray spectrometry, but in a few cases X-ray spectrometry was also applied. The targetry related to charged-particle irradiations has reached a high level of sophistication, since often highly-enriched, rather expensive, stable isotopes are used as target materials, necessitating their recovery. The chemical isolation of the desired radionuclide from the matrix activity made use of both dry and wet chemical procedures and the quality control measures extended to radionuclidic, radiochemical and chemical purity. The final product consisting of GBq amount of the radionuclide must be concentrated in a very small volume of the solution (<1 mL) and should be free of all metallic impurities (radioactive and inactive) to allow its efficient conversion to the desired metal-complex for application. The prospects of further improvement of the developed processes will be discussed. In general, the use of radionuclides of metals in medicine is increasing. Some emerging and potential applications of the novel radionuclides, e.g. theragnostic approach, combination of PET and MRI, use of radionanoparticles in therapy, etc. will be outlined.

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AN OVERVIEW OF OUR WORK IN NUCLEAR CHEMISTRY

A. V. R. Reddy

Formerly Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai – 400085, India;
Present address: Professor in Chemistry, V.S. University, Nellore 524001, AP, India,
e-mails: avreddy52@yahoo.com, avramanareddy1@gmail.com

Keywords: nuclear chemistry, nuclear fission, NAA, radiotracer

Research in Nuclear and Radiochemistry (NRC) in India got impetus with availability of neutrons from APSARA research reactor and during the last six decades, its horizon expanded to various areas towards understanding reaction mechanism and applications of radioisotopes and radiations. One of the major areas has been neutron induced fission of actinides in which mass, charge and kinetic energy distributions were experimentally determined to unravel the mechanism of nuclear fission. These studies were extended to medium to higher energy using charged particles and the focus was on mass, charge and mass resolved angular distribution studies. These studies resulted in quality data that were useful to understand the structural effects and role of excitation energy. Besides, significant contributions were made to understand the influence of entrance channel on the reaction mechanism from the recoil range distribution measurements and online measurements that helped to apportion CF and ICF contributions. Radiochemical separations were employed to study some rare isotopes. Another area is application of Neutron activation analysis (NAA) to analyze samples belonging to various areas of research with emphasis on geological and environmental samples. Whereas radiotracers are being continuously used in chemical studies *including trace element speciation*. Bhabha Atomic Research Centre (BARC) has become host to researchers from a large number of Indian Universities to carry out their work and the proceeding of NUCAR symposia, NAC and ARCEBS reflect the work that is being carried out. During mid-eighties of last century, a paradigm shift in overreliance of instrumental methods has taken place and a few nuclear probe based techniques in NRC have come into *force.* They are positron annihilation spectroscopy, perturbed angular correlation studies, PGNAA and Single comparator NAA (k_0-NAA) to name a few besides extending radiotracers to some interesting studies like elucidating mechanism and *trace element* speciation.

In this talk, a few of the above mentioned topics will be described with some of our contributions. An overview of the present scenario and future prospects will be presented.

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NUCLEAR AND RADIOANALYTICAL TECHNIQUES IN METALLOBIOCHEMISTRY RESEARCH: STUDIES OVER 50 YEARS

Enrico Sabbioni

CeSI, Aging Research Center, "G. d'Annunzio" University Foundation, 66100 Chieti, Italy; LASA, University of Milan and INFN-Milan, 20090 Segrate, Milan, Italy, e-mail: enrico.sabbioni@alice.it

Keywords: trace elements, risk assessment, neutron activation analysis, radiotracers, nanoparticles

Human health is inseparably linked to the presence in the body of trace and ultratrace elements (T&U), many of which follow the Paracelsus principle in a narrow concentration range, i.e. the essentiality or toxicity of an element is determined by its concentration. Exposure of humans to T&U raises serious concerns in terms of environmental, occupational and consumer safety. In this context, the use of an integrated strategy (parallelogram approach) based on data derived from human studies, animal experimentation and *in vitro* cellular and non-cellular assays forms the basis for an appropriate health risk assessment associated with the exposure to T&U.

The aim of this work is to provide a brief historical overview of 50 years development and applications of nuclear and radioanalytical techniques (N&R) in human health-related metallobiochemistry research. In analyzing the applications reported with time different periods can be distinguished, from the pioneer period to that of the growing competition of advanced spectrochemical (GFAAS, ICPMS) techniques, till the present day where N&R are finding a prominent place in nanotoxicology, an emerging discipline for a safety assessment of nanomaterials. In this context, selected applications of particular relevance for the two components of the risk assessment paradigm (exposure assessment and hazard identification) are discussed:

– NAA of human tissues. The multielement character and the high sensitivity for many elements of instrumental and radiochemical separation NAA contributed to the explosion of data concerning the total concentration of essential and "exotic" (without a known biological role) elements in tissues and body fluids of general population, occupational workers and pathological subjects. In addition, NAA, in combination with bioanalytical techniques (gel filtration, differential centrifugation, ion exchange chromatography, ultrafiltration) as well as cellular and molecular biology tools, was applied to speciation studies, resolving the total concentration of T&U into different chemical species, a fundamental basis for the mechanistic interpretation of metal toxicity.

– Radiolabelling of T&U. Radioisotopes with high specific radioactivity, produced at the nuclear reactor and at the cyclotron, have proven to be a potent analytical tool for *in vivo* delineation of metabolic patterns of environmental doses of T&U in laboratory animals (toxicokinetics, uptake, intracellular distribution, binding with intracellular components); and for *in vitro* metallomics experiments by cell cultures of animal and human origin (i.e. determination of T&U in whole cells, their distribution over different cell compartments and association with specific class of biomolecules).

– NAA and radiolabelling of metal-based nanoparticles. Nanotoxicology, a new frontier of toxicology, represents a great challenge for the further development and future applications of N&R in metallobiochemistry research.

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HOW FAR CAN WE GET? LATEST PROGRESS IN ACCELERATOR MASS SPECTROMETRY

H.-A. Synal

Laboratory of Ion Beam Physics, ETH Zurich, Otto-Stern-Weg 5, 8093 Zurich, Switzerland, e-mail: synal@phys.ethz.ch

Keywords: AMS, radiocarbon, instrumental developments

The technical evolution of Accelerator Mass Spectrometry (AMS) over the last ten years is summarized. A key characteristic of AMS is destruction of molecular interferences and subsequent analyses of atomic ions. It makes the extreme abundance sensitivity possible (in specific cases, below isotopic ratios of 10^{-16}). Today, 1+ charge state is used, molecular interferences are destroyed in multiple collisions with stripper gas atoms or molecules, and a high yield of atomic ions is reached at energies of a few hundred keV. Thus, AMS instruments develop towards lab size or tabletop devices. The use of He as stripper gas has further improved performance with respect to overall detection efficiency and reproducibility of measurement conditions. In parallel, implementation of permanent magnets into dedicated radiocarbon AMS system is progressed. This reduces complexity of the instruments and significantly reduces operation and installation costs. In addition, hybrid ion sources have been developed which can analyser either solid graphite samples or CO_2 gas. Using CO_2 directly enables a reduction of sample sizes down to 5–50 microgram of carbon. The related advancements in measurement technology have a strong impact on applications. But, low energy AMS is not limited to Radiocarbon only and there is a great potential for ^{10}Be, ^{26}Al, ^{129}I and actinides measurements at compact AMS systems. These developments have launched the wide spread use of AMS in various research fields and has resulted in a boom of new AMS facilities. I will present some specific examples to demonstrate opportunities related to these improvements.

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PROGRESS IN SUPERHEAVY ELEMENT RESEARCH

Andreas Türler

Laboratory of Radiochemistry, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland; Laboratory of Radiochemistry and Environmental Chemistry, University of Bern, CH-3012 Bern, Switzerland; Albert Einstein Center for Fundamental Physics, University of Bern, CH-3012 Bern, Switzerland, e-mail: andreas.tuerler@psi.ch

Keywords: superheavy elements, transactinides, nuclear structure, chemical properties

Investigations of superheavy elements are an exciting field of basic research in radiochemistry [1]. The success of ^{48}Ca induced heavy ion fusion reactions on actinide targets has led to the synthesis of all elements up to atomic number 118 and the discovery of more than sixty new nuclides in the heavy element region over the past two decades [2]. Thus, the 8th row of the Periodic Table has been completely filled. While first experiments focused only on the synthesis of new transactinide elements, recently, detailed nuclear structure investigations were shown to be possible with the newest generation of detection set-ups. Most noteworthy are experiments where decay spectroscopy in element 115 decay chains was successfully performed [3, 4]. Also, independent confirmation experiments that largely confirmed earlier findings, but revealed also new features, were of major importance to the field, such as the independent synthesis of elements 114 through 117 and their progeny [5–7], while the attempted synthesis of elements 119 and 120 has failed so far.

Experiments elucidating the chemical properties of heavy actinide and transactinide elements have made significant progress. Recently, the first ionization potential of lawrencium ($Z = 103$) was experimentally determined in excellent agreement with advanced theoretical calculations [8], seaborgium ($Z = 106$) was shown to form volatile hexacarbonyl complexes similar to its lighter homologs W and Mo [9], and, copernicium ($Z = 112$) and flerovium ($Z = 114$) showed an interesting, not yet conclusive behaviour that needs further clarification [10–12].

In summary, the progress made in recent years in superheavy element research is impressive and many new challenges lie ahead.

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X-RAY SPECTROMETRY FOR ENVIRONMENT AND CULTURAL HERITAGE

René Van Grieken

Department of Chemistry, University of Antwerp, B-2610 Antwerp, Belgium

X-ray spectrometry (XRS) in its various forms has nowadays many applications in many fields of research, including environmental research (e.g. concerning sediments and air pollution and global climate change). Recently, XRS has been used often in studies of the effect of air pollution on human health. Some illustrations will be given.

Nowadays, XRS is also very popular in conservation and cultural heritage (CH) research, e.g. due to the advent of portable instruments to be used in museums. Indeed, XRS, in its many forms, is one of the most relevant analysis techniques, concerning the methodology used by the artists, provenancing and the discovering of forgeries, and in the preparation for restorations, mostly because of its non-destructive nature. But also in “preventive conservation” (= studying the environment around a work of art with the intention to improve it and hence to extend the lifetime of a work of art), XRS is predominant, especially since in the last decades, much interest had shifted to the indoor environment and to particulate atmospheric material. XRS has indeed since long been the method of choice for the characterization of the inorganic composition of atmospheric aerosols.

Over the last two decades, we have intensively used various forms of XRS, namely energy-dispersive X-ray fluorescence e.g. with polarized high-energy beam excitation, and automated electron probe X-ray microanalysis, but always together with ion chromatography, micro Raman analysis, on-line soot determinations, etc., to identify particle types and their sources in indoor museum environments, while also gaseous indoor pollutants were assessed. We have studied atmospheric aerosols in and around some 40 museums in Europe, USA, Japan and South America, always with the intent to propose remedies to reduce the abundance of harmful particles. Some examples will be discussed, both some simple and successful ones and some very recent ones, namely concerning the Correr Museum in Venice, Italy, the Altamira Caves in NW Spain and the Alhambra complex in Granada, Spain.

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NEW TRENDS IN RADIOPHARMACEUTICALS

Hans-Jürgen Wester

Chair of Pharmaceutical Radiochemistry, Technische Universität München, Germany, e-mail: h.j.wester@tum.de

Keywords: radiopharmaceuticals, PET, targeted radiotherapy, GMP, quality control

Clinical Molecular imaging is an emerging technology that allows to determine the extent and the kinetics of a disease. In particular, positron emission tomography (PET) offers picomolar sensitivity and is a fully translational technique. On the other hand, targeted radiotherapy by means of radiolabeled peptides or small molecules has become a very powerful methodology for selective treatment of cancer tissue. Consequently, modern Pharmaceutical Radiochemistry has become a very active field of research that covers a broad range of interdisciplinary and translational oriented activities, such as the development of new labeling strategies by new chelators, kit-like technologies, rapid introduction of radiohalogens, design of innovative and highly selected probes, *in vitro* evaluation and *in vivo* characterization in suitable animal models, the development of reliable automated production strategies, the implementation of such strategies into the clinical environment under good manufacturing practice (GMP), incl. rapid analytical techniques for quality control of short lived isotopes and finally the translation into first proof-of-concept studies in humans and clinical study support. The presentation will give a brief overview on exemplary and selected state-of-the-art developments in the field, spanning from important innovations in chelator and labeling chemistry, new and powerful radiopharmaceuticals and corresponding applications in diagnosis and treatment of cancer.

INVITED LECTURES

Actinide analytical chemistry

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CERTIFICATION OF URANIUM REFERENCE MATERIALS FOR TRACE-ABUNDANCE U ISOTOPES

Richard Essex[1], *Paul Croatto*[2], *Jeffrey Morrison*[3]

[1]National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD, USA, e-mail: Richard.essex@nist.gov
[2]New Brunswick Laboratory, 9800 South Cass Avenue, Argonne, IL, USA, e-mail: Paul.Croatto@science.doe.gov
[3]Department of Homeland Security – Domestic Nuclear Detection Office, Stop 0552, 245 Murry Lane, Washington, DC, USA, e-mail: Jeffrey.Morrison@hq.dhs.gov

Keywords: reference material, U-233, U-232, isotope, nuclear forensics

Two certified reference materials (CRM) for U isotope-amount ratios have been re-certified to include isotope-amount ratios for ^{232}U and ^{233}U, which occur at trace levels in the materials. ^{232}U and ^{233}U are produced during neutron irradiation of ^{232}Th-bearing materials and are often present at trace levels (ppm or lower) in U that includes a reprocessed component. These isotopes are of particular interest for nuclear forensics due to the potentially characteristic information that can be derived. The presence and relative abundances of ^{232}U and ^{233}U can be highly representative material signatures; the relative proportion of the trace U isotopes may provide an indication of the irradiation conditions for reprocessed U material; and both isotopes are potentially useful as radiochronometers.

As part of an ongoing effort to enhance nuclear forensic measurement capabilities the US Department of Homeland Security, Domestic Nuclear Detection Office has funded the certification of additional attributes for New Brunswick Laboratory CRMs U045 and U630. CRM U045 is 4.5% ^{235}U-enriched material provided as an ampoulated nitric acid solution and U630 is a 63% ^{235}U-enriched U_3O_8 powder. These CRMs were previously certified for the relative proportions of ^{234}U, ^{235}U, ^{236}U, and ^{238}U. For this project, traceable measurements of $n(^{233}\mathrm{U})/n(^{238}\mathrm{U})$ ratio for U045 and the $n(^{233}\mathrm{U})/n(^{235}\mathrm{U})$ ratio for U630 were made by thermal ionization mass spectrometry (TIMS) using two different secondary electron multiplier – Faraday cup analytical routines. The $n(^{232}\mathrm{U})/n(^{238}\mathrm{U})$ ratio for U045 and the $n(^{232}\mathrm{U})/n(^{235}\mathrm{U})$ ratio for U630 were determined by measuring the $n(^{232}\mathrm{U})/n(^{234}\mathrm{U})$ ratio by alpha spectrometry and converting the ratios using previously certified $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{234}\mathrm{U})/n(^{235}\mathrm{U})$ ratio values, respectively.

The newly determined isotope-amount ratios and expanded uncertainties (k ≈ 2) for U045 are $n(^{232}\mathrm{U})/n(^{238}\mathrm{U}) = 8.6\times10^{-12} \pm 1.3\times10^{-12}$ and $n(^{233}\mathrm{U})/n(^{238}\mathrm{U}) = 2.438\times10^{-7} \pm 0.032\times10^{-7}$. The ratios and expanded uncertainties (k ≈ 2) for U630 are $n(^{232}\mathrm{U})/n(^{235}\mathrm{U}) = 7.31\times10^{-10} \pm 0.15\times10^{-10}$ and $n(^{233}\mathrm{U})/n(^{235}\mathrm{U}) = 2.372\times10^{-6} \pm 0.078\times10^{-6}$. To evaluate homogeneity and measurement repeatability, multiple characterization samples of each material were processed for analysis and at least duplicate measurements were made of each sample. The data were compared to verification analyses performed by a second lab and/or to additional data sets that are independent of certification analyses. The CRM units did not show any discernible sample-to-sample variability and are highly consistent with independent data sets. The newly determined attribute values will be included in revised certificates of analysis along with measurement uncertainties that are compliant with international standards (i.e. GUM).

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DETERMINATION OF GALLIUM IN PLUTONIUM BY ISOTOPE DILUTION MASS SPECTROMETRY

Joshua King, Tony Huggins, Phil Kaye

AWE, Aldermaston, RG7 4PR, United Kingdom

Keywords: plutonium, gallium, analysis, IDMS

The Actinides Analysis Group at AWE specialises in the chemical analysis of bulk actinide materials and analyses a wide array of actinide materials in support of various AWE programmes. A range of processes are carried out from high precision assay of major actinide elements through to the determination of trace amounts of a range of elements across the periodic table.

The current method for determination of gallium in plutonium samples at AWE involves dissolution of 1g of plutonium, pH adjustment, anion exchange separation to remove the plutonium followed by WDXRF measurement of the gallium.

The preparation and separation stage is time consuming, labour intensive, generates significant aqueous radioactive waste and contributes to increased doses to the analytical staff both in the sample analysis and processing of waste produced.

To remove this separation stage we show that the high sensitivity and low detection limits achievable by High Resolution ICP-MS can be utilised to measure the gallium content directly. The Isotope Dilution Mass Spectrometry (IDMS) technique is used, as it provides high precision and is less prone to errors from short or long term changes or drifts in instrument sensitivity. Work has been carried out to prove that IDMS analysis of gallium in plutonium materials, by a method involving dissolution, spiking with Ga-71 and dilution only, provides quantitative recoveries from a range of gallium concentrations, with a precision that satisfies customer requirements.

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ACTINIDE ANALYTICAL CHEMISTRY ASSOCIATED WITH NUCLEAR FORENSICS CHARACTERIZATION OF BULK SPECIAL NUCLEAR MATERIALS: AN OPERATIONAL AND RESEARCH & DEVELOPMENT PERSPECTIVE

Lav Tandon, Jung Rim, Jamie Doyle, Kevin Kuhn, Ann Schake*

Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87544, USA, *e-mail: tandon@lanl.gov

Keywords: actinide analytical chemistry, nuclear forensics, chronometry, ISO GUM uncertainty

Nuclear forensics is the analysis of intercepted illicit nuclear material and any associated material to provide evidence for determining the history of the confiscated material. Specific chemical and physical characteristics of the interdicted special nuclear material can be unique “fingerprints” or signatures for identifying manufacturing processes, intended use, point of origin, and route attribution. Total actinide content, actinide isotopic abundances, and metal and non-trace element concentrations are an integral part of a forensic investigation. Los Alamos National Laboratory (LANL) has been at the forefront of nuclear forensics research and is a support laboratory for the multi-agency Bulk SNM Analysis Program (BSAP). The pre-detonation actinide analytical chemistry team at LANL has recently participated in multiple nuclear material exchanges emphasizing inter-laboratory comparisons of analysis methods and measurement to maintain ISO 17025 accreditation for “operational” purposes. Results from some of those studies will be presented along with the associated bulk special nuclear material characterization capabilities. There is also a sustained effort to improve analytical chemistry methods through research and development in the areas of minor actinide analysis, separation science, and radiochronometry for plutonium, uranium and neptunium samples. Keys to routine method performance and method improvement acceptance are the application of defensible quality assurance protocols and demonstrating long term “statistical control” of quality control data. Examples of special nuclear material characterization with a statement of uncertainty derived using ISO/IEC Guide 98-3:2008 – Uncertainty of Measurement – Part 3: Guide to the Expression of Uncertainty in Measurement (GUM: 1995) will be discussed. This document has been reviewed and assigned publication number: LA-UR-15-26937.

Advances in radiochemistry supporting the nuclear fuel cycle

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THE NATURE OF THE VOLATILE TECHNETIUM SPECIES FORMED DURING VITRIFICATION OF BOROSILICATE GLASS

Bradley C. Childs[1], *Frederic Poineau*[1], *Ken R. Czerwinski*[1], *Alfred P. Sattelberger*[2]

[1]Department of Chemistry, University of Nevada Las Vegas, Las Vegas, NV 89154, USA, e-mails: childsb2@unlv.nevada.edu, poineauf@unlv.nevada.edu, czerwin2@unlv.nevada.edu
[2]Energy Engineering and Systems Analysis Directorate, Argonne National Laboratory, Lemont, IL 60439, USA, e-mail: asattelberger@anl.gov

Keywords: technetium, volatile, vitrification, X-ray absorption spectroscopy

The vitrification of sodium pertechenate into borosilicate glass was performed under air at 1100 °C. A glass with a composition similar to the one developed for vitrification of the low activity waste at the Hanford site was used. During the process, a red volatile species was observed above 600 °C. The nature of the red species was studied by XAFS spectroscopy. The EXAFS results indicate the environment of the absorbing atom to be constituted by 2.9(6) O atoms at 1.73(2) Å, 2.2(4) O atoms at 2.02(2) Å, and 0.8(2) O atoms at 2.18(2) Å. The results are consistent with the presence of a mononuclear species with a structure closely related to the one of $TcO_3(OH)(H_2O)_2$.

The volatile red technetium compound was also formed from the reaction of technetium dioxide with oxygen at 250 °C. Initial results indicate a linear correlation between the production of the volatile species with time of reactions. The mechanism of formation of $TcO_3(OH)(H_2O)_2$ and the role of water on the nature of the volatile technetium species during vitrification will be discussed.

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CHALLENGES IN DEVELOPING RADIOCHEMICAL METHODOLOGY FOR SAVANNAH RIVER SITE WASTE TANK CLOSURE CAMPAIGNS

D. P. DiPrete

Savannah River National Laboratory, Savannah River Nuclear Solutions, Aiken, SC 29808, USA

Waste cleanup efforts currently underway at the Savannah River Site, as well as other DOE nuclear sites, have created an ongoing need to characterize the inventories of the various waste tank heels prior to tank closure. The heels of each tank slated for closure often have unique chemical constituents as well as unique radiological distributions compared to previous tank heels characterized. Continuous programmatic evaluations of allowable closed tank radiological inventories result in steadily decreasing detection limit targets for isotopes that are required to be characterized. Numerous target isotopes are often required to be characterized to levels as much as 10 orders of magnitude lower radioactive concentrations than interfering isotopes. New isotopes continue to appear on the evolving characterization lists. Method development to generate protocols to characterize said isotopes must be worked in parallel to the larger characterization effort to ensure tank closure schedules can be met.

Tank Closure Program have required characterization of 54 radioisotopes on 36 high activity waste samples over a several month time frame. Dose rates of samples were at levels requiring initial manipulations to be carried out in remote manipulated Shielded Cells facility prior to hands-on radiohood operations. Radioanalytical methodology for numerous isotopes had to be developed from the ground up. Methodology used for a number of previously analyzed radioisotopes often have to be modified to reach lower detection limit targets in tank heels consisting of unusual sample matrices compared to previously analyzed SRS tank bottom samples. An overview of methodology and available resources used to rapidly develop protocols capable of meeting these Tank Closure radiological characterization requirements will be discussed as well as some specifics arising from recent program efforts.

Mass spectometry

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SOME INTERESTING APPLICATIONS OF ACCELERATOR MASS SPECTROMETRY TO ^{14}C, ^{10}Be AND ^{129}I

A. J. Timothy Jull[1]*, *Ching-Chih Chang*[1], *George S. Burr*[1, 2], *J. Warren Beck*[2] , *Jennifer McIntosh*[3], *Claire Tritz*[3], *Fusa Miyake*[4]

[1]Department of Geosciences, University of Arizona, Tucson, AZ 85721 USA, *e-mail: jull@email.arizona.edu
[2]University of Arizona AMS Laboratory, Physics Building, Tucson, AZ 85721, USA, e-mail: burr@email.arizona.edu
[3]Department of Hydrology and Water Resources, University of Arizona, Tucson, AZ 85721 USA, e-mail: mcintosh@hwr.arizona.edu
[4]Solar Terrestrial Environment Laboratory, Nagoya University, Chikusa ku, Nagoya 464 860, Japan, e-mail: fusa.miyake@gmail.com

Keywords: accelerator mass spectrometry, carbon-14, iodine-129, beryllium-10

The radionuclides carbon-14, beryllium-10 and iodine-129 are important as tracers of environmental processes, as opposed to the classical idea of dating have been developed in recent decades. These applications would not be possible without the sensitivity of accelerator mass spectrometry. We will review some applications and give some examples from our own research, as well as some new developments.

We highlight some interesting events recorded in the ^{14}C record in tree-rings, which are increasingly used not just for dating and reconstruction of the calibrated curve, but also as archives of past cosmic-ray events or "space weather" events, such as the well-documented rapid excursions at 774–775AD, to which similar phenomena have now been added. We also discuss ^{10}Be evidence for similar events and geomagnetic excursions. Third, we also summarize a number of applications using ^{129}I. These studies focus on both ocean studies, since ^{129}I is a conservative tracer originating from anthropogenic sources such as reprocessing plants. Recently, there has been great interest in radionuclides related to the Fukushima nuclear accident, but also to the development of ^{129}I as a possible tracer of modern groundwater recharge. The Fukushima study includes monitoring of ^{129}I in Pacific Ocean water samples collected on a regular basis at the Scripps Institution of Oceanography in La Jolla, CA, other coastal locations in California and also sample collection in Kaoshiung, Taiwan. This monitoring has been undertaken since shortly after the Fukushima event in 2011. A newer study is concentrated on water in semi-arid environments. We have begun a small pilot project to demonstrate the possible usefulness of ^{129}I as an age-tracer of recent recharge to shallow aquifers in the Tucson Basin. Iodine-129 concentrations have been measured in precipitation, surface water, and groundwater samples. Results from some of these interesting applications of these nuclides will be presented.

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DETERMINATION OF LONG-LIVED COSMOGENIC RADIONUCLIDES BY ACCELERATOR MASS SPECTROMETRY

Silke Merchel[1]*, *Nasrin B. Khojasteh Mohammadi*[1], *Stefan Pavetich*[1, 2], *Georg Rugel*[1], *Andreas Scharf*[1], *DREAMS-Users*[3], *DREAMS-Friends*[3]

[1]Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany, www.dresden-ams.de, *e-mail: s.merchel@hzdr.de
[2]Present address: Department of Nuclear Physics, Australian National University, Canberra, ACT 2601, Australia
[3]ANSTO, ANU, ASTER, AWI, U Bern, ETH, MPI Mainz, TANDAR, TU Munich, U Poznan, Senckenberg, VERA, VKTA. All over the world.

Keywords: accelerator mass spectrometry AMS, cosmogenic nuclides

Applications: Long-lived radionuclides with half-lives of 0.1–16 Ma have nowadays thousands of exciting applications, especially within environmental and geosciences. In nature, the so-called cosmogenic nuclides (CNs) are products of nuclear reactions induced by primary and secondary cosmic rays. Hence, they can be found in extraterrestrial material such as meteorites – originating from the asteroid belt, the Moon or Mars – and lunar samples in higher concentrations (e.g. ~10^{10} ^{10}Be atoms/g or <0.5 mBq/g). A combination of several CNs is used to reconstruct the exposure history of this unique material while in space (irradiation age) and on Earth (terrestrial age).

Though, in terrestrial material the concentrations are typically only on the order of 10^4–10^9 atoms/g (i.e. μBq/g–nBq/g) for ^{10}Be produced in the Earth's atmosphere, then transported to the surface and further absorbed and incorporated at and in, e.g. sediments or ice. Some of the lowest ^{10}Be concentrations (~10^3 atoms/g), produced *in-situ* by neutron- and muon-induced nuclear reactions from e.g. O and Si in quartz, can be found in samples taken from the Earth's surface. The concentrations of atmospheric or *in-situ* produced CNs record information that is used to reconstruct sudden geomorphological events such as volcanic eruptions, rock avalanches, tsunamis, meteor impacts, earthquakes and glacier movements. Additionally, glacier movements and data from ice cores give hints for the reconstruction of historic climate changes and provide information for the validation of climate model predicting future changes. Slower processes such as sedimentation, river incision and erosion rates can also be investigated and last but not least, indirect dating of bones as old as several Ma's is possible.

Anthropogenic production by release from nuclear reprocessing, accidents and weapon tests led to increased levels of CNs in surface water and soil (^{129}I,…), ice (^{36}Cl,…) and material from nuclear installations themselves (^{41}Ca,…). Some of the CNs can, thus, be used as tracers to follow pathways in oceanography, to date and identify sources of groundwater, to perform retrospective dosimetry and to study aspects in radioecology and pharmacology.

Method: The analytical method of choice for CN determination is accelerator mass spectrometry (AMS). After simple radiochemical separation, AMS reduces background and interfering signals resulting from molecular ions and isobars enormously. Thus, AMS provides much lower detection limits compared to conventional MS or decay counting. The DREAMS (DREsden AMS) system at HZDR offers excellent measurement capabilities (Akhmadaliev et al., *NIMB* 294 (2013) 5) also for external users (see www.hzdr.de/ibc).

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ENVIRONMICADAS: A C-14 AMS FOR NUCLEAR ENVIRONMENTAL PROTECTION IN HUNGARY

Mihály Molnár, Róbert Janovics, Anita Molnár, László Rinyu, Mihály Veres, A. J. Timothy Jull*

Hertelendi Laboratory of Environmental Studies, MTA Atomki- Isotoptech Zrt, Debrecen, Hungary, *e-mail: mmol@atomki.hu

Keywords: radiocarbon, nuclear, AMS

Among the radionuclides potentially emitted into the environment by nuclear power plants and nuclear waste disposal facilities, usually radiocarbon is the most significant regarding the collective effective dose contribution. Therefore, the determination of radiocarbon from various environmental media is of high importance during the environmental monitoring of nuclear facilities.

In 2011, a compact accelerator mass spectrometer (MICADAS-AMS) was installed in the HEKAL Laboratory within the framework of a cooperation between Isotoptech Co. Ltd., MTA Atomki and the Swiss Federal Institute of Technology (Zürich). Compared to the radiometric techniques, AMS requires orders of magnitude lower amount of samples to perform a radiocarbon measurement of appropriate accuracy. Our aim was to adapt and develop sample treatment methods making possible the preparation of various sample types for AMS radiocarbon measurements. One of our main objective was to determine the radiocarbon contribution of the Hungarian nuclear facilities, as reflected by the surrounding environmental elements not investigated so far, among others by the investigation of the organic components of groundwater and the incorporation of the emitted atmospheric radiocarbon into plants.

We have investigated the effect of the Paks Nuclear Power Plant on the ^{14}C concentration of a nearby tree The specific radiocarbon concentration of the annual rings of the tree in the vicinity (400 m) of the Paks Nuclear Power Plant was slightly, but systematically higher than that of a background (20 km away) tree in Dunaföldvár. As an analogue we studied the effect of the Püspökszilágy radioactive waste treatment and disposal facility on the ^{14}C concentration of a nearby tree. The specific radiocarbon concentration of the annual rings of the trees in the vicinity of the vaults of the Püspökszilágy radioactive waste treatment and disposal facility is significantly influenced by the gaseous radiocarbon emitted from the site. We have conducted an investigation of radiocarbon contamination in the groundwater of nuclear facilities**.** By the separate measurement of the inorganic and organically bound radiocarbon content of the groundwater of the Paks Nuclear Power Plant that the radiocarbon contamination getting into the groundwater of the power plant is emitted mostly in inorganic form and the organic fraction does not have significant radiocarbon contribution and has an activity close to the natural background.

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ICP-MS/MS AND SF-ICP-MS FOR THE DETERMINATION OF RADIOCESIUM ISOTOPES IN ENVIRONMENTAL SAMPLES

Jian Zheng[1], Keiko Tagami[1], Wenting Bu[2], Shigeo Uchdai[1]*

[1]Research Center for Radiation Protection, National Institute of Radiological Sciences, Anagawa 4-9-1, Inage, Chiba 263-8555, Japan,
*e-mail: jzheng@nirs.go.jp
[2]Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, Sichuan, 621900, China,
e-mail: buwenting2006@pku.edu.cn

Keywords: radiocesium isotopes, environmental samples, ICP-MS/MS, SF-ICP-MS, ^{135}Cs/^{137}Cs atom ratio

Radiocesium isotopes are high yield fission products up to 6.535% and 6.236% for Cs-135 (half-life 2×10^6 y) and Cs-137 (half-life 30.2 y), respectively, from thermal neutron fission of U-235. They can be released into the environment in nuclear events like the detonation of a nuclear weapon or nuclear reactor accident. In the fission chains for Cs-135 and Cs-137, a shielding of Cs-135 occurs, which causes a high degree of variance of Cs-135/Cs-137 isotope ratio with source. Thus, the ratio of Cs-135/Cs-137 will be characteristic of the reactor operation and shutdown conditions. In addition, the isotope ratio of Cs-135/Cs-137 is very important in many aspects in radioecological studies, including source identification of radioactive contamination, dispersion modeling of fission products in the environment after a nuclear accident, long-term estimation of environmental behavior of Cs, and development of accurate sediment geochronology.

The determination of Cs-135 by radiometric methods is very difficult and quite insensitive because of its long half-life and low-energy β-decay. Neutron activation analysis and thermal ionization mass spectrometer have been investigated for Cs-135 activity and Cs-135/Cs-137 isotope ratio analysis in environmental samples, but these techniques are expensive and not widely available. Recently, the analytical potential of ICP-MS have been studied, but the analysis of environmental samples remains to be a great challenge. The main difficulties for environmental samples analysis using ICP-MS techniques are: (1) polyatomic interferences, such as ^{95}Mo^{40}Ar$^+$, ^{119}Sn^{16}O$^+$ for Cs-135, and ^{97}Mo^{40}Ar$^+$, and ^{121}Sb^{16}O$^+$ for Cs-137; (2) isobaric interferences, for example, Ba-135 (abundance 6.592%) and Ba-137 (abundance 11.232%); and (3) interferences from the stable Cs-133, for low level environmental samples containing global fallout Cs-135, an abundance sensitivity of 10e-9 is required. To overcome these analytical difficulties, we investigated the analytical potential of three ICP-MS, namely, SF-ICP-MS (Element 2), reaction cell ICP-MS (Agilent 7500c) and a triple quadrupole ICP-MS (ICP-MS/MS) (Agilent 8800) for the determination of cesium isotopes. The advantages and disadvantages of these different ICP-MS were explored and compared. And the applications of developed ICP-MS method for radiocesium isotopes determination in Fukushima environmental samples for release source identification will be discussed.

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Neutron activation analysis

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FOUR DECADES OF k0-NAA: AN APPRAISAL

Frans De Corte

(ex) Fund for Scientific Research-Flanders and University of Gent-Belgium/Institute for Nuclear Sciences/Laboratory of Analytical Chemistry, B-9921 Vinderhoute, Belgium, e-mail: fransmans@skynet.be

Keywords: NAA, k_0-standardization

Four decades ago, the NAA k_0-method was introduced to get rid of the doubtful quality of the nuclear data used in the absolute standardization, and this led to the introduction of experimental composite nuclear data (k_0's) which are since then the kernel of the development of the k_0-method. Following milestones such as the ADNDT library (De Corte/

Simonits, 2003) and the IUPAC Access database (Kolotov/De Corte, 2004), the k_0-Nuclear Data Committee (2009) released the "classic" k_0-database (Jaćimović et al., JRNC 2012) as a stepping stone for its upgraded 2015-version. In these compilations not only k_0's are dealt with, but also associated data such as Q_0 (thermal cross section/resonance integral), E_r (effective resonance energy), F_{Cd} (Cd transmission factor) and Westcott's g and s_0 factors, not to forget half-lives and activation/decay schemes with their related data. Recently, the evaluation of these data was assisted by an IAEA INDC project (Trkov et al., 2015), notably helpful for the quality improvement of Q_0, E_r, F_{Cd} and g, but somewhat ambiguous since it might be understood as the re-introduction of k_0-factors calculated from combination of cross-sections and gamma-intensities. Next to the nuclear data, in the course of the years large attention went to the practical and general applicability of the k_0-method. This was achieved by developing reliable, robust and user-friendly procedures for the characterization of the irradiation and counting parameters. As to the irradiation, protocols were worked out for measuring Ryves' epithermal shape factor α next to the well-known thermal/epithermal flux ratio f; both involve the knowledge of k_0 and associated data for the monitors selected, thus revealing a non-negligible correlation. As to the counting parameters, attention was paid both to the accurate/precise determination of the detection efficiency over a broad energy range and to the evaluation of the peak-to-total ratio for the correction of gamma summing effects. This correction requires the knowledge of the decay schemes and their parameters, and although this has been the topic of some of our studies, it has known little follow-up. Next to the efforts for enhancing the k_0-method's applicability, it is essential to mention the development of dedicated computer programs, for instance Blaauw's k0-IAEA and van Sluijs' Kayzero_for_Windows (KAYZERO/SOLCOI). The performance of both has been extensively tested by analysing reference samples, including the SMELS materials that were especially developed for k_0-NAA. It has to be emphasized that, starting the k_0-method in the mid-1970s as a pure Budapest-Gent cooperation, it has evolved since then into an international discipline, involving numerous laboratories providing new data and insights, among which the PGAA contribution is noteworthy, e.g. from the Budapest group (Zsolt, Szentmiklósi et al.). This internationalization, with respect to both development and application, can best be documented by the series of International k_0 Users Workshops, the 1st edition held in Gent, 1992 and the 7th one scheduled in Montreal, 2017.

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RADIOCHEMICAL SEPARATION OF MOSTLY SHORT-LIVED NEUTRON ACTIVATION PRODUCTS

Jan Kučera, Jan Kameník

Department of Nuclear Spectroscopy, Nuclear Physics Institute, The Czech Academy of Sciences, 25068 Husinec-Řež 130, Czech Republic, e-mails: kucera@ ujf.cas.cz, kamenik@ujf.cas.cz

Keywords: RNAA, vanadium, iodine, manganese, mercury, selenium, uranium, neptunium, protactinium

Radiochemical separation of neutron activation products in so-called radiochemical neutron activation analysis (RNAA) provides the lowest element detection limits achievable of all neutron activation analysis modes, especially if short-lived products are employed. The most frequently RNAA procedures used at the Nuclear Physics Institute (NPI) and their applications for assay of namely biological materials are presented. Various separation methods can be used for the given purpose. In case of short-lived radionuclides, extraction is most frequently employed, because of the separation speed and high radiochemical purity attainable. The radionuclide with the shortest half-life, which we determine in biological materials by RNAA, is ^{52}V ($T_{1/2}$ = 3.74 min). For this purpose, we use extraction of vanadium with a solution of N-benzoyl-N-phenyl hydroxylamine in toluene. The RNAA procedure had previously been used for the vanadium determination in blood at the sub-μg kg^{-1} level, and recently for the value assignment of vanadium at the μg kg^{-1} level in the new NIST SRM 1577c Bovine Liver. Extraction of elementary iodine into chloroform is basis of our RNAA procedure using ^{128}I ($T_{1/2}$ = 24.99 min) with a detection limit down to the μg kg^{-1} level. This procedure is mainly used for assay of human diet and pet food samples. This procedure also allows for subsequent determination of manganese via ^{56}Mn ($T_{1/2}$ = 2.579 h) using either hydrated MnO_2 precipitation or extraction of Mn(III) complex with diethyldithiocarbamate (DDC) into chloroform. The Mn detection limit in the sub-μg kg^{-1} range has been achieved. Another pair of elements, which can be determined by RNAA either individually or subsequently, is Hg and Se. For Hg determination via ^{203}Hg ($T_{1/2}$ = 46.6 d), extraction with $Ni(DDC)_3$ into chloroform is used, while

^{75}Se ($T_{1/2}$ = 119.8 d) is precipitated in elemental form by ascorbic acid. The above procedures have mainly been used for quality control purposes of the Hg determination in polluted soils and for the Se determination in agricultural studies concerning Se supplementation of crops. In both cases the detection limit down to µg kg^{-1} level is achieved. For determination of sub-ng amounts of U, we use extraction of ^{239}U ($T_{1/2}$ = 23.45 m) with tributylphoshate or separation of daughter ^{239}Np ($T_{1/2}$ = 2.36 d) by a combination of coprecipitation and solid phase extraction with TEVA resin, whereas for determination of Th via daughter ^{233}Pa ($T_{1/2}$ = 26.98 d) we employ coprecipitation and extraction with trioctylphosphine oxide. The purpose of the last three RNAA procedures is to arrive at a lower limit of detection of U and Th than can be achieved by radiometric measurements in, e.g., shielding materials for low-level counting.

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NAA – THE METHOD WITH NEARLY UNLIMITED MEASUREMENT RANGE

Borut Smodiš

Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia, e-mail: borut.smodis@ijs.si

Keywords: neutron activation analysis, measurement range

Most of conventional chemical analytical techniques for determination of trace elements are limited in their linear range, i.e. linear relationship between signal and concentration of the measurand. Furthermore, a calibration curve is frequently needed within a relatively narrow measurement range. It is often overlooked that this is not the case with neutron activation analysis (NAA), where relationship between the signal (i.e. gamma-ray intensity of the formed radionuclide) and the measurand's content in a sample is linear throughout the whole concentration range. This feature, stemming from the activation equation, which definitely represents comparative advantage of NAA in comparison with other, non-nuclear analytical techniques, is taken for granted by analysts and usually not emphasised enough. In the contribution, this fact is re-emphasised and further discussed, for both radiochemical and instrumental modes of NAA. Typical examples from the practice are presented, showing almost unlimited possibilities with respect to measurement ranges of particular measurands to be determined, ranging from ng g^{-1} or even lower levels to up to tenths of percent content levels. Furthermore, the physical characteristic of gamma-ray detection process also allows for unique compensation of signal intensity, if needed, by simply changing distance between the detector and the measured sample.

Nuclear forensics

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RESULTS FROM THE GALAXY SERPENT WEB-BASED TABLE TOP EXERCISE UTILIZING THE CONCEPT OF NUCLEAR FORENSICS LIBRARIES

James Borgardt[1]*, Jodi Canaday*[2]*, David Chamberlain*[2]

[1]Office of Weapons of Mass Destruction Terrorism, U.S. Department of State, Washington, DC, USA (on detail from Juniata College, Huntingdon, Pennsylvania, USA), e-mail: borgardt@juniata.edu
[2]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA,
e-mails: jodi.canaday@anl.gov, david.chamberlain@anl.gov

Keywords: sealed radiological source, nuclear forensics, national nuclear forensics library, Galaxy Serpent, database

Key lessons learned and methodologies used in the second version of Galaxy Serpent, a unique, virtual, web-based international tabletop exercise concerning the concept of a national nuclear forensics library (NNFL), are presented. The three phase exercise involved thirty-five teams of scientists from twenty-eight countries and three international organizations. In Phase 1, teams were provided synthetic sealed radiological source data which was used to compile a model NNFL. In Phases 2 and 3, this library served as a comparative instrument. Phase 2, based upon synthetic data from a hypothetical intact sealed source recovered out of regulatory control, was designed to allow teams using provided information and making warranted assumptions to down-select to three potential matches in their model inventory. Phase 3, utilizing simulated field information obtained from a hypothetical detonated radiological dispersal device, was designed to allow teams to identify a single source in their holdings as a potential match. Teams were also asked to evaluate the confidence underlying their reported findings. The methodologies utilized and aggregate results of the exercise will be presented, along with challenges encountered and benefits realized. The exercise has yielded insightful lessons regarding the vital role NNFLs can provide in concert with traditional forensics to strengthen investigations of nuclear or other radioactive materials encountered outside of regulatory control. The exercise also provides practical insights into how a country can develop their own NNFL. The success and efficacy of the exercise has initiated the development of a third version of the exercise, similar in scope and intent, which uses data pertaining to uranium ore concentrate (UOC). This tabletop exercise was conducted under the auspices of the Nuclear Forensics International Technical Working Group (ITWG) and funded and organized by the U.S. Department of State with technical expertise provided by Argonne National Laboratory.

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AGE DATING OF BULK PLUTONIUM MATERIALS

Brogen Dawkins, Philip Kaye, Pamela Thompson, Robert Watson

AWE, Aldermaston, RG7 4PR, United Kingdom

Keywords: plutonium, age dating, analysis, nuclear forensics

The Actinides Analysis group at AWE specialises in the bulk chemical analysis of actinide materials, with a particular emphasis on plutonium and uranium metals. Recently, we have started to investigate the application of this capability to forensic analysis of nuclear materials.

A particular area of interest within the nuclear forensic community is the age dating of actinide materials, specifically the determination of a ‘model age’ for discovered material by the study of radio-chronometry pairs.

As part of quality control activities at AWE, plutonium materials are routinely analysed for plutonium isotope ratio composition by Thermal Ionisation Mass Spectrometry (TIMS) and assayed for total plutonium content by potentiometric titration. Americium and neptunium content is determined by High Resolution Gamma Spectrometry (HRGS) and uranium content by Wavelength Dispersive X-Ray Fluorescence (WDXRF). Extending the analysis to uranium isotope ratios thus allows access to the Pu-238-U-234, Pu-239-U-235, Pu-240-U-236, Pu-241-Am-241, and Am-241- Np-237 radio-chronometers. The analytical techniques used will be discussed, and the age dating of plutonium materials will be considered with particular reference to the effect of low precision analytical techniques such as XRF on the model age.

The relationship between the calculated model ages for different radio-chronometry pairs and the known production history of plutonium materials will be discussed.

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^{233}Pa TRACER CALIBRATION FOR URANIUM RADIOCHRONOMETRY

Amélie Hubert[1], Ross W. Williams[2]

[1]CEA, DAM, DIF, F91297 Arpajon, France, e-mail: amelie.hubert@cea.fr
[2]Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA94550, USA, e-mail: williams141@llnl.gov

Keywords: age determination, uranium, protactinium, secular equilibrium

The age determination of a nuclear material gives information on the time elapsed since the last chemical purification undergone by the material. A “model age” can be obtained by measuring the ratio between one isotope of the element of interest (for example ^{234}U or ^{235}U) and its decay product (^{230}Th or ^{231}Pa). The “model” assumptions are that (1) the uranium decay products have been completely removed during the production and (2) the material has been kept as a closed system. When the first condition is not fulfilled (Th or Pa impurities still in the material), the material looks older than it is in reality. The use of two radiochronometers allows the validity of these assumptions to be tested through comparison of the ages obtained.

The quantification of the different isotopes is performed by isotope dilution mass spectrometry (IDMS). For ^{231}Pa analyses, there are two ways to obtain the isotopic tracer ^{233}Pa: (i) by milking from ^{237}Np, (ii) by neutron activation of ^{232}Th. Both CEA DAM and LLNL laboratories purify ^{233}Pa milked from ^{237}Np. ^{233}Pa has a relatively short half-life ($T_{1/2}$ = 27 days), and it is of importance to exactly know the concentration of this isotope at a precise date. One of the major difficulties in making ^{231}Pa analyses is the calibration of the ^{233}Pa tracer. Two different rocks at secular equilibrium (equal activity between ^{235}U and ^{231}Pa), Table Mountain Latite (TML) and Basalt from Columbia River (BCR-2), were used in both laboratories to calibrate the ^{233}Pa solutions. Both rocks were solubilized and the amount of ^{235}U was measured by IDMS. ^{231}Pa amount in those solutions was then calculated using the assumption of secular equilibrium. The ^{233}Pa tracer was then mixed with each rock solution, Pa was separated and purified, the ^{233}Pa/^{231}Pa ratio was measured, andthe ^{233}Pa concentration was calculated using the known ^{231}Pa amount. The results from both TML and BCR-2 are in agreement, which validates the assumption of secular equilibrium, and both are suitable surrogate interim standards for calibrating ^{233}Pa tracers until ^{231}Pa reference materials become available.

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CHALLENGES AND UNCERTAINTIES IN AGE DATING OF URANIUM AND PLUTONIUM

Klaus Mayer[1]*, *Mateusz Monterial*[2], *Zsolt Varga*[1]

[1]European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany, *e-mail: Klaus.Mayer@ec.europa.eu
[2]University of Michigan, Ann Arbor, MI 48105, USA, e-mail: mateuszm@umich.edu

Keywords: age dating, uranium, plutonium, half-life, uncertainty

The radioactive decay of uranium and plutonium isotopes, in combination with a few assumptions, can be used as built in “chronometer” for determining the “age” of the material. More precisely, the time elapsed since the last chemical separation of parent and daughter nuclides determines the relative amounts of these nuclides. In turn, the accurate knowledge of the parent-daughter ratio enables to calculate a model age of the material in question. “Age dating” is a vital technique employed in nuclear forensics in order to characterize the material of unknown history. The relative abundance of parent-daughter pairs are measured through mass spectrometric or radiometric methods. The uncertainty budget includes the contributions from the measurements themselves, calibrations, and physical constants such as half-lives of the nuclides. In this paper we will examine the major uncertainty contributions, the validity of some of the assumptions to be made for establishing the model age and experimental options for further improving the uncertainty in radiochronometry.

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MORPHOLOGY AND CHEMICAL SPECIATION OF ACTINIDE MATERIALS FOR FORENSIC SCIENCE

Marianne P. Wilkerson

Chemistry Division, Los Alamos National Laboratory, P.O. Box 1663, MS-J514, USA, e-mail: mpw@lanl.gov

Keywords: chemical speciation, forensic science, morphology, plutonium, uranium

Chemical speciation and morphology of uranium oxide and plutonium oxide materials may provide information important for understanding provenance and history of unknown samples [1, 2]. We recently reported that chemical signatures common to nuclear processes may become incorporated into uranium oxide materials, and that subtle changes in chemical speciation from oxidation and/or hydration following storage under humidity are detectable [3]. These studies to identify chemical signatures in uranium oxide materials were conducted using tools commonly employed to measure chemical structure. Complementary studies from the field of nuclear fuels have been published to understand morphologic properties of uranium oxide materials in an effort to improve material performance, and this information may be of value to nuclear forensics science [2].

We have investigated the use of morphology to characterized images of materials, and X-ray diffraction analysis and synchrotron-based X-ray absorption spectroscopy to probe temporal changes in chemical speciation of additional uranium oxide materials and plutonium oxide samples. These latter materials are intriguing systems that readily form on plutonium metal surfaces, forming an olive colored "rust" of PuO_2. Studies of plutonium materials have been conducted with an eye towards a variety of applications, such as environmental transport & fate and stockpile stewardship. Our limited understanding of the complexity of plutonium oxide systems, their morphologies, and chemical behaviors, however, challenges our ability to develop viable and quantitative forensic signatures from these systems.

We will discuss our studies to characterize morphologic and chemical speciation from a set of uranium and plutonium oxide materials. LA-UR-15-27363

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Nuclear instrumentation and methodology

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GAMMA^3, AN ADVANCED ULTRA-LOW BACKGROUND GAMMA SPECTROMETER

O. Delaune, A. Cagniant, G. Douysset, J.-P. Fontaine, P. Gross, G. Le Petit*

CEA, DAM, DIF, F-91297 Arpajon, France, *e-mail: olivier.delaune@cea.fr

Keywords: low-level gamma spectrometry, high purity Germanium detectors, background analysis

The CEA/DAM in Bruyères-le-Châtel has recently developed a new gamma spectrometer composed of three different BEGe5030P Hyper-Pure Germanium detectors from Canberra company. State-of-the-art techniques have been used in order to reduce as much as possible its background. Thus, the shielding is composed by three different layers of increasing purity lead, several plastic scintillators used as cosmic vetoes, an inner layer of borated polyethylene used to capture secondary neutrons and an injection of radon-free gas in the measurement chamber in order to remove radon descendants that emit γ-rays from the detection chamber. Consequently, the spectrometer background count rate is 4.4 counts per minute and per kilogram of Germanium over the 40–2500 keV energy range. Thus, this spectrometer located at ground level (2 meters of water equivalent) offers similar background level that underground spectrometers.

The gamma^3 setup is operated using a digital acquisition system. It is composed by a PIXIE-4 module from XIA LLC. The PIXIE-4 module records the energy and the timestamp of each event. Recording the timestamp allows to consider only events in a given time range, to reconstruct coincident events, to identify short lifetime nuclides, … Examples illustrating the interest of digital acquisition will be presented.

The particular disposition of the detectors allows us to measure with high efficiency different kind of sample geometries, such as F100, BP20 or SG500 geometries for environmental measurements.

In addition, the use of two or three Germanium detectors permits to perform coincidence measurement as well as to increase the detection efficiency. In particular, the coincidence measurements allow us to extract from the background in active samples, nuclides that would remain invisible in direct measurement.

The gamma^3 spectrometer and its background will be presented. Coincidence measurement powerfulness will be discussed and the usefulness of the digital electronics will be illustrated.

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DIGITAL COINCIDENCE GAMMA SPECTROMETER – INITIAL TESTS, RESULTS AND PERSPECTIVES

*Paweł Janowski, Jerzy W. Mietelski**

The Henryk Niewodniczanski Institute of Nuclear Physics, Polish Academy of Sciences (IFJ PAN), Radzikowskiego 152, Krakow, 31-342 Poland, *e-mail: Jerzy.Mietelski@ifj.edu.pl

Keywords: gamma spectrometry, digitizer, coincidences, germanium detectors

A setup of two HPGe detectors with digital spectrometer tracks was constructed at our Institute in Krakow. Basically it consists of coaxial and planar HPGe detectors and 14 bit CAEN digitizer. The detectors are in/at perpendicular axis. It was also tested using two 30% efficiency coaxial HPGe detectors from our whole body spectrometer. These two were facing each other. Spectra are collected in a form of tables with registered energy and time of registration with resolution of 10 ns. Especially written software is used to analyse any kind of coincidence/anticoincidence between registered photons and enables also to analyse delayed coincidences. Achieved results will be presented during conference.

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GEANT4 SIMULATIONS OF THE BUDAPEST COMPTON-SUPPRESSED PGAA SPECTROMETER

László Szentmiklósi, Tamás Belgya*

Centre for Energy Research, Hungarian Academy of Sciences, Budapest, Hungary, *e-mail: szentmiklosi.laszlo@energia.mta.hu

Keywords: prompt-gamma activation analysis, geant4

In prompt-gamma activation analysis, the source of the analytical information is in most cases the (n, γ) reaction. The energy range of the spectra is consequently broad, spans from 45 keV to 11 MeV. There is a Compton-plateau for each full energy peak, containing the majority of the counts. The Compton-suppressed detection of photons reduces the level of the baseline by about one order of magnitude, so that it is of great importance to achieve low detection limits and accurate nuclear data.

In order to better understand the operation of the detector assembly used at the Budapest PGAA and NIPS facilities, and to allow the unfolding of spectra for nuclear physics purposes, we made simulations earlier with MCNP5 and MCNP-CP for the complete PGAA and NIPS setups, and more recently with geant4, but only for the bare HPGe detector. As a continuation of these earlier studies, this time we report about the results of geant4 calculations for the entire PGAA detector, in both unsuppressed and suppressed modes.

Nuclear safeguards

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ROLE AND EVOLUTION OF NON-DESTRUCTIVE ASSAY FOR IAEA SAFEGUARDS VERIFICATIONS

Andrey Berlizov, Alain Lebrun

Department of Safeguards of the International Atomic Energy Agency, Wagramerstrasse 5 PO box 100, Vienna, Austria,
e-mails: a.berlizov@iaea.org, a.lebrun@iaea.org

Keywords: non-destructive assay, international safeguards

IAEA verification of the correctness and completeness of State declarations under their safeguards agreements is based on a number of techniques ranging from analysis of open source literature, analysis of commercial satellite imagery, international trade analysis, field activities conducted by IAEA inspectors and destructive analysis of samples in laboratory environment. A large part of field activities involves instrumentation operated by inspectors or permanently installed at facilities and running in unattended mode. Instrumentation aims at supporting verification of multiple parameters associated with State declarations. Therefore, multiple techniques are involved, including optical surveillance, sealing and radiation detection, such as neutron coincidence counting or gamma spectrometry.

Systematically verifying declared nuclear material using the ultimately accurate technique would induce enormous costs comparable to all costs induced by process or quality control by facility operators. To control both cost and probability to detect diversions, inspectors implement staged verifications methods with associated sampling plans ensuring adequate detection probability.

Non-destructive assay techniques are applied in the field to confirm the nature and presence of declared nuclear material at the item level by attribute testing. Attribute is a specific measurable characteristic of a verified item which when observed allows concluding that the verified item is present. To verify that a substantial part of a declared item has not been diverted, partial defect test method is used which normally involves more sophisticated measurement such as quantitative gamma spectrometry or neutron coincidence counting. To detect protracted diversion, most accurate methods have to be employed. The so-called bias defect methods most of the time induce the need sample analysis in laboratories.

Fortunately, because the number of gross, partial and bias defects respectively increases to result into the diversion of a significant quantity, corresponding tests have to be carried out in decreasing numbers to maintain the detection probability irrespective of the envisaged diversion scenario.

In the recent years, accuracy of non-destructive assay technique have improved and contributed reducing the number of destructive analysis. Combined procedures have also been applied to use quantitative gamma spectrometry in the field on fully controlled samples. Example of such reduction of uncertainties will be presented including usage of Combined Procedure for Uranium Concentration and Enrichment Assay (COMPUCEA), Advanced *In-Situ* Object Counting (A-ISOCS) and other specialized gamma spectrometry applications applied to Uranium and Thorium. The presentation will also underline the crucial role played by improvement of simulation capabilities to accurately calibrate the instruments and appropriately correct for identified biases.

Production of radionuclides

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NUCLEAR DATA FOR THE PRODUCTION OF MEDICAL RADIONUCLIDES

Roberto Capote[1], Marie-Martine Bé[2], Mark A. Kellett[2], Brett V. Carlson[3], Alex Hermanne[4], Mazhar Hussain[5], Anatoly Ignatyuk[6], Tibor Kibédi[7], Guinyun Kim[8], Filip Kondev[9], Ondrej Lebeda[10], Aurelian Luca[11], Yasuki Nagai[12], Haladhara Naik[13], Alan L. Nichols[14], Meiring Nortier[15], J. W. Engle[15], Ingo Spahn[16], Ferenc Tárkányi[17]

[1]International Atomic Energy Agency, Vienna, Austria, e-mail: r.capotenoy@iaea.org
[2]Laboratoire National Henri Becquerel CEA-Centre d'Etudes de Saclay Saclay, France
[3]Instituto Tecnologico de Aeronautica, Sao Paulo, Brazil
[4]Vrije Universiteit Brussel, Brussels, Belgium
[5]Government College University, Lahore, Pakistan
[6]Institute for Physics and Power Engineering, Obnink, Russia
[7]Dep. of Nuclear Physics, Australian National University, Canberra, Australia
[8]Kyungpook National University, Busan, Korea
[9]Argonne National Laboratory, Argonne, USA
[10]Physics Institute (NPI), Academy of Sciences of the Czech Republic, Czech Republic
[11]National Institute of Physics and Nuclear Engineering "Horia Hulubei", Bucharest – Magurele, Romania
[12]Japan Atomic Energy Agency, Tokai-mura, Japan
[13]Bhabha Atomic Research Centre, Mumbai, India
[14]University of Surrey, Guildford, UK
[15]Los Alamos National Laboratory, Los Alamos, USA
[16]Forschungszentrum Jülich Gmbh (FZJ), Jülich, Germany
[17]Institute for Nuclear Research, Hungarian Academy of Sciences, Debrecen, Hungary

Keywords: medical isotopes, decay data, cross section data, evaluated databases

Cancer management is a major medical and economic issue because of the increasing incidence of the disease in the world. The need for radioisotopes in both cancer diagnosis and therapy is very well established. These needs have been addressed through a series of IAEA Coordinated Research Projects running for the last 20 years.

Experimental data compilations, theoretical calculations and evaluations were carried out for many of the reactions of interest for isotope production and beam monitoring. The recommendations for both established and emerging radionuclides, and validation/testing of the cross-section production library are discussed. Issues in decay data and cross section evaluations will also be presented. The on-going project on "Nuclear Data for Charged-particle Monitor Reactions and Medical Isotope Production" and the recently developed IAEA Medical Portal designed for dissemination of isotope production will be reviewed.

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THIN LAYER ACTIVATION, RADIOACTIVE TRACERS AND NUCLEAR DATA

Ferenc Ditrói, Sándor Takács, Ferenc Tárkányi*

Institute for Nuclear Research, Hungarian Academy of Sciences, Bem tér 18/c, Debrecen, Hungary, *e-mail: ditroi@atomki.hu

Keywords: Thin Layer Activation (TLA), radioisotope production, radioactive tracers, wear measurement, production cross section

In the frame of a systematic study for establishment a data base for nuclear data of charged particle induced excitation function, cross sections and yield of radioisotopes suitable for Thin Layer Activation (TLA) base radioactive tracing are also collected separately. Taking into account the most important condition for a radioisotope to be suitable for TLA, a series of charged particle induced nuclear reactions have been measured and evaluated in order to establish a useful public database for the users of the radioactive tracing community.

These radioisotopes have been selected according to their large enough cross sections in the energy range of the available charged particle beams, according to their half-life proper to produce them, process them, deliver them and perform the corresponding measurements in a reasonable time interval. The proper gamma energy and its intensity is also a selection criteria.

The largest group of materials to be investigated is the construction materials used in industry, technology, nuclear industry, etc. These materials consist of pure elements such as iron, copper, aluminium, etc., but most of them are alloys containing more elements proper for activation as radioactive tracers. Another groups of technical materials, which does not contain any element proper for activation based on the above conditions. In this case the radioactive tracers should be produced separately and process it in a suitable physical and chemical form, and add it to the material in question with a properly chosen method (implantation, diffusion, mixing, etc.).

This work presents the principles and technical details of the wear, corrosion and erosion measurements by using thin layer activation with radioactive tracers as well as present the most recent results achieved in the field of nuclear data measurements for this purpose.

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CYCLOTRON PRODUCTION OF ^{99m}TC – REVIEW OF THE CURRENT STATUS

Ondřej Lebeda[1]**, Jan Ráliš*[1]*, Pavel Hradilek*[1]*, Adam Čepa*[1]*, Tomáš Vrba*[2]

[1]Department of Radiopharmaceuticals, Nuclear Physics Institute of the CAS, v.v.i., Husinec-Řež 130, Řež, CZ 250 68, Czech Republic,
*e-mail: lebeda@ujf.cas.cz
[2]Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Břehová 7, Praha 1, CZ 115 19, Czech Republic,
e-mail: tomas.vrba@fjfi.cvut.cz

Keywords: Tc-99m, cyclotrons, Mo-100, Mo-99 supply crisis, radionuclidic impurities, quality control

Radionuclide ^{99m}Tc ($T_{½}$ = 6.01 h) plays up to now the key role in nuclear medicine, being used in ca 80% of diagnostic imaging worldwide. It is now obtained from radionuclide generators ^{99}Mo/^{99m}Tc, where the parent ^{99}Mo ($T_{½}$ = 65.96 h) is produced in a few research nuclear reactors by fission of ^{235}U. Since 2008, the world of nuclear medicine experienced several severe shortages of the ^{99}Mo supply due to the unexpected shutdowns. This experience and risk associated with the age of the largest reactors resulted naturally in exploring alternative ways of ^{99}Mo or ^{99m}Tc production.

A promising concept seems to be highly decentralized cyclotron production of ^{99m}Tc via the ^{100}Mo(p,2n)^{99m}Tc. The installed number of medical cyclotrons (over 1000 worldwide) represents a natural network for simultaneous supply of ^{99m}Tc as pertechnetate for kit labellings and positron emitters for PET imaging.

We shortly summarize experimental data necessary for the yield calculation and for reliable forecast of the radionuclidic impurities content in the product. Actually, the profile of potential radionuclidic impurities is the only significant difference between the ^{99}Mo/^{99m}Tc generator eluate and the cyclotron-produced Sodium (^{99m}Tc) pertechnetate. Its impact on the on patient's radiation burden for expected range of production parameters (target enrichment, irradiation and cooling times, expiry time) is estimated and discussed.

We describe the key moments of the cyclotron production (targetry, target processing, ^{100}Mo recycling, compatibility of the cyclotron-produced ^{99m}Tc with established kits for production of radiopharmaceuticals, regulatory issues) and address its technical and economic challenges. We also give a survey of a set of analytical control methods that are implemented in a proposed monograph on Sodium (^{99m}Tc) pertechnetate (cyclotron-produced) in the European Pharmacopoeia.

Prompt gamma activation analysis

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DETERMINATION OF THERMAL NEUTRON CAPTURE CROSS SECTIONS FROM PROMPT GAMMA-RAY DATA

Richard B. Firestone

Department of Nuclear Engineering, University of California, Berkeley, CA 94720 USA; Lawrence Berkeley National Laboratory, MS-88R0192, Berkeley, CA 94730, USA

Keywords: γ-ray energy, γ-ray cross section, total radiative thermal neutron cross section, neutron beams

Thermal neutron capture cross sections are important for the production of radioisotopes, reactor calculations, activation analysis, dosimetry, nuclear medicine and a host of other applications. Precise γ-ray energies and cross sections were measured with thermal neutron beams at the Budapest Research Reactor for all natural elemental targets, except He, and compiled into the Evaluated Gamma-ray Activation File (EGAF) [1] as part of an IAEA Coordinated Research Project (CRP). These measurements were precisely standardized using stoichiometric compounds and mixtures [2] containing elements whose γ-ray cross sections are well known. Additional measurements have subsequently been mode on isotopically enriched targets at the Budapest and Garching FRM-2 Research reactors.

We have used these γ-ray cross sections to determine total radiative thermal neutron cross sections. In the case of light isotopes the neutron capture decay scheme is complete and we determine the cross section from the sum of γ-ray cross sections deexciting the capture state and feeding the ground state. For heavier isotopes the decay schemes are not complete because γ-rays from the continuum cannot be experimentally resolved yet contribute significantly to the total cross section. In those cases we use statistical models to calculate the continuum contribution and determine the total cross section by the equation $\sigma_0 = \Sigma\sigma_\gamma(\mathrm{GS})_{\mathrm{exp}} + \Sigma\sigma_\gamma(\mathrm{GS})_{\mathrm{calc}}$ where the continuum contribution feeding the ground state is calculated with the statistical model code DICEBOX [3]. In many cases we have also measured the cross sections for activation γ-rays and the total cross section can be determined from the decay scheme normalization or conversely the decay scheme normalization can be calculated from the total cross section. These methods typically give precisions of 1–2% and are usually more accurate than earlier measurements.

In this talk I will discuss the analysis techniques we have used with our measurements to determined cross sections and the statistical models that we have used. I will also discuss our progress on updating the EGAF database and developing a new database of thermal neutron capture cross sections.

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Radiation chemistry

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WATER PURIFICATION BY IONIZING RADIATION

László Wojnárovits, Erzsébet Takács*

Department of Radiation Chemistry, Institute for Energy Security and Environmental Safety, Centre for Energy Research, Hungarian Academy of Sciences, 1121 Budapest, Konkoly Thege út 29–33, Hungary, *e-mail: wojnarovits.laszlo@energia.mta.hu

Keywords: advanced oxidation processes, wastewater, hydroxyl radical, irradiation technology

The contamination of surface waters with recalcitrant, poorly degradable organic molecules, pesticides, pharmaceuticals, surfactants, etc. forces the chemists to develop new technologies for water treatment [1]. In the so-called Advanced Oxidation Processes (AOPs), highly reactive radical intermediates, mainly the hydroxyl radicals induce the degradation of organic molecules. These technologies mainly differ in the way of hydroxyl radical generation. In water treatment by ionizing radiation the radiolysis of water supplies the hydroxyl radicals. Due to the simple way of radical generation, as well as the well developed steady-state (irradiation with γ-rays and analysis of final products) and transient (irradiation with accelerated electrons and observation of the short-lived intermediates by optical spectroscopy) techniques radiolysis is very often used for investigation of the kinetics and mechanism of advanced oxidations. The number of research and technical papers on this field is well above 1000. The basic radiation chemistry and in some cases the details of chemical reaction are now well understood. The investigations refer to the decay of the starting compounds (discoloration) but very often the scientists follow the fate of the products till complete transformation to H_2O, CO_2 and other inorganic substances (mineralization). In the case of mineralization usually group parameters are measured such as the chemical oxygen demand, the biological oxygen demand and the total organic carbon content. Many studies are supplemented by toxicity measurements as well.

Irradiation technology is used in a large number of pilot plants and in a few full scale installations for wastewater treatment [2, 3]. All the installations use electron accelerator for this purpose and continuous flow through systems. The pilot plants may treat several hundred m^3 a day, whereas the capacity of full scale installations goes up 10,000 m^3/day.

In the lecture the theoretical background of water treatment by ionizing radiation is discussed showing the reaction kinetics and mechanism of pollutant degradation. From the point of view of economics of large scale application one of the most important questions is the selection of the electron accelerator. The applicable high-power electron accelerators will also be discussed together with the prices of installations and everyday operations. With the present knowledge the treatment price with 0.1–0.2 kGy absorbed dose is c.a. 0.1–0.2 USD/m^3.

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Radio- and nuclear analytical methods

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PHOTOCATALYTIC ABILITY AND ^{57}Fe-MÖSSBAUER STUDY OF IRON-CONTAINING SILICATE GLASS

S. Kubuki[1], Y. Iida[1], B. Kobzi[1], Z. Homonnay[2], E. Kuzmann[2], M. Ristić[3], S. Krehula[3], T. Nishida[4]

[1]Tokyo Metropolitan University, 1-1 Minami Osawa, Hachi-Oji, Tokyo 192-0397, Japan
[2]Eötvös Loránd University, Pázmány P. s. 1/A, 1117 Budapest, Hungary
[3]Ruđer Bošković Institute, Zagreb 10000, Croatia
[4]Kinki University, Kayanomori 11-6, Iizuka, Fukuoka 820-8555, Japan

A relationship between visible light photocatalytic ability and structure of iron-containing silicate glass with the composition of 15 Na_2O • 15 CaO • (70–x) • SiO_2 • $x$$Fe_2O_3$ (abbreviated as xNCFS, $0 \leq x \leq 50$ mass%) was investigated by ^{57}Fe-Mössbauer spectroscopy and methylene blue degradation test. ^{57}Fe-Mössbauer spectrum of xNCFS glass with 'x' of 50 heat treated at 1000 °C for 100 min composed of a paramagnetic doublet with the isomer shift *(d)* of 0.24 mm s^{-1} and quadrupole splitting *(D)* of 0.99 mm s^{-1} due to distorted $Fe^{III}O_4$ tetrahedra, and a magnetic sextet with d of 0.36 mm s^{-1} and internal magnetic field (H_{int}) of 51.8 T due to hematite [1]. Remarkable decrease in MB from 10.0 to 0.0 mmol with the rate constant *(k)* of 2.87×10^{-2} h^{-1} was observed for the degradation test using heat-treated 50 NCFS glass under visible light irradiation [1]. The larger k value of 9.26×10^{-2} min^{-1} was estimated for heat-treated iron aluminosilicate glass [2], indicating that iron silicate glass is an effective visible-light activated photocatalyst.

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Radioanalytical methods of long-lived radionuclides

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FAST, SENSITIVE AND ACCURATE: CHALLENGES TO RADIOANALYTICAL METHODS FOR DIFFICULT-TO-DETECT RADIONUCLIDES

Xiongxin Dai

China Institute for Radiation Protection, Taiyuan, China; Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Suzhou, China, e-mail: daixx@yahoo.com

Keywords: radioanalytical methods, difficult-to-detect radionuclides, environmental and biological samples

Over the past 70 years, the development of nuclear fission for nuclear weapon testing and nuclear power generation have led to global spread of both natural and artificial radionuclides in the environment at ultra-trace levels. This presents a potential threat to human health, since many of the fission/activation products are long-lived alpha- or beta-emitting radionuclides with high radio-toxicities (e.g., actinides and Sr-90). Thus, monitoring of the release of these radionuclides from the sources and understanding of their environmental behaviour are of high importance. However, sensitive and accurate determination of these radionuclides in low level environmental and biological samples is often very difficult, as many current radioanalytical methods are quite laborious, time-consuming and insufficient to meet the sensitivity requirements. Furthermore, rapid methods are urgently needed to shorten the sample analysis turn-around time for quick decision making in the event of a radiological/nuclear (RN) emergency. Even a small scale incident may generate hundreds of samples, and faster methods with increased sample analysis throughput are highly desired. Therefore, development of rapid methods for difficult-to-detect radionuclides with good speed and accuracy, using modern radiometric and advanced mass spectrometric techniques as well as emerging radiochemical separation technologies, is essential but remains a great challenge to radioanalytical chemists.

In this presentation, some newly developed methods for rapid determination of various difficult-to-detect radionuclides (including actinides, Ra-226, Po-210, Sr-90, Pm-147 and Fe-55) in a wide variety of environmental and biological samples (e.g., water, swipe, urine and faecal samples) will be overviewed, along with their applications in the fields of environmental radioactivity monitoring, emergency radioassay, nuclear forensics, and radio-hazard characterization, etc.

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RAPID DETERMINATION OF ACTINIDES IN SEAWATER SAMPLES

Sherrod L. Maxwell[1]*, *Brian K. Culligan*[1], *Jay B. Hutchison*[1], *Robin C. Utsey*[1], *Dan. R. McAlister*[2]

[1]Savannah River Environmental Laboratory, Aiken, SC, USA, *e-mail: sherrod.maxwell@srs.gov
[2]PG Research Foundation, Inc. Lisle, IL 60532, e-mail: dmcalister@eichrom.com

Keywords: actinides, rapid method, seawater, emergency

In light of the nuclear accident at Fukushima Daiichi Nuclear Power Plant in March, 2011, there is a need for rapid methods to determine actinide levels in seawater samples that can be applied quickly, with high chemical yields and effective removal of interferences. Laboratory methods that take one to two weeks to determine actinide levels in seawater are simply not rapid enough following a radiological release. The theft of nuclear material in Mexico [1] in 2013 highlights the need for nuclear safeguards and raises concerns about a radiological dispersive device (RDD) or "dirty bomb", again illustrating the need for rapid environmental methods. The measurement of actinide levels in seawater can be quite challenging, due to the difficulty of the seawater matrix and low detection limits required. Surface concentrations of plutonium in seawater, for example, are usually very low (<5 μBqL^{-1}), except for contaminated areas such as in the Irish Sea. [2] While fresh water sample aliquots taken for analysis are often 1 liter or less, seawater aliquots up to 200 liters or more have been analyzed to lower detection limits as much as possible. Unfortunately, many of the methods used provide chemical yields of only 30–60%. The time frame needed to determine actinide levels in environmental samples, including seawater samples, after a nuclear accident is in hours, not weeks, to allow appropriate assessment of environmental contamination as well as protection of the public and marine ecosystems.

A new rapid method for the determination of actinides in seawater samples has been developed at the Savannah River Environmental Laboratory. The actinides can be measured by alpha spectrometry or inductively-coupled plasma mass spectrometry (ICP-MS). The new method employs novel pre-concentration steps to collect the actinide isotopes quickly from 80–100 L of seawater. Following these rapid matrix removal steps, the actinides are separated using extraction chromatographic resins. Stacked TEVA Resin and TRU Resin cartridges are used to rapidly separate Pu, U, and Np isotopes from seawater samples. TEVA Resin and DGA Resin were used to separate Pu, Am and Cm isotopes in seawater for measurement. This robust method is ideal for emergency seawater samples or the routine analysis of seawater samples for oceanographic studies to enhance efficiency and productivity. Sample preparation time for this new method is <8 hours.

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SIMULTANEOUS DETERMINATION OF ACTINIDES USING DGA RESIN

*Nóra Vajda**, *Judit Groska, Patrícia Szeredy, Márton Zagyvai, Zsuzsa Molnár, Edit Bokori*

Radanal Ltd., Konkoly-Thege M. út 29–33, 1121 Budapest, Hungary, *e-mail: vajdanor@gmail.com

Keywords: actinides, DGA resin

A new procedure was developed for the separation of uranium, thorium, plutonium, neptunium and americium based on extraction chromatography using the N,N,N',N' tetraoctyldiglycolamide sorbed onto Amberchrom CG-71 (available as DGA resin® from Triskem International).

The dissolved sample was loaded from a reductive media in 4M HCl and the actinides were sequentially eluted changing the nature and the acidity of the eluents, the oxidation states of the given actinides, the concentration of the complexing agent, and the temperature. Conditions of the sequential elution were optimized by series of model experiments. 0.5 M HNO_3 solution was selected as the elution media for all actinides except Am. The following elution sequence was realized: (i) The least retained uranium species were stripped from DGA as U(VI) after on-column oxidation under moderate conditions using 4M HNO_3 at 30 °C. During this process the oxidation of Pu and Np to non-retained species of Pu(V), Pu(VI) and Np(V), Np(VI) was neglectable. (ii) Oxalic acid as a strong complexing agent was selected to strip the tetravalent actinides, i.e. Th and Np(IV). It was proved that trivalent actinides form less stable complexes with oxalic acid than tetravalent ones. Therefore Pu was on-column reduced to Pu(III) and kept on the DGA together with Am(III) while Th and Np(IV) were stripped. (iii) Pu(III) was oxidized on-column to Pu(IV) or to higher oxidation states using the strong oxidizing agent $K_2S_2O_8$. It was stripped from DGA probably as oxalate complex while Am was still retained on DGA. (iv) Finally, Am was stripped with 0.5M HCl. It was recognized that the extraction chromatographic processes on DGA at room temperature are often slow and irreproducible. The chromatograms became reproducible after a strict temperature control. Slight increase of the temperature could accelerate the oxidation reaction and the elution, as well. E.g., on-column oxidation of uranium with 4M HNO_3 at 30 °C was possible, and the temperature increase to 40 °C accelerated the rather slow elution of Th and Np(IV) complexes.

Alpha sources were prepared by micro-co-precipitation from the strip solutions without further processing.

The method was successfully applied for the determination of the alpha emitting isotopes of U, Th, Np, Pu and Am in radioactive waste samples after destruction and pre-treatment (co-precipitation with $Fe(OH)_2$) of the samples. The method was also applied for the determination of Am in urine samples without any pre-treatment (destruction, pre-concentration) of urine. Overall recoveries for all actinides were higher than 50%. The alpha sources were free of contaminants of other actinides.

Radioecology and environmental radioactivity

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ON THE PLUTONIUM ISOTOPIC COMPOSITION IN EAST ATLANTIC SURFACE WATERS, LEVELS AND TRENDS

Mats Eriksson[1], Isabelle Levy[2], Elena Chamizo[3], Janine Gastaud[2], Kirsi Ämmälä[4], Jan Scholten[5]*

[1]Swedish Radiation Safety Authority, SE-171 16 Stockholm, Sweden, e-mail: mats.eriksson@ssm.se
[2]Environment Laboratories, International Atomic Energy Agency, MC 98000 Monaco, e-mail: I.N.Levy@iaea.org
[3]Centro Nacional de Aceleradores (Universidad de Sevilla, Consejo Superior de Investigaciones Científicas, Junta de Andalucía).
Thomas Alva Edison 7, 41092, Seville, Spain, e-mail: echamizo@us.es
[4]Laboratory of Radiochemistry, University of Helsinki, Finland
[5]Institute of Geosciences, University Kiel, 24118 Kiel, Germany, e-mail: js@gpi.uni-kiel.de
*(1956–2011)

Keywords: plutonium isotopes, ratios, sea water, Atlantic, GEOTRACES, AMS, alpha spectrometry

The South Atlantic Ocean has the lowest concentration and inventory of plutonium of the world’s oceans due to the low input from stratospheric fallout. Furthermore, no major known nuclear tests resulting in local fallout and nuclear reprocessing have been conducted in the area. Due to the global ocean circulation system, dissolved plutonium can be transported over large distances that eventually can result in an increase of Pu in the south Atlantic. It is well established that the Pu-isotopic composition in the Pacific Ocean differs from the stratospheric global fallout found on land and from the composition in North Atlantic and Arctic Ocean. These differences enable us to use dissolved plutonium in seawater as an oceanographic tracer. So far, few data exist on seawater Pu concentrations and isotopic composition in the South Atlantic.

During GEOTRACES pre-cruise ANT XXX-1 in 2005 from Bremerhaven, Germany, via Vigo (Spain) to Cape Town, (South Africa) surface water samples from 19 stations were obtained. Plutonium was sampled using an *in-situ* absorption MnO_2 cartridge system. Large volumes (956 l – 2700 l) of surface water were sampled by passing seawater at a flow rate of 2.8±0.7 l/min through the system. All samples were taken to the home laboratory for further radiochemical purification. After chemical purifications, Pu isotopes were measured by alpha spectrometry, and selected Pu cartridges samples were analysed by an Accelerator Mass Spectrometry (AMS) to determine $^{240}Pu/^{239}Pu$ isotopic ratios.

The highest surface water Pu concentrations were found in the region of the Canary Islands and the West African coast (~3.7 µBq/l of ^{239,240}Pu) probably indicating aeolian input from Sahara. The lowest concentration was found in the oligotrophic Angola basin (~0.3 µBq/l of ^{239,240}Pu). From the Angola basin towards the Cap basin concentrations increase. The ^{238}Pu/^{239,240}Pu activity ratios increase from the northern stations (~0.04) towards the southern stations (~0.1). The lower ratios at the Northern stations agree with the stratospheric fall out ratio (~0.03). The higher ratios in the eastern South Atlantic could be a result of Pu released during the SNAP 9A satellite re-entry over the Mozambique Channel in 1964 that increased the ^{238}Pu/^{239,240}Pu ratio in the Southern hemisphere. The ^{240}Pu/^{239}Pu atom ratio shows a linear trend from 0.18 in the Northern stations to 0.21 in the Southern stations. This might indicate that some surface water originates from the Pacific Ocean (where the ^{240}Pu/^{239}Pu ratio is about 0.23) or that an unknown source of Pu with a higher ratio than the global fallout is present in the South Atlantic.

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MODIFICATION OF THE UPTAKE OF ^{239}Pu AND ^{241}Am BY WHEAT PLANTLETS BY APPLICATION OF INORGANIC FERTILIZERS

Francisco Javier Guillén[1]*, *Juan Gabriel Muñoz-Muñoz*[1], *Antonio Baeza*[1], *Alejandro Salas*[1], *Nicolae Mocanu*[2]

[1]LARUEX. Department of Applied Physics, Faculty of Veterinary Science, University of Extremadura, Avda. Universidad, s/n, 10003, Cáceres, Spain, *e-mail: fguillen@unex.es
[2]Department of Life and Environmental Physics, Horia Hublei National Institute of Research and Development for Physics and Nuclear Engineering, 30 Reactorului Street, Magurele-Bucharest, Ilfov, P.O. Box MG-6, RO-077125, Romania

Keywords: plutonium, americium, wheat, transfer, plant, fertilizer

Inorganic fertilizers have been used as agricultural countermeasures to reduce the uptake of anthropogenic radionuclides released into the environment. They were mainly focused on radiocaesium and radiostrontium, and there are fewer data on other radionuclides also released, such as ^{239}Pu and ^{241}Am. Wheat plantlets were grown under controlled laboratory conditions on a limited amount of soil with a known activity of ^{239}Pu and ^{241}Am, in order to analyze the influence of two common inorganic fertilizers, NPK and diammonium phosphate (DAP) at different rates. As these rates increased, the uptake of ^{239}Pu and ^{241}Am to the whole plantlet also increased compared to control experiences, in which no fertilizer was added. This increase was higher for DAP fertilizer than for the NPK one, which might be due to the higher supply of P_2O_5 and NH_4^+ provided by DAP fertilizer to the soil in comparison with NPK fertilizer. The radionuclide distribution within the plantlet was not homogeneous. Root content was higher than shoots for control and fertilized experiences, suggesting low mobility of ^{239}Pu and ^{241}Am within the plantlet. The ^{239}Pu and ^{241}Am content in root increased with the fertilizer rate, but practically no effect was observed in shoots. Their content remained almost the same, and only decreased slightly with NPK.

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SIMPLIFIED MODELING IN DYNAMIC COLUMN TECHNIQUE FOR THE DETERMINATION OF RADIONUCLIDE TRANSPORT PARAMETERS IN SYSTEMS OF SOLID GRANULAR MATERIALS AND GROUNDWATER

*Š. Palágyi**, *K. Štamberg*, *D. Vopálka*

Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, 115 19 Prague, Czech Republic, *e-mail: istvan.palagyi@email.cz

Keywords: crushed crystalline rock and soil columns, pulse and continual groundwater inlets, linear and non-linear equilibrium sorption/desorption isotherms, 1-D advection, dispersion equation, breakthrough curves

Deep geological disposal of high-level radioactive waste and spent nuclear fuel into earth crust formations requires studies on the behavior of the surrounding environment towards transport of radionuclides, which may enter the groundwater as a possible source of drinking or irrigation water in case of the failure of engineering barriers of a repository. For the evaluation of the ability of environment to retain radionuclides and prevent them to transfer into groundwater is necessary to know some important transport parameters. The most important amongst them are the retardation *(R)* and dispersion *(K_d)* coefficients. The retardation coefficient can be calculated indirectly from the distribution coefficient, determined in batch test, which is a convenient laboratory method. However, the distribution coefficient determined by static batch method for the characterization of the retardation properties of the environment, in the so-called K_d-model, seems too simple to represent the complex host rock-groundwater system, especially if a non-linear equilibrium isotherm holds.

For the determination of K_d it is more effective to use dynamic transport process, where the groundwater flows through the column of a porous (granular) solid material (core or fractured rock, soil, or sediment). In this laboratory technique, the retardation coefficient can be evaluated directly using the experimental through-flow data and then distribution coefficient is calculated from *R* and by hydraulic data. Moreover, dynamic column experiments make possible to observe the sorption, or desorption during transport of a contaminant by water through the bed under saturated or unsaturated conditions. Contrary to static method, the hydrodynamic dispersion coefficient *(D_d)* can also be determined by this column technique.

In comparison with the batch operation (closed arrangement), there are several substantial advantages of the column operation (open arrangement). Above all the dynamic arrangement is much closer to conditions existing in the environment, the aqueous volume to mass ratio is incomparable more realistic, the build-up of interfering products is greatly limited, the change of material quality during test is insignificant, there is a possibility to apply undisturbed materials (core samples), it enables to keep a fine structure and specificity of the sample, and allows easier differentiation of reversible and irreversible portions of sorbed and desorbed contaminants. On the other hand, the advantages of static, batch method lie in a much more simple experimental apparatus, the possibility to attain equilibrium radionuclide distribution state and the better reproducibility of results.

The most widely used column technique and their evaluation is given in this paper. The evaluation is based on the application of the analytical solution a 1-D advection-dispersion equation (ADE) under defined boundary conditions, namely for both pulse and continual input of a radioactive solute. The determination of transport parameters in both input techniques are solved by the construction and fitting the experimental breakthrough curve, which is a function of a relative radioactivity concentration on the number of pore volumes at the column outlet. The experimental breakthrough curve is dependent, beside the input conditions, also on the sorption and desorption equilibrium isotherms, equilibrium or non-equilibrium dynamics, and physical properties of the column, etc.

It has been shown that the method of evaluation can be used in the case of validity of linear (K_d-model), or a non-linear (Freundlich – model) sorption isotherm. The experimental data are fitted on a point wise basis using the Newton-Raphson multidimensional non-linear iteration procedure, in which the regression function consists of the above mentioned AD equation and equation for the retardation coefficient including the K_d quantity, or the first derivative of Freundlich equation. Values of basic parameters, namely K_d or two Freundlich equation parameters (K_F and n) and Peclet number, are sought in the course of the regression procedure. Applicability of the method has been demonstrated on the evaluation of breakthrough curves of several hygienically important radionuclides obtained by dynamic flow column experiments.

The aim of this presentation is to inform on the work carried out in our department on the determination of transport parameters of radionuclides in systems made of various solid crushed granitic and soil materials, sands and disturbed or undisturbed soil cores with synthetic groundwater, containing nonreactive and/or reactive tracers.

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FOOD SAFETY AFTER FUKUSHIMA: THE BEEF ISSUE

Georg Steinhauser

Leibniz Universität Hannover, Germany

After the Fukushima nuclear accident Japanese authorities dedicated enormous efforts to secure food safety for the public. Although our recent analyses have shown that the monitoring has been very effective for most food categories, beef proved to be the only major food category that has been more problematic. Our analyses revealed a much lower effectiveness of the monitoring action for beef. The author speculates that, by following the governmental monitoring manual (which gives “meat” only second priority), the sudden exceedances caught the monitoring agencies unprepared and triggered a much higher density monitoring of beef with the delay of several weeks. Even then, many above limit items reached the market (mainly because the monitoring during this period had focused on the post-market). Therefore, it is likely that some above-limit beef has been consumed by the public.

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USE OF MOSSES FOR MONITORING ATMOSPHERIC DEPOSITION OF RADIONUCLIDES – POSSIBILITIES AND LIMITATIONS

Eiliv Steinnes

Department of Chemistry, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway, e-mail: eiliv.steinnes@ntnu.no

Keywords: atmospheric deposition, radionuclides, monitoring, moss samples

Samples of naturally growing moss have been extensively used in Europe over the last 40 years for large-scale monitoring of atmospheric deposition of trace metals. As radioactive isotopes of an element behave the same way as the corresponding stable isotopes under equilibrium conditions there is no reason why moss sampling could not be used for monitoring of radionuclides as well, provided that the moss technique works for the corresponding stable elements. There have been some reports in the literature on the use of this approach for the study of radionuclides in natural (^{7}Be, ^{210}Pb, ^{210}Po – –) as well as anthropogenic processes (^{131}I, ^{137}Cs, ^{90}Sr, ^{95}Zr-^{95}Nb, ^{140}Ba-^{140}La, ^{239}Pu, ^{240}Pu, ^{241}Am), but most of these efforts have been limited in time and space, and very few of them have considered in detail the mechanisms involved in the fixation of the radionuclides to the moss surface and the character and strength of the binding.

From studies of trace element deposition it is known that metals may be fixed to the moss surface bound to particles as well as attached to the moss surface in free state by electrostatic or chemical bonds, and the feasibility of the moss monitoring technique for an element depends on the chemical property of the elements and its physical or chemical association with other substances in the atmosphere. These facts have not always been considered critically in monitoring studies employing moss samples for mapping deposition of radionuclides. Several investigations have been reported on geographic distribution of ^{137}Cs in moss, but most frequently without considering the interaction of Cs with the moss. It has been shown that the Cs ion is transported in the moss plant from the older to the younger annual growth increment [1, 2]. This was clearly demonstrated in a study from Belarus where the original atmospheric deposition pattern from the Chernobyl accident was evident in moss samples collected over 20 years after the accident [3].

The present talk will briefly review the literature on monitoring of radionuclides in air using mosses and discuss some of the possible problems based on general experience with this technique applied to stable forms of trace elements.

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Radiolabeled compounds and radiopharmaceuticals

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DEVELOPMENT OF A THERANOSTIC LIPOSOMAL DRUG DELIVERY SYSTEM FOR RADIONUCLEOSIDES

Zoltán Varga[1], Rita Dóczi[2], Krisztián Szigeti[3], Ildikó Horváth[3], Dániel S. Veres[3], Domokos Máthé[4], Marion Roller[5], Agnieszka Morgenroth[5], Nils Bornwasser[6], Uwe Königs[5, 6], Andreas Vogg[5]

[1]Biological Nanochemistry Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar tudósok körútja 2, H-1117 Budapest, Hungary, e-mail: varga.zoltan@ttk.mta.hu
[2]Institute of Nuclear Techniques, Budapest University of Technology and Economics, H-1111 Budapest, Hungary
[3]Department of Biophysics and Radiation Biology, Semmelweis University, H-1094 Budapest, Hungary
[4]CROmed Translational Research Centers, H-1047 Budapest, Hungary
[5]University Hospital of the RWTH Aachen, Clinic for Nuclear Medicine, D-52057 Aachen, Germany
[6]FH Aachen, University of Applied Sciences, Campus Jülich, D-52428 Jülich, Germany

Keywords: endoradiotherapy, nucleoside analogs, targeted drug delivery, multimodal imaging

Many cancerous cells exhibit intensified metabolism, which also concerns the enhanced uptake of the building blocks of DNA, namely the nucleosides. Nucleoside analogues containing a radioactive isotope which emits Auger radiation effectively degrade the DNA of the cancer cells, but on the other hand the efficiency of this approach is limited by the fact that only a small fraction of the intravenously administered radionucleosides reaches the target cells. The main aim of this work was to establish a multimodal liposomal drug delivery platform for radionucleosides for combined diagnostic and therapeutic use in cancer treatment (theranostics).

In the present work we have developed a liposomal nanocarrier system for the delivery of a thymidine analog, [I-125]5-iodo-2'-deoxyuridine (IdUrd) by using its lipid conjugate. Esterification was performed with hexanoic and oleic anhydride, and the product was purified by reverse phase HPLC. Incorporation of the lipid conjugated IdUrd into the liposomes was monitored by size exclusion chromatography.

Labeling of the liposomes with 68-Ga for PET imaging was performed by using a DTPA-conjugated phospholipid, while fluorescent labeling was achieved with a nitrobenzoxadiazole (NBD) fluorophore conjugated phospholipid.

Antigen specific targeting of the liposomal nanocarrier to cancer cells was achieved by covalent attachment of a prostate-specific membrane antigen (PSMA) ligand, namely the dipeptide Glu-urea-Lys. PSMA is highly overexpressed in prostate cancer, therefore it presents an excellent target in some novel diagnostic and therapeutic treatments. The PSMA-ligand containing a primary amine-group was attached to the liposomes by incorporating an N-hydroxysuccinimide activated polyethylene glycol – lipid conjugate (DSPE-PEG2000-NHS).

In vitro binding with PSMA-targeted and fluorescently labelled liposomes in MDA-MB231 (PSMA positive) and PC-3 (PSMA negative) cell lines was evaluated by flow cytometry analysis, which revealed specific binding of the PSMA-targeted liposomes to the PSMA positive cells.

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SYNTHESIS AND EVALUATION OF ^{18}F-LABELED INDOLE-BASED ANALOGS AS HIGHLY SELECTIVE SIGMA-2 RECEPTOR PROBES

Liang Wang[1], *Jiajun Ye*[1], *Winnie Deuther-Conrad*[2], *Yingfang He*[1], *Jinming Zhang*[3], *Jörg Steinbach*[2], *Peter Brust*[2], *Hongmei Jia*[1]*

[1]Key Laboratory of Radiopharmaceuticals (Beijing Normal University), Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, China, *e-mail: hmjia@bnu.edu.cn

[2]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Radiopharmaceutical Cancer Research, Department of Neuroradiopharmaceuticals, 04318 Leipzig, Germany

[3]Nuclear Medicine Department, Chinese PLA General Hospital, Beijing 100853, China

Keywords: F-18, sigma-2 receptors, indole-based analogs

Objectives: The sigma-2 (σ_2) receptors are overexpressed in a wide variety of human and rodent tumor cells and play a pivotal role in cancer biology [1, 2]. Moreover, they showed an approximately 10-fold higher expression in proliferating tumor cells compared to that in quiescent tumor cells. And thus, they proved to be a unique receptor-based biomarker of cell proliferation in solid tumors [3]. Herein we report the synthesis and evaluate of a series of indole-based analogs with 5,6-dimethoxyisoindoline or 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline moiety as highly selective σ_2 receptor ligands.

Results and discussion: The newly synthesized indole-based analogs showed low nanomolar affinity for σ_2 receptors ($K_i(\sigma_2)$ = 1.79–5.23 nM) and excellent subtype selectivity ($K_i(\sigma_1)/K_i(\sigma_2)$ = 56–708). The carbon chain length of the linker between the indole group and 5,6-dimethoxyisoindoline or 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline moiety displayed significant influence on the subtype selectivity. The compounds with a butyl linker exhibited highest subtype selectivity. We synthesized 2-(4-(4-(2-[^{18}F]fluoroethoxy)-1*H*-indol-1-yl)butyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline and 1-(4-(5,6-dimethoxyisoindolin-2-yl)butyl)-4-(2-[^{18}F]fluoroethoxy)-1*H*-indole. The log *D* values of the above radioligands are 2.17 ± 0.13 and 2.14 ± 0.02, respectively. The *in vivo* biological evaluations are in progress.

Conclusions: These findings suggest that ^{18}F-labeled indole-based ligands warrant further evaluation as potential PET radiotracers for σ_2 receptor imaging.

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PREPARATION AND APPLICATIONS OF ^{99m}TC LABELED DITHIOCARBAMATE COMPLEXES AS RADIOPHARMACEUTICALS

Junbo Zhang

Key Laboratory of Radiopharmaceuticals, Ministry of Education; College of Chemistry, Beijing Normal University, Beijing, 100875, China, e-mail: zhjunbo@bnu.edu.cn

Keywords: ^{99m}Tc, labeled, dithiocarbamate, radiopharmaceuticals

Dithiocarbamate compounds have been the focus of medicinal chemistry in recent years because of their unique molecular structure with a variety of biological properties, such as anti-tumor and anti-bacterium. Due to the favourable characteristics of ^{99m}Tc (ideal half-life, optimal γ-energy, inexpensive cost and in-house availability) and larger number of single photon emission computed tomography (SPECT) scanners in the world, there has been great interest in developing novel ^{99m}Tc-labeled radiotracers for SPECT imaging. Among ^{99m}Tc labeled radiopharmaceuticals, dithiocarbamate compounds contain two sulfur atoms that can easily chelate with ^{99m}Tc, thus making it feasible to prepare several stable ^{99m}Tc complexes as novel potential radiopharmaceuticals. This review summarizes the preparation and potential applications in nuclear medicine of previous reported ^{99m}Tc labeled dithiocarbamate complexes and discusses future prospects of this class of imaging agents.

Radionuclide separation

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ISOLATION OF NO-CARRIER-ADDED RADIOMANGANESE FOR POSITRON EMISSION TOMOGRAPHY

Martin Buchholz, Ingo Spahn, Heinz H. Coenen, Bernd Neumaier*

Institut für Neurowissenschaften und Medizin, INM-5: Nuklearchemie, Forschungszentrum Jülich, 52425 Jülich, Germany,
*e-mail: i.spahn@fz-juelich.de

Keywords: radiomanganese, $^{51, 52m, 52g}$Mn, non-standard PET nuclides, ion exchange chromatography

The natural mono-isotopically occurring ^{55}Mn is an essential trace element in the mammalian body and is currently increasingly used in animal research studies with Manganese Enhanced Magnetic Resonance Imaging (MEMRI). The divalent manganese ion can enter neuronal cells via voltage gated calcium channels and is in addition a strong T_1 contrast enhancing agent. Due to its increased uptake in excited nerve cells it can be used for the visualization of neuronal activity in the heart and especially in the brain. In the case of brain imaging, it enables tracing the neuronal pathways and even displaying the complete cytoarchitecture after systemic dose application by MEMRI in animals. However, high doses of free manganese cations have neurotoxic effects in the brain and may lead to symptoms similar to Parkinson's disease. Therefore, MEMRI operates normally at the lowest mass of contrast agent possible, but has still not been approved for application in humans. Its use for bi-modal PET/MR-imaging might be a valuable evaluation tool, bringing this method closer to human application.

The $^{nat.}$Cr(p,xn)-process is a very efficient route for production of ^{52g}Mn ($T_{1/2}$ = 5.59 d). Based on measurements of distribution coefficients with different media and ion-exchange resins, an optimized chromatographic separation of radiomanganese from ^{nat}Cr with the resin Amberlite CG400 was developed. Using this system ^{nat}Cr is eluted first with an acetic acid/methanol 1:1 mixture at room temperature and ^{52g}Mn thereafter with 3 M HCl at 50 °C. Within a separation time of 4 h the method yielded 99.5% of the n.c.a. ^{52g}Mn in 2–3 mL of 3 M HCl. An ICP-MS analysis revealed a chromium impurity of 0.07 mg (0.014%) in the final solution. Thus this separation method provides the purest form of ^{52g}Mn so far.

In search for a new and more facile method for the radiochemical separation of ^{52g}Mn from ^{nat}Cr for future use, e.g. labelling of T_1 MRI contrast agents, the measurement of distribution coefficients proved an indispensable tool to evaluate the viability of different chromatographic separation systems. Using an acetic acid/methanol 1:1 mixture on the anion exchange resin Amberlite CG400, a nearly quantitative adsorption of ^{52g}Mn was found, with nearly no adsorption of ^{nat}Cr.

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CONVERTER TARGET CHEMISTRY – A NEW CHALLENGE TO THE RADIOANALYTICAL CHEMISTRY

Susanta Lahiri[1], Moumita Maiti[2], Dibyasree Choudhury[1]*

[1] Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata-700064, India, *e-mail: susanta.lahiri@saha.ac.in
[2] Department of Physics, Indian Institute of Technology Roorkee, Roorkee-247667, India, e-mail: moumifph@iitr.ac.in

Keywords: converter targets, lead bismuth eutectic (LBE), astatine radionuclides, precipitation

The next generation RIB facilities plan to use huge volume of converter target, which will be bombarded by 1.4 GeV high flux proton beam to convert proton to neutrons. The emitted neutrons will hit the kilogram amount of fissile materials to produce radioactive ion beams of at least 100 times enhanced intensity than the current facilities including very recently commissioned HIE-ISOLDE at CERN or SPIRAL2 at GANIL. The proposed converter targets are liquid Hg or liquid lead bismuth eutectic. Besides the use of converter target in RIB facilities, they can also be a huge source of useful radionuclides for the benefit of mankind, which became more relevant after the Fukusima incident. Recently an inventory of radionuclides produced in LBE matrix by the impact of 1.4 GeV proton beam has been made [1]. The separation of these radionuclides from manifold scaled up target materials is a challenge to the radioanalytical chemists. According to reference [2] ^{211}At will be produced in very thick LBE target when bombarded by 1.4 GeV proton beam through complex nuclear process. In addition, large amount of radiotoxic polonium radionuclide will also be produced in the LBE matrix.

We have simulated above condition using low energy accelerators. We irradiated 6.5 mg/cm^2 LBE target by 40 MeV alpha particles for 7.3 h with an average beam current 0.3 mA and total integrated charge of 6266 mC. The irradiation was carried out at Variable Energy Cyclotron Centre, Kolkata, India. The irradiated matrix was assayed for quantitative analysis of various radionuclides produced in the matrix. In the experimental condition 3.9 MBq ^{210}At, 0.2 MBq ^{209}At along with 0.9 MBq ^{207}Po and 0.02 MBq ^{205}Po were produced in the matrix. Afterwards the irradiated sample was dissolved in 0.1 M HCl. The precipitation technique was applied with oxalic acid, $K_2Cr_2O_7$, NH_3 and $AlCl_3$. It has been found that $AlCl_3$ is the most efficient agent for separation of At radionuclides from bulk lead and bismuth as well as from radiotoxic polonium radionuclides. When drop wise $AlCl_3$ was added in ammoniacal condition to the solution bulk lead and bismuth along with polonium quantitatively precipitated leaving 98.6% astatine in the supernatant. The developed method is rapid, quantitative and from the green chemistry point of view it requires no organic or carcinogenic reagents.

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OPTIMIZATION OF RADIOISOTOPE QUALITY BY BOND RUPTURE

Bert Wolterbeek[1, 2], Marcel de Bruin[2], Rupali Bhardwaj[2], Josette Moret[2], Pablo Serra Crespo[2], Jorge Gascon[3], Ruud van Ommen[3], Antonia Denkova[2]

[1]Reactor Institute Delft (RID), Mekelweg 15, 2629 JB Delft, the Netherlands, e-mail: H.T.Wolterbeek@tudelft.nl
[2]Department of Radiation Science and Technology, Delft University of Technology, Delft, Faculty of Applied Sciences, the Netherlands
[3]Department of Chemical Engineering, Delft University of Technology, Delft, Faculty of Applied Sciences, the Netherlands

Apart from yield in radioisotope production, today's nuclear medicine asks for more and more attention for (radiochemical, chemical) purity and high specific radioactivity [1]. Here, purity applies not only to the direct medical application, but also to eventual management of hospital waste: possible coproduced longer-lived activity that is not discarded before use of the intended radioisotope may not only seriously affect treatment options, but has also consequences for later procedures and options (legislation) in disposal. Here, the concepts of specific activity, radioactivity concentration, carrier, carrier-free, and no-carrier-added have been [2–4] and should be continuously discussed as to their relevance, clarity, consistency, and to how these radioisotope characteristics contribute to radioisotope quality in nuclear medicine applications.

The presentation addresses these issues, and focuses on bond rupture processes in radioisotope production. Bond rupture should be interpreted here as the splitting off of the intended radioisotope from its chemical and/or radiochemical environment, by whatever process, to reach the intended high quality end-product. Examples are given that show both the absence of the need for the highest possible specific activity (e.g. ^{99}Mo) and the need for "as-near-as-possible to massless" and of the highest possible radiochemical purity (e.g. ^{99m}Tc, ^{177}Lu), in all cases in dependence of the radionuclide's position in the production and application chain and its eventual use in nuclear diagnostics or – therapy.

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ORAL PRESENTATIONS

Actinide analytical chemistry

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U(V) STABILIZATION IN OXO-MATERIALS: ALIOVALENT SUBSTITUTION AND EXTREME PRESSURE EFFECT

Evgeny V. Alekseev[1, 2]**, Bin Xiao*[1]*, Philip Kegler*[1]*, Sergey Novikov*[3]*, Dirk Bosbach*[1]*, Ivan Pidchenko*[4]*,*
Tonya Vitova[4]*, Piotr Kowalski*[1]

[1]Institut für Nukleare Entsorgung, Forschungszentrum Jülich, 52428 Jülich, Germany, *e-mail: e.alekseev@fz-juelich.de
[2]Institut für Kristallographie, RWTH Aachen University, Jägerstraße 17–19, 52066 Aachen, Germany
[3]Samara State University, Akademik Pavlov Street 1, 443011 Samara, Russian Federation
[4]Institut für Nukleare Entsorgung, KIT, D-76344 Eggenstein-Leopoldshafen, Germany

Keywords: uranium, oxides, valence states, extreme conditions, polymorphism, synthesis

Actinides show a great diversity in their chemistry due to the complex structure of *5f* electron shells. One of the most remarkable properties of early actinides is multi valence which has a very strong influence on their chemical and physical properties. Uranium owns the valences from II to VI in solid state, where IV and VI are the most usual and stable. In spite of the environmental importance and fundamental interest, the reports on pentavalent uranium remain quite rare. The facile methods of pentavalent uranium materials stabilizing are still of great challenge. Here we present two methods of U(V) stabilization: by aliovalent substitution and reactions under extreme conditions.

The first case is a complex system where the oxidation state of uranium can be rationally altered through incorporation of cations with different sizes and charges, so called aliovalent substitution. We can demonstrate that the hexavalent uranium (U(VI)) and pentavalent uranium (U(V)) can be stabilized in $Ca(U^{VI}O_2)W_4O_{14}$ and $[Ln(U^{V}O_2)W_4O_{14}]$ (Ln = Nd, Sm, Eu, Gd, and Yb), respectively. The studied phases are structurally similar to *iriginite*, a natural U(VI) mineral and the Ln cations are the surrogate elements for trivalent actinides such as Am^{3+} and Cm^{3+}. The detailed crystal structures, proposed charge-compensating mechanism and spectroscopic investigations of these compounds were performed in respect to uranium valence state and lanthanide cations influence on U(V) stabilisation within the framework. We confirmed U(V) stabilization using state of the art methods such as U M_4 edge high energy resolution X-ray absorption near edge structure (HR-XANES). This study demonstrates a possibility to precisely tune and stabilize U(V) within the complex oxo-phases.

The second case is a U(VI) conversion to U(V) via UO_3 transformation into a new modification of U_2O_5 with an extraordinary high density. We have showed that under very high pressure and temperature (10GPa/1200 °C), UO_3 can be reduced to U_2O_5 within the oxo-borate matrix. The crystal structure of resulting HP (high pressure)-U_2O_5 is dramatically differs from ambient pressure polymorph so called delta-U_2O_5. The structure of HP-U_2O_5 is more related to the cubic UO_2 than to the layered delta-U_2O_5. Using state of the art ab initio methods we reveal the stability ranges of both ambient and high pressure forms of U_2O_5 and demonstrated a potential pathway of their behaviour under ambient pressure and air atmosphere. This research is a first look on the U(V) oxide chemistry under extreme conditions of pressure and temperature.

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COMPLEX FORMATION OF EUROPIUM AND CURIUM WITH THE DIGESTIVE ENZYME ALPHA-AMYLASE

Astrid Barkleit[1], *Anne Heller*[2], *Atsushi Ikeda-Ohno*[1], *Gert Bernhard*[1]

[1]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstr. 400, 01328 Dresden, Germany,
e-mails: a.barkleit@hzdr.de, a.ikeda@hzdr.de, g.bernhard@hzdr.de
[2]Technische Universität Dresden, Institute of Zoology, Division of Molecular Cell Physiology and Endocrinology, Dresden, Germany,
e-mail: anne.heller@tu-dresden.de

Keywords: lanthanides, actinides, body fluids, saliva, laser-induced fluorescence spectroscopy

In case of the incorporation of radioactive heavy metal ions, they would represent a serious health risk to humans due to their chemo- and/or radiotoxicity. Trivalent actinides (An(III)) like Am(III) or Cm(III) are man-made radioactive elements exclusively generated in nuclear reactors, whilst non-radioactive lanthanides (Ln(III)) are naturally occurring elements having wide technological and medical applications. These heavy metals have a potential risk of intake into humans with different pathways. Since Ln(III) and An(III) are considered to have no significant essential function in the human body, little is known about their biochemical behaviour from the uptake, *in-vivo* transport to the final accumulation or excretion.

Our recent studies on the speciation of U(VI) and Cm(III) in body fluids (*e.g.,* saliva) suggested α-amylase as a potential binding partner of these actinides [1, 2], which would finally affect the biochemical behaviour of these elements *in-vivo*. The enzyme α-amylase is one of the major enzymes in salivary and pancreatic secretions of mammals and catalyses the hydrolysis of polysaccharides like starch or glycogen. In order to further understand the potential role of α-amylase in the *in-vivo* speciation and complexation of Ln(III) and An(III), we investigated the complexation of Eu(III) and Cm(III) with α-amylase over a wide pH range by using time-resolved laser-induced fluorescence spectroscopy (TRLFS). Based on the obtained spectroscopic results, stability constants were determined at ambient and physiological temperature. The data were further extrapolated to infinite dilution to make the obtained data compatible with the existing thermodynamic database. The speciation of Eu(III) and Cm(III) in the saliva studied were determined based on these new data and will be presented.

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ANALYSIS OF ACTINIDES IN SOLID SAMPLES AFTER DIGESTION BY LITHIUM BORATE FUSION

Ljudmila Benedik, Miha Trdin

Jožef Stefan Institute, Ljubljana, Slovenia, e-mails: ljudmila.benedik@ijs.si, miha.trdin@ijs.si

Keywords: uranium, americium, plutonium, alkaline fusion, separation techniques, alpha-particle spectrometry

One of the most important requirements in radiochemical analysis is total digestion of a solid sample before radiochemical separation. It is well known that soil samples are often considered one of the most difficult matrices to digest. This is due to the fact that natural radionuclides such as uranium and thorium are incorporated into the structure of difficultly soluble minerals – such as zircon, apatite, titanite, allanite, etc. On the other hand, most authors presume that the artificial radionuclides such as plutonium and americium are attached to the surface of the sample particles. This, however, is probably not strictly correct due to the growth of mineral particles since the beginning of the nuclear era. Current techniques for determination of radionuclides in solid samples can take up to several days if acid digestion utilizing mineral acids is used to decompose the samples. Alternatively, thermal fusion and microwave digestion are known as a tool to shorten the digestion process. However, in the vast majority of the digestion methods the solid residue (silicates, zirconium, etc.) remains and is removed prior to the radiochemical separation.

On the other hand, available results show that a significant amount of some radionuclides can remain in this solid residue. A digestion method allowing a sample to be loaded on a separation resin without any residue is therefore of great interest.

The aim of the present work was a development of a fast digestion method for various solid samples (soil, sediments and foodstuffs). This was achieved by employing thermal fusion utilising Li borate as a fusion agent. Actinides were separated by using different chromatographic separation techniques such as ion exchange and extraction chromatography. The results obtained showed that no solid residue remained in the solution after the digestion process. No filtration was thus needed prior to the loading of the sample on the resin. When the results obtained were compared to those obtained by a classical digestion by mineral acids the activity concentrations of determined radionuclides were slightly higher. The developed method was tested by radiochemical analysis of reference materials.

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URANIUM DISSOLUTION IN HYPERALKALINE TMA-OH SOLUTIONS: PRELIMINARY RESULTS

C. Cachoir[1], *S. Salah*[1], *T. Mennecart*[1], *K. Lemmens*[1]

SCK•CEN- Belgian Nuclear Research Centre, Boeretang 200, 2400 Mol, Belgium,
e-mails: ccachoir@sckcen.be, ssalh@sckcen.be, tmenneca@sckcen.be, klemmens@sckcen.be

Keywords: uranium dioxide, dissolution, alkaline pH, TMAOH

The Supercontainer design is the current reference design for the geological disposal of spent nuclear fuel in Belgium [1]. The main characteristic of this design is to provide a highly alkaline environment. In 2005, a research programme was started at the Belgian Nuclear Research Centre (SCK• CEN), supported by ONDRAF/NIRAS, to evaluate the stability of UO_2, as analogue of real spent fuel in such environment. In a previous work [2], it was demonstrated that the high pH did not increase the soluble U(IV) concentrations in the synthetic pore water, but it increased the soluble U(VI) concentrations due to formation of uranyl-hydroxocomplexes. However, we stressed that presence of alkali and/or alkaline-earth elements, especially Ca^{2+} may strongly increase the U release in solution by U-coprecipitation and/or by formation of U-colloids, as precursor of Ca- U(VI) phases. Experiments in tetramethylammonium hydroxide solution (TMAOH) have been recently initiated to better understand the processes taking place in cementitious systems.

Leaching experiments were performed at ambient temperature under Ar atmosphere with depleted UO_2 (pellet and/or powder) in TMAOH solutions at pH 13.5 and 12.5, and at different UO_2 surface area to volume of solution (SA/V) ratios.

The preliminary results show that we have no indication of U-colloids in the TMAOH systems (as expected) in contrast to experiments performed in cementitious waters. These results suggest that the colloid formation in cementitious systems was presumably promoted by the presence of Ca. As demonstrated for the cementitious systems, we found that uranium release in solution was dominated by U(VI) species for the two TMAOH systems. The uranium concentrations increased when increasing the pH from 12.5 to 13.5 and by increasing the SA/V ratio up to 100 m^{-1}, with is considered to be the threshold value (beyond this SA/V value, the U-concentration did not increase anymore). Furthermore, it was observed that the UO_2 morphology influences the UO_2 dissolution, i.e. showing different dissolution behaviour for pellet and powder. These experimental results were also supported by geochemical calculations performed with Geochemist's Workbench [3].

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MULTI-STEP EXCITATION SHEMES IN LASER SPECTROSCOPY AND DETECTION OF ACTINIDES AND LANTHANIDES IN SOLUTIONS

Igor Izosimov

Joint Institute for Nuclear Research, Dubna, 141980 Joliot Curie 6, Russia, e-mail: izosimov@jinr.ru

Keywords: luminescence, chemiluminescence, actinides, lanthanides, detection, solutions

The use of laser radiation with tunable wavelength allows [1–3] selective excitation of actinide/lanthanide species with subsequent registration of luminescence or chemiluminescence. The practical application of laser spectroscopy to analysis of different samples is confronted with one essential difficulty, namely the element to be detected must be permanently located in the area of interaction with laser radiation. Therefore the use of solutions of the substances to be analyzed is the most attractive from the practical standpoint. When the pulse (1ns) UV radiation produced by nitrogen laser is used for lanthanide and actinide excitation in solutions the UV radiation is absorbed with different molecules and as a consequence the background radiation is increased. Using short laser pulses for excitation of molecules and ions in liquids and time resolution for registration of luminescence and chemiluminescence produced by actinide and lanthanide ions we can efficiently separate target signals from short-lived background luminescence [1–3]. Selective excitation of detectable molecules can additionally decrease the intensity of background radiation. In addition, UV radiation is absorbed with chemiluminogen (luminol in our experiments) molecules, which makes difficult interpretation of the results of chemiluminescence registration. Therefore, a key problem of chemiluminescence application to detection of lanthanides and actinides in solutions is an increase in the selectivity of detection. Appropriate selectivity of lanthanide or actinide molecules excitation can be reached by initiation of transitions within 4f- or 5f-electron shell, which correspond to visible spectral range of absorbed laser radiation. Since the energy of one-quantum excitation in visible range may be insufficient for initiation of chemiluminescence it was proposed to excite lanthanide or actinide ion by multi-quantum absorption of visible light [1–3]. The scheme [1–3] *two step-one color,* i.e. in irradiation of actinide-containing solution by one laser (two photons absorbed from one laser pulse) and the scheme *two step-two color,* when a solution is irradiated by two lasers operating at different wavelengths (two photons absorbed from two synchronized laser pulses) were used for excitation of actinide ions in the range of 5f electron transitions.

The details of multi-step excitation of luminescence/chemiluminescence in solutions are considered. It is shown that a multi-step scheme of luminescence/chemiluminescence excitation increase both the sensitivity and selectivity of detection of substances.

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^{234}U/^{238}Pu AGE DATING OF PLUTONIUM MATERIALS USING HIGH RESOLUTION ICP-OES AND SECTOR FIELD ICP-MS

Michael Krachler, Rafael Alvarez-Sarandes, Gert Rasmussen*

European Commission-Joint Research Centre-Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany,
*e-mail: michael.krachler@ec.europa.eu

Keywords: ICP-OES, high resolution, ICP-MS, U-234, Pu-238, age dating

The assessment of the production age of a nuclear material helps to identify its potential origin as well as its intended use. In plutonium (Pu) bearing samples such age dating can be performed utilising the α decay of ^{238}Pu to ^{234}U. The ingrowth of the daughter nuclide ^{234}U into the original ^{238}Pu material can be calculated via the well-established radioactive decay equations. The daughter-to-parent ratio, i.e. ^{234}U/^{238}Pu ratio, is referred to as a chronometer which enables the determination of the elapsed time since the start of the decay of the original amount of ^{238}Pu [1]. While ICP-MS is frequently employed for isotope ratio measurements in the nuclear domain, high resolution (HR-)ICP-OES is gaining importance in this field [1, 2]. The improved optical resolution (<5 pm) of HR-ICP-OES instruments allows to detect the splitting of prominent Pu and U emission wavelengths into their isotopic contributions. This spectroscopic effect, called the isotope shift or isotope splitting, provides the potential for isotope ratio measurements using HR-ICP-OES. In this study the amounts of both ^{234}U and ^{238}Pu will be determined isotope-specifically in various Pu materials employing HR-ICP-OES. Applying ^{234}U/^{238}Pu chronometry, the age of these specimens will be subsequently calculated. These ages will be compared to the corresponding values that were obtained via sector field ICP-MS analysis.

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LIGHT SCATTERING STUDIES ON POLYMERIZATION AND COLLOID FORMATION OF ACTINIDES IN AQUEOUS SOLUTIONS

N. Priyadarshini, M. Sampath, Shekhar Kumar, U. Kamachi Mudali*

Process Development and Equipment Section, MPEDG, Reprocessing Group, IGCAR, Kalpakkam – 603102, Tamil Nadu, India,
*e-mail: shekhar@igcar.gov.in

Keywords: actinides, hydrolysis, polymers, colloids, light scattering

The inordinate tendency of tetravalent plutonium to form polymeric complexes and colloids has been the focus of interest for many years. Due to the complexity of plutonium aqueous chemistry, predicting the exact mechanism of formation of polymers and colloids pose major challenge. Though colloids in general offer great advantages in various fields, formation of actinide colloids in aqueous solutions has to be strictly avoided mainly because, it can play an important role in the transport of radioactive nuclides in the environment, loss of Pu in aqueous waste, emulsification in solvent extraction and it can lead to criticality hazard due to accumulation of Pu metal. Hence for long term safety assessments of radioactive waste repositories and to avoid polymer formation during processing of spent nuclear fuel, it is very important to know about the size distribution, relative stability and chemical composition of actinide colloids formed in aqueous solutions. Since aquatic colloids are very delicately balanced systems and sensitive to handling, a non-invasive and *in-situ* technique can allow the possibility of characterizing these colloids without disturbing the whole system. Hence light scattering technique was chosen for the present study to probe the polymerization reactions of Zr(IV) taken as surrogate for Pu(IV) and actinides such as U(IV), U(VI) and Th(IV) leading to colloid formation. The onset of colloid formation was observed using spectroscopic technique such as UV-visible and ATR-FTIR. Size distribution and molecular weight of the colloidal polymers were determined using dynamic and static light scattering technique. The second virial coefficient, a parameter which measures the solute-solvent interaction was also determined and the stability of the colloidal dispersion was arrived. The results obtained from above systems, clearly shows that the tetravalent Zr, U and Th behaves in similar manner as that of Pu(IV), whereas U(VI) behaviour is contradictory. The present paper includes a comparison of the results obtained from the investigation done on the aqueous systems of Zr(IV), U(IV), U(VI) and Th(IV).

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SIMULTANEOUS ANALYSIS OF U, Np, Pu, Am, AND Cm ISOTOPES AT ULTRA-TRACE LEVELS IN GROUNDWATER SAMPLES WITH AMS AND A COMPARISON WITH SF-ICPMS

F. Quinto[1]*, *M. Lagos*[1], *M. Plaschke*[1], *T. Schäfer*[1], *P. Steier*[2], *H. Geckeis*[1]

[1]Institut für Nukleare Entsorgung, Karlsruher Institut für Technologie, Hermann-von-Helmholtz-Platz 1,
76344 Eggenstein-Leopoldshafen, Germany, *e-mail: francesca.quinto@kit.edu
[2]VERA Laboratory, Faculty of Physics, University of Vienna, Währinger Straße 17, 1090 Vienna, Austria

Keywords: AMS, ultra-trace analysis, actinides, groundwater samples

The safety of the deep geological disposal of nuclear waste is intensely studied in laboratory and field experiments focusing on the geochemical behaviour of the actinides. In radionuclide tracer tests at the Grimsel Test Site (Switzerland) [1], ^{233}U, ^{237}Np, ^{242}Pu and ^{243}Am were injected in dipoles of a water conducting granodiorite shear zone fracture in order to investigate the colloid mediated transport and retention of actinides. In the groundwater eluent fractions, concentrations of actinides above 10 fg/g were determined with SF-ICPMS. Groundwater samples collected in the tailing of the tracer breakthrough curves, and bearing actinide levels below the detection limits (DL) of SF-ICPMS, were investigated with accelerator mass spectrometry (AMS). Abundance sensitivities (AS) for ^{236}U, ^{237}Np and ^{239}Pu relative to ^{238}U at levels $\leq 10^{-15}$ and DL of 10^4 atoms make AMS one of the most sensitive analytical technique allowing for accurate determinations below fg/g. Since the ultra-trace analysis of ^{237}Np and of ^{243}Am is limited by the non-availability of pure enough isotopic tracers for mass spectrometry, we have developed a new method involving the use of non-isotopic tracers. A group separation of the actinides from the matrix elements was performed with a $FeOH_3$ co-precipitation and the actinide nuclides were measured sequentially without previous chemical separation from each other, exploiting the exceptional AS of AMS [2]. For a direct comparison of the two employed analytical methods, AMS was also performed for selected samples previously analysed by SF-ICPMS. For AMS analysis, ^{233}U, ^{237}Np and ^{242}Pu were determined by using ^{239}Pu, while ^{243}Am by using ^{248}Cm as yield tracers. Groundwater samples were sized according to the expected concentration of the actinides from 0.1 g to 250 g. The detection of the injected actinides by AMS down to the levels of ag/g was successful. However, the use of non-isotopic tracers led to higher uncertainties in the determination of ^{233}U, ^{237}Np and ^{243}Am than of ^{242}Pu. While the maximum relative uncertainty on the measured values of ^{239}Pu, due solely to the counting error, is of a few percent, the relative uncertainties for ^{233}U, ^{237}Np and ^{243}Am can reach up to ~30%. Even though the developed method does not provide the same high precision of SF-ICPMS, it enables long-term field studies of multiple actinide tracers at unrivaled low concentration levels.

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BULK PLUTONIUM CHEMICAL ANALYSIS AT MICROSCALE

Ning Xu[1]*, *Rebecca M. Chamberlin*[1], *Pam Thompson*[2]

[1]Los Alamos National Laboratory, P.O. Box 1663, MS G740, Los Alamos, NM, 87545, USA, *e-mail: ningxu@lanl.gov
[2]Atomic Weapon Establishment, Aldermaston, RG74RP, UK, e-mail: thopmson@awe.co.uk

Keywords: plutonium analysis, small sample

Around the world, a common issue faced by the nuclear industry is decommissioning the aged nuclear facilities due to the expiration of their operational safety basis. Often times analytical chemistry operation in such a facility has been/will be moved into a low hazard category radiological/nuclear facility. This was driven by the high cost of building a nuclear facility, also by the fact that many of these chemical analyses require highly dexterous manipulations of very minute amount of samples in open-front hood or gloveboxes with light weight gloves. At the Los Alamos National Laboratory in USA, the analytical chemistry operation in the Chemistry Metallurgy Research (CMR) nuclear facility is undergoing a transition to a new low hazard category Radiological Laboratory Utility Office Building (RLUOB).

The success of this transition requires chemists to develop new methodologies to reduce the plutonium sample size for chemical analysis. ICP-OES/MS are commonly employed to determine trace impurities in bulk plutonium samples at Los Alamos. Recently, we have evaluated two types of major instrumental modifications for the ICP-OES/MS and have achieved an average of 10-to-1 reduction in sample size. This reduced sample is realized through integrating the ICP instruments with either a novel sample introduction system or a software amendment, both coupled with a flow rate nebulization technology. We have proven that these integrated ICP systems were capable of analyzing plutonium metal samples at one-tenth of the original size without compromising the measurement sensitivity and the precision. Moreover, in order for this reduced sample requirement at the instrument to be realistically beneficial, the upstream sample process must also be reduced in a similar scale. Three of such microscale and automated analytical sample preparation techniques are also under developing at Los Alamos.

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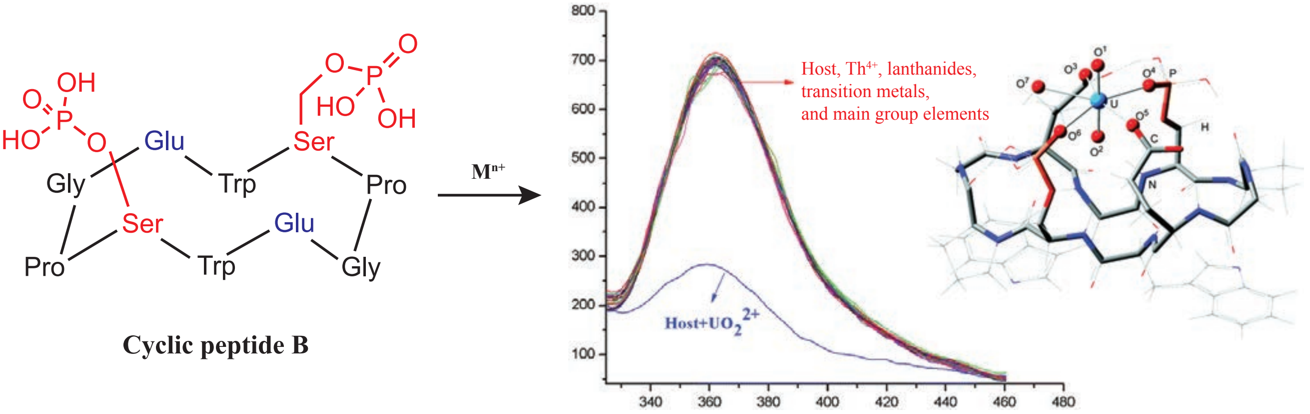
FLUORESCENT RECOGNITION OF URANYL IONS BY A PHOSPHORYLATED CYCLIC PEPTIDE

Chu-Ting Yang, Xiaolin Wang, Sheng Hu

Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, Sichuan, 621900, P. R. China



The development of new analytical methods for uranium, materials for its separation, effective antidotes, and more efficient remediation methods for pollution have become the focus of radiochemistry. Herein, we provide the first case of fluorescent identification of uranyl ions using a polypeptide. The cyclic peptide B and uranyl ions formed a 1:1 complex, and phosphorylated functional groups and pre-organized structure are key structural parameters. Cyclic peptide B is highly selective to uranyl ions (compared with the other competition metal ions such as VO^{2+} and Th^{4+} etc). In addition, B was successfully used as a fluorescent sensor in the detection of uranyl ion in river water. The structure of this uranyl-specific binding polypeptide will hopefully facilitate the future design of new materials for the separation of uranyl ion.

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PILLAR[5]ARENE-BASED FLUORESCENT SENSOR FOR DETECTION OF THORIUM(IV) ION

*Lihua Yuan, Yuyu Fang, Xiangyang Yuan, Lei Wu, Wen Feng**

Institute of Nuclear Science and Technology, Key Laboratory for Radiation Physics and Technology of Ministry of Education,
College of Chemistry, Sichuan University, Chengdu 610064, China, *e-mail: wfeng9510@scu.edun.cn

Keywords: pillar[5]arene, fluorescent probe, thorium(IV) ion

Pillararenes are a new class of macrocyclic compounds for supramolecular chemistry after cyclodextrins, crown ethers and calixarenes [1, 2]. We have recently demonstrated the unique complexation and extraction behaviour of pillar[5]arenes functionalized with phosphine oxides (PO), diglycolamide (DGA) and CMPO moieties in separation of actinides and lanthanides [3]. The recognition of metal ions by these host molecules is the prerequisite for the complexation to occur. Given the importance of thorium element as uranium resources and as a model of radioactive tetravalent actinides, we report herein a fluorescent probe based on non-symmetric pillar[5]ararene (NSP) **1** bearing five triazole-linked 8-oxyquinolines at one rim and five alkyl chains at the other (Scheme 1). The other ten chelating groups-substituted pillar[5]arene **2** was also synthesized as a control. The NSP **1** showed sequential fluorescent sensing for Th(IV) followed by fluoride ion. The difference in the ability of Th(IV) recognition between **1** and **2** was discussed. This work along with our previous reports indicates the great potential of pillararene macrocycles for design of fluorescent sensors towards actinide/lanthanide metal cations.

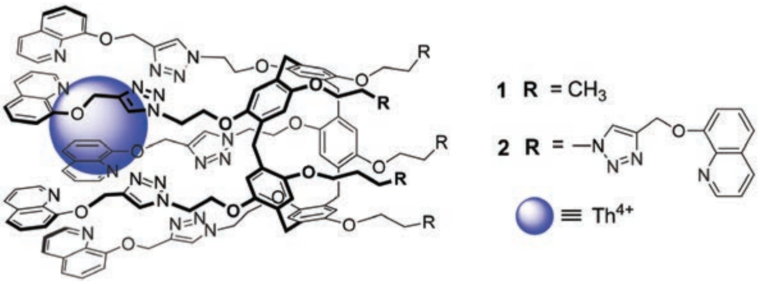

Fig. 1. Chemical structure of pillar[5]arene-based 8-oxyquinolines and its Th^{4+} complex

Acknowledgements

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Advances in radiochemistry supporting the nuclear fuel cycle

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POLONIUM EVAPORATION FROM LIQUID LEAD BISMUTH EUTECTIC COOLANT FOR ACCELERATOR DRIVEN SYSTEMS

Alexander Aerts[1], *Borja Gonzalez*[1], *Jörg Neuhausen*[2]

[1]Chemistry and Conditioning Programme (CCP), Belgian Nuclear Research Centre, Boeretang 200, Belgium,
e-mails: alexander.aerts@sckcen.be, borja.gonzalez.prieto@sckcen.be
[2]Radwaste Analytics, Paul Scherrer Institute, Switzerland, e-mail: joerg.neuhausen@psi.ch

Keywords: polonium, LBE, MYRRHA, ADS

Accelerator driven nuclear systems (ADS) using lead-bismuth eutectic (LBE) as coolant and spallation target are being developed in several countries worldwide. Such systems in principle allow flexible use of nuclear fuel and benefit from a relatively short life and quantity of their waste products. Specific to the use of LBE is the formation of significant quantities of the radiotoxic element polonium in the primary coolant. For the development and licensing of an ADS, accurate predictions of polonium release from LBE as well as properties that determine its migration, especially in the gas phase, are needed.

In an ADS a variety of conditions may prevail, both in normal operation and during accidents, for which polonium release from LBE needs to be quantified. To this aim, knowledge of the thermochemical properties of polonium and its compounds in a system consisting of liquid LBE in contact with a gas phase, both containing various impurities, is a fundamental requirement. However, because of the difficulty of working with macroscopic amounts of polonium, many traditional methods to determine these thermochemical properties are out of reach.

Our methodology therefore relies on experiments in which the released polonium activity from small LBE samples doped with trace amounts of polonium is measured. The results of these experiments are compared with calculated released quantities based on theoretical estimations of thermochemical data, obtained for example by extrapolation of properties of the lighter chemical homologues of polonium, or by quantum chemical calculations.

In this contribution, we present the results of this methodology based on experiments and calculations performed mainly in the frame of the MYRRHA ADS project. In case of the thermal release of polonium from LBE at high temperatures, typically above 600 °C, this approach has led to a relatively consistent picture of the involved polonium chemical species and reactions. At lower temperatures, however, this approach has had only partial success until now, because of the complexity of the experimentally observed polonium release phenomena and the absence of accurate thermochemical data.

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DISSOLUTION PERFORMANCE OF PLUTONIUM NITRIDE BASED FUEL MATERIALS

Emma Aneheim, Marcus Hedberg

Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg SE41296, Sweden

Keywords: dissolution, plutonium zirconium nitride, PuN, (Pu,Zr)N

Nitride fuels have been regarded as one viable fuel option for Generation IV reactors due to their positive features compared to oxides. To be able to close the fuel cycle and follow the Generation IV concept, nitrides must, however, demonstrate their ability to be reprocessed. This means that the dissolution performance of actinide based nitrides has to be thoroughly investigated and assessed. As the zirconium stabilized nitrides show even better potential as fuel material than does the pure actinide containing nitrides, investigations on the dissolution behavior of both PuN and (Pu,Zr)N has been undertaken. If possible it is desirable to perform the fuel dissolutions using nitric acid. This, as most reprocessing strategies using solvent-solvent extraction are based on a nitride containing aqueous matrix.

(Pu,Zr)N/C microspheres were produced using internal gelation. The spheres dissolution performance was investigated using nitric acid with and without additions of HF and Ag(II). In addition PuN fuel pellets were produced from powder and their dissolution performance were also assessed in a nitric acid based setting.

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AMERICIUM LOSSES IN PLUTONIUM NITRIDE DURING NITRIDE FABRICATION AND PELLET SINTERING

Marcus Hedberg, Aneta Sajdová

Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Kemivägen 4, Sweden, e-mail: marhed@chalmers.se

Keywords: nitride fuel, carbothermal reduction, PuN, AmN

Nitride based materials has been identified as a potential alternative to traditional oxide based nuclear fuel. Nitride based nuclear fuel possess several characteristics that are advantageous compared to the oxide counterparts such as far higher thermal conductivity while maintaining high melt temperature and higher fissile material density. Downsides associated with production of nitrides compared to oxides include having to produce the nitride in air free environment to avoid oxidation of the nitride and higher volatility of the nitrides. In this work PuN has been fabricated from PuO_2 powder containing small amounts of ^{241}Am from ^{241}Pu decay by carbothermal reduction in N_2 + 5% H_2 environment. XRD measurements have been used to characterize and confirm formation of PuN matrix material. HPGe measurements have been performed to evaluate the degree of AmN loss by vaporization in the material during carbothermal reduction and pellet sintering. Results show that AmN containing PuN pellets can be sintered up to 1800 °C and still retain AmN in the pellet matrix.

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RUTHENIUM VOLATILISATION FROM REPROCESSED SPENT NUCLEAR FUEL – STUDYING THE BASELINE THERMODYNAMICS OF Ru(III)

Sukhraaj K. Johal[1], *Colin Boxall*[1], *Colin Gregson*[2], *Carl J. Steele*[3]

[1]The Lloyd's Register Foundation Centre for Nuclear Engineering, Engineering Department, Lancaster University, Bailrigg, Lancashire, LA1 4YR, UK
[2]National Nuclear Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG, UK
[3]Sellafield Ltd., Sellafield, Seascale, Cumbria, CA20 1PG, UK

Spent Fuel Management at Sellafield includes the reprocessing of spent nuclear fuel from stations across the UK and also the reprocessing of spent fuel from overseas customers. At Sellafield, methods have been developed for the processing of high level wastes, including highly active liquor 10174 (HAL), which is a result of reprocessing irradiated nuclear fuel.

This Highly Active (HA) raffinate / waste stream is concentrated in evaporators and storage tanks in the Highly Active Liquor Evaporation & Storage (HALES) facility before feeding to the Waste Vitrification Plant (WVP). Here, the resultant HAL feed is calcined and combined with glass before pouring into containers to produce an immobilised HA wasteform.

Ruthenium is a fission product possessed of two relatively long lived stable isotopes: Ru-103 ($t_{1/2}$ = 39.8 days) and Ru-106 ($t_{1/2}$ = 1 year). Both isotopes form part of the inventory of HA waste raffinate during reprocessing of spent fuel. Volatilisation of fission products in nuclear waste generally occurs at high temperature – apart from ruthenium where volatilisation occurs at the lower temperature stages of the vitrification process.

Given its volatile nature and high specific radioactivity, ruthenium presents a strong challenge to the nuclear industry in effectively managing its abatement. Part of the challenge is to fully understand the highly complex solution chemistry under conditions relevant to HA waste streams and associated abatement systems.

Experimental work within the National Nuclear Laboratory (NNL), UK has demonstrated that the presence of oxidising metal ions in HA waste (e.g. Ce(IV)) can enhance the volatility of ruthenium through a chemical conversion of Ru(III) species to what is assumed to be RuO_4. A better understanding of these species, their electrochemical processes and reaction kinetics is required to underpin the empirical evidence gathered to date, in particular to develop gravimetric, electrochemical and spectroscopic analytical methods that will improve the understanding of ruthenium speciation in high nitric acid environments, establish the kinetics of inter-conversion between ruthenium species and establish the mechanism by which metal ions such as Ce(IV) may oxidise ruthenium.

We have studied the electrochemical behaviour of ruthenium and present here the thermodynamics of NO-complexed and uncomplexed ruthenium. Electrochemical, spectroscopic and surface analytical methods have been used to characterise the products of NO-complexed and uncomplexed Ru(III) redox. A surprising methodological observation is that as-purchased Ru(III) in the form of $RuCl_3$ is a mixture of Ru(III) and Ru(IV). Subsequently, a method to electroreduce the mixture to a pure Ru(III) solution was developed. Complexed $RuNO^{3+}$solutions show no sign of any Ru(IV) present, indicating NO stabilises against Ru(III) to (IV) oxidation, a conclusion confirmed by subsequent electrochemical and microgravimetric study of solution phase $RuCl_3$ and $RuNO^{3+}$. These studies have shown that, in uncomplexed Ru(III) systems, Ru(III) oxidation to Ru(IV) occurs prior to any Ru(VIII) generation. Once Ru(IV) has formed, tetroxide generation occurs, in both complexed and uncomplexed systems at 1.2V vs. Ag/AgCl. These results suggest the Ru(III) to (IV) transition is the key precursor process for volatilisation, implying nitrate complexation plays no role in promoting volatilisation and volatility of ruthenium is an intrinsic ruthenium problem coupled with nitric acid chemistry.

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SPECTROSCOPIC CHARACTERIZATION OF URANYL(VI) AND NATURAL ORGANIC MATTERS IN GROUNDWATER USING LASER-INDUCED LUMINESCENCE SPECTROSCOPY

E. C. Jung[1], M. H. Baik[2], H.-R. Cho[1], H. Kim[1], W. Cha[1]*

[1]Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 34057, Republic of Korea, *e-mail: ecjung@kaeri.re.kr
[2]Radioactive Waste Disposal Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 34057, Republic of Korea, e-mail: mhbaik@kaeri.re.kr

Keywords: uranium, natural granite groundwater, natural organic matters, carbonate, luminescence

The aim of the present study is to examine the luminescence characteristics of uranyl(VI) complexes and natural organic matters (NOMs) in natural granite groundwater using time-resolved laser fluorescence spectroscopy (TRLFS). The groundwater used in this study was sampled from a borehole with a depth of 500 m in a granite bedrock formation. It was located at KURT (KAERI Underground Research Tunnel) within the KAERI (Korea Atomic Energy Research Institute) area in Daejeon, Korea. Samples were taken from six different depths in the borehole where a multi-packer system was installed. TRLFS was conducted using two different laser systems. A pulsed nanosecond Nd:YAG laser at 266 nm (Continuum, Minilite) and a femtosecond laser at 267 nm (Coherent, Vitra and Legend Elite, frequency mixing of fundamental wavelength of Ti:Sapphire laser at 800 nm and its 2nd harmonic wavelength) were used as the excitation light sources. The laser beam passed through the sample cell. The luminescence perpendicular to the direction of propagation of the laser beam was delivered to an inlet slit of the Czerny-tuner-type monochromator (Horiba Jobin Yvon, iHR320) or spectrograph (Andor, SR-303i) using an optical fibre bundle. The luminescence signal was measured using the photo-multiplier tube (PMT) or ICCD system (Andor, DH-720/18U-03 iStar 720D). In the first step, the quantitative determination of uranium in groundwater was performed using a newly developed analytical technique based on the simultaneous measurement of the time-resolved luminescence of U(VI) and Raman scattering of water. In this technique, a calibration curve was simply obtained by measuring the ratio of the luminescence intensity of U(VI) to the Raman scattering intensity of water. The limit of detection of approximately 0.03 mg/L was achieved for the uranium determination. In the next step, the peak wavelengths and luminescence lifetime of U(VI) species in groundwater were determined. These luminescence characteristics were compared with those of $Ca_2UO_2(CO_3)_3(aq)$ and $UO_2(CO_3)_3^{4-}$ species, which were carefully prepared in a laboratory. Luminescence characteristics of NOMs in groundwater were also investigated. Several types of luminescence spectra of NOMs were observed and these spectra were compared with those of humic acids. The luminescence of NOMs may interrupt the speciation of U(VI) complexes owing to the spectral overlap in the luminescence between NOMs and U(VI) complexes. It was observed that the luminescence intensities of NOMs were severely weakened through a photodecomposition effect. We show that the high repetition rate and high peak power of a femtosecond laser beam make it possible to accumulate single-shot spectra rapidly with the elimination of overlapped luminescence of NOMs.

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ALPHA SOURCE TERM TREND IN TERMS OF DOSE RATE REDUCTION IN NUCLEAR POWER PLANT BEZNAU

Irene Mailand, René Hoffmeister

[1]Dept. Chemistry, RadProt and RadWaste, Nuclear Power Plant Beznau, Switzerland,
e-mails: irene.mailand@axpo.com, rene.hoffmeister@axpo.com

Keywords: alpha radiation, source term trend, dose rate reduction, *in-situ* gamma spectrometry, NPP Beznau

The Nuclear Power Plant Beznau consists of two identical 380 MWe PWR units with two loops each, commissioned in 1969 and 1971. Westinghouse was responsible for the primary part of the plant and BBC, nowadays ABB for the secondary part. In the last 25 years the plant has undergone an extensive modernisation programme in which more than

1.5 billion Swiss Francs have been invested. One of the main measures was the replacement of the steam generators with Inconel 690 tube material, realized at unit 1 in 1993 and at unit 2 in 1999. In 2015 the reactor vessel head of both units were replaced, which is another brand new project.

To keep the dose rate at permanently low levels, the minimisation of activity build-up on the surfaces of the primary components is always the main focus of the chemistry and radiation protection. A large number of measures to decrease the dose rates have been realized in the past, which are connected with permanent improvements of the primary coolant and shutdown chemistry.

The shutdown chemistry is capable to remove activated corrosion products as well as iodine and noble gases during shutdown before opening of the primary system. This process is supported by dosing hydrogen peroxide at 80 °C. The contamination level and the deposited activities have been measured by *in-situ* gamma spectrometry at several locations, like steam generator and main circulation pipe surfaces.

Besides the measuring of dose rate the knowledge about the alpha emitters is also of great importance especially regarding incorporation because of their high radio toxicity.

To characterize the alpha source term, the knowledge of historical fuel cladding defects and transuranic activity in the crud layers on fuel cladding surfaces are of importance.

Transuranic nuclides, such as americium, plutonium and curium are formed in irradiated uranium fuel by neutron activation and decay predominantly by alpha emission in the energy range of 4 to 6 MeV.

Most alpha emitters are long lived and will not be removed by decay. They therefore remain in the systems for a long time. The significance of alpha contamination depends on its relative abundance compared to beta-gamma contamination. It is therefore convenient to define the term “activity ratio”. Normally smears are being taken from primary plant areas and systems, where transuranic nuclides are most likely to be present and analyzed for beta-gamma and alpha activity.

One of the most important characterization is the examination of contamination in crud on fuel elements, or on components removed from the primary system.

In Beznau NPP CRUD scraping campaigns were performed in 2007, 2010 and 2015 to characterize fuel cladding deposit (CRUD) and to identify correlations to water chemistry parameters. The current presentation presents the results of shutdown chemistry and CRUD scraping analysis at Beznau NPP.

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NUCLEAR FUEL CYCLE MODELLING USING MESSAGE

Zhang Guiying[1, 2]*, Li Gaoliang*[1]*, Cao Lei*[2]*, Xu Guoliang*[2]*, Li Jue*[2]*, Ni Bangfa*[1]*, Xiao Caijin*[1]*, Jin Xiangchun*[1]*,*
Yao Yonggang[1]*, Guo Zeqin*[2]*, Wang Zhichao*[2]*, Qiu Yutong*[2]

[1]China Institute of Atomic Energy, Fangshan District, Beijing, China, e-mail: 23593448@qq.com
[2]Beijing Institute of Occupational Medicine for Chemical Industry, Beijing, China, e-mail: 18600668652@163.com

Keywords: MESSAGE, fuel cycle

In order to demonstrate the possibilities of application of MESSAGE tool for modelling of Nuclear Energy System at a national level, One of the possible open nuclear fuel cycle options based on thermal reactors has been modelled using MESSAGE. The referenced nuclear fuel cycle includes 3 types of reactors: light water reactor (LWR), heavy water reactor (HWR) and advanced light water reactor (ALWR). The steps of the front-end and back-end of nuclear fuel cycle and nuclear reactor operation were described. The model gives an optimal structure for Nuclear Power Development and optimal schedule for introducing various reactor technologies and fuel cycle options; infrastructure facilities, nuclear material flows and wastes, investments and other costs. Type or copy the abstract here. Please note that the whole text should fit to this single page.

Mass spectometry

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AUTOMATIC MULTI-COLLECTOR TOTAL EVAPORATION MEASUREMENTS WITH ION COUNTER INITIALISATION

Claudie Black, Phil Freedman*

Nu Instruments Ltd, Wrexham Industrial Estate, LL13 9XS, UK, *e-mail: claudie.black@nu-ins.com

Keywords: total evaporation, uranium, TIMS, safeguards, forensics

Multicollector total evaporation measurement of uranium isotopes is a technique that has been used for many years in thermal ionisation mass spectrometry (TIMS) to minimize the loss of sample and remove errors associated with mass fractionation, in order to increase both measurement accuracy and precision.

The traditional total evaporation method uses a small amount of the sample beam, ~5%, at the start of the measurement, for tuning and peak centring. This can lead to the preferential loss of the lower isotopes at the start of the measurement, potentially introducing errors.

The Nu TIMS utilises the ion counting Daly detector as part of an automatic total evaporation method to find and tune the beam before it is measured on the Faraday detectors. Therefore minimising the amount of beam lost at the beginning of the measurement. Following peak centring, tuning and turret optimisation using the Daly, the program then switches the beam onto the Faraday detectors for multi-collector total evaporation analysis.

The data presented in this poster is an overview of Uranium standards in the 50–100 ng size range that have been analysed using this fully automatic total evaporation measurement technique.

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RECONSTRUCTION OF THE ^{129}I/^{236}U INPUT FUNCTION AND ITS APPLICATION FOR TRANSIENT TRACER STUDIES IN THE NORTH ATLANTIC AND ARCTIC OCEAN

Marcus Christl[1], Núria Casacuberta[1], Christof Vockenhuber[1], Christoph Elsässer[2], Pascal Bailly du Bois[3], Jürgen Herrmann[4], Hans-Arno Synal[1]*

[1]Laboratory of Ion Beam Physics, ETH Zurich, Switzerland, *e-mail: mchristl@phys.ethz.ch
[2]Institute for Environmental Physics, University of Heidelberg, Germany, e-mail: Christoph.Elsaesser@iup.uni-heidelberg.de
[3]IRSN/PRP, Laboratoire de Radioécologie, Cherbourg-Octeville, France, e-mail: pascal.bailly-du-bois@irsn.fr
[4]Bundesamt für Seeschifffahrt und Hydrographie, Hamburg, Germany e-mail: juergen.herrmann@bsh.de

Keywords: uranium-236, iodine-129, nuclear reprocessing, North Atlantic Ocean, radionuclide tracers

Recent developments in accelerator mass spectrometry (AMS) allow the determination of heavy ions with compact, low energy AMS systems at highest sensitivity and at lowest background levels. This combination makes compact AMS a robust and easy to handle tool for the determination of ultra-trace amounts of heavy and long lived radionuclides in environmental samples.

The presentation focusses on two long lived radionuclides ^{129}I ($T_{½}$ = 15.7 Myr) and ^{236}U ($T_{½}$ = 23.5 Myr) measured by compact AMS in North Atlantic and Arctic Ocean waters. These anthropogenic nuclides have been introduced into the oceans by nuclear fallout from the atmospheric nuclear bomb tests. Another, more local source of ^{129}I and ^{236}U are the liquid releases of radionuclides from the two European nuclear reprocessing facilities located in Sellafield (GB) and La Hague (F). In ocean waters, the two sources (nuclear fallout and reprocessing) can be easily distinguished by their ^{129}I/^{236}U atom ratio. While the ^{129}I/^{236}U ratio in nuclear fallout is significantly below 1, the releases from nuclear reprocessing facilities have a much higher ratio. In addition, our recent reconstruction of the ^{129}I/^{236}U input function from nuclear reprocessing indicates that the ^{129}I/^{236}U ratios was steadily increasing since the 1990s from about 100 to about 400 in recent times. This not only allows determining the source of radionuclides in a water mass in the North Atlantic and Arctic Ocean (global fallout or reprocessing), the transient character of the $^{129}I/^{236}U$ ratio in the releases additionally can be used to trace and to date the labelling of a water mass when it was passing by the North Sea region.

In this presentation, first, the analytical tool (compact AMS) will be briefly discussed, including the most recent technical developments. Then we will show how the $^{129}I/^{236}U$ input function for the Northeastern North Atlantic Ocean was reconstructed based on the systematics found in the isotopic signatures of the releases from La Hague. Finally the $^{129}I/^{236}U$ input function will be used to determine transit times of Atlantic water masses in the Arctic Ocean.

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DETERMINATION OF RADIUM 226 IN GROUNDWATER BY SF-ICP-MS: A REVISED AND OPTIMIZED METHOD

Lorenzo Copia[1], *Stefano Nisi*[2], *Wolfango Plastino*[3], *Marta Ciarletti*[4], *Pavel P. Povinec*[5]

[1]Department of Mathematics and Physics, Roma Tre University and Section of Roma Tre, National Institute of Nuclear Physics, Rome, Italy, e-mail: copia@fis.uniroma3.it
[2]Gran Sasso National Laboratory, National Institute of Nuclear Physics, Assergi, Italy, e-mail: stefano.nisi@lngs.infn.it
[3]Department of Mathematics and Physics, Roma Tre University and Section of Roma Tre, National Institute of Nuclear Physics, Rome, Italy, e-mail: plastino@fis.uniroma3.it
[4]Department of Mathematics and Physics, Roma Tre University and Section of Roma Tre, National Institute of Nuclear Physics, Rome, Italy, e-mail: ciarletti@fis.uniroma3.it
[5]Department of Nuclear Physics and Biophysics, Comenius University, Bratislava, Slovakia, e-mail: pavel.povinec@fmph.uniba.sk

Keywords: SF-ICP-MS, Ra-226, groundwater, extraction chromatography, polyatomic interferences

Ra-226 detection in groundwater samples by SF-ICP-MS has been investigated for precise estimation, as required by time series analysis, applying a modified [Lariviere et al., Analytica Chimica Acta (2005) 2:528] method, to which pre-concentration was added. The separation and pre-concentration protocol, consisting of a sequential application of ion exchange and extraction chromatography, was optimized, assessing related polyatomic interferences and matrix effects affecting signal on Ra-226 peak window and achieving, on 12 replicates, a Ra-226 recovery efficiency of (100±3)% on waters spiking at 22 fgg^{-1} Ra-226. The instrumental detection limit was 0,089 fgg^{-1}, considering a 3σ criterion, with an absolute detection limit of 0.0489 fg equivalent to 1.95* 10^{-18} gmL^{-1} on a 25 mL liquid sample [Copia et al., Journal of Analytical Science and Technology (2015) 6:22]. This method was applied on nine groundwater samples, collected from three different sampling sites inside the Gran Sasso aquifer (central Italy), in order to assess measurement uncertainties and to evaluate the applicability to measurement surveys.

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ULTRA-SENSITIVE ANALYSIS OF ACTINIDES USING COMPACT ACCELERATOR MASS SPECTROMETRY

Xiongxin Dai[1, 2], *Marcus Christl*[3], *Sheila Kramer-Tremblay*[2], *Hans-Arno Synal*[3]

[1]China Institute for Radiation Protection, Taiyuan, China, e-mail: daixx@yahoo.com
[2]Canadian Nuclear Laboratories, Chalk River, Ontario K0J 1J0, Canada, e-mail: sheila.kramer-tremblay@cnl.ca
[3]Laboratory of Ion Beam Physics, ETH Zurich, 8093 Zurich, Switzerland, e-mail: mchristl@phys.ethz.ch

Keywords: accelerator mass spectrometry, actinide, radiobioassay, nuclear forensics

Ultra-trace analysis of actinide isotopes is often required in a number of important applications, including radiobioassay, nuclear forensics, environmental radiochemistry research, biological tracer studies, and geochronology. However, many radiometric and non-radiometric methods currently available for the determination of actinides in low-level environmental and biological samples are tedious, very time consuming and/or not sufficiently sensitive to meet the growing analytical demands. Accelerator mass spectrometry (AMS) is an extremely sensitive technique for the analysis of intermediate- and long-lived radionuclides. As a result of its high rejection of molecular isobaric interferences and low susceptibility to adverse matrix effects, the AMS technique (particularly compact AMS) allows for simplification of the sample preparation chemistry with a good potential for high sample analysis throughput and reduced cost for ultra-low level radioassays. This is of particular interest for extremely low-level analysis of actinide signature (especially Pu, Am, Cm and Cf isotopes) in bioassay and nuclear forensic samples, where other mass spectrometric (e.g., inductively coupled mass spectrometry (ICP-MS) and thermal ionization mass spectrometry (TIMS)) and radiometric techniques (e.g., alpha spectrometry) may not be adequate to meet analytical sensitivity or throughput requirements.

Over the past decade, compact AMS system has been dramatically improved and has become the most sensitive and robust tool for actinide analysis. Our recent works have demonstrated the feasibility of compact AMS for the analysis of actinides (e.g., Pu, Np, Am, Cm and Cf) at fg/L levels or less in large-volume urine samples using low energy Tandy system at ETH Zurich. With the improvements on both instrumentation and target preparation chemistry, compact AMS has surpassed large conventional AMS systems and become the most cost effective tool for ultra-low level detection of actinides down to attogram range. This would open the door for new radiobioassay, forensic and environmental applications.

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RESONANCE IONIZATION MASS SPECTROMETRY FOR ACTINIDE ISOTOPE MEASUREMENTS: MODELING AND SIMULATIONS

Sean Gates[1], Michael Savina[1], Brett Isselhardt[1], Colin Thomas[2], Kim Knight[1], Andrew Kucher[1] and Michael Kristo[1]*

[1]Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore CA, USA,
*e-mail: gates24@llnl.gov
[2]Georgia Institute of Technology, Atlanta, GA, USA

Keywords: mass spectrometry, actinides, isotopic analysis

The accurate measurement of actinide isotope ratios is critical for assessing the production, processing and irradiation history of nuclear materials. Resonance Ionization Mass Spectrometry (RIMS) is a technique that enables rapid, isobar – free quantification of actinide isotope ratios. RIMS is predicated upon the utilization of a laser resonant scheme to solely ionize ground state neutral atoms of a specific element. The presence of isobaric interferences, typically inherent to multicomponent actinide material, is therefore eliminated *in situ* during RIMS analysis. Modeling and simulation capabilities have been developed to identify and optimize the experimental conditions for the RIMS analysis of actinides. Measurements require relatively high useful yields and, more importantly, the ability to accurately quantify low abundance isotopes. We first present results demonstrating close agreement between a simulated actinide spectrum and one obtained through experiments. The effect of different laser ionization volumes on the useful yield and dynamic range are then explored. We present data indicating that smaller ionization volumes, while slightly reducing the useful yield, significantly increase the dynamic range of the measurements by eliminating the peak tailings associated with larger ionization volumes. Specifically, we show that by modifying the ionization geometry from a 1.5 mm diameter cylinder to a 1.5 mm diameter sphere we reduce the useful yield by a factor of 1.4 while increasing the dynamic range by three orders of magnitude.

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PLUTONIUM IN ATMOSPHERIC ENVIRONMENT

Katsumi Hirose

Department of Material and Life Sciences, Sophia University, 7-1 Kioi-cho, Chiyoda-ku Tokyo 102-8554, Japan,
e-mail: hirose45037@mail2.accsnet.ne.jp

Keywords: plutonium, plutonium isotope ratio, atmosphere, temporal variation, nuclear explosion

Plutonium and its isotopes in the environment are concerned by public because of its chemical and radiological toxicity and fissile material. Researchers in the fields of atmospheric chemistry, chemical oceanography and others have been interesting in plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu) in the environment as a unique transient tracer of atmospheric, oceanic, terrestrial and biogeochemical processes. Since explosions of the New Mexico and Nagasaki atomic bombs in 1945, global environment has contaminated with plutonium as a result of atmospheric nuclear weapons tests, satellite accidents and nuclear reactor accidents. Especially, large quantities of plutonium were released during atmospheric tests of nuclear weapons conducted by USA and former Soviet Union mainly during the 1950s and early 1960s. Atmospheric behaviour of plutonium has been frequently studied during the past 50 years. As a result, during the large-scale nuclear weapons tests of hydrogen bombs, radioactive debris including plutonium reached the stratosphere, which became then the main reservoir of plutonium. The stratospheric plutonium was transported into troposphere as an apparent stratospheric residence time of 1–2 years due to exchange processes between the stratosphere and the troposphere [1]. Although the stratospheric plutonium decreased to negligible level after 1990, plutonium has been detected in dust and deposition samples collected in Japan, Europe and US, in which current levels of $^{239,\,240}$Pu are 0.1–10 nBq m^{-3}, 0.05–10 mBq m^{-2}Mon^{-1} for surface airborne dust and deposition, respectively. Sources of the atmospheric plutonium since 1990 are considered to be resuspension of deposited plutonium, including plutonium-bearing soil particles blew up by storms [2] and large-scale biomass burning.

Plutonium in environmental samples has been measured by alpha spectrometry. Recent development of mass spectrometric measurements such as ICP-MS, AMS and others allows us to determine ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu atom ratios in the environmental samples [3], which depend on scale of nuclear explosion and sources such as nuclear reactor accident. As results of measurement of archived samples, we have new knowledge about long-term variation of ^{240}Pu/^{239}Pu atom ratios in the atmospheric samples (deposition and dust). This knowledge is important to have better understanding of terrestrial and oceanic processes of plutonium.

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AMS AND ICP-MS FOR MEASUREMENT OF LOW LEVEL RADIONUCLIDES

Xiaolin Hou

Technical University of Denmark, Center for Nuclear Technologies, 4000 Roskilde, Denmark, e-mail: xiho@dtu.dk; Xi’an AMS Center,
Institute of Earth Environment, CAS, 710061 Xi’an, China

Keywords: AMS, ICP-MS, mass spectrometry, long-lived radionuclides, environmental radioactivity

Radionuclides are conventionally measured by detecting their characteristic radiation using alpha spectrometry, beta counting including liquid scintillation counting and gamma spectrometry depending on their decay modes, these methods are high sensitive for short half-lived radionuclides. Mass spectrometry, typically used to measure isotopes of elements, can be also used for measurement of radionuclides. In these methods, the atoms of the radionuclide of interest are directly measured. Therefore, mass spectrometry methods are normally sensitive for the measurement of long-lived radionuclides. Among various inorganic mass spectrometric methods, inductively coupled plasma mass spectrometry (ICP-MS) and accelerator mass spectrometry (AMS) are two most popular used mass spectrometry techniques for the measurement of radionuclides, especially long-lived radionuclides. With the improvement of ICP-MS technique and more instruments to be installed, the application of this technique is becoming more popular tool for measurement of radionuclides. By hyphenation with automated separation system, ICP-MS will play a critical role in rapid determination of radionuclide for emergency analysis. AMS is the most sensitive analytical technique for many long-lived radionuclides, the new development of this techniques, especially the miniaturization of AMS system significantly reduce the cost of instrument as well as maintenance and operation, this stimulated and enhanced the application of this technique in the environmental researches. This work present the application of ICP-MS and AMS in the measurement of most important radionuclides, such as ^{99}Tc, ^{129}I, ^{135}Cs, ^{236}U, ^{237}Np, ^{239}Pu, ^{240}Pu, especially the new progress in the analytical methods of these radionuclides for environmental researches.

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FUKUSHIMA-DERIVED RADIOCESIUM IN THE WESTERN NORTH PACIFIC IN 2014

Yuichiro Kumamoto[1], Michio Aoyama[2], Yasunori Hamajima[3], Hisao Nagai[4], Yoshimi Kawai[1], Eitaro Oka[5], Atsushi Yamaguchi[6], Keiri Imai[7], Akihiko Murata[1]*

[1]Research and Development Center for Global Change, Japan Agency for Marine-Earth Science and Technology, 2-15 Natushima-cho, Yokosuka, Kanagawa 237-0061, Japan, *e-mail: kumamoto@jamstec.go.jp
[2]Institute of Environmental Radioactivity, Fukushima University, 1-1 Kanayagawa, Fukushima, Fukushima 960-1296, Japan, e-mail: r706@ipc.fukushima-u.ac.jp
[3]Low Level Radioactivity Laboratory, Kanazawa University, Wake, Nomi, Ishikawa 923-1224, Japan, e-mail: hamajima@se.kanazawa-u.ac.jp
[4]Department of Chemistry, College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajousui, Setagaya Ward, Tokyo 156-8550, Japan, e-mail: hnagai@chs.nihon-u.ac.jp
[5]Atmosphere and Ocean Research Institute, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8564, Japan, e-mail: eoka@aori.u-tokyo.ac.jp
[6]Graduate School of Fisheries Sciences, Hokkaido University, 3-1-1 Minato-cho, Hakodate, Hokkaido 041-8611, Japan, e-mail: a-yama@fish.hokudai.ac.jp
[7]School of Fisheries Sciences, Hokkaido University, 3-1-1 Minato-cho, Hakodate, Hokkaido 041-8611, Japan, e-mail: imai@fish.hokudai.ac.jp

Keywords: radiocesium, Fukushima Dai-ichi Nuclear Power Plant accident, North Pacific

Accident of Fukushima-Dai-ichi Nuclear Power Plant on 11 March 2011 resulted in a large amount release of radiocesium into the North Pacific Ocean. Since just after the accident, the Government of Japan, Tokyo Electric Power Co., and lots of oceanographers from countries of the North Pacific Rim have been measured concentration of dissolved radiocesium in seawater. They found that along surface currents between 40°N and 50°N approximately the released radiocesium had been transported eastward and reached the west coast of the North American Continent by April 2015. On the other hand, some of it were conveyed southward due to subduction of the subtropical mode water (STMW). Maximum of radiocesium concentration in subsurface layer (200–400 m depth), which is derived from the subduction of STMW, should be spreading in the subtropical area of the western North Pacific during the past four years. However, behaviour of the subsurface maximum is still unknown. We collected seawater samples from surface to about 800 m depth at 14 stations between 15°N and 41°N in the western North Pacific in 2014 and revealed vertical profiles of Fukushima-derived radiocesium at each station. At a station (34°N/148°E) in the just south of the Kuroshio Extension, where STMW was formed just after the accident, activity concentration of ^{137}Cs in the subsurface layer has been decreasing; about 50 Bq/m^3 in October 2011, 20 Bq/m^3 in January 2012, 10 Bq/m^3 in November 2012, and 5 Bq/m^3 in July 2014. At a station (30°N/148°E) located about 400 km directly south of the above station, the subsurface activity concentration increased from about 8 Bq/m^3 in January 2012 to 15 Bq/m^3 in November 2012. Then it has fallen to about 5 Bq/m^3 by July 2014. At a station (22°N/165°E) further south, the activity concentration in the subsurface layer rose from about 2 to 5 Bq/m^3 between June 2012 and December 2014. These temporal changes in the activity concentration of ^{137}Cs suggest that Fukushima-derived radiocesium has been spreading southward through the subsurface layer along circulation of STMW in the subtropical area.

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THE APPLICATION OF MASS SPECTROMETRIC TECHNIQUE FOR ANALYZING PLUTONIUM ISOTOPES IN THE ENVIRONMENTAL SAMPLES INCLUDING FOOD STUFFS

Sang-Han Lee

Korea Research Institute of Standards and Science Ionizing Radiation Center, South Korea, e-mail: s.lee@kriss.re.kr

The ^{239}Pu and ^{240}Pu are important isotopes because of their long half-lives, high abundance and their radiological toxicity and the atom ratio of ^{240}Pu/^{239}Pu has been known as a powerful tool to identify its sources. Since the Fukushima Daiichi Nuclear Power Plant's disaster in Japan on March 11, 2011, public's concerns regarding of radiological hazards in the environment and in the foods have been growing with a fear of the use of nuclear power plants (NPPs) in Korea. Therefore, it is very important to monitor the artificial radionuclide around the NPP as well as the non-NPP sites to assess the radiological contamination.

For this purpose, the environmental samples and food stuffs were collected near the NPPs and the non-NPPs in Korea and analyzed the plutonium isotopes using a radiometric (alpha spectrometry) and non-radiometric (ICP-MS) method. All results will be informed in detailed later on.

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MASS SPECTROMETRY TECHNIQUES FOR TRACER STUDIES OF ENVIRONMENTAL PROCESSES

Galina Lujanienė

SRI Center for Physical Sciences and Technology, Vilnius, Lithuania

Keywords: AMS, ICPMS, ^{14}C, $^{239, 240}$Pu, tracer studies

Recent developments in analytical techniques of long-lived radionuclides, mainly in accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICPMS), have enabled to apply radioactive isotopes introduced into the environment after nuclear weapon tests, as well as released during accidents in tracer environmental studies. These ultra-sensitive techniques are especially useful for studies based on the compound specific analyses which require measurements at ultra-low levels.

Concentrations of radionuclides as well as characteristic Pu activity and atom ratios in the atmosphere, soil, suspended particulate matter and bottom sediments were measured using gamma- and alfa-spectrometry, ICPMS and AMS, while δ^{13}C and δ^{15}N by a Thermo Scientific Delta V Advantage mass spectrometer (Thermo Finnigan Delta plus). Analyses of airborne radioactive aerosols were carried out in daily samples collected in Vilnius (1993–2011), as well as in 10-day samples at the background station in Preila (on the Baltic Sea shore, Lithuania) [1–3]. ^{137}Cs, ^{241}Am and Pu isotopes were also analyzed in soil, seawater, sediments and suspended particulate matter samples collected in the Baltic Sea and the Curonian Lagoon during 1997–2014 [4, 5]. Speciation studies were performed for better understanding the behaviour of radionuclides in the environment. Pu redox speciation was studied in laboratory experiments [6].

Pu isotopes, Δ^{14}C and δ^{13}C of total organic carbon as well as lipid and phospholipids (PL) fractions of the sediments were applied to study the sources of pollutants including chemical warfare agents (CWA) [7]. The compound-specific δ^{13}C analysis, PL-derived fatty acid biomarkers and an end-member mixing model were used to estimate a relative contribution of the marine, terrestrial and fossil, petroleum hydrocarbon sources to organic carbon in the sediments, to assess a possible effect of petroleum hydrocarbon contamination on radiocarbon signatures and to elucidate a possible leakage of CWA at the Gotland Deep dumpsite [8]. Application of radioactive (^{14}C, ^{134,137}Cs, ^{238,239,240}Pu, ^{241}Am, ^{7}Be, Th, Pb, etc.) and stable (C, N) isotopes as well as their activity and isotope ratios in tracer studies will be discussed. The special emphasis will be given to the physical and chemical characteristics of the tracers.

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SORPTION BEHAVIOR OF Cs, Pu AND Am TO NATURAL CLAY: EFFECT OF VARIOUS COMPONENTS

Galina Lujanienė[1], Loreta Levinskaitė[2], Remigijus Juškėnas[1], Karol Štamberg[3], Audrius Kačergius[4], Ieva Kulakauskaitė[1], Martynas Gavutis[1], Sergej Šemčuk, Dušan Vopalka[3]

[1] SRI Center for Physical Sciences and Technology, Savanorių ave 231, Vilnius, LT-02300, Lithuania
[2]SRI Nature Research Centre, Žaliųjų ežerų 49, Lt-2021, Vilnius, LT-2600, Lithuania
[3]Department of Nuclear Chemistry, CTU, 11519 Prague 1, Brehova 7, Czech Republic
[4]Lithuanian Research Centre for Agriculture and Forestry Žalioji Sq. 2, Trakų Vokė, LT-02232 Vilnius, Lithuania

Keywords: natural clay, Cs(I), Pu(IV), Pu(V) and Am(III)

Natural clay has been often used to protect the environment from a harmful impact of radionuclides released from a repository of radioactive waste. Retardation of radionuclides is rather complicated in the heterogeneous natural minerals and can be affected by various factors, e.g. type of mineral, pH and redox potential. Recent studies have shown that various microorganisms found in nature may also result in changes of the Pu oxidation state.

The main aim of this study was to estimate the effect of various components naturally present in the clay minerals on sorption of Cs(I), Pu(IV), Pu(V) and Am(III) as well as their impact on the Pu oxidation state distribution. Three well characterized samples of Triassic clay with different amounts and composition of iron minerals were used in sorption experiments. In addition, sorption experiments were performed with fungi (*Trichoderma* sp. M-1, *Penicillium sp.*14 M and *Penicillium chrysogenum* 21RM) and bacterium (*Bacillus sp.* 2mH*, Bacillus sp. 3bm, Bacillus sp.* 6br) isolated from groundwater and the Triassic clay.

The composition of clay mineral coatings and their leaching during the SE procedures were studied using the Mössbauer spectroscopy and X-ray diffraction. Pu (IV), (V) or (VI) was added to achieve their initial concentration of 3×10^{-10} mol·L^{-1} in 0.154 mol/L NaCl. Solids and biomass were separated by centrifugation at 6000×g after desired time. Pu activity concentrations were measured by alpha spectrometry. The oxidation state distribution analysis was performed using thenoyltrifluoroacetone (TTA), bis(2-ethylhexyl) hydrogen phosphate (HEDHP) and 1,3-diphenyl-1,3-propanedione (DBM) solvent extraction and Pu(III, IV), Pu(V), Pu(VI), Pu(IV) and Pu(IV polymeric) were separated. Ultrafiltration and alpha spectrometry as well as ICP-MS were employed to characterize the oxidation states of the formed plutonium species.

It was found that in spite of the Pu(V) fast reduction the Pu speciation in the clay coatings was determined to be different in comparison with that of the Pu(IV) experiments. Pu was associated with exchangeable and carbonate fractions indicating its possible higher mobility in the environment. The maximum of Pu biosorption to bacterium and fungi was observed at pH of ~7 and 4, respectively. In the liquid-phase (LP) the plutonium oxidation state distribution was found to be as follows: Pu(IV) – 36%, Pu(IV-polymeric) – 58%, Pu(V) – 2% and Pu(VI) – 4%.

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ADVANCES OF THERMAL IONIZATION CAVITY SOURCES FOR MASS SPECTROMETRY APPLICATIONS (TIMS)

Colin Maden[1], Heinrich Baur[1], Amélie Hubert[2], Anne-Laure Fauré[2], Fabien Pointurier[2], Bernard Bourdon[3]*

[1]Department of Earth Sciences, ETH Zurich, Clausiusstrasse 25, CH-8092 Zurich, Switzerland, *e-mail: maden@erdw.ethz.ch
[2]Commissariat à L'Energie Atomique, CEA-DAM, Ile-de-France, Bruyères-le-Châtel, Arpajon Cedex, France
[3]Laboratiore de Géologie de Lyon, ENS Lyon and UCBL, UMR 5276, CNRS, France

Keywords: thermal ionization mass spectrometry, cavity source, ionization efficiency, charged particle simulation, space charge, cavity geometry

Thermal ionization cavity (TIC) sources are known to provide higher ionization efficiencies than conventional filament sources used in thermal ionization mass spectrometry (TIMS), e.g. [1]. This is because evaporating sample atoms can have multiple contacts with the hot inner surfaces of the cavity rather than being lost in the vacuum chamber of the ion source as is the case for sample atoms evaporating from a conventional TIMS filament. Each surface contact provides another possibility to be thermally ionized with a probability calculated via the Saha-Langmuir equation.

Contrary to the prevailing interpretation of the relevant physical processes inside a hot cavity (T > 500 K), which includes the presence of a non-thermal-equilibrium plasma in the volume of the cavity, we suggest that at lower temperatures and cavity volumes no plasma is developed, and sample ions can fly freely through the volume of the cavity only interacting at a macroscopic scale via the extracting electric potential, which is shaped by the space charge of ions and thermally emitted electrons. As a result, the geometry of the cavity becomes relevant for the ionization efficiency of the source.

We have developed a unique simulation code that allows numerical determination of the ionization efficiency of a cavity by simulating the trajectories of ions, electrons, and neutral atoms – including their space charge – and surface adsorption/re-emission processes within the cavity. The code has been successfully tested against problem sets with analytical solutions and by reproducing experimentally determined TIC ionization efficiencies.

With the help of the simulation code a new cavity geometry has been identified, which can have more than 100 times higher ionization efficiency than predicted by the Saha-Langmuir equation. This would be about ten times more than the reported ionization efficiencies achieved with tube geometry cavities, which themselves are about ten times higher than the ionization efficiencies measured with conventional filament sources, e.g. [2].

The code also offers an explanation why the tube geometry cavities are particularly suited to efficiently ionize particle type samples, for example dust particles or elements adsorbed to ion exchange resin beads, e.g. [3] and references therein.

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DETERMINING SPECIATION OF U AND Pu IN SPENT NUCLEAR FUEL VIA ELECTROSPRAY IONIZATION MASS SPECTROMETRY

Luther W. McDonald IV[1], *James Campbell*[2], *Thomas Vercouter*[3], *Sue B. Clark*[4]

[1]Department of Civil and Environmental Engineering, University of Utah, Salt Lake City, UT 84112, USA
[2]Chemical and Biological Signature Sciences Group, Pacific Northwest National Laboratory, Richland, Washington 99352, USA
[3]CEA, DEN, DANS, Department of Physico-Chemistry, F-91191 Gif-sur-Yvette, France
[4]Department of Chemistry, Washington State University, Pullman, Washington 99164, USA

Keywords: scanning electron microscopy, uranium oxides, synthesis, nuclear forensics

Used nuclear fuel (SNF) contains almost one-third of the periodic table. A selective separation of the long-lived actinides (An) from the fission products of intermediate life-time (^{90}Sr, ^{137}Cs, ^{99}Tc, and ^{131}I), and the relatively shorter lived lanthanides (Ln) reduces both the amount and radiotoxicity of the waste. Nonetheless, a fundamental understanding of the thermodynamic properties of complex formation and speciation in solvent extraction systems is needed for the development of advanced spent nuclear fuel reprocessing systems. In this work, methods have been developed using electrospray ionization – mass spectrometry (ESI-MS) to characterize the speciation of U and Pu with tributyl phosphate (TBP) and dibutyl phosphate (DBP) as would be found in the PUREX process. The polarity of the ionization source was altered to observe both positive and negative gas phase ions. U and Pu complexed to TBP resulted in complexes that could be observed as positive ions, but no negative ion species were observed. In contract, U and Pu complexed to DBP could be observed as both positive and negative ions. Using the relative abundance of ions observed in the gas phase, apparent stability constants were calculated to enable comparison of the gas phase species to known solution species. The protocols developed in these studies help determine fundamental actinide complexation chemistry in solvent extraction systems, and demonstrate the potential of ESI-MS for process control monitoring in spent nuclear fuel reprocessing facilities.

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LOW AND HIGH-ENERGY RADIOISOTOPE MASS SPECTROMETRY VS. RADIOMETRICS

Pavel P. Povinec

Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, 84248 Bratislava, Slovakia, e-mail: povinec@fmph.uniba.sk

Keywords: ICPMS, TIMS, AMS, HPGe gamma-spectrometry

Recent developments in low and high-energy mass spectrometry (mainly associated with ICPMS – Inductively Coupled Plasma Mass Spectrometry, and TIMS – Thermal Ionization Mass Spectrometry), and in high energy mass spectrometry (AMS – Accelerator Mass Spectrometry) have made them dominant techniques for analysis of long-lived radioisotopes (e.g. 10Be, 14C, 36Cl, 41Ca, 53Mn, 99Tc, 129I, uranium and plutonium isotopes) in various types of samples from meteorites to deep ocean seawater. In the radiometrics sector the most important development has been associated with underground operation of large volume HPGe detectors, which have been dominating analyses of short and medium-lived radioisotopes emitting gamma-rays. Applications of these analytical methods in isotope oceanography will be discussed, specifically for studying transport of water masses, and for investigations of processes in the water column.

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RESONANCE IONIZATION MASS SPECTROMETRY FOR ACTINIDES: PLUTONIUM ANALYSIS

Michael Savina[1], Brett Isselhardt[1], Kim Knight[1], Andrew Kucher[1], Sean Gates[1], David Ruddle[1], Bruce King[2]*

[1]Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore CA, USA,
*e-mail: savina1@llnl.gov
[2]The University of Newcastle, Newcastle, Australia

Keywords: mass spectrometry, actinides, isotopic analysis

Actinide isotope ratios hold important information in the forensic analysis of solid materials such as nuclear fuel and interdicted samples. Resonance Ionization Mass Spectrometry (RIMS) uses tunable lasers to selectively ionize specific elements such as uranium and plutonium prior to mass analysis, and holds the promise of rapid, isobar-free quantification of actinide isotope ratios. The challenges to routine measurements include laser-induced isotopic fractionation (i.e. the preferential ionization of one isotope over another) and the strong tendency of actinides, particularly uranium, to vaporize from solids as oxide molecules or in low-lying excited states, both of which are transparent to the resonance lasers used to ionize ground state neutral atoms that are essential for accurate, precise RIMS analysis. We discuss various sources of spectroscopic fractionation, such as isotope shifts and hyperfine splitting, and present strategies for mitigating them. We present recent progress in measuring actinide isotope ratios directly in solids with minimal sample consumption and no or minimum sample preparation. In addition, we present first data from a new RIMS facility at Lawrence Livermore National Laboratory, and discuss ion optical simulations performed to improve instrument design and performance.

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DETERMINATION OF LOW LEVEL ^{129}I IN BIOLOGICAL SAMPLES USING ACCELERATOR MASS SPECTROMETRY MEASUREMENT

Yanyun Wang[1], *Xiaolin Hou*[1, 2]

[1]SKLLQG, Shaanxi Key Laboratory of AMS Technology and Application, Xi´an AMS Center, Institute of Earth Environment, CAS, Xi'an 710061, China
[2]Center for Nuclear Technologies, Technical University of Denmark, Risø Campus, Roskilde 4000, Denmark

Keywords: iodine-129, vegetation, environmental tracer, bioavailability, combustion

Iodine is an important biophilic element, and enriched in human thyroid via the food chains. Environmental ^{129}I, as the only long-lived isotope ($t_{1/2}$=1.57×10^7 years), is mainly originated from anthropogenic nuclear activities, and the ^{129}I/^{127}I ratio in the terrestrial organisms was significantly increased since 1940s. It is important to investigate transfer of radioactive iodine in ecosystem, variation of vegetation and animal samples need to be analysis and to evaluate the radiological impact of radioactive iodine to the environment and population due to nuclear activities. This requires analysing various environmental and biological samples radioactive isotopes of iodine including ^{129}I. Among all possible measurement methods, accelerator mass spectrometry (AMS) is the most sensitive method, and only method for determination ^{129}I in low level environmental samples. Many methods for determination of ^{129}I in soil, sediment and water samples have been reported. While, the method on determination of ^{129}I in biological samples such as vegetation and animal tissues are not well established.

This work aims to develop an effective method for separation of iodine from large size of vegetation samples for AMS measurement of ^{129}I in low level biological samples.

Based on volatility of iodine at high temperature, combustion method using a tube furnace was investigated. Due to the complexity of plant constituents and high organic content, it is critical to burn the sample at a suitable temperature to prevent producing a large amount gas in a short time and explosion. The results showed that the ignition temperature of most vegetation ranges 220–300 °C. The speed of temperature increase is another key parameter to prevent the rapid burn of sample causing an incompletely combustion, the experimental results showed that at least three hours is needed to ensure a smooth burning of the biological samples. In addition, combustion at a high temperature up to 800 °C and for relative longer combustion time up to 3 hours are needed to completely release iodine from sample. In optimal condition, a recovery of more than 80% for iodine was measured in this step using ^{125}I tracer. The effect of the type of trap solution was also investigated, and found that $NaHSO_3$ in trap solution does not significantly affect the recovery of iodine, and the optimal concentration of alkali solution is 0.2 mol/L. Iodine in the trap solution is further purified using solvent extraction and prepared as AgI for AMS measurement. Based on this investigation, a method for determination of ^{129}I in different vegetation samples such as lichens, pine needles, grass and, spinach has been established. The overall recoveries of iodine in whole procedure range from 75%–90%. The procedure blanks was also prepared and measured to be (1–2)×10–^{13}, this is more than 2 orders of magnitude lower than the present environmental level. Compared to alkaline ashing method reported in literature, the developed method is simple, fast, high in chemical recovery and less cross-contamination. This method has been successfully applied to analyse more than 100 vegetation samples collected in north China.

Neutron activation analysis

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DELAYED NEUTRON ACTIVATION ANALYSIS AT ANSTO

Mellodee Anvia, Susan A. Brown

ANSTO Minerals, New Illawarra Road, Lucas Heights NSW 2234, Australia, e-mails: mellodee.anvia@ansto.gov.au, susan.brown@ansto.gov.au

Keywords: DNAA, neutron, uranium, activation, nuclear, reactor

Activation analysis techniques including neutron activation analysis (NAA) and delayed neutron activation analysis (DNAA) are sensitive techniques which allow the rapid determination of several elements, including uranium and thorium, down to trace levels. ANSTO Minerals is an international mining consultancy within ANSTO, which provides expertise to mining companies on a range of areas including rare earth elements, critical metals and uranium ore processing, and on the removal of radioactivity from ores. ANSTO has dedicated NAA and DNAA facilities at the OPAL (Open Pool Australian Lightwater) nuclear research reactor. DNAA is regularly employed by ANSTO Minerals for the quantification of uranium concentrations in a wide variety of sample types from the copper, uranium, rare earth and other metals processing industries. In most cases, DNAA is a highly accurate means of measuring uranium concentrations in solids, and is often also a superior alternative to quantification by XRF analysis or fusion digest/ICP. However, the presence of some elements in a sample matrix, such as the rare earth elements, may compromise DNAA results. Here, the application of DNAA to a wide variety of sample matrices from the mining and minerals processing industries will be presented, and the limitations of the technique for the analysis of various sample types will be discussed. The application and/or development of correction methods at ANSTO Minerals to samples containing significant elemental interferences and high natural uranium concentrations will also be presented.

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INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS APPLIED TO ICE CORES

Giovanni Baccolo[1, 2, 3], *Massimiliano Clemenza*[3, 4], *Barbara Delmonte*[2], *Massimiliano Nastasi*[3, 4], *Ezio Previtali*[3, 4], *Valter Maggi*[2, 3]

[1]Department of Earth Sciences, University of Siena, Siena, Italy
[2]Department of Environmental Sciences, University of Milano-Bicocca, Milano, Italy
[3]INFN section of Milano-Bicocca, Milano, Italy
[4]Physics Department, University of Milano-Bicocca, Milano, Italy

Keywords: ice core, atmospheric dust, neutron activation analysis, trace elements

Ice cores are considered one of the most important natural archives for the reconstruction of the climate. The analysis of the chemical and physical properties of the ice strata and of its content allowed to reconstruct the atmospheric history of the last 800,000 years. From the analytical point of view the development of protocols and methods dedicated to such samples, characterized by very low concentrations and reduced availability, lead to extreme analytical performances. We report here the development and the application of a new method based on instrumental neutron activation analysis for the elemental characterization of the atmospheric mineral dust entrapped in polar and non-polar ice cores. The possibility to obtain an accurate and complete geochemical fingerprint of the material deposited at these remote sites in different climatic periods give us the possibility to identify and to highlight new and unexpected climatic and environmental processes.

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ELEMENTAL ANALYSIS OF INFANT FORMULAS BY INAA AND ICP-MS. COMPARISON OF ESTIMATED INTAKES WITH THE SAFETY LIMITS FOR TRACE ELEMENTS

Ewelina Chajduk, Marta Pyszynska, Halina Polkowska-Motrenko*

Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland, *e-mail: e.chajduk@ichtj.waw.pl

Keywords: elemental content, infant formulas, NAA, ICP-MS

During infancy, a period of rapid growth, nutrient requirements per pound of body weight are proportionally higher than at any other time in the life cycle. Breast milk is recommended as an only source of infant nutrition for the first months of life. However, data show that only 3% of European babies are entirely breast fed. Therefore, milk-based formulas and/or milk substitutes have to be used then it is difficult to bring up an infant on mother's milk. A number of commercial infant ready to feed infant food are available, intended for the infants aged 0–6 months. Depending on producers of the infant formula and food, data concerning selected essential elements concentration is given. Most essential trace elements in infant formula have received very little attention.

Neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS) has become a

mainstay of biochemical trace elements research due to their several important advantages. One of them is a detection limit – both have been shown to be applicable to the analysis of many elements at sub-picogram amounts. In the case of INAA, the another advantage is freedom from analytical blank and other problems related to sample dissolution.

The aim of this study was the critical evaluation of analytical performance of ICP-MS and INAA for the determination of selected elements in infant formulas. The complementary use of NAA and ICP -MS to study the elemental composition of the food samples, allows to obtain reliable and richer analytical information. In the case of As, Fe and Se determinations, definitive methods based on radiochemical NAA, as the methods of the highest metrological quality, have been used to check the accuracy of obtained results.

The daily intake of selected elements in the age 0–6 months for non-breast fed infants was estimated and compared with present safety limits. The current study provides a broad overview of the intake of essential non-essential trace elements in commercially available baby foods, and can be useful for further studies in health risk assessments.

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THE HISTORY OF NEUTRON SELF-SHIELDING CORRECTIONS IN NEUTRON ACTIVATION ANALYSIS

Cornelia Chilian, Gregory Kennedy*

Dept. of Engineering Physics, Ecole Polytechnique, Montreal, Canada, *e-mail: cornelia.chilian@polymtl.ca

Keywords: neutron activation analysis, neutron self-shielding

Neutron activation analysis is usually considered as relatively free of matrix effects but for materials containing strong neutron absorbers the measurements are often subject to significant neutron self-shielding, which should be corrected using an appropriate model. The problem is divided into thermal and epithermal neutron self-shielding. Thermal neutron self-shielding was considered simpler and, since the 1950s, models based on the capture and scattering cross-sections have been developed and put into use in many laboratories to calculate the thermal neutron self-shielding correction factors for samples of different shapes, sizes and chemical composition. In 2012 it was pointed out that five thermal neutron self-shielding correction routines in common use gave widely differing self-shielding factors for the same sample. All the models had neglected the effect of neutrons reflecting back into the sample from surrounding materials; further investigation is needed.

The capture of epithermal neutrons has always appeared more complicated since each nuclide has its own pattern of resonances. The only resonance self-shielding calculations were the deterministic and Monte-Carlo calculations carried out for reactor development and these were not available to the NAA community. The only means of obtaining reliable epithermal neutron self-shielding factors was to measure them for specific cases, such as by irradiating stacks of foils. With time the Monte-Carlo calculations improved and were useful for developing physical models. A breakthrough occurred in 2003 when Salgado discovered that the curves of epithermal neutron self-shielding factor vs amount of element were the same for all nuclides, just as for thermal neutrons, making possible the development of a model with only one parameter for each nuclide. Chilian developed this for NAA, determining the epithermal neutron absorption cross-sections for all nuclides used in NAA, using the Salgado weighted mean of the resonances. Trkov achieved a similar result by integrating over the cross-sections in the resonance region. Now epithermal self-shielding factors for any cylindrical sample can be calculated by Chilian's spreadsheet with the sigmoid function or by Trkov's MATSSF package.

To be useful for routine NAA work, the correction software needs to be automated to use the mass fractions measured for batches of samples. Since the correction factors depend on the measured mass fractions, the calculation must be iterative. Chilian has demonstrated the feasibility of iterative self-shielding corrections and automated them for routine NAA.

The presentation will recount the history and describe current and foreseen future developments. A project has just begun to incorporate the best features of the self-shielding models into a user-friendly and all-encompassing software package.

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LOW BACKGROUND NEUTRON ACTIVATION ANALYSIS: A HIGH SENSITIVITY TECHNIQUE FOR PHYSICS OF RARE EVENTS

Massimiliano Clemenza

Department of Physica Università degli Studi di Milano Bicocca; INFN division of Milano Bicocca
Piazza della Scienza, 3 20126 Milano Italy, e-mail: massimiliano.clemenza@mib.infn.it

Keywords: LBNAA, physics of rare events, lead, copper PTFE

The Low Background Neutron Activation Analysis (LBNAA) foresee to minimize all sources of noise that limit the sensitivity of the NAA technique, as the contamination in materials containers used during sample irradiation, the radioactive background due to the major and minor elements of the sample matrix through radiochemical techniques or radioactive background suppression methods (gamma-gamma coincidences) as well as the use of detector with very low intrinsic radioactive background. In present work it show an application of LBNAA in the materials selection for physics of rare events experiments.

In fact, the new generation of Physics of rare events experiments need increasing constraints in the radio-purity of materials. The natural radioactive background can cover the signal of extremely rare processes, such as neutrino oscillation, double beta decay, and dark matter searches. Normally these experiments are situated in underground labs in order to reduce the natural background due to cosmic radiations, but not from the one due to the experimental apparatus itself. For example, the radiations emitted from radionuclides present in the experimental set-up can often have the same energy signature of the rare processes studied.

In order to reduce the intrinsic background of these experiments is widespread the utilization of shielding and structure made of ultra-pure materials. In these latest years it has become of great importance to found an optimal method to estimate limits on the radio-purity of the materials of 10–12–10–13 g of contaminants / g of materials. In this way also the evaluation of 232Th and 238U contaminations in ultra-pure materials becomes very important, because this two radionuclides are the principal cause of radioactive background due to the detectors facilities.

In particular the goal of the present work was to determine 232Th and 238U contaminations in ultra-pure materials like High purity Copper, High purity Lead (modern and ancient roman lead), PTFE, High purity Silicon and others. These materials can be used in almost all the radiation detectors with low background facilities and for the shielding of many experiments of Physics of Rare Events (CUORE, GERDA, MAJORANA).

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DEVELOPING A METHOD BASED ON NEUTRON ACTIVATION ANALYSIS TO DETERMINE THE ORIGIN OF METALS USED IN ANTIQUITY

Alessandro Contini[1, 2], Massimiliano Clemenza[3, 4], Giovanni Baccolo[4, 5], Massimo Carpinelli[1, 2], Ettore Fiorini[3, 4], Ezio Previtali[4], Valeria Sipala[1, 2], Gabriele Mulas[2], Stefano Enzo[2], Sebastiano Garroni[2]*

[1]INFN section of Cagliari, Monserrato, 09042, Italy
[2]University of Sassari, Via Vienna 2, Sassari, 07100, Italy, *e-mail: alessandro.contini@hotmail.com
[3]Physics Department, University of Milano-Bicocca, Milano, 20126, Italy
[4]INFN section of Milano-Bicocca, Milano, 20126, Italy
[5]University of Siena, Siena, 53100, Italy

Keywords: neutron activation analysis, archaeometallurgy, ancient Roman Lead, cultural heritage

The study of the production and trade of metals in antiquity poses difficult questions to solve as about the origin of materials brought to light by archaeologists. In particular, the trade associated with the archaeo-metallurgy were developed by ancient civilizations distributing goods along routes even far away for thousands of kilometers with amazing results.

To determine the origin of metals used in antiquity in particular for those in the form of ingots, the methods normally used are the study of the archaeological context, the type and the epigraphy eventually reported on the finds. In absence of these information the study of the chemical composition and the determination of the isotopic ratios of lead constitutes a valid supports for archaeologists.

In the present work six ingots of ancient Roman Lead, retrieved from Mal Di Ventre sea (Sardinia-Italy) and associated to three different foundries located in Sierra de Cartagena in Spain (SOCPONTILIENORUMMF, QAPPCF and MCPONTILIENORUMMF) has been chosen to develop a method based on Neutron Activation Analysis and a Multivariate statistical procedure (Principal Component Analysis PCA). This approach allows to define the elemental “fingerprint” of the sample with a non-destructive technique, covering a very important request coming from cultural heritage authorities.

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INVESTIGATION OF PARTICULAR SPECIES OF MOSSES AND LICHENIZED FUNGI FROM ANTARCTICA: INFLUENCE OF ALTITUDE AND SUBSTRATES ON THE ELEMENTAL CONTENT

O. A. Culicov[1, 2], *L. Yurukova*[3], *O. G. Duliu*[1,4], *I. Zinicovscaia*[1, 5]

[1]Joint Institute for Nuclear Research, Frank Laboratory of Neutron Physics, 141980, Dubna, Russian Federation
[2]National Research and Development Institute for Electrical Engineering, (ICPE-Advanced Research), 30, Splaiul Unirii, 74204, Bucharest, Romania
[3]Bulgarian Academy of Sciences, Institute of Botany, Acad. G. Bonchev Str., Block 23, 1113 Sofia, Bulgaria
[4]University of Bucharest, Department of Structure of Matter, Earth and Atmospheric Physics and Astrophysics, 405, Atomistilor str., 077125 Magurele (Ilfov), Romania
[5]Moldavian Academy of Sciences, Institute of Chemistry, 3, Academiei str., 2028 Chisinau, Moldova

The Antarctic region, being the least polluted in the world and having extreme climatic conditions, offers a possibility to perform a large spectrum of investigations regarding natural phenomena. Mosses and lichens are well-established bioindicators and biomonitors of the environmental status, therefore, it is very important to know the environment (substrate, altitude of location where they grow) influence on their elemental content. Samples of mosses and lichenized fungi, as well as neighboring soil collected, from different altitudes of the Livingston Island (Antarctica) were analyzed. Total content of 38 elements was determined by INAA at the IBR-2 reactor. This allowed calculating the enrichment factor with respect to the soil. The data, interpreted within the model of the Reference Plant and the Upper Continental Crust, were compared with the previous studies regarding the same species of mosses in the same area.

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NEUTRON ACTIVATION ANALYSIS AND MICROSCOPY OF EXTRA-TERRESTRIAL MATERIALS

Marina Frontasyeva

Department of Neutron Activation Analysis and Applied Research, Division of Nuclear Physics, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, str. Joliot-Curie, 6, Dubna, 141980, Moscow Region, Russian Federation, e-mail: marina@nf.jinr.ru

Keywords: instrumental NAA, radiochemical NAA, epithermal NAA, major and trace elements, lunar rocks, meteorites, manganese micronodules, moss, peat bog cores, cosmic dust

A brief review of the results obtained by radiochemical neutron activation analysis of lunar rocks and fine-grained lunar “soil,” (Apollo missions 1969–1972) [1, 2] is given. Examples are demonstrated of applying instrumental epithermal NAA at the reactor IBR-2 in FLNP JINR, Dubna for determination of major and trace elements (Na, Al, Cl, Mn, K, Ca, Ti, Fe, Sc, V, Cr, Ni, Co, Zn, Cu, As, Sr, Rb, Zr, Mo, Sn, In, Sb, Ba, Cs, La, Ce, Nd, Eu, Sm, Tb, Dy, Yb, Hf, Ta, W, Th, U) in manganese micronodules from the North Pacific Ocean Clarion-Clipperton abyssal plane [3]. To classify meteorites of unknown origin according to their element contents, a total of 38 elements were determined. Applying Principle Component Analysis, meteorites of carbonaceous chondrite and iron types were distinguished. Attempts were made to employ NAA in combination with microanalysis (SEM, TEM) for search for cosmic dust in natural moss planchettes from Russian Western Siberia, Arctic (Northern Norway) and Antarctica (King George Island), as well as in melting ice of the Arktu glacier in the Altay Mountains. Peat bog cores in Poland [4] and Russia were used for retrospective studies of deposition of micrometeorites, anthropogenic and cosmic dust. Nowadays neutron activation analysis which proved to be a powerful tool for studying trace elements finds more and more applications in investigation of extra-terrestrial materials.

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APDC/MIBK AND WATER EXTRACTABLE INORGANIC ARSENIC(III) AND ARSENIC(V) SPECIES IN JAPANESE HIJIKI BY NEUTRON ACTIVATION ANALYSIS

Michiko Fukushima[1], *Jatechan Channuie*[2], *Arporn Busamongkol*[2], *Sirinart Laoharojanaphand*[2], *Amares Chatt*[3]

[1]Department of Science and Engineering, Ishinomaki Senshu University, 1 Minamisakai, Ishinomaki, Miyagi, 986-8580, Japan, e-mail: fukusima@isenshu-u.ac.jp

[2]Thailand Institute of Nuclear Technology, 9/9 Moo 7 Tumbon Saimoon, Ongkharak, Nakhonnayok 26120, Thailand, e-mails: jatechan.c@gmail.com, arpornbusa@yahoo.com, l.sirinart@gmail.com

[3]Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, 6274 Coburg Road, Room 212, PO BOX 15000, Halifax, NS, B3H 4R2, Canada, e-mail: chatt@dal.ca

Keywords: arsenic, speciation, hijiki, NAA

Edible seaweeds are known to contain a number of elements. Some of them are of nutritional importance for Japanese population groups. Although the biological role of arsenic for human beings has not been fully established yet, some physico-chemical form of the element can be toxic at certain levels. Among the various arsenic species that exist in nature, inorganic As(III) species is said to be most toxic followed by inorganic As(V). Hijiki, one of edible seaweeds, is well known for its rather high levels of arsenic. Therefore, it is of interest to have simple methods available for the determination of low levels of inorganic As(III) and As(V) species in Japanese hijiki samples. Various types of atomic absorption spectrometry (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) are commonly used for arsenic speciation analysis. Neutron activation analysis (NAA) is one of the most sensitive methods available for the analysis of arsenic in seaweeds. In this work, the total amount of arsenic in several reference materials, namely NMIJ 7405a Hijiki, NIES No. 9 Sargasso and NMIJ CRM 7402a Cod Meat were analyzed by instrumental neutron activation analysis (INAA) for the validation of the method. Levels of inorganic As(III) and As(V) in these materials and hijiki samples were also measured by separation of these species followed by NAA. The separation method consisted of solvent extraction by APDC/MIBK and back extraction of the species in nitric acid. The samples were irradiated for 3 h at a neutron flux of 1×10^{12} cm^{-2} s^{-1} at the Thailand Institute of Nuclear Technology (TINT). After a decay of one day, arsenic was quantitatively assayed using ^{76}As (559 keV, half-life 1.08 d) by gamma-ray spectrometry. The ratios of As(III) and As(V) to total arsenic for hijiki samples were 0.01–0.05 and 0.07–0.44, respectively.

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CYCLIC NEUTRON ACTIVATION ANALYSIS OF LARGE SAMPLES WITH A PULSED 14 MeV NEUTRON SOURCE

Frank Mildenberger, Eric Mauerhofer

Institute of Energy and Climate Research – Nuclear Waste Management and Reactor Safety, Forschungszentrum Juelich GmbH, 52425 Juelich, Germany

Keywords: large samples, 14 MeV neutron sources, cyclic neutron activation, prompt and delayed gamma-rays

Prompt gamma neutron activation analysis using a 14 MeV neutron generator is a promising analytical technique to determine nonradioactive elements in 200 L radioactive waste drums [1, 2]. However further information on the elemental composition of the waste may be obtained measuring the delayed gamma rays of short-lived radionuclides (e.g. ^{16}N, ^{24m}Na, ^{27}Mg, ^{28}Al, ^{52}V and ^{207m}Pb) induced by fast and thermal neutron reactions. In a previous study dealing with the die-away time of thermal neutrons in various large samples [3] we showed that a waiting of about 12 ms after the end of the neutron pulses is required to measure delayed gamma rays without appreciable interferences of prompt gamma rays.

Cyclic neutron activation i.e. the subsequent measurement of prompt and delayed gamma rays between fast neutron pulses is applied for the analysis of the 200 L drum filled with concrete and a large lead sample. The neutron generator was operated in pulse mode at a neutron emission of about 8×10^7 n·s^{-1}. The length of the neutron pulses was set to 2 ms and the repetition time to 40 ms. Using two multi channel analyzers the prompt gamma-rays were measured directly after the neutron pulses for 20 ms and the delayed gamma-rays for 20 ms after a waiting time of 18 ms from the end of the neutron pulses. Prompt and delay gamma-ray spectra were recorded for total counting time of 3600 s. In this work the methodology to determine the elemental composition of concrete is presented. It includes the evaluation of the fast and thermal neutron flux using the steel drum as monitor as well as correction factors based on thermal neutron die-away times for quantification through the prompt gamma rays measured in a decaying thermal neutron flux. The results are compared with those obtained by setting irradiation and counting conditions preferably for the measurement of thermal neutron capture gamma rays [2]. Finally characterization of a large lead sample using thermal neutron capture gamma rays and delayed gamma rays of the short-lived isotope ^{207m}Pb ($T_{½}$ = 805 ms) induced by (n,2n)-reaction with fast neutrons is described.

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ACTIVATION ANALYSIS IN GEOCHEMICAL CHARACTERIZATION OF MOLDAVITES AND THEIR PARENT MATERIALS

Jiří Mizera[1], Zdeněk Řanda[1], Jan Kameník[1], Karel Žák[2]

[1]Nuclear Physics Institute, The Czech Academy of Sciences, Hlavní 130, 250 68 Řež, Czech Republic,
e-mails: mizera@ujf.cas.cz, randa@ujf.cas.cz, kamenik@ujf.cas.cz
[2]Institute of Geology, The Czech Academy of Sciences, Rozvojová 269, 165 00 Praha 6, e-mail: zak@gli.cas.cz

Keywords: moldavite, Ries Impact Structure, Upper Freshwater Molasse, INAA, IPAA

The Central European tektites – moldavites – have been linked to the Ries Impact Structure (Nördlingen, Germany), based on correspondence of their age (~14.5 Ma) and similarity of chemical composition of moldavites with their supposed source materials – unconsolidated surface sediments dated to the Middle Miocene, the so-called Obere

Süßwassermolasse (OSM, Upper Freshwater Molasse), which covered a major part of the pre-impact Ries area. The study presents geochemical characterization of a large collection of more than one hundred moldavites from the major parts of the Central European tektite strewn field (Southern Bohemia, the Cheb Basin in Western Bohemia, Moravia, and Lusatia in Germany), and selected samples of unconsolidated sediments and bedrock samples collected in the Ries area. Most attention was paid to various OSM sediments, marginally also Miocene karst residues and Triassic and Jurassic sedimentary rocks were sampled as potential source materials present at the target area. Detailed geochemical characterization of moldavites and Ries sediments and rocks was based on determination of about fifty major and trace elements, using various modes of instrumental neutron activation analysis, supplemented by instrumental photon activation analysis.

The geochemical data for moldavites and their probable source materials have been compared in terms of major elements. Despite similarity in the chemical composition of some OSM samples with moldavites, there are some significant differences in the major element contents, namely significantly higher contents of Al, Na and Fe, and lower contents of K, Ca and Mg in the sediments than in moldavites. These differences can be partly solved by recalculation of the composition of the sediments to their volatile-free bases, since water, carbon and other volatiles escaped during the impact process and moldavite formation. Nevertheless, another component rich in K, Ca and Mg is highly probable. Presence of an uncombustible residue of biomass and soils, which would contribute to high K, Ca and Mg levels in moldavites, may be applicable to modeling composition of moldavites with extremely high K/Na ratios, but their proportion in a majority of moldavites was probably low. Comparison of the chemical composition of moldavites and residual karst sediments exclude also these materials as a dominant component of the moldavite parent mixture. The observed differences between the source materials and moldavites cannot be explained by a single process or factor. Clearly, multiple factors influenced the element ratios during the moldavited formation processes.

Acknowledgements
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DETERMINATION OF ^{235}U AND ^{239}Pu IN RADIOACTIVE WASTE USING CYCLIC NEUTRON ACTIVATION

T. Nicol[1, 2], E. Mauerhofer[2], C. Carasco[1], B. Perot[1], J. Collot[3]*

[1]CEA, DEN, Cadarache, Nuclear Measurement Laboratory, F-13108 Saint-Paul-lez-Durance, France

[2]FZJ, Institute for Energy and Climate Research – Nuclear Waste Management and Reactor Safety, Wilhelm-Johnen-Straße, D-52428 Jülich, Germany, *e-mail: e.mauerhofer@fz-juelich.de

[3]Laboratoire de Physique Subatomique et de Cosmologie, Université Grenoble Alpes, CNRS/IN2P3, Grenoble, France

Keywords: neutron activation analysis, fission delayed gamma rays, radioactive waste characterization

In the frame of collaboration between Forschungszentrum Jülich GmbH (Germany) and CEA Cadarache (France), the possibility to determine ^{235}U and ^{239}Pu in 200 L radioactive waste drums by measuring fission delayed gamma rays is being studied. Following preliminary performance assessment reported in [1], a 200 L drum filled with concrete or polyethylene was irradiated in the MEDINA (Multi Element based on Instrumental Neutron Activation) facility [2] using a pulsed 14 MeV neutron generator and gamma rays were measured with a High Purity Germanium detector (HPGe). The length of the neutron pulses was set to 10 ms and the repetition time to 50 ms. During the first 10 ms following each neutron pulse, the prompt gamma rays emitted from the main element of the waste or package are measured and used to evaluate the average thermal neutron flux within the waste. After this 10 ms delay, thermal neutron have almost vanished and delayed gamma rays are counted during the next 30 ms without appreciable interferences of prompt gamma rays. The cycle [10 ms pulse – 10 ms prompt gamma measurement – 30 ms delayed gamma measurement] is repeated with a 20 Hz frequency. Moreover, delayed gamma-ray spectra were acquired after the shutdown of the neutron generator, during 15 minutes and 5 hours using two different multi-channel analysers, in view to record gamma rays emitted by medium- and long-lived fission products, respectively. Measurements were also performed with and without ^{60}Co and ^{137}Cs sources to simulate the background due to gamma emission of radioactive waste. In this work, an analytical approach to determine detection limits of ^{235}U and ^{239}Pu is presented, and the results are compared to those obtained by MCNPX simulations.

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INVESTIGATION OF ISTANBUL'S NEOLITHIC AGE ANIMAL FINDINGS BY NEUTRON ACTIVATION ANALYSIS

Ayse Tuba Ongül[1], Sevilay Haciyakupoglu[1], Johannes H. Sterba[2], Sema Erenturk[1]*

[1]Energy Institute, Istanbul Technical University, Istanbul, Turkey, *e-mail: haciyakup1@itu.edu.tr
[2]Atominstitut, Technische Universität Wien, Vienna, Austria, e-mail: jsterba@ati.ac.at

Keywords: Istanbul, NAA, Neolithic, shell

In the study, the shells of Gastropods, Mytilus galloprovincialis, Acanthocardia spinosa, Ostrea edulis, several fish vertebras as well as a tortoise shell were analyzed by neutron activation analysis. Results were compared to those from the literature to contribute some subjects such as Istanbul's oldest animals lived in Neolithic age by evaluation of the results. Findings were collected from various depths from Marmaray-Metro Project Archaeological Excavations at Yenikapı, Istanbul. Neutron Activation Analysis technique was applied by irradiation of samples at the TRIGA Mark II Research Reactor of the Atominstitut of Vienna University of Technology. In this frame concentrations of Na, K, Sc, Cr, Fe, Co, Ni, Zn, As, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th and U elements were determined.

The distribution of the elements in the shells was categorized into three groups. Of these, first 7 elements (Na, K, Fe, Co, Cr, Ni, and Zn) were grouped together because of their contribution to living organisms. Their average concentrations changes from 0.243 to 11.33 mg×kg^{-1}. Second ten elements (Sc, As, Rb, Sr, Zr, Sb, Cs, Ba, Hf, and Ta) are not essential to living organisms, nevertheless may provide additional information regarding e.g. pollution of the sea with further discussion. Their concentrations are between 0.016 and 3.142 mg×kg^{-1}. The remaining ten elements consists from Lanthanides and Actinides (La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Th and U) which often called "Rare Earth Elements" are the most commonly investigated elements with NAA. Their average concentration varies between 0.078 and 5.523 mg×kg^{-1} throughout species. The main contribution of Zn and U comes from fish bones and tortoise shell in accordance with the differences in chemical composition between shells and bones of marine animals.

The characteristics of the 27 elements were studied separately in samples. It is known that, in mollusk taxonomy, the elements have unique values. In other words, element concentrations in various mollusk shells depend mainly on the taxonomic characteristics of mollusks. In different bionomic environments, various element distributions of the same species are attributed to the different geochemical characters of the each environment. Considering that the organisms are the most active and deterministic factors of the environment, data obtained in this study will serve as a database for future research.

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PERFORMANCE OF NAA LABORATORIES IN THE ASIA-PACIFIC REGION IN DETERMINING RARE EARTH ELEMENTS

A. Stopic[1], J. W. Bennett[1], G. Damdinsuren[2], M. Ebihara[3], M. S. Hamzah[4], D. M. Ho[5], M. A. Islam[6], I. Silachyov[7], Sutisna[8], C. Xiao[9]*

[1]Neutron Activation Group, Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia, *e-mail: attila.stopic@ansto.gov.au
[2]Institute of Physics and Technology, Mongolian Academy of Sciences, Mongolia
[3]Division of Chemistry, Tokyo Metropolitan University, Japan
[4]Analytical Chemistry Application Group, Nuklear Malaysia, Malaysia
[5]Nuclear Research Institute, Vietnam Atomic Energy Institute, Hanoi, Vietnam
[6]Institute of Nuclear Science & Technology, Atomic Energy Research Establishment, Savar, Dhaka, Bangladesh
[7]Institute of Nuclear Physics, National Nuclear Centre of the Republic of Kazakhstan, Kazakhstan
[8]National Nuclear Energy Agency of Indonesia (BATAN), Serpong, Tangerang, Indonesia
[9]Department of Nuclear Physics, China Institute of Atomic Energy, Beijing, China

Keywords: NAA, inter-laboratory comparison, rare earth elements

The Forum for Nuclear Cooperation in Asia (FNCA) aims to demonstrate and promote the use of nuclear methods and technologies for socio-economic benefit in the Asia-Pacific region. Mining is an important industry for many countries in the region and in recent years there has been an upsurge in demand for rare earth elements (REEs). Neutron activation analysis (NAA) is a suitable method to quantify the concentration of many REEs in samples of soils, sediments and rocks. The FNCA organized an inter-laboratory comparison using three certified reference materials as a means for participating NAA laboratories to benchmark their performance and subsequently to engage with potential end-users of their services.

Packets of three certified reference materials covering a range of REE concentrations were purchased from a commercial supplier and distributed to participants. The three materials were chosen to test the ability of an NAA laboratory to deal with different levels of complexity. Different self-shielding corrections were required in the analysis and one sample had a relatively high concentration of uranium, requiring a significant correction for fission products.

Seven laboratories participated in the NAA inter-comparison: Australia, Bangladesh, China, Indonesia, Kazakhstan, Malaysia and Vietnam. Both the relative and k_0 methods of standardisation were variously employed. Two other laboratories, Japan and Mongolia, analysed the samples using inductively coupled plasma mass spectrometry (ICP-MS) as an independent method.

The paper presents the results from each laboratory and assesses performance using z-scores. Comments are made about the various influencing factors, from choice of standards through to adequacy of self-shielding and fission product corrections.

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A MULTI-DETECTORS INTEGRATED AUTOMATION SYSTEM OF ROUTINE INAA

Yonggang Yao, Caijin Xiao, Xiangchun Jin, Long Hua, Pingsheng Wang, Bangfa Ni

Department of Nuclear Physics, China Institute of Atomic Energy, P.O. Box 275-50, Beijing, China, e-mail: yaoyonggang@ciae.ac.cn

Keywords: routine INAA, integrated automation, pneumatic transfer system, ADVNAA

An instrumental neutron activation analysis (INAA) measurement system with fully automation, high accuracy and three detectors was successfully established at China Institute of Atomic Energy (CIAE). The characteristics include: (1) The Kingview software was employed to control all the system which includes pneumatic transfer system (PTS), programmable logic controller (PLC) and step motor. Of course, the manual switch is also designed for each step of sample transfer. (2) The sample rack have a capability of 200 samples which is assigned in a line-up of 10 rectangle boxes, each box contains 20 sample rabbits stand in a line. The sample is sent to the detector from bottom of the box. After counting, the rabbit will return back to the top of same box in queue automatically for the next time counting. (3) The high efficiency and accuracy: Three detectors can be run simultaneously at 24 hours continuously. Photoelectric sensor was fixed at each sample input and output point of pneumatic transfer system. The radio frequency identification (RFID) tag was installed on each sample capsule/rabbit. The RFID reader was installed each HPGe detector chamber in order to keep the consistence of the sample ID with counting spectrum. (4) Each sample counting condition can be optimized through the automatic adjustment of sample counting position to maintain a reasonable dead time. (5) The operation interface was designed as menu style. All the status of sample position, detectors, counting spectrum and sample transfer can be displayed on the screen. (6) The NAA software with the functions of relative method, K0 method, interference correction as well as NAA report, etc. is also connected with the counting system. The NAA data management can be carried at any time through batch or single sample analysis.

This integrated automation system has been demonstrated more than 100 times for each step automatically. The results indicated the system is successful for routine INAA.

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INAA CONTRIBUTIONS TO THE CERTIFICATION OF ARSENIC SPECIES AND OTHER TRACE ELEMENTS IN SRM 3232 KELP

Rolf Zeisler, Rabia Oflaz, Rachel Stanoyevitch, Lee Yu*

Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899 USA, *e-mail: rolf.zeisler@nist.gov

Keywords: activation analysis, extraction of As species, liquid chromatography, nutritional supplements, uncertainty

The National Institute of Standards and Technology (NIST) is developing a standard reference material (SRM) for kelp in support of US Food and Drug Administration's (FDA) food safety and nutrition measurements program, and to meet the needs in the food industry for compliance with the current good manufacturing practice (cGMP) and the Food Safety Modernization Act (FSMA). Instrumental neutron activation analysis (INAA) is contributing results on trace element mass fractions, which are used for assessment of homogeneity and are combined with results from other techniques for value assignment. A special effort is dedicated to the determination of arseno-sugar compounds, which are representing about 60% of the total arsenic measured in the kelp. INAA is used for the direct determination of As in the original material, the aqueous extracts containing the As species, the extracted material, and in the fractions separated by liquid chromatography (LC) that contain the individual As compounds. The latter step provides the needed calibration for the inductively coupled mass spectrometry (ICP-MS) measurements of the same species in the extracts after LC. Results are evaluated for uncertainty and, where appropriate, compared with other techniques' analytical results.

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SPIRULINA PLATENSIS AS BIOSORBENT OF HEAVY METALS FROM MODEL SOLUTIONS AND INDUSTRIAL EFFLUENTS

I. Zinicovscaia[1, 3], *L. Cepoi*[2], *O. A. Culicov*[1, 4], *M. V. Frontasyeva*[1]

[1]Joint Institute for Nuclear Research, Joliot-Curie Str., 6, 1419890 Dubna, Russia
[2]Institute of Microbiology and Biotechnology of the Academy of Science of Moldova, 1, Academiei Str., 2028 Chisinau, R. Moldova
[3]The Institute of Chemistry of the Academy of Sciences of Moldova, 3, Academiei Str., 2028 Chisinau, R. Moldova
[4]National R&D Institute for Electrical Engineering ICPE-CA, 313, Splaiul Unirii, District 3, 030138, Bucharest, Romania

The time-dependent accumulation of heavy metals (Zn, Cr, Co, Fe, and Cu) from model systems (single- and multi-component) and residual waters of an engineering plant was investigated using cyanobacteria *Spirulina platensis*. Two analytical techniques, neutron activation analysis and atomic adsorption spectrometry, were used to trace the the uptake of metals by spirulina biomass. In the experiment on the metal biosorption from model solutions the efficiency of studied metal uptake changes in the following order Fe(III) > Zn(II) > Cu(II) > Co(III) > Cr(IV) (single-metal solutions) and Fe(III) > Cu(II) > Zn(II) > Co(III) > Cr(IV) (multi-metal system). The degree of metal retention present in wastewater increased rapidly in the first 5–15 min of the reaction, then stayed approximately at the same level or slightly decreased. Fourier transform infrared spectroscopy was used to identify functional groups responsible for metal binding.

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IDENTIFICATION OF ELEMENTAL SIGNATURES IN URANIUM SAMPLE FROM NUCLEAR FUEL CYCLE BY PIXE, PIGE AND NRA METHODS USING 3 MV TANDETRON PARTICLES ACCELERATOR

A. I. Apostol[1,2]*, *A. Pantelica*[1], *O. Sima*[2], *V. Fugaru*[1]

[1]Horia Hulubei National Institute for Physics and Nuclear Engineering (IFIN-HH), Bucharest-Magurele, Romania,
*e-mail: andrei.apostol@nipne.ro
[2]University of Bucharest, Faculty of Physics, Bucharest-Magurele, Romania

Keywords: nuclear forensics, uranium, metallic impurities, IBA, gamma spectrometry

This paper describes three non-destructive analytical methods for identification of elemental signatures in uranium samples from nuclear fuel cycle. The measurements are based on Particles Induced X-ray Emission (PIXE), Particles Induced Gamma-Ray Emission (PIGE), and Nuclear Reaction Analysis (NRA) applied to nuclear fuel cycle uranium samples of different origins. The uranium samples were irradiated by 5 MeV protons at the 3 MV Tandetron particle accelerator of IFIN-HH. The prompt X and gamma rays, as well as gamma rays resulted from the activation reactions were measured using High Purity Germanium (HPGe) detectors. The GUPIX and GAMMAW software were used for the determination of major, minor and trace elements present in the studied samples.

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THE RADIOLOGICAL SEALED SOURCE LIBRARY: A COMPILATION OF FORENSIC SIGNATURES AND DISTRIBUTION PATHWAYS

Jodi L. Canaday[1]*, *David B. Chamberlain*[1], *Seema R. Naik*[1], *Yu Tang*[1], *Martha R. Finck*[2], *Kevin P. Carney*[2]

[1]Nuclear Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, U.S., *e-mail: jodi.canaday@anl.gov
[2]Idaho National Laboratory, Idaho Falls, U.S., e-mail: Martha.Finck@inl.gov

In the event of a terrorist obtaining and possibly detonating a device with radiological material, radiological forensic analysis of the material and source capsule could provide law enforcement with valuable clues to the origin of the material; this information could then provide further leads on where the source or material was obtained.

The concept of nuclear forensic signatures for interdicted nuclear materials is generally understood to include isotopic ratios, trace element impurity ratios, material age and morphological aspects of the material. In contrast, radiological forensic signatures for radiological sealed sources focus more on the physical design and chemical composition of the radioactive material and attributes of the source capsule or containers in which the material is contained.

Argonne and Idaho National Laboratories have been working since 2003 on understanding signatures that could be used to identify specific source manufacturers. These signatures include elemental and isotopic abundance, source materials of construction, dimensions, weld details, of the radioactive material. These signatures have been collected in a library, known as the Radiological Sealed Source Library. Data, collected and validated through collaborative agreements with regulatory agencies and source manufactures, is supplemented through other diverse, open source data streams. Details of the Radiological Sealed Source Library will be described.

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CAPABILITIES AND EXPERIENCE OF THE INSTITUTE OF NUCLEAR PHYSICS IN THE REPUBLIC OF KAZAKHSTAN IN NUCLEAR FORENSICS

Petr Chakrov, Viktor Gluchshenko, Alexandr Pustovoy, Vladimir Solodukhin*

Institute of Nuclear Physics, Ibragimov St. 1, Almaty, 050032, Republic of Kazakhstan, *e-mail: vik.inp.kz@gmail.com

Keywords: nuclear forensics, radioactive sources, nuclear materials, radionuclide analysis, elemental analysis

One of the main direction of activities of the Institute of Nuclear Physics (INP) located in Almaty, Kazakhstan, is the development and application of nuclear-physical methods for analysis of the environmental objects and mineral raw materials. Having retained the scientific capabilities through the collapse of the Soviet Union, in recent years the Institute has upgraded its instrumentation and methodological frameworks in this area. Currently, the complex of analytical methods based on the up-to-date spectrometric and analytical equipment is available in INP, including the elemental analysis such as X-ray fluorescence analysis, inductively-coupled plasma mass spectrometry, neutron activation analysis, and also the instrumental and radiochemical techniques for analysis of radionuclide and isotopic composition. In particular, this analytical complex along with specially developed procedures is applied for forensic examinations of various nuclear and radioactive materials delivered by law enforcement agencies. The set of techniques applied for forensic examination is different in each specific case, depending on features of the material and requirements of the investigators. Short-term material categorization techniques such as visual inspection, dose rate measurement and gamma-spectrometry are used in all cases.

The Institute is licensed for handling of ionizing radiation sources, nuclear materials, radioactive substances and waste, and for providing the services such as determination of radionuclide content in various materials. INP has specialized laboratories and qualified staff for this kind of work. Quality management system at the Institute is certified for compliance with the ISO 9001 international standard, and the Center of Complex Ecological Research of INP engaged in nuclear forensics activities is accredited to meet the requirements of ISO/IEC 17025-2007 standard “General requirements for the competence of testing and calibration laboratories”. Quality of analyses is confirmed also by successful participation in international inter-laboratory comparisons and proficiency tests organized by the IAEA.

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NUCLEAR FORENSICS CENTER IN THAILAND

Kalaya Changkrueng, Harinate Mungpayaba, Arug Wititteeranon*

Office of Atoms for Peace, 16 Vibhavadi Rangsit Road, Lardyao, Chatuchak, Bangkok Thailand 10900, *e-mail: anne778@hotmail.com

Keywords: Nuclear Forensics Centre, CBRN Centres of Excellence, JRC-ITU

Thailand established Nuclear Forensics Centre in 2013 at Office of Atoms for Peace (OAP), Ministry of Science and Technology. Before OAP started the Centre, there are many activities preparing for the Project; Round Table Meeting, ASEAN Regional Forum Workshop, Training (Scientist, Forensic Science, Crime Scene Detection Police). Furthermore OAP submitted “Project 30: Network of Nuclear Forensics in South East Asia Region” to CBRN Centres of Excellence. European Commission Joint Research Centre – Institute for Transuranium Element (JRC-ITU) is an advisor. The objective of the project is to reinforcing public security by upgrading capabilities and methodologies to comprehensively assessment involving radioactive and nuclear materials and technology and to collect radioactive and nuclear materials information and develop database system. For the next activities, OAP would be the training of Nuclear Forensics Officer among South East Asia Countries.

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PYROLYSIS GAS CHROMATOGRAPHY MASS SPECTROMETRY ANALYSIS OF ORGANICS WITHIN AUSTRALIAN URANIUM ORE CONCENTRATES FOR SOURCE ATTRIBUTION

Tim G. Ditcham[1], Andrew Wotherspoon[2], Paul Kirkbride[1], Claire E. Lenehan[1], Rachel S. Popelka-Filcoff[1]*

[1]School of Chemical and Physical Sciences, Flinders University, Bedford Park SA 5042, Australia, *e-mail: tim.ditcham@flinders.edu.au
[2]Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, NSW 2234, Australia

Keywords: nuclear forensic science, organic analysis, pyrolysis gas chromatography mass spectrometry, uranium ore concentrate

One important facet of the nuclear forensic science discipline is the determination of the provenance of an unknown nuclear or radioactive material (source attribution), to support criminal investigations and prevent the further proliferation of material. Uranium ore concentrates (UOCs) are of particular interest to nuclear forensic science, as they contain greater than 65% uranium by weight and are a commodity traded internationally for the production of nuclear fuel. While several signatures have previously been identified within UOCs, the development of new signatures and analytical methodologies are necessary to advance the capabilities of source attribution in nuclear forensic science.

Recently, a sorptive extraction method has identified a number of organic compounds in UOCs used during the solvent extraction (SX) process in their production [1]. Purification of uranium via SX is a complex process, often requiring 2–3 different classes of organic compounds: an extractant (a complexing agent), a diluent (often kerosene) and possibly a modifier (to increase the solubility of uranium-extractant complex in the organic phase). Given the number of different organic compounds that can be used in the SX process and their state of purity, the organic profile of an interdicted UOC sample may be used to elucidate the SX processing method used in its production.

Research described in this presentation concerns the novel use of pyrolysis gas chromatography mass spectrometry (py-GC-MS) to investigate the organic content of Australian UOCs. Py-GC-MS thermally decomposes organic compounds into smaller, more volatile fragments that are introduced into the GC-MS system. As the organic compounds are liberated directly from the UOC, py-GC-MS requires minimal sample preparation and a nominal amount of UOC (<5 mg), whereas in contrast, the previous sorptive extraction method required 100 mg of material, and involved multiple preparative steps requiring >4 hrs per sample. This paper describes how the py-GC-MS technique is amenable to analysing seized UOC samples in small quantity.

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A NOVEL CERTIFIED REFERENCE MATERIAL – ^{243}Am

A. Fankhauser[1], R. Jakopič[1], Y. Aregbe[1], M. Crozet[2], C. Maillard[2], S. Richter[1], C. Rivier[2], D. Roudil[2]

[1]European Commission, Joint Research Centre (JRC), Institute for Reference Materials and Measurements (IRMM), Retieseweg 111, B-2440 Geel, Belgium, e-mails: adelheid.fankhauser@ec.europa.eu, rozle.jakopic@ec.europa.eu, yetunde.aregbe@ec.europa.eu, stephan.richter@ec.europa.eu
[2]Commissariat à l'énergie atomique et aux énergies alternatives (CEA/DEN), Centre de Marcoule, BP 171, 30207 Bagnols-sur-Cèze cedex, France, e-mails: marielle.crozet@cea.fr, christophe.maillard@cea.fr, cedric.rivier@cea.fr, danielle.roudil@cea.fr

Keywords: americium, plutonium, actinides, certified reference material, IDMS, TIMS

Americium is a transuranium element, produced by neutron capture in nuclear reactions. In spent nuclear fuel, as an example, ^{241}Am contributes, especially by its daughter ^{237}Np to the long-lived radioactive waste. Currently there is no ^{243}Am spike reference material commercially available, although a certified reference material (CRM) is indispensable for accurate measurements of ^{241}Am in nuclear materials for security, safety and safeguards. Furthermore, it can be applied in nuclear forensics by using the ^{241}Pu/^{241}Am chronometer (^{241}Pu, $t_{1/2} = 14.325 \pm 0.024$ a) to determine the elapsed time since the last chemical purification of plutonium and enables to calculate an age of (seized) nuclear material.

In order to meet the recommendation from the IAEA 2014 Technical Meeting on Nuclear Reference Materials for Destructive Analysis to fill this gap, CEA/CETAMA (CEA/DEN Marcoule, France) and JRC-IRMM initiated a joint project for the preparation and certification of a ^{243}Am spike CRM. The base material, about 3 mg of Am (88% ^{243}Am and 12% ^{241}Am) was made available and purified by extraction chromatography by CEA/LAMM (Material Analysis and Metrology Laboratory), and subsequently shipped to JRC-IRMM for further processing and certification in compliance with ISO Guide 34. About 580 units were prepared, each containing about 3.5 mL of diluted nitric acid solution with an americium mass fraction of about 1.5 µg/g.

For the determination of the ^{243}Am amount content in this reference material by ID-TIMS, in principle, a certified spike of another Am isotope is required. In absence of such a spike, a ^{241}Am in-house spike had been prepared from a highly enriched ^{241}Pu material (99.3%), which was characterised by ID-TIMS using IRMM-049d (^{242}Pu CRM). A three-fold purification was performed by anion exchange in order to remove the decay product ^{241}Am. The completeness of this purification was confirmed by γ-ray spectrometry. The ingrown ^{241}Am, produced by beta decay of ^{241}Pu, since the last purification (10th June 2014), is used as in-house spike for the ID-TIMS analyses to certify the novel ^{243}Am reference material. It will be certified for ^{243}Am, ^{241}Am and total Am amount contents, and ^{241}Am/^{243}Am and ^{242m}Am/^{243}Am amount ratios by ID-TIMS and TIMS, respectively. The approach for characterisation and value assignment in line with ISO Guide 34 and normalised results will be presented. An inter-laboratory comparison (ILC) exercise will be organised by CEA/CETAMA prior to the release of this novel ^{243}Am CRM.

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SPECTRAL METHODS FOR ELEMENTAL AND ISOTOPIC ANALYSIS OF NUCLEAR FORENSICS OBJECTS IN THE INSTITUTE OF NUCLEAR PHYSICS IN THE REPUBLIC OF KAZAKHSTAN

Viktor Gluchshenko, Dmitriy Zheltov, Alexander Bychenko, Amina Kalieva, Mariya Edomskaya*

Center of Complex Environment Research, Institute of Nuclear Physics, Ibragimov Str. 1, Almaty, 050032, Republic of Kazakhstan,
*e-mail: zheltovda@gmail.com

Keywords: quadrupole mass spectrometry, optical-emission spectrometry, nuclear forensics objects, uranium concentrate, national nuclear forensic library

The Institute of Nuclear Physics developed and widely applies the methods of quadrupole mass- and optical-emission spectrometry (Q-ICP-MS and ICP-OES) on a base of Perkin Elmer instruments for elemental and isotopic analysis of nuclear and radioactive materials. The most widely-applied and effective methods of microwave digestion and fusion are used for sample preparation of “composite” objects.

Q-ICP-MS and ICP-OES methods are providing the rapid and accurate investigation of the trace-, minor- and macro-elements in the objects of nuclear forensics. Q-ICP-MS also enables to determine the long-lived radionuclides and the isotopic composition of the nuclear forensics objects, primarily uranium, plutonium and other transuranic elements. Using the data obtained by Q-ICP-MS and ICP-OES we can obtain the unique signature of the nuclear forensics object and make the conclusions about the type of chemical compound, structure materials, production technology and probable origin.

The presentation provides data of elemental and isotope composition of 10 samples of uranium concentrate as an example, seized on the territory of the Republic of Kazakhstan. The obtained data enabled us to perform the identification of the uranium concentrate as the radioactive material containing the natural uranium and answer the question about probable type of concentrate chemical compound and its place in the technological chain of the nuclear fuel cycle used in the nuclear plants in Kazakhstan. However, it was not possible to make an unambiguous conclusion about the origin of the studied uranium concentrates. For this purpose the national nuclear forensic library is required, which is not available in the Republic of Kazakhstan at present moment.

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ADVANCES IN THE DEVELOPMENT OF A DISSOLUTION METHOD FOR THE EVALUATION OF IRIDIUM SOURCE MATERIALS

Andrew Hodgson[1, 2]*, Robin Grimes*[2]*, Kym Jarvis*[3]*, Olivia Marsden*[1]

[1]AWE plc, Aldermaston, Reading, Berkshire, RG7 4PR, United Kingdom
[2]Department of Materials, Imperial College London, Royal School of Mines, Exhibition Road, London SW7 2AZ, United Kingdom
[3]Faculty of Natural Sciences, Centre for Environmental Policy, Imperial College London, South Kensington Campus, London SW7 1NA, United Kingdom

Keywords: dissolution, iridium targets, sample speciation, nuclear forensics

Iridium-192 sources are generated in nuclear reactors through the irradiation of stable target materials. However, variation in: neutron energy, flux and irradiation time; target material characteristics and purity; the activation cross sections of the desired reactions; decay and daughter progeny in-growth; and any post irradiation processing, can play a key part in determining the isotopic and chemical composition of the material produced. These isotopic ratios, together with those of any activated elemental impurities, therefore have the potential to provide information relating towards not only the material's production date, but also the source's production route, irradiation history and original elemental and isotopic composition.

A computational study to evaluate the effect that neutron flux spectra have on radionuclide production within such materials has indicated a number of potential signatures. These signatures though need to be validated using materials of known production history. As part of this process, a new method is being developed to enable the dissolution of iridium sources without biasing the signature of the embedded impurities. Details of this method will be provided, and the various issues that have been encountered during the transition towards source material analyses will be discussed.

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RAPID ANALYSIS OF $^{89/90}$Sr IN NUCLEAR FORENSICS SAMPLES

Jun Jiang, Ashley Davies, Kieran Thorne, Chris Gilligan*

AWE plc, Aldermaston, Reading, RG6 4PR, UK, *e-mail: jun.jiang@awe.co.uk

Keywords: $^{89/90}$Sr, liquid scintillation counting, Cerenkov counting, nuclear forensics

Strontium measurement is of interest for a number of reasons, including analysis in nuclear forensic scenarios. ^{89}Sr and ^{90}Sr are important fission products with high fission yields of 4.7% and 5.8% from the irradiation of ^{235}U by thermal neutrons, and 1.7% and 2.0% from the irradiation of ^{239}Pu by fission spectrum neutrons. Both radiostrontium nuclides are pure beta emitters. ^{89}Sr decays to stable ^{89}Y. ^{90}Sr decays to ^{90}Y, which further beta decays to stable ^{90}Zr. Immediately after irradiation, the activity of ^{89}Sr is much higher than that of ^{90}Sr due to the differences in half lives – 51 days versus 29 years. The measurement of radiostrontium is complicated because ^{89}Sr and ^{90}Sr can not be chemically separated and ^{90}Y, the daughter of ^{90}Sr, ingrows after the separation of strontium and yttrium.

Several papers have been published in which ^{89}Sr and ^{90}Sr activities have been simultaneously measured by Cerenkov counting. However, the measurement of ^{89}Sr has to be carried out as soon as possible after yttrium removal and there is an additional step to separate ^{90}Y after ingrowth. An alternative is to use a combined counting method using Cerenkov and liquid scintillation counting. Although this method is efficient, the published study requires preparations of four calibration sources (^{89}Sr, ^{90}Sr, ^{90}Y, and mixed ^{90}Sr/^{90}Y) and Cerenkov/LSC efficiency calibrations for each of them. The procedures are complicated and the preparation of accurate ^{90}Sr and ^{90}Y sources are difficult.

A rapid method has been developed for the analysis of $^{89/90}$Sr by a combination of Cerenkov and Quantulus liquid scintillation counting. The counting efficiencies were determined using certified ^{89}Sr and ^{90}Sr (in equilibrium with ^{90}Y) solutions without the need of ^{90}Sr/^{90}Y separation. A ^{90}Sr/^{90}Y ingrowth curve and a LSC efficiency versus delay time chart were plotted using the obtained efficiencies and used in the calculation. Results can now be available within 3 to 5 days using this method and the method has been validated using recent inter-laboratory comparison samples. This talk discusses the developed method, its validation and nuclear forensic type sample analysis results.

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PREPARATION OF VOLATILE CHELATES OF TRIVALENT AND TETRAVALENT NEPTUNIUM

Aaron T. Johnson, Jana K. Pfeiffer, Martha R. Finck, Kevin P. Carney*

Idaho National Laboratory, Idaho Falls, Idaho, USA, *e-mail: aaron.johnson@inl.gov

Keywords: neptunium, volatile, reference material, electrochemistry

The sensitivity in thermal ionization mass spectrometry is governed by the vapor pressure of the element or compound, ionization efficiency, and transmission characteristics of the mass spectrometer. Plutonium has a low vapor pressure combined with a low ionization potential which results in moderate sensitivities in thermal ionization mass spectrometric analyses. However, the vapor pressure of neptunium is an order of magnitude higher than plutonium, but because its ionization potential is significantly higher, TIMS sensitivity is lower. An efficient method of introducing neptunium compounds into a mass spectrometer is desirable to reduce the mass of samples necessary for analysis. This is particularly desired in the handling and analysis of transuranic elements. Chemical modification of neptunium to increase its volatility adds complexity to this approach. Perhaps the best example of chemical modification to volatilize actinide compounds is uranium hexafluoride (UF_6), used to enrich ^{235}U by gaseous diffusion to make nuclear fuel. NpF_6 exhibits similar volatility; however F is highly corrosive to the sensitive internals of the mass spectrometer. Iodine (which is more volatile than F and the other halides) may be a viable alternative. Two approaches for the synthesis of volatile neptunium compounds have been considered. First were neptunium iodide complexes, which have not previously been considered for this application. Electrochemical manipulations, combined with solvent extraction techniques were used to create both NpI_3 and NpI_4 as confirmed by absorbance and FTIR spectroscopy. Second, the relatively high volatility of β-diketone chelates makes them an ideal candidate for use in this application. Tetrakis β-diketone chelates with trivalent and quadrivalent neptunium and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (FOD) were synthesized as confirmed by FTIR and NMR. The volatilities the iodide and β-diketonate compounds were then investigated by thermogravimetric analysis. Ultimately, vapor pressures of these compounds at variable temperatures and pressures can be determined using the Knudsen effusion method. The work reported here presents novel, low-hazard routes to the creation of volatile neptunium chelates for introduction into thermal ionization mass spectrometers.

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THE NEXT FRONTIER FOR NUCLEAR FORENSIC SIGNATURES: MICROANALYSIS OF NUCLEAR FUEL PELLETS

Ruth Kips, Michael Kristo

Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA 94551, USA, LLNL-ABS-678817

Ceramic uranium oxide is the most commonly used fuel type in nuclear reactors worldwide, with standard fuel fabrication methods producing hundreds of uranium pellets per minute. Investigating nuclear forensic signatures in fuel pellets is imperative, given the number of cases of theft and illicit trafficking of nuclear fuel pellets that have occurred in the past. LLNL has applied a wide range of analytical techniques to the analysis and identification of nuclear fuel pellets. In this work, we will describe our analyses of different types of fuel pellets at the microscale. The fuel pellets investigated include the fuel pellet material provided as part of the most recent Collaborative Materials Exercise (CMX-4) organized by the Nuclear Forensics International Technical Working Group (ITWG). Scanning electron microscopy (SEM) and NanoSIMS secondary ion mass spectrometry were used to characterize the fuel pellets' grain size and grain structure, porosity, isotopic homogeneity and impurities. These various microstructural attributes of a fuel pellet that influence the fuel properties and its subsequent behavior in a reactor may also be of value in a nuclear forensics investigation, potentially linking the fuel to a particular production process, feedstock material and/or fuel fabrication facility.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory (under contract DE-AC52-07NA27344).

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DEVELOPMENT OF A NATIONAL NUCLEAR FORENSIC LIBRARY IN HUNGARY

Eva Kovacs-Szeles, Katalin Talos, Bernadett Henn, Zsuzsana E. Meszar, Kornel Fel, Peter Volgyesi*

Hungarian Academy of Sciences Centre for Energy Research, Nuclear Security Department, Konkoly-Thege M. út 29–33,
1121 Budapest, Hungary, *e-mail: eva.szeles@energia.mta.hu

Illicit trafficking of nuclear and other radioactive material is a subject of serious concern due to the radiological hazard to the public and the environment as well as the security risks associated nuclear and other radioactive material out of regulatory control. The problem of theft or loss of nuclear materials has affected countries on all five continents emphasizing the international scale of this issue.

To increase confidence in determining the origin and history of questioned materials, analysis of numerous comparison samples from the same and also different confiscations and batches with different origin is necessary. Another necessary element is the development by States of a national nuclear forensics library to aid in national level comparisons of material out of regulatory control.

Besides, following the experiences of inter-laboratory comparison exercises and analysis of different type of samples it was concluded that it is important to identify the really relevant signatures for origin assessment of nuclear materials because some of the often used signatures seem uncertain.

To increase confidence in determining the origin and history of questioned materials, analysis of numerous comparison samples from the same and also different confiscations and batches with different origin is necessary. Following statistical evaluations of the large database originated from analysis of numerous samples determination of the relevance and applicability of the individual signatures can be more effective.

Confiscated nuclear materials obtained during past seizures by the Hungarian authorities stored at the Centre for Energy Research. In our work analysis of these nuclear materials was performed to obtain relevant signatures useful for the development of a national nuclear forensics library. Using different techniques which are available at the Centre for Energy Research such as optical and scanning electron microscopy, gamma-spectrometry and mass spectrometry, X-Ray diffraction, electron spectrometry techniques, such as XPS (ESCA) and Auger spectrometry (AES), a relatively large and informative database could be obtained and analyzed.

In the presentation evaluation of analysis results and some conclusions for relevance of the individual signatures connected to uranium-oxide base materials will be discussed.

Besides our aim was also to identify physical, chemical and radiological characteristics of sealed and unsealed radioactive sources which could be used as signatures in the attribution phase of forensic investigations of sources out of regulatory control (typically seized or found samples with unknown origin). Another aim was to find relevant signatures of other type of nuclear materials like salts, and other chemicals available in Hungary to extend the Library.

First analysis data will be also demonstrated. In connection with the establishment of the library in order to make its use easier a special searching database handling system was also initiated.

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ALPHA SPECTROMETRY FOR BASIC CHARACTERIZATION OF NUCLEAR FORENSIC SAMPLES

Stephen LaMont[1], Lisa Hudston[1], Donald Dry[1], James Blankenship[2], Sarah Fendrich[3], David Schnaars[3], Vovik Atoyan[4], Konatantin Pyuskyulyan[4]

[1]Nuclear and Radiochemistry, Los Alamos National Laboratory, PO Box 1663 / MS J514, Los Alamos, NM 87545 USA,
e-mails: lamont@lanl.gov, lisahudston@lanl.gov, dry@lanl.gov
[2]CBRN Sciences Unit, FBI Laboratory, Quantico, VA 22135 USA, e-mail: james.blankenship@ic.fbi.gov
[3]Counter Nuclear Smuggling Unit, US Department of State, 2401 E Street, NW, Washington, DC 20037, USA,
e-mails: FendrichSE@state.gov, SchnarsDD@state.gov
[4]Armenia Nuclear Power Plant, Laboratory, 091 Metsamor, Armivir Marz, Republic of Armenia,
e-mails: vovik.atoyan@anpp.am, pyuskyulyan@bk.ru

Keywords: alpha spectrometry, nuclear forensics, uranium enrichment

Nuclear forensic evidence examinations are used to identify and quantify nuclear and radioactive materials recovered from outside of regulatory control, provide necessary evidence for prosecuting criminal activity, and ultimately help determine the provenance of the material. As part of an ongoing collaborative project between the United States and Armenia, we are working to demonstrate how alpha spectrometry can contribute to nuclear forensics examinations and produce reliable and defensible uranium enrichment data. Gamma-ray spectrometry is frequently used to determine uranium enrichment, but can be challenging for forensic samples that are often in non-standard counting geometries and require self-absorption corrections that make estimating enrichment difficult for laboratories that do not routinely practice these measurements. Given the serious nature of incidents involving enriched uranium, and the relatively ubiquitous nature of depleted and natural uranium materials, it is critical that accurate enrichment data is available to investigators, and gamma-ray spectrometry data may not easily provide an accurate measure of enrichment. As a compliment to gamma-ray spectrometry, alpha spectrometry can provide reasonably accurate uranium enrichment measurements that are generally much easier to interpret. There are a number of other advantages to employing alpha spectrometry as well, including the relatively low cost of equipment, robust nature of the hardware, its ease of operation, and straightforward data interpretation. The disadvantage is that samples generally cannot be counted directly, and need to be prepared into thin sources with limited self-absorption. However, there are a number of source preparation techniques that require only basic radiochemistry expertise and produce data sufficient for estimating uranium enrichment. This paper will discuss the training materials developed for applying alpha spectrometry to nuclear forensic investigations along with methods for preparing samples and evaluating data to determine uranium enrichment.

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ISOTOPIC TECHNIQUES IN RESOLVING NUCLEAR FORENSIC SIGNATURES FOR U & Th MINING AND PROCESSING

Manny Mathuthu, Ntokozo Khumalo, Refilwe N. Maretela, Malayitha M. Baloyi

North-West University (Mafikeng), Centre for Applied Radiation Science and Technology (CARST)
P Bag X2046, Mmabatho, 2735, NW, RSA, e-mails: manny.mathuthu@nwu.ac.za, rnmaretela@gmail.com, ntokozohkhums@gmail.com, maxon@live.co.za

Keywords: nuclear forensics, signatures, forensic library, isotopic ratio, ICP-MS

The risks of smuggling of radiological and nuclear materials as well as trafficking of these materials has increased and become a real threat to the National Security of many countries including South Africa. There is a need to build a national nuclear forensic library which contains all the possible nuclear materials for a proper working database of the different materials originating from South African mines and those brought in. The researchers sought to properly characterize the signatures of the different nuclear materials and develop a database or library. These signatures are used to establish the origins of the seized nuclear material, the material nature, the age of the material as well as the intended use of the material by detection of major, minor as well as trace elements in the material. Major elements define the identity of the nuclear material, minor elements helps to define the function of the material and different rock types contain very different trace elements which indicates how the Uranium or Thorium was processed from the ore. Isotopic signatures of the material involves identifying the fission, decay or neutron capture products, which designate that the material has been in a nuclear reactor and is a representative fingerprint for the type and operating conditions of a given reactor. In this preliminary work we report on the trace and major elements identified by ICP-MS, after soil samples from a Gold mine in the Gauteng Province of South Africa were digested using the Aqua Regia method. Results show that there are elevated concentration levels (ppm) of some trace elements: Co (15.966–365.483); Cr (0.015–2.094); Cu (0.014–1962.253); Mg (0.06–11.914, a high diamond indicator in kimberlite bedrock); Mn (677.548–14439.569); and Zn (0.002–0.019) and that Th (3.978–36.525); U (0.54–637.962) were associated with the following heavy elements (ppm): Al; B (0.0001–0.004, no coal fired plant activity in the mine); Ba (39.695–546.871, heavy granite geogenic enrichment in the bedrock); Ca (1.285–27.386, from lime used as smelter in high temperature processing of U/Th extraction); K (1.728–6.468); Cl (37.149–2538.377, processing using HCl); P (0.008–0.054, use of phosphoric acid in processing too); Na (0.019–1.949); Ni (11.183–1427.872, from Co-60 decay too); Pb (0.001–162.487). The high values of U and Th in the tailing of the investigated mine indicate a Granite lithology underground. Absence of La, Sr, and Y show that the Gold mine does not use open cast mining and there are no alkaline intrusion lithologies.

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THE EXPERIENCE OF SOUTH AFRICA NECSA NUCLEAR FORENSICS LABORATORY PARTICIPATION IN THE INTERNATIONAL TECHNICAL WORKING GROUP (ITWG) FOURTH COLLABORATIVE MATERIAL EXERCISE (CMX-4)

A. N. Nelwamondo, B. L. Kokwane, K. D. Mulibana, M. K. Mogale*

South Africa Nuclear Energy Corporation (NECSA), Pretoria 0001, Republic of South Africa (RSA), GAUTENG,
*e-mail: Aubrey.nelwamondo@necsa.co.za

Keywords: nuclear forensics, analytical techniques, CMX-4, experiences, lessons learned

NECSA is the main organization responsible for the national nuclear science and technology research and development, and for performing the analysis of nuclear and radioactive materials found out of regulatory control on behalf of the government of South Africa. As an organization NECSA lacked certain critical infrastructure to adequately perform nuclear forensic analysis in support of law enforcement investigations, and has embarked on a critical path in the building and enhancement of national nuclear forensic analysis capacity and gaining international exposure. NECSA as the organization primarily responsible for national technical nuclear forensics took charge of the fourth comparative material exercise (CMX-4) analysis. The NECSA dedicated nuclear forensics laboratory, the available instruments, the nuclear analytical techniques and the experiences accumulated over the past decades, and the nuclear forensics expertise acquired in the past recent years were all utilized as bases for the CMX-4 analysis. The experience, challenges and lessons learned from participation in CMX-4 investigations will be presented in this paper.

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URANIUM AGE-DATING USING *IN-SITU* ISOTOPE RATIOS FOR NUCLEAR FORENSICS

Ayako Okubo[1]*, Nobuo Shinohara*[1]*, Masaaki Magara*[2]

[1]ISCN, Japan Atomic Energy Agency, Ibaraki, Japan, e-mails: okubo.ayako@jaea.go.jp, shinohara,nobuo@jaea.go.jp
[2]Safeguards Analytical Chemistry Research Group, Japan Atomic Energy Agency, Ibaraki, Japan, e-mail: magara.masaaki@jaea.go.jp

Keywords: nuclear forensics, uranium age-dating, secular equilibrium, isotopic equilibrium, ID-TIMS

As an effort of strengthening nuclear security in the world, the capacity building of nuclear forensics in each state has been required. The age-dating of nuclear material is to estimate an elapsed time since the final purified date of the nuclear material. Because the age-dating result could enable us to better constrain the origin of unidentified material, which is recognized as an important parameter for nuclear forensics.

The isotope dilution mass spectrometry (ID-MS) method is recognized as the most reliable method to estimate ^{234}U/^{230}Th ratio for uranium age-dating. The amount of ^{234}U and ^{230}Th in a uranium material are respectively measured by ID method using spikes (^{233}U and ^{229}Th). The isotopic equilibrium between the isotopes *in-situ* the sample and added spikes is assumed in ID method. In order to obtain the accurate concentrations of ^{234}U and ^{230}Th, the precise measurement of sample weight and the control of spike concentration are necessary.

We have developed a new method to estimate ^{234}U/^{230}Th ratio without spike addition for uranium age-dating. In this method, using secular equilibrium between ^{238}U and ^{234}Th (^{234}Th/^{238}U = 1.45 E-11), ^{234}U/^{230}Th ratio is calculated from measured isotope ratios of U (^{234}U/^{238}U) and Th (^{230}Th/^{234}Th).

20 mg of LEU was dissolved in nitric acid, and Th fraction was purified with two steps anion exchange column. The decontamination factor of the two steps anion exchange was estimated to be 10^{-11}. The total time of purification of Th fraction was 6h. The remaining U in the Th fraction was further separated in filament heating step using the difference of optimum ionization temperature between U and Th at TIMS measurement. At the beginning of Th isotope measurement, the ion count of ^{234}U was estimated to be below detection limit from ^{238}U ion counts (typically <100 cps). The estimated ^{234}U/^{230}Th ratios by this new method were agreed with the result of ID-MS method within the difference of 3–5%.

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COMBINATORY USE OF TOF-SIMS AND SECTOR-FIELD SIMS IN THE PRELIMINARY ESTIMATION OF ELEMENTAL AND ISOTOPIC COMPOSITION OF NUCLEAR FORENSIC SAMPLE

Jinkyu Park[1]*, *Tae Hee Kim*[1], *Sang Ho Lim*[1, 2], *Chi-Gyu Lee*[1], *Sun Ho Han*[1], *Kyuseok Song*[1]

[1]Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daejeon, Korea, *e-mail: jinku1004@kaeri.re.kr
[2]Department of Radiochemistry and Nuclear Nonproliferation, University of Science and Technology, Daejeon, Korea

Keywords: TOF-SIMS, sector-field SIMS, nuclear forensic analysis

Nuclear forensics is the complete scientific analysis of nuclear or other radioactive material, providing insight to origin and history of the material. Many analytical techniques including SEM-EDS, TIMS and ICP-MS have been employed to investigate the material of interest acquiring morphological data, elemental composition and isotopic ratio, etc. Among others, SIMS has been very useful for isotopic analysis of nuclear materials, because of its pg-level sensitivity, and of fast and easy sample measurement compared to other techniques. A type of SIMS commonly used in nuclear forensic analysis is sector-field SIMS (SF-SIMS) which is capable of isotopic measurement for selected elements with high sensitivity, and with high lateral and depth resolution. Since the instrument analyzes isotopes one by one while varying magnetic field, it is not appropriate for scanning a wide range of masses to investigate an unknown sample. TOF-SIMS is another type of SIMS which is able to analyze a full range of masses from one to thousands simultaneously, although it has relatively low sensitivity. In this study, a combinatory use of these two types of SIMS was tested for nuclear forensic analysis. TOF-SIMS and SF-SIMS with APM (Automated Particle Measurement) mode were used to investigate simulated samples containing uranium particles and other metal elements such as molybdenum, gadolinium and lead, which possibly co-exist in the nuclear samples. The results demonstrated that both techniques together provide preliminary information for the nuclear forensic analysis.

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THE STATE OF PRACTICE AND ART OF NUCLEAR FORENSIC ANALYSIS: HIGHLIGHTS FROM THE 4TH COLLABORATIVE MATERIALS EXERCISE (CMX-4) OF THE NUCLEAR FORENSICS INTERNATIONAL TECHNICAL WORKING GROUP (ITWG)

Jon M. Schwantes[1], *Olivia Marsden*[2]

[1]National Security Directorate, Pacific Northwest National Laboratory, Richland, WA, USA, e-mail: jon.schwantes@pnnl.gov
[2]AWE, Aldermasten, UK, e-mail: Olivia.Marsden@awe.co.uk

Keywords: nuclear forensics, Nuclear Forensics International Technical Working Group (ITWG), Collaborative Materials Exercise (CMX-4)

Founded in 1996 upon the initiative of the “Group of 8” governments (G8), the Nuclear Forensics International Technical Working Group (ITWG) is an ad hoc organization of official Nuclear Forensics practitioners (scientists, law enforcement, and regulators) that can be called upon to provide technical assistance to the global community in the event of a seizure of nuclear or radiological materials. The ITWG is supported by and is affiliated with nearly 40 countries and international partner organizations including the International Atomic Energy Agency (IAEA), EURATOM, INTERPOL, EUROPOL, and the United Nations Interregional Crime and Justice Research Institute (UNICRI). Besides providing a network of nuclear forensics laboratories that are able to assist the global community during a nuclear smuggling event, the ITWG is also committed to the advancement of the science of nuclear forensic analysis, largely through participation in periodic table top and Collaborative Materials Exercises (CMXs). Exercise scenarios use “real world” samples with realistic forensics investigation time constraints and reporting requirements. These exercises are designed to promote best practices in the field and test, evaluate, and improve new technical capabilities, methods and techniques in order to advance the science of nuclear forensics. Past efforts to advance nuclear forensic science have also included scenarios that asked laboratories to adapt conventional forensics methods (e.g. DNA, fingerprints, tool marks, and document comparisons) for collecting and preserving evidence comingled with radioactive materials. The ITWG recently completed its 4th CMX in the 20 year history of the organization. This was also the largest materials exercise to date, with participating laboratories from 16 countries or organizations. Three samples of Low Enriched Uranium were shipped to these laboratories as part of an illicit trafficking scenario, for which each laboratory was asked to conduct nuclear forensic analyses in support of a fictitious criminal investigation. An objective review of the state of practice and art of international nuclear forensic analysis based upon the outcome of this most recent exercise is provided.

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MEASUREMENT AND ASSESSMENT OF NUCLEAR TESTING FALLOUT IN THE SOUTHWEST UNITED STATES

Robert Steiner[1], Stephen LaMont[1], William Eisele[2], Philip Fresquez[2], Michael McNaughton[2], Jeffrey Whicker[2]*

[1]Nuclear and Radiochemistry, Los Alamos National Laboratory, Los Alamos, NM, USA, *e-mail: steiner@lanl.gov
[2]Environmental Stewardship Services, Los Alamos National Laboratory, Los Alamos, NM, USA

Keywords: global fallout, isotopic signature

During the past 70 years approximately 12,000 TBq of plutonium has been distributed throughout the global biosphere by atmospheric thermo nuclear weapons testing. The resultant global plutonium fallout ^{240}Pu/^{239}Pu atom ratio is 0.176 + 014. The make-up of global fallout results from a complex mixing in the atmosphere whose ^{240}Pu/^{239}Pu atom ratio is a function of the design and yield of the devices tested. However, the ^{240}Pu/^{239}Pu atom ratio at any location may differ significantly from the global fallout value. Plutonium has also been released regionally by discharges and accidents associated with the commercial and weapons related nuclear industries. At many locations contributions from this plutonium significantly perturb the ^{240}Pu/^{239}Pu atom ratios from those observed in global fallout. We have measured the ^{240}Pu/^{239}Pu atom ratios in environmental samples collected from many locations in North America. This presentation will summarize the analytical results from these measurements. Special emphasis will be placed on interpretation of the significance of the ^{240}Pu/^{239}Pu atom ratios measured in environmental samples collected in the western portions of the United States.

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IRMM-1000A, IRMM-1000B AND REIMEP-22 – IMPROVING THE METROLOGICAL BASIS FOR URANIUM AGE DATING

C. Venchiarutti[1], Z. Varga[2], S. Richter[1], R. Jakopič[1], A. Nicholl[2], J. Krajko[2], K. Mayer[2], Y. Aregbe[1]*

[1]European Commission, Joint Research Centre (JRC), Institute for Reference Materials and Measurements (IRMM), Retieseweg 111, B-2440 Geel, Belgium, *e-mail: Celia.VENCHIARUTTI@ec.europa.eu
[2]European Commission, Joint Research Centre (JRC), Institute for Transuranium Elements (ITU), P.O. Box 2340, 76125 Karlsruhe, Germany, e-mail: Zsolt.VARGA@ec.europa.eu

Keywords: certified reference materials, nuclear forensics, age determination, uranium, thorium

In support to the Nuclear Forensics, in particular to the International Technical Working Group (ITWG), the Institute for Reference Materials and Measurements (IRMM) and the Institute for Transuranium Elements (ITU) of the Joint Research Centre of the European Commission (EC-JRC) joined efforts to produce two uranium reference materials (CRM) certified for the production date, IRMM-1000a and IRMM-1000b, based on the ^{230}Th/^{234}U radiochronometer. These CRMs were prepared from low-enriched uranium $m(^{235}\mathrm{U})/m(\mathrm{U})$ of 3.6% by a complete separation of all thorium decay products as verified by gamma spectrometry and mass spectrometry at a well-known time, which is referred to as the certified production date of IRMM-1000a and IRMM-1000b. The elapsed time since the production date, commonly referred to as the “age” of a material is measured in nuclear forensics among other parameters to support the identification of the origin of an unknown material. Therefore CRMs such as IRMM-1000a and IRMM-1000b are indispensable for the establishment of the accurate age of a nuclear material using validated mass spectrometric or radiometric techniques. The preparation and certification of these materials were done in compliance with ISO Guide 34 and ISO 17025, including characterisation, homogeneity and stability studies on randomly selected units to establish the certified value and its final expanded uncertainty. The certified reference material is available as dried uranyl nitrate in two sizes: 20 mg (IRMM-1000a) for mass spectrometric techniques and 50 mg uranium for radiometric techniques (IRMM-1000b). The certified value for the production date for both materials is the 9th July 2012 with an expanded uncertainty of 13 days ($k = 2$).

Prior to the release of the CRMs, the REIMEP-22 interlaboratory comparison on 'U Age Dating – Determination of the production date of a uranium certified test sample' was organised using the same material. This was the first exercise of this kind and included the participation of eleven international laboratories, six of them were part of the ITWG. The individual results of the participants were evaluated against the certified production date and the laboratory performances evaluated according to ISO 13528. In general the laboratories performed well in REIMEP-22 considering the analytical challenge to accurately date a young uranium sample with a very low amount of radiogenic thorium present.

Nuclear instrumentation and methodology

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GAMMA³/PIPSBOX: A HIGH EFFICIENCY AND HIGH RESOLUTION ELECTRON/PHOTON SPECTROMETER FOR RADIOXENON TRACE DETECTION

Antoine Cagniant, Gilbert Le Petit, Philippe Gross, Olivier Delaune, Guilhem Douysset*

CEA, DAM, DIF – F91297 ARPAJON (France), *e-mail: antoine.cagniant@cea.fr

Keywords: electron/photon coincidence spectrometry, ultra-low background, radioxenon, CTBTO

For the verification of the Comprehensive nuclear Test Ban Treaty (CTBT), the measurement of fission products trace levels in the environment is fundamental. Such measurement is a key indicator of a nuclear explosion. For constant amelioration of these measurements, the CEA/DAM-Ile de France has developed and installed a new dedicated surface spectrometer. Named Gamma³, it is equipped with three germanium detectors and includes an optimized shielding (see *Fig. 1*). It can be coupled to a dedicated gas cell fitted with two silicon detectors (the PIPSBox detector) for radioactive noble gases (see *Fig. 2*).

This shielding reduces greatly the interference of environmental photons, muons and neutrons with the detectors. The residual radiological background measured inside the shielding is the community's lowest for a surface laboratory. This set of high energy resolution detectors allows the operator to optimize a measurement according to the sample geometry, activity or nature. In the case of radioactive noble gas quantification, photon/electron coincidence measurements are performed.

Fig. 1. The Gamma³ spectrometer

Fig. 2. The PIPSBox detector

Combining optimized shielding and optimized measurement configuration, Minimum Detectable Activities required for CTBT certifications are obtained quicker than in the 6 days recommended by the treaty. Efficiency measurement and simulation as well as background measurement and simulation supporting this point will be presented. Finally, obtained MDA for ^{131m}Xe, ^{133m}Xe, ^{133}Xe and ^{135}Xe will be provided.

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IMPROVING RADIO DETECTION FOR HIGH RESOLUTION RADIO-UPLC

Rory de Zanger, Erik de Blois, Wouter Breeman*

Department of Nuclear Medicine, Erasmus MC, Wytemaweg 12, Rotterdam, the Netherlands, *e-mail: r.dezanger@erasmusmc.nl

Keywords: radio detection, resolution, sampling frequency, signal conversion, accuracy, reproducibility

Introduction: The determination of the quality or radiochemical purity (RCP) of (short lived) radiopharmaceuticals depends on two main criteria: separation method and radio detection. The first has been thoroughly investigated and is assumed to be optimised but the latter is not. At least not for radio-UPLC set-ups. Therefore, investigations were focused on the radio detection part of the measurement.

Objective: High resolution radio detection measurement on a chromatograph such as a UPLC is determined by properties such as sampling frequency (detector electronics and software), interaction time between radioactivity and detector, signal conversion and electronics. All these affect parameters such as the accuracy, resolution, detection limit and reproducibility. The aim was to determine the influence of each factor on the mentioned parameters and optimize the settings for the properties to improve radio detection measurement. Thus improving overall quality of the radio chromatogram.

Method & Materials: Our set-up consisted of a Waters Acquity H-class UPLC system which included a radio detection system consisting of a NaI(Tl) crystal attached to either an Osprey multichannel analyser (MCA, Canberra) and amplifier box (Canberra) or a bPAD/VR single channel analyser (SCA, Brightspec). In both cases the connection between radio detection set-up and the UPLC was made using a Waters E-SAT/IN box. ^{111}In-DOTA^0,Tyr^3-Octreotate was the model of choice and analysed multiple times, both with bPAD/VR SCA or Osprey MCA connected, while varying parameters as mentioned above.

Results: Reduction in number of signal conversion steps led to reduction in loss of data points. Moreover, the number of collected data points was increased due to a 2 fold higher sampling frequency and a longer time of interaction between radioactivity and detector (2 to 2.5 times longer). This last parameter also improved the counting statistics in the measurement.

Conclusion: Replacement of the Osprey MCA with the bPAD/VR SCA resulted in a decrease in signal conversion steps and faster overall electronics. All the alteration to the above mentioned parameters led to an improved accuracy, resolution, detection limit and reproducibility.

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COMPARISON OF TWO SPECTROMETRIC COUNTING MODES FOR FAST ANALYSIS OF SELECTED RADIONUCLIDE ACTIVITY

Magdalena Długosz-Lisiecka

Technical University of Lodz, Institute of Applied Radiation Chemistry, Wróblewskiego 15, 90-924 Łódź, Poland, e-mail: mdlugosz@mitr.p.lodz.pl

Keywords: anticoincidence, Compton suppression

The two counting modes: a normal with a single HPGe detector and second with the additional anti-compton shield of the annular NaI(Tl) detector have been compared for fast determination of the activity concentration of thorium ^{232}Th in the solid environmental samples including building materials. The ^{232}Th (in secular equilibrium with ^{228}Th) activity concentration was calculated by measurement of its decay products: ^{212}Pb (238 keV), ^{212}Bi (727 keV) and ^{208}Tl (583 keV) as well as ^{228}Ac (911 keV) content. Although the Compton suppression mode applied in gamma spectrometry systems in general increase sensitivity of the analysis. But in case of 583 keV the most abundant ^{208}Tl γ-line, the significant reduction of photon counting rate was observed and resulting figure of merit (FOM) was lower than for normal mode ^{208}Tl counting.

In this study developed anticoincidence system with a Compton suppression shield integrated with a primary HPGe detector, which is used for measuring low level activity in environmental samples has been used. Due to Compton scattering, only part of initial photon energy is absorbed within the active volume of the germanium counter.

In routine γ spectrometry measurement, ^{228}Ac and/or ^{212}Bi and/or ^{208}Tl and/or ^{212}Pb radionuclides are often chosen for this analysis.

The anticoincidence counting mode can substantially reduce the count rate of the photons emitted in cascade decay, particularly for the most abundant (84.5%) 583 keV photons of ^{208}Tl. In that case, practically at the same time (which is shorter than settled anticoincidence intervals), photons with energies 277, 727, 511 and 2614 keV are simultaneously emitted. The high-efficiency γ – γ coincidence events rejected from the anticoincidence spectrum can significantly disturb regular spectrometric measurements and as a result reduce the activity concentration of analyzed radionuclides.

The ^{232}Th radionuclide was measured in various different solid materials, including building materials and environmental samples. The described procedure makes it possible to quickly determine the activity concentration of ^{232}Th in small solid (<50 g) samples. The FOM criterion was calculated in order to choose the best counting parameters. For the 583 keV line of ^{208}Tl in single HPGe counting mode, the FOM criterion achieved the highest value. In AC mode average only 21% of photons with energy 583 keV for ^{208}Tl radionuclide in relation to single HPGe has been identified correctly. Sophisticated electronic AC systems applied for activity concentration analysis of such radionuclides seems to be useless or at best can lead to significant mistakes in routine analysis.

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HPGe DETECTOR FULL-ENERGY PEAK EFFICIENCY CALCULATION FOR INHOMOGENEOUSLY ACTIVATED SAMPLES

Lojze Gačnik[1, 2], *Radojko Jaćimović*[1, 2]

[1]Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[2]Jozef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia, e-mails: lojze.gacnik@ijs.si, radojko.jacimovic@ijs.si

Keywords: HPGe detectors, effective solid angle ratio, full-energy peak efficiency, efficiency transfer method

We present and evaluate a program for the semi-empirical calculation of the full-energy peak efficiency of a hyper-pure germanium detector, by using the efficiency transfer method. Using simple Monte-Carlo integration and constructive solid geometry, we are able to calculate the effective solid angle for a wide range of HPGe detector and sample geometries. However, the main advancement is including in our calculations the inhomogeneity of the sample activity, caused by the inhomogeneous neutron flux when performing neutron activation analysis (NAA). This reduces systematic error in the standard procedure of NAA. To increase usability, the input and output file formats used are compatible with the program SOLANG, which belongs to the Kayzero for Windows software.

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QUENCHING OF THE SENSITIVITY OF GEL DOSIMETERS AND RADIOCHROMIC FILMS IN HIGH LET RADIATION

Grazia Gambarini[1, 2]*, *Marco Felisi*[1], *Gabriele Camoni*[1], *Ivan Veronese*[1, 2]

[1]Department of Physics, Università degli Studi di Milano, via Celoria 16, 20133 Milano, Italy, *e-mail: grazia.gambarini@mi.infn.it
[2]National Institute of Nuclear Physics (INFN), Section of Milan, via Celoria 16, 20133 Milano, Italy

Keywords: chemical dosimeters, LET, protons, thermal neutrons

Radiation therapy techniques are in continuous progress, with particular interest to charged particles such as protons or carbon ions, exploited in Hydrotherapy, or the particles generated by the interaction of thermal neutrons with some specific isotopes, exploited in boron neutron capture therapy (BNCT). The charged particles give the advantage of achieving well-shaped regions with high dose where the linear energy transfer (LET), and then the radiobiological effectiveness (RBE), are high. Owing to the high dose gradients, dosimetry methods for the control of the dose calculated by treatment planning system require the capability of spatial dose imaging with high precision and high spatial resolution. To this aim, chemical dosimeters, as radiochromic films and gel dosimeters, that allow measures of the spatial distribution of the absorbed dose, are currently studied to investigate their suitability in these radiation fields. The main faced problem is the dependence of the sensitivity of these dosimeters on LET. In fact, for high LET the recombination in the ion track causes a decrease, i.e. quenching, of the dosimeter response. The difficulty of the problem is increased by the fact that in each position of the irradiated volume the absorbed dose is the addition of contributions of radiations with different LET values, and then such contributions should be separated and individually amended. The dependence of the response of the various dosimeters on LET is not yet fully known and it is now studied by many research groups.

In our laboratory, experiments have been carried out to investigate the effect of quenching of the response of radi-

ochromic films irradiated, in a water phantom, with proton beams of different energies, thus obtaining Bragg peaks at different depths, and it was evaluated the ratio between the measured and the absorbed dose as a function of depth for each energy. A method for correcting the experimental dose images, taking into account all the proton beams that contribute to the absorbed dose in each position, is in development.

Other studies are aimed at investigating the quenching of the response of gel dosimeters irradiated with neutron beams characteristic of BNCT. In this case the situation is different, principally because in each position the absorbed dose can be due to different charged particles, and the contributions have to be separated, but the charged particles produced in the reactions of thermal neutrons with a given isotope have always the same energy, which is locally released. A method for separating the various dose contributions by means of gel dosimeters has been developed and improvements on the precise determination of the under-response coefficient for the charged particles of interest are in progress.

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CHARACTERIZATION OF HPGe DETECTORS USING COMPUTED TOMOGRAPHY

A. Hedman[1, 2]*, J. Bahar Gogani*[1]*, M. Granström*[1]*, L. Johansson*[2]*, J. S. Andersson*[2]*, H. Ramebäck*[1, 2, 3]

[1]Swedish Defence Research Agency, Division of CBRN Defence and Security, SE-90182 Umeå, Sweden
[2]Umeå University, Department of Radiation Sciences, Radiation Physics, SE-90187 Umeå, Sweden
[3]Chalmers University of Technology, Department of Chemical and Biological Engineering, Nuclear Chemistry, SE-41296 Göteborg, Sweden

Keywords: gamma spectrometry, HPGe, computed tomography, Monte Carlo modelling, Gespecor, semi-empirical calibration

Computed Tomography (CT) high-resolution imaging have been used to investigate differences in detector parameters when cooling a small n-type HPGe detector and a medium sized p-type HPGe detector to operating temperatures. The findings were compared to calculated linear temperature expansions of different parameters inside the detector and detector dimension data made available by the manufacturer. Parameters investigated were *e.g.* the air gap between crystal and end cap. The air gap increased by (0.38±0.07) mm for the n-type detector and by (0.40±0.15) mm for the p-type detector when the detectors were cooled compared to at room temperature. Monte Carlo calculations indicate that these differences have a significant impact on the efficiency in close geometries (<5 cm). In the energy range of 40–700 keV with a source placed directly on endcap, the change in detector efficiency with temperature is 1.9–2.9% for the n-type detector and 0.3–2.1% for the p-type detector. The measured air gap thickness when cooling the detector was 1.1 mm thicker than manufacturer data for the n-type detector and 0.2 mm thicker for the p-type detector. In the energy range of 40–700 keV and with a source on endcap, this result in a change in detector efficiency of 5.2–7.1% for the n-type detector and 0.2–1.0% for the p-type detector, i.e. the detector efficiency is overestimated using data available by the manufacturer.

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OPTIMIZED DETECTOR FOR *IN SITU* LOW ENERGY GAMMA SPECTROMETRY IN CLOSE GEOMETRIES

A. Hedman[1, 2]*, G. Ågren*[1]*, L. Johansson*[2]*, J. Bahar Gogani*[1]*, H. Ramebäck*[1, 2, 3]

[1]Swedish Defence Research Agency, Division of CBRN Defence and Security, SE-90182 Umeå, Sweden
[2]Umeå University, Department of Radiation Sciences, Radiation Physics, SE-90187 Umeå, Sweden
[3]Chalmers University of Technology, Department of Chemical and Biological Engineering, Nuclear Chemistry, SE-41296 Göteborg, Sweden

Keywords: gamma spectrometry, *in situ,* low energy, surface contamination, Monte Carlo modelling, MCNP

In situ gamma spectrometry is a fast, important and reliable method for measurements of radionuclide contaminated surfaces. The aim of this work was to find the best possible detector for contamination measurements of low energy gamma radiation in close geometries. Simulations have been made using MCNP (Monte Carlo N-Particle code) where different detector parameters e.g. window material and crystal size, have been varied to find the best combination from a sensitivity point-of-view for close measurements of a contaminated surface with a background spectra of natural radionuclides. The detection limit and the minimum detectable activity (MDA) was calculated. The detection limit increases with larger crystal diameter and thickness while the MDA decreases with larger diameter and thinner crystal.

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LIMITATIONS OF GAMMA-RAY SPECTROMETRY IN THE QUANTIFICATION OF ^{238}U AND ^{232}Th IN RAW MATERIALS AND BY-PRODUCTS

Young-Yong Ji, Chang-Jong Kim, Kun Ho Chung, Jong-Myoung Lim, Hyuncheol Kim, Geun-Sik Choi, Mun Ja Kang*

Korea Atomic Energy Research Institute, Daejeon 305-353, Republic of Korea, *e-mail: yyji@kaeri.re.kr

Keywords: gamma-ray spectrometry, ^{238}U, ^{232}Th, density, disequilibrium, raw materials, by-products

According to the protective action guidelines of the Nuclear Safety and Security Commission (NSSC) in Korea, concerns regarding the radioactivity of naturally occurring radioactive materials (NORM) are increasing to protect the public from them. Therefore, the concentration of ^{238}U, ^{232}Th, and ^{40}K in raw materials and by-products is regulated and managed in a domestic distribution. Because gamma-ray spectrometry is widely used to analyse those nuclides in NORM samples owing to the time and cost constraints, the evaluation of its accuracy is overlooked even though the method of validation using a gamma-ray spectrometry, such as accuracy, precision, and ruggedness, has been well established. In particular, the analysis of ^{238}U and ^{232}Th using gamma-ray spectrometry demands an indirect measurement of their progenies under the secular equilibrium state between those nuclides and their own progenies in a sample. However, this equilibrium in raw materials and by-products can be easily broken due to the artificial process of manufacturing those materials into processed products, such as chemical treatment, owing to the difference in the solubility of nuclides, which is called elemental fractionation. In this study, two CRMs, NBS SRM 600 (Bauxite) and NIST SRM 1633c (Coal fly ash), were first analysed using gamma-ray spectrometry and an ICP-MS. Reliable results of ^{238}U and ^{232}Th using gamma-ray spectrometry could be achieved compared with ones of ICP-MS. This means gamma-ray spectrometry still has an effect on the assessment of natural radionuclides in NORM samples in the case of no chemical treatment. However, when real samples for raw materials and by-products in a domestic distribution were analysed through aforementioned methods, the difference between the two methods was distinctly shown, especially in the ^{232}Th. This means a radioactive evaluation of ^{238}U and ^{232}Th using gamma-ray spectrometry can then induce serious errors in the case of chemically processed products from raw materials and by-products.

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DEVELOPMENT OF GAMMA RAYS IMAGE PLATE FOR SINGLE PHOTON COUNTING USING PLASTIC SCINTILLIATOR

Jiseok Kim, Gwang Min Sun, Hani Baek, Sy Minh Tuan Hoang

Korea Atomic Energy Research Institute (KAERI), 111, Daedeok-Daero, 989 Beon-Gil, Yuseong-gu, Deajeon, Republic of KOREA,
e-mail: geesuck@kaeri.re.kr

Keywords: gamma, imaging, scintillator, single photon counting

The array of thick scintillator has been widely used for getting a high energy of gamma-rays or a high efficiency gamma-ray imaging. Two dimensional distributions of gamma-rays can be analyzed by applying a small piece of scintillator with a density arrangement. However, one of the drawbacks in the application of the thick scintillator is that secondary radiations are generated by a Compton scattering effect from the initial position. This problem is a reason cause to reduce the quality of image.

The Compton noise in the gamma-ray imaging was reduced by applying the single photon counting method with a coincidence analysis between each scintillator.

The results of this study suggest using the PET-like image plate in the gamma-ray imaging. It is determined that the high resolution can be achieved by limiting the secondary radiation events in the gamma-ray imaging.

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DIRECT MEASUREMENT OF CORRECTION FACTORS FOR GAMMA-GAMMA TRUE-COINCIDENCE

András Kocsonya, László Lakosi, Koppány Pázmán, Zsuzsanna Kovács*

Hungarian Academy of Sciences Centre for Energy Research, Konkoly-Thege Miklós út 29–33, 1121 Budapest, Hungary,
*e-mail: kocsonya.andras@energia.mta.hu

Keywords: gamma-spectrometry, true coincidence

Gamma-spectrometry analysis of low activity samples requires detectors with large active volume and close sample-detector geometries. In case of multi-line gamma-emitters the true gamma-gamma coincidence effect became rather significant, therefore correction procedures are necessary both for efficiency calibration and for precise activity measurements. There are several experimental and mathematical methods are available for coincidence correction, however all of them have their limitations which restricts the precision or make difficult to transfer the correction to other cases. A new method is developed which gives directly the count-loss ratio caused by the true coincidence effect. Our method is based on a calibration with multi-line gamma-emitter to be analysed together with a single line emitter applied as coincidence-less marker. This test sample is measured in different geometries extending from close to far enough geometries, where the true coincidence effect is negligible. The decrease of intensity ratio between the multi- and single-line gamma-emitter directly refers to the coincidence-loss.

The method is demonstrated on ^{60}Co, ^{110m}Ag and ^{214}Bi nuclides measured on coaxial and well-type gamma-detectors with 30–60% relative efficiencies.

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CHARACTERIZATION OF NUCLEAR FUEL ASSEMBLIES BY GAMMA-RAY SPECTROMETRY

Péter Völgyesi, András Kocsonya, István Almási, Zoltán Hlavathy, László Lakosi*

Nuclear Security Department, Hungarian Academy of Sciences, Centre for Energy Research, Konkoly-Thege Miklós út 29–33, 1121 Budapest, Hungary, *e-mail: volgyesi.peter@energia.mta.hu

Keywords: fresh and spent fuel, non-destructive analysis, enrichment, burn-up

While destructive methods are not recommended to characterize nuclear assemblies due to radiation protection and other practical reasons, high-resolution gamma-spectrometry (HRGS) is a suitable analytical tool. Both fresh and spent fuel assemblies of VVER-440 reactors at Paks Nuclear Power Plant (NPP) were measured by using this non-destructive method. It provides an independent enrichment verification of fresh fuel and supports nuclear inventory for nuclear safeguards aspects. In the case of spent fuel analysis it helps to optimize the fuel operation allowing better approach of burn-up limits, detects possible burn-up anomalies (e.g. neutron distribution anomaly within the reactor) and also supports nuclear inventory.

Fresh fuel measurements were carried out in the fresh fuel storage of the power plant by a 95 cm^3 HPGe detector, placed to the detector holder rack at the half-height of the assembly. This method enables the measurement of the outer fuel pins in an assembly in different rotating angles (0°, 120°, –120°) with 3.8% and 4.2% enrichment. Enrichment verification relied on the measurement of the 186 keV energy gamma-rays of ^{235}U, as compared to reference assemblies of 1.6% and 2.4% enrichment. Laboratory measurements and Monte Carlo simulations were also carried out to determine how many pins in which row with different enrichment can be detected by the detector.

The burn-up measurements were carried out by a 45 cm^3 HPGe detector placed behind a collimator built into the concrete wall of the service pit. Spent fuel assemblies were transported to measurement position and moved up and down as well as rotated under water by the refueling machine in the front of the collimator hole. Assemblies with different burn-up and cooling time were selected and ana-

lyzed with different rotating angles. ^{137}Cs activities and ^{134}Cs/^{137}Cs activity ratios were measured (662 keV of ^{137}Cs and 605 keV and 796 keV of ^{134}Cs) and also calculated theoretically. The measured parameters are proportional to the burn-up of the fuel, therefore correlation between measured activities/ ratios and calculated burn-out confirms the validity of burn-up calculations.

This method is applicable to determine the uranium enrichment (in %) of fresh fuel assemblies with 0.05% absolute error (2σ).

On the basis of the comparison made among measured results of the assemblies, the dispersion of Cs ratios varied between 1–3% in the case of assembly groups of higher burn-up and shorter cooling time.

These results verify the versatility of gamma-ray spectrometry also in nuclear fuel operation.

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SIMULATION AND FIRST PROOF-OF-CONCEPT OF NEXT GENERATION, MICRO-ORDER SPATIAL RESOLUTION THERMAL NEUTRON DETECTOR

Xiaodong Zhang[1]*, *Joseph Conner*[1], *Michael Moore*[1], *Harish Bhandari*[2], *Vivek Nagarkar*[2], *Jason Hayward*[1, 3]

[1]Department of Nuclear Engineering, University of Tennessee, TN, USA, 37996, *e-mail: xzhang39@utk.edu
[2]RMD Inc., Watertown, MA, USA, 02472
[3]Oak Ridge National Laboratory, Oak Ridge, TN, USA, 37831

Keywords: micro-order spatial resolution, thermal neutron detector, CsI:Tl scintillation columnar array, intensified charge coupled device

To unravel and control the complexity that determines functionality at the meso-scale, new imaging tools must be developed to observe the evolution of defect formation and evolution *in situ* with micron-order resolution. Thermal neutron scattering techniques are well appropriate for these kinds of measurements, especially for the characterization of lithium and corresponding defects dynamic distribution in lithium batteries and the hydrogen behaviour inside hydrogen polymer electrolyte fuel cells. But the current, best available neutron detection system for such applications is fundamentally limited by its spatial resolution. This is mainly caused by the ranges of the charged particles produced by the neutron reaction, which occurs in neutron sensitive materials. To overcome this fundamental limitation, a next generation thermal neutron detector with charged particle tracking capability is proposed for the first time and is being studied with simulations and experiments. Its tracking capability makes its position resolution finer than that allowed by the state-of-the-art, where no tracking is used. The detector consists of a CsI:Tl scintillation columnar array fabricated by RMD, Inc., a microscope objective lens for magnification, and an image intensified charge coupled device (ANDOR iStar DH334T-18U-63 ICCD). The CsI:Tl scintillation columns have a diameter of 1 μm, are 100 μm in length, and have a pitch of 1.5 μm. The gaps among these columns are filled with ^{6}LiF through a chemical vapour deposition process. The whole detection system has been modelled first with Geant4. A Hough transform was used to recognize the tracks of tritons and alphas produced in the neutron and ^{6}Li reaction. The reaction location–which is the interface between the alpha and triton tracks – can be precisely resolved based on the intrinsic energy loss differences of two different energetic charged particles. Combined both algorithms, the simulated achievable spatial resolution of the thermal neutron detector is 0.97 μm and 0.75 μm FWHM along X- and Y-axes, respectively. The difference in resolution along different axes is caused by the asymmetrical structure of CsI columns. Specifically, this detector has an intrinsic gamma rejection capability due to their track differences, i.e., electrons produced by gammas have tortuous tracks; while tritons and alphas produced by neutrons have straight ones. To further prove the concept experimentally, the whole detection system has been tested at the neutron beamline at Oak Ridge National Laboratory. The detail experiment results will be discussed in the full paper and reported on the conference.

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Nuclear safeguards

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A SIMPLE METHOD FOR REPLACING/COMPLEMENTING THE TRADITIONAL IMAGE RECONSTRUCTION TECHNIQUES FOR SPENT NUCLEAR FUEL

Dina Chernikova[1]*, *Kåre Axell*[1, 2], *Syed Naeem*[1]

[1]Department of Applied Physics, Nuclear Engineering, Chalmers University of Technology, Fysikgården 4, SE-412 96 Göteborg, Sweden, *e-mail: dinac@chalmers.se
[2]Swedish Radiation Safety Authority (SSM), SE-171 16 Stockholm, Sweden

Keywords: radon transform, imaging, spent nuclear fuel

For the imaging of spent nuclear fuel originally a set of parallel projections (a line integral of an object along a line) is taken at multiple angles. In mathematical terms this represents the so-called Radon transform of a two dimensional object *f(x,y)*. The data are then fed into different reconstruction techniques such as, Back Projection, Filtered Back Projection, Maximum Entropy, Neural Networks, Algebraic Reconstruction Techniques etc. to obtain the two dimensional object *f(x,y)*. To sum it up, all these techniques are aimed to answer the following question: *"If one is measuring outside an object, is it possible to make conclusions about the inside of the object?"* In most of the cases it depends on the properties of the object itself (scattering and absorption properties) and the reconstruction technique used. Interesting to notice is that the methods applied to the imaging of the spent fuel assemblies are not different from what is already used in medical field or radio astronomy. However, in the medical field the *f(x,y)*-function (object) is assumed to be unknown and therefore, can not be represented in a form of a simple analytical expression. In our view it is not the case of spent nuclear fuel. Therefore, we elaborate on this assumption taking into account the specific nature of the imaging task of the spent nuclear fuel. In particular, the fact that all spent fuel assemblies have fixed geometry allows us to describe the function *f(x,y)* (our object) in a simple analytical form, as a sum of Gaussian functions with specific intensity *(b,k)* and positions *(xi,yi)*. The Radon transform of this function (data measured around an object at different angles and positions) can be easily calculated. In the case of the gross, partial and bias defects present, "the experimental" Radon transform (sinogram) will differ from the one which is predicted theoretically. Thus, the presence of defects can be determined. This paper describes theoretical and numerical investigations of this method.

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DETECTION OF ACTINIDES WITH GALLIUM NITRIDE ALPHA PARTICLE DETECTOR

Padhraic Mulligan[1], *Max Chaiken*[1], *Michael Simpson*[2], *Tom Blue*[1], *Lei Cao*[1]*

[1]Nuclear Engineering, Department of Mechanical Engineering, The Ohio State University, Columbus, Ohio, USA, *e-mail: Cao.152@osu.edu
[2]Department of Metallurgical Engineering, University of Utah, Salt Lake City, USA

The vulnerability of a closed fuel cycle comes from the risk of diversion of special nuclear materials (SNM) for ill-purposed use. The ability to monitor actinides to prevent and detect the misuse of SNM throughout the fuel cycle is of paramount concern to global security. There is a critical need to monitor the concentration of actinides in the salt, and preferably this monitoring should involve an on-line monitoring method. While many other approaches have been proposed and are promising, none have yet been proven to be both practically implementable and sufficiently accurate. We have fabricated sensor prototypes based on gallium nitride (GaN) for measurement of actinide concentrations in molten salt in high temperature. The novel approach using in-salt electro-deposition to pre-concentrate salt onto sensor before measurement will greatly increase the accuracy in actinides quantification for use in material accounting. We have electrodeposited a thin film actinide from high temperature salt onto a 1 cm × 1 cm × 0.1 cm tungsten substrate to use as a testing source for the sensor response. Less than a gram of U-238 and less than a gram of Th-232 deposited on the surface produces an aerial source activity of 0.1 uCi. A group GaN schottky structure devices have been fabricated from a wafer of carrier concentration at 10^{14} cm^{-3}. Sensor is fully depleted and alpha spectroscopy can be used to determine the amounts of actinide isotopes in the deposit. This can then be correlated back to the concentration of these actinides in the salt. The benefit over voltammetry using alpha spectroscopy is improved ability to quantify specific actinides that might have similar electrochemical reduction potentials and even isotopes that are electrochemically indistinguishable. Notably, the sensor is reusable; because the actinide film on the detector can be reversibly removed through application of an oxidizing potential after the sensor is placed back into the salt.

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INFLUENCE OF Bi X-RAYS ON URANIUM ISOTOPE RATIOS DETERMINED BY GAMMA SPECTROMETRY

Tomas Rüther[1, 2], *Jozsef Zsigrai*[1], *Tam Cong Nguyen*[3], *Andrey Berlizov*[4]

[1]EC Joint Research Centre - Institute for Transuranium Elements, Karlsruhe, Germany
[2]University of West Bohemia, Faculty of Electrical Engineering,Department of Electrical Power Engineering and Ecology, Pilsen, Czech Republic
[3]Centre for Energy Research of the Hungarian Academy of Sciences (EK), 1525 Budapest 114, P.O. Box 49, Hungary
[4]International Atomic Energy Agency, Vienna International Centre, PO Box 100, 1400 Vienna, Austria

Keywords: uranium, isotopic composition, gamma spectrometry, MGAU, FRAM

The isotopic composition of uranium for safeguards purposes is often determined from its gamma spectrum using the MGAU or FRAM software codes. Both codes can provide, in principle, results with relative accuracies close to 1%. However, if X-ray fluorescence peaks of Bi are present in the gamma spectra, biases of up to 7% have been observed. The most common origin of Bi X-rays in the spectra of uranium is the presence of Bi in the detector, in the sample cladding or in the sample itself. In this work we determined the bias of the ^{235}U enrichment given by MGAU and FRAM as a function of Bi mass present in the measurement setup. We also propose a solution for removing this bias from the results of FRAM. For accurate measurements of the ^{235}U enrichment by MGAU and FRAM the presence of Bi should be avoided. If this is not possible, the corresponding bias has to be taken into account.

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A COUPLED FRAMEWORK TO ESTIMATE URANIUM MULTIPLICATION AND ENRICHMENT IN TAGGED NEUTRON MEASUREMENTS

Matthew Tweardy[1]*, *Seth McConchie*[2], *Jason P. Hayward*[1]

[1]Department of Nuclear Engineering, University of Tennessee, Knoxville, TN, USA, *e-mail: mtweardy@vols.utk.edu
[2]Nuclear Materials Detection and Characterization Group, Oak Ridge National Laboratory, Oak Ridge, TN, USA

Keywords: uranium enrichment, multiplicity measurements, point kinetics

Coincidence and multiplicity counting techniques are widely used in the characterization of special nuclear material for safeguards and arms control applications. Assay of uranium objects presents a particularly difficult challenge in that it typically requires an active source to induce a measurable coincident neutron signal. Tagged neutron measurement systems currently under development use an associated particle D-T neutron generator to perform simultaneous transmission and multiplicity measurements of uranium objects. We present an extended coupled framework to calculate the expected reduced factorial moments of the prompt neutron multiplicity distribution in terms of model parameters that represent some interesting physical characteristic of a uranium object. The three model parameters are the probability of a source neutron inducing fission in the object, the probability of a source neutron (n,2n) interaction in the object, and the object's total self-multiplication. The one-group point kinetics model is assumed for the fission chain propagation within the fissile object. However, transmission imaging information and knowledge of the source neutron energy and time-of-flight allow for the source neutron coupling parameters to be related to the uranium enrichment via attenuation physics.

The three model parameters can be uniquely solved from three measured values in a tagged neutron measurement. We demonstrate that using the singles, doubles, and either the triples or the neutron path length through uranium, determined from transmission imaging, can be used to numerically solve for the unique set of characteristic parameters using a cubic spline fitting algorithm. Data from tagged neutron measurements of enriched and depleted uranium annular castings, as well as Monte Carlo simulated measurements, are used to evaluate the accuracy of estimating total self-multiplication and enrichment using the new framework and methods.

Production of radionuclides

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CROSS SECTION DATA FOR THE PRODUCTION OF THERANOSTIC ^{195M}Pt VIA THE DOUBLE NEUTRON CAPTURE IN ^{193}Ir

Nikolay Aksenov, Sarkis Karamian, Gospodin Bozhikov*

Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, Joliot-Curie 6 141980 Dubna, Russia,
*e-mail: nikolay.aksenov@jinr.ru

Keywords: platinum radionuclides, Auger-emitters, double neutron capture, theranostics, radionuclide production, radiochemical separation, iridium target

The advantage of using the Auger electron emitter ^{195m}Pt ($T_{1/2}$ 4.02 days) in medical radiotherapeutic applications is high yield of low energy beta/gamma radiation, where each decay leads to 33 secondary electrons. Effective ways for optimization of the Pt isomer yield at low impurity content must be investigated [1]. Here we report investigation of the possibility of production of isomer ^{195m}Pt by double neutron capture by the ^{193}Ir target nucleus with consequent population of ^{195m}Pt through β-decay. This approach allows isolation of carrier-free Pt isotopes from the irradiated target using radiochemical methods. Time-integrated mean flux of slow neutrons reaches a value of 2.3×10^{12} cm$^{-2} \times$ s^{-1} at the irradiation port near the active zone of the IBR-2 pulsed reactor of JINR. This is enough to detect the double neutron capture products by the activation method. We developed a rapid and efficient method for dissolution of Ir metal based on anodic dissolution in aqueous solutions and subsequent chemical separation of ^{195m}Pt from solution using extraction chromatography.

A high capture cross section is deduced in the present experiment for intermediate radioactive ^{182}Ta and ^{194g}Ir target nuclides. The ^{nat}Ta targets were also irradiated over the experiment as monitor, and they have demonstrated a great cross section for the second neutron capture by radioactive ^{182}Ta. The cross sections of neutron capture by the odd-odd radioactive targets, like ^{194g}Ir, ^{182}Ta, and ^{198}Au, exceeding 10^4 b, are of importance for understanding within the nuclear reaction theory. The determined now cross sections are enough to evaluate the activity yield at a high neutron flux reactor. The equilibrium activity of ^{195m}Pt could reach a level of 1.0 Ci per mg of the ^{193}Ir target material.

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CHARACTERISATION OF A HYDROXAMATE BASED EXTRACTION CHROMATOGRAPHIC RESIN AND ITS APPLICATION TO Zr/Y, Ti/Sc AND Ge/Ga SEPARATION

Carina Dirks, Steffen Happel, Aude Bombard*

TrisKem International, 3 Rue des Champs Géons ZAC de, L'Éperon, 35170 Bruz, France, *e-mail: shappel@triskem.fr

Keywords: hydroxamate resin, extraction chromatography, Zr/Y separation, Ti/Sc separation, Ge/Ga separation

Zr separation chemistry is of increasing interest in various domains. Long-lived Zr-93 (t½ = 1.61(6) a, Eb-,max = 90.3(15) keV [1]) frequently needs to be determined in decommission and radioactive waste samples. It is often quantified by mass spectrometry, accordingly isobaric interferences and matrix elements need to be removed very thoroughly before measurement. Zr-89 on the other hand is gaining more and more interest in immuno-PET due to its favorable physical properties (t½ = 78.42(13), 100% EC/b+, Eg = 908.97(3) with P = 99.03(2)% [1]). It is cyclotron produced via a (p,n) reaction from natural Y (Y-89) targets. Hydroxamate based resins as described e.g. by Holland et al. [2] are frequently used to separate Zr from the Y target material. The synthesis of the described resin involves the use of irritating (GHS07) and hygroscopic reagents such as 2,3,5,6-tetrafluorophenol. In order to overcome this drawback a stable and ready to use hydroxamate based extraction chromatographic resin, now commercially available under the designation of ZR Resin, was developed and characterized. The characterization of the resin included the determination of DW values of selected elements in varying HCl, HNO3 and oxalic acid concentrations as well as the determination of its capacity for Zr. Based on the obtained data, elution studies were performed in order to find suitable conditions for the separation of Zr from Y targets, Ti from Sc targets and Ge from Ga targets, further its potential use as a support for Ti-44 generators is evaluated. Results of these studies will be presented.

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PRODUCTION AND SEPARATION OF RADIOACTIVE BERYLLIUM ISOTOPES AT PSI

Stephan Heinitz[1]*, Emilio Maugeri*[1]*, Marin Ayranov*[2]*, Dorothea Schumann*[1]

[1]Laboratory of Radiochemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland
[2]European Commission, DG-ENER, L-2557 Luxembourg, Luxembourg

The Paul Scherrer Institute operates one of the most powerful accelerators worldwide generating 590 MeV protons with currents up to 2.5 mA. The protons pass several stages of the facility and are finally guided towards a solid lead target, where neutrons are produced inside the Swiss neutron spallation source SINQ. Materials in the environment of the accelerator complex and the SINQ become highly activated. They contain a number of exotic radionuclides, which hardly can be produced by other means and are urgently needed in several scientific application fields like nuclear astrophysics, basic nuclear physics, environmental science and others.

While ^{7}Be ($T_{1/2}$ = 53.22 d) is currently under investigation in astrophysical research related to the primordial ^{7}Li problem, the long-lived isotope ^{10}Be ($T_{1/2}$ = 1.387 Ma) is a useful nuclide for geochemical processes relevant in soil and ice core dating. We here report on the production and separation of both beryllium isotopes at different stages of the PSI accelerator complex and will briefly focus on the production of targets made of these nuclides.

^{7}Be is produced in considerable amounts in the D2O cooling water of the SINQ facility by spallation reactions on ^{16}O with the generated fast neutrons. A special by-pass-filter, consisting of mixed bed ion exchanger, has been installed into the moderator cooling circuit in order to collect the wanted activity. A remotely controlled separation setup has been developed for the purification of several hundred GBq of ^{7}Be in one batch.

Large amounts of ^{10}Be are produced at the PSI myon production facility by high-energy proton spallation in polycrystalline graphite. For the extraction of ^{10}Be out of massive amounts of carbon, pyrolysis and a wet chemical procedure have been tested. Approx. 270 g of graphite from Target E92, which had received a total proton charge of 29 Ah between 2002 and 2005, have been burned at 1000 °C in a stream of oxygen. The volatile radioactive oxidation products $^{3}H_2O$ and $^{14}CO_2$ were trapped in 3 water bubblers connected in series. The remainder, a white hygroscopic solid material mainly consisting of $^{6/7}Li_2O$, $^{9/10}BeO$ and $^{10/11}B_2O_3$, was dissolved in HF and was further purified by ion exchange chromatography. Radioactive impurities such as ^{22}Na, ^{26}Al, ^{44}Ti, ^{54}Mn, ^{60}Co, ^{101}Rh, ^{133}Ba, ^{172}Hf and ^{207}Bi have been separated from the final product. The purified material represents a mixture of approx. 6 mg ^{9}Be and 4 mg (3.8 MBq) ^{10}Be. It is ready to be used for scientific investigations requiring large amounts of this precious isotope.

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INVESTIGATION OF PRODUCTION AT LIGHT CHARGED PARTICLE ACCELERATORS OF MEDICAL RADIOISOTOPES IN THE RARE EARTH REGION

A. Hermanne[1]*, F. Tarkanyi*[2]*, F. Ditroi*[2]*, S. Takacs*[2]*, A. V. Ignatyuk*[3]

[1]Cyclotron Laboratory, Vrije Universiteit Brussel (VUB), Brussels, Belgium
[2]Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Debrecen, Hungary
[3]Institute of Physics and Power Engineering(IPPE), Obninsk, Russia

Keywords: rare earths, experimental excitation functions, light charges particles, model calculation

Numerous candidate diagnostic and therapeutic radioisotopes in the rare earth region have been identified in the literature. They can be produced via light charged particle activation of rare earth targets and optimization of irradiation parameters should be based on reliable nuclear reaction data. Only very few experimental activation cross section data on these elements were available due to the relatively rare practical use, the difficult chemical behavior and targetry problems. We initiated a systematic study of proton and deuteron induced reactions on rare earth elements (including a few alpha induced reactions) to investigate production routes of medical radioisotopes. Activation cross sections with proton (80 MeV), deuteron (50 MeV) and alpha-particle (40 MeV) beams were measured by using stacked foil irradiation technique and off-line gamma spectroscopy. Among others excitation functions were determined for formation of ^{177}Lu, ^{169}Yb, ^{166}Yb, ^{165}Er, ^{166}Ho, ^{161}Ho, ^{152}Tb, ^{155}Tb,^{153}Sm, ^{149}Pm ^{140}Nd- ^{140}Pr medically relevant radioisotopes and for contaminating reactions.

A summary of our earlier investigation will be given and new data are presented for the Ce+p, La+p, Nd,+p, Tm+d and Pr+d reactions. In most cases no earlier experimental data are available, or only the low energy range was investigated. The data were measured on targets with natural isotopic composition. The results help however to estimate cross sections and impurity levels for highly enriched targets.

The data are compared with the results of theoretical calculations using the ALICE, EMPIRE and TALYS codes.

Low and medium energy charged particle induced reactions are in general not competitive with (n,γ reactions using research reactors, especially for production of long lived isotopes. It is however impossible to produce significant amounts of these products at reactors. The neutron route is mostly not carrier free and result in low specific activity, not fulfilling the requirements of nuclear medicine applications.

It should be mentioned the most of these isotopes can be produced with high yields through high energy spallation on tungsten and tantalum. Due to the large generated activity and the large number of reaction products the specific product should be separated/purified with a ion mass separator set up (see ISOLDE-CERN project).

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EXCITATION FUNCTION MEASUREMENTS FOR ^{103}Pd PRODUCTION BY DEUTERON BEAMS IRRADIATION

Simone Manenti[1]**, Maria del Carmen Alí Santoro*[2]*, Giulio Cotogno*[3]*, Charlotte Duchemin*[4]*, Ferid Haddad*[4, 5]*,*
Uwe Holzwarth[3]*, Flavia Groppi*[1]

[1]LASA, Università degli Studi di Milano and INFN-Milano, via F.lli Cervi 201, I-20090 Segrate, MI, Italy, *e-mail: simone.manenti@mi.infn.it
[2]Comisión Nacional de Energía Atómica, Centro Atómico Ezeiza, Presb. González y Aragón 15, B1802AYA Ezeiza, Argentina
[3]Institute for Health and Consumer Protection, Joint Research Centre, European Commission, TP 500, I-21020 Ispra, VA, Italy
[4]Laboratoire SUBATECH, CNRS/IN2P3-EMN-Université, 4 rue Alfred Kastler, 44307 Nantes, France
[5]GIP Arronax, 1 rue Aronnax, 44817 Saint-Herblain, France

Keywords: nuclear medicine, accelerator produced isotopes, deuteron beams, Pd-103

Brachytherapy was developed to treat prostate cancer 50 years ago. It consists in the implantation of titanium or stainless steel seeds containing suitable radionuclides. Nowadays only three radioactive isotopes are available for use in low dose rate prostate brachytherapy: ^{125}I ($t_{1/2}$ = 59.4 d, mean photon energy emitted: 26 keV), ^{103}Pd ($t_{1/2}$ = 17 d, mean photon energy emitted: 19 keV), and ^{131}Cs ($t_{1/2}$ = 9.7 d, mean photon energy emitted: 28 keV). ^{103}Pd is an effective alternative to ^{125}I: the higher photon energy is, the fewer radioactive seeds are required and, given the differences in dose rates, ^{103}Pd may have an advantage for high grade, rapidly growing cancer because of its faster dose rate that also raise concerns for possible differences in normal tissue complication. So it is important to study the production optimization of ^{103}Pd radionuclide.

Nowadays the accelerator production method for ^{103}Pd is based on the irradiation of rhodium metal with 18 MeV protons via the ^{103}Rh(p, n)^{103}Pd reaction. We are studying the production by deuteron beams irradiation.

We present our contribution to the systematic study of the activation cross-sections of deuteron induced nuclear reactions, with new measurements and dataset, experimentally determining excitation functions of the ^{103}Rh(d,2n)^{103}Pd nuclear reaction. The stacked-foil activation technique irradiating at different energies thin targets of ^{103}Rh was used. The irradiations were carried out at the JRC Cyclotron, Ispra – VA, Italy and at ARRONAX, Saint-Herblain, France. The irradiated targets were analysed at LASA Laboratory in Milano. Due to the half- life of the radionuclide, the first measurements of the samples were generally started few hours or one day after the end of bombardment depending on the activity of the targets. Our new set of excitation function for this nuclear reaction is compared with the only other three sets present in literature. The thin-target yields have been plotted as a function of their average energy into the targets and were fitted with the best mathematical functions. The integration of these functions allowed gaining the calculated thick target yields, in order to find the optimized couple of energy irradiation and energy loss inside the thick target to maximize the production of the radionuclide of interest.

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THE CHALLENGE OF HIGH PERFORMANCE TARGETS PREPARATION FOR NUCLEAR PHYSICS EXPERIMENTS

Andreea Mitu[1], Marius Dumitru[2], Nicoleta M. Florea[1], Nicolae M. Marginean[1],*
Gheorghe Cata-Danil[3], Maria Dinescu[2]

[1]Department of Nuclear Physics, Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), Reactorului Street, no. 30, Bucharest-Magurele, Romania, *e-mail: andreea.mitu@nipne.ro
[2]Department of PPAM/ Lasers, National Institute for Laser, Plasma and Radiation Physics (INFLPR), 409 Atomistilor Blvd., Bucharest-Magurele, Romania
[3]Department of Physics, University Politehnica of Bucharest, 313 Splaiul Independentei, Bucharest, Romania

Keywords: enriched isotopic thin films, nuclear structure experiments, pulsed laser deposition

During the last years the demand for enriched isotopic thin films used as targets for different types of nuclear structure experiments, performed at the 9 MV FN tandem accelerator in IFIN-HH, Romania and other international research facilities where the research groups have scientific collaborations, has increased significantly. In present, the target preparation laboratory from IFIN-HH is developing and produces thin layers on backings and thin self-supporting layers using evaporation in vacuum (thermal evaporation, electron-gun evaporation, sputtering) and rolling methods [1].

The success of the nuclear physics experiments is strongly influenced by the characteristics of the used targets (purity, composition, thickness, uniformity). The above-mentioned evaporation techniques allow preparation of well-controlled, good quality thin films materials with high vaporization temperatures (~4000 °C). However, there is an increased demand for thin films of materials with extremely high vaporization temperatures in the range of 4500–5500 °C (e.g. Os, Hf, W). Pulsed lased deposition (PLD) is one of the most popular and simple technique used for deposition of thin films of a wide range of materials: it can be applied to simple metals, binary or multicomponent compounds (ceramic) layers, polymers, etc. Using this technique thin film with high density, thickness uniformity on the defined surface, controllable thickness, high purity and durability can be obtained [2].

In this research study various types of thin layers of materials with extremely high vaporization temperatures will be prepared using PLD technique.

In order to determine the features of the obtained thin films multiple characterization methods (e.g. RBS, AFM, SEM-EDX, SIMS, XRD) will be performed.

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PRODUCTION OF HIGH PURITY LANTHANIDE ISOTOPES FROM THE SPONTANEOUS FISSION OF Cf-252

Jana K. Pfeiffer[1], *Kevin P. Carney, Mathew S. Snow, Christopher A. McGrath*[2]

[1]Idaho National Laboratory, Idaho Falls, Idaho, USA, e-mail: jana.pfeiffer@inl.gov
[2]Idaho State University, Pocatello, Idaho, USA

Keywords: californium-252, fission products, isotopes, lanthanides

The global national security community needs certified reference materials to develop detection methods and verify confidence in non-proliferation, counter-proliferation, and nuclear forensics measurements. The sparse availability of fast fission sources in the United States makes the development of isotope mixtures emulating the fast fission spectra of uranium and plutonium an interesting research challenge. To address this challenge, Idaho National Laboratory is pursuing the collection and purification of isotopes from the spontaneous fission of Cf-252; a readily available source of isotopes over the mass range of 70–170 amu that does not require reactor irradiation of fissionable materials. Successful deployment of this research presents several challenges including 1) carrier-free isolation of single isotopes from the complex isotope mixture generated by Cf-252, 2) efficient and rapid isotope purification to ensure provision of short-lived fission products, and 3) development of analytical methods to enable efficient, quality analysis of the purified products. This work reports a method combining extraction chromatography with high performance liquid chromatography (HPLC) to perform rapid, quantitative purification of carrier free quantities of lanthanide fission products collected from Cf-252 for addition to working materials used to enhance nuclear forensics analysis.

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STANDARDISATION OF A ^{68}(Ge+Ga) SOLUTION WITHIN THE CCRI(II)-K2.Ge68 KEY COMPARISON

Maria Sahagia, Aurelian Luca, Andrei Antohe, Mihail-Razvan Ioan, Constantin Ivan*

Horia Hulubei National Institute of Physics and Nuclear Engineering, IFIN-HH, Bucharest-Magurele, Romania, *e-mail: msahagia@nipne.ro

Keywords: PET ^{68}Ga radiopharmaceuticals,^{68}(Ge – Ga) generator, absolute and relative standardization of solution, CIPM-MRA, key comparison, international equivalence

^{68}Ga, a short half life radionuclide, decays both by electron capture and positron emission and is used as a radiopharmaceutical in PET investigations. It is the daughter of ^{68}Ge, decaying by pure electron capture; this is the reason to prepare ^{68}(Ge – Ge) generators and to elute ^{68}Ga from them in nuclear medicine units. On the other hand, a standard solution of this mixture, at equilibrium, can be used as a mock (surrogate) solution for the calibration and check of the radionuclide calibrators, measuring ^{11}C, ^{13}N, ^{15}O, ^{18}F, ^{68}Ga. For this reason, the international equivalence of the National or Designated Metrology Institutes standards is necessary to be established within the international system of reference (SIR). On this purpose, it was decided by the CIPM-CCRI(II) to organise a type II key-comparison, codified as CCRI(II)-K2.Ge68. The pilot laboratory, who prepared the solution, sent it to the participant laboratories, and engaged himself to gather the comparison reports and process the measurement data in cooperation with BIPM, was NIST-USA, responsible person, Dr. Jeffrey Cessna.

Our laboratory took part in the comparison and reported the measurement results. Four methods of standardisation were used on this purpose: the absolute methods (i) the 4γβ(PC)-γ coincidence method, efficiency extrapolation variant, using the previous experience in the field [1, 2] and improving it, (ii) the liquid scintillation counting in the variant of triple to double coincidence ratio (LSC-TDCR), and the relative methods using calibrated secondary installations – (iii) gamma-ray spectrometer [3] and (iv) well-type ionisation chamber [4].

The paper describes all the measurement methods and their specific problems which were overcome. The final results, mean activity concentration of the solution (kBq g^{-1}) and its uncertainty, were calculated and reported to NIST, from all results of the four methods. The new method “power moderate weighted mean (PMM)” used by the CCRI(II) to calculate the key comparison reference value (KCRV) and its standard uncertainty within key comparisons [5] was used. The standardization results will be presented in relative figures, taking as reference the 4γβ(PC)-γ result (taken as 100 kBq g^{-1}) because the comparison result is not yet published.

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CONVERSION OF HIGH-ENRICHED (98.5%) $^{98}MoF_6$ TO ^{98}Mo AND ^{98}MoC NANOCRYSTAL TARGETS IN RF PLASMA

Petr Sennikov[1], Roman Kornev[1], Dmitry Chuvilin[2]*

[1]Plasma-Chemistry Department, G.G. Devyatykh Institute of High-Purity Substances of RAS, 49 Tropinin Str., 603950 Nizhny Novgorod, Russian Federation, *e-mail: pgsen@rambler.ru
[2]National Research Centre “Kurchatov Institute”, Kurchatov Sq. 1, 123182 Moscow, Russian Federation, e-mail: Chuvilin_DY@nrcki.ru

Keywords: molybdenum isotopes, plasma chemical conversion, molybdenum hexafluoride

The most popular radio-pharmaceutical drugs based on ^{99m}Tc are originated by ^{99}Mo with half-life of 66.02 hours. The reactor ^{99}Mo production method, which is based on high enrichment ^{235}U nuclear fission process, is the only commercial one. But then, a lot of reactors which work on HEU fuel are closing nowadays as a result of a worlds’ modern global nuclear safe policy. The radioactive capture method of ^{99}Mo production from ^{98}Mo targets is very promising among all other non-reactor alternatives. It uses the following reaction:

$$^{98}\mathrm{Mo}(n,\gamma)^{99}\mathrm{Mo} \rightarrow \beta\text{-decay} \rightarrow {}^{99m}\mathrm{T} \qquad (1)$$

A new ^{99}Mo production method, based on nuclear reaction (1) using structured molybdenum (preferably ^{98}Mo isotope containing) nanoparticles as target material, was proposed in “Kurchatov institute” National Research Centre. Calculations have been shown that in case of constructing of a special target consisting of 10 nm nanoparticles of molybdenum or molybdenum-containing compounds surrounded by binding buffer will be able to localize ^{99}Mo recoil atoms in this buffer during the radioactive process and separate them from the target material.

In this paper the first step of the process, (1), namely, the production of ^{98}Mo isotope particles in form of metal and ^{98}MoC compound from enriched $^{98}MoF_6$ is described. The process of plasma chemical conversion of $^{98}MoF_6$ in RF (13.56 MHz) capacitive-coupled and arc discharges was investigated. In both types of discharges the formation of metal (bulk) and powder nano-dispersed molybdenum as well as of fluoromolybdens of $^{98}MoF_n$ fluorides was found. The mechanism of plasma chemical reduction of $^{98}MoF_6$ by hydrogen under considered experimental conditions was suggested. The isotopic and impurity composition of prepared nano-powder and bulk samples of ^{98}Mo as well as of their structure was determined. Samples of ^{98}Mo isotope and its carbide ready for neutron irradiation have been prepared.

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INVESTIGATION OF CROSS SECTIONS OF DEUTERON INDUCED NUCLEAR REACTIONS ON NATURAL LUTETIUM

S. Takács[1], F. Tárkányi[1], A. Hermanne[2], R. Adam Rebeles[2]

[1]Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), 4026 Debrecen, Hungary
[2]Cyclotron Laboratory, Vrije Universiteit Brussel (VUB), Laarbeeklaan 103, 1090 Brussels, Belgium

In a systematic study of light charged particle induced nuclear reactions we investigated the excitation functions of deuteron induced nuclear reactions on natural lutetium targets. Experimental excitation functions of deuteron induced reactions up to 50 MeV on high purity natural lutetium were determined using the standard stacked foil activation technique. High resolution off-line gamma-ray spectrometry was applied to assess the activity of each foil. From the measured activity independent and/or cumulative elemental or isotopic cross-section data for production of Hf and Lu radioisotopes were determined. The experimental data were compared to the data published earlier by other authors and to results of TALYS theoretical code taken from TENDL-2014 database. Thick target yields for the investigated radionuclides were calculated from the excitation functions deduced as an analytical fit to our experimental cross section data points.

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PRODUCTION OF MEDICAL RADIOISOTOPES OUT OF STANDARD PROTON BEAM AND ENERGY RANGES

Ferenc Tárkányi[1], Sándor Takács[1], Ferenc Ditrói[1], Alex Hermanne[2], Anatolij V. Ignatyuk[3], Syed M. Qaim[4], Mamoru Baba[5]*

[1]Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI), Debrecen, Hungary, *e-mail: tarkanyi@atomki.hu
[2]Cyclotron Laboratory, Vrije Universiteit Brussel (VUB), Brussels, Belgium
[3]Institute of Physics and Power Engineering (IPPE), Obninsk, Russia
[4]Institut für Neurowissenschaften und Medizin, INM-5: Nuklearchemie, Forschungszentrum Jülich, Jülich, Germany
[5]Cyclotron and Radioisotope Center (CYRIC), Tohoku University, Sendai, Japan

Keywords: medical isotopes, charged particle reactions, production routes

The number of routinely used medical radioisotopes produced at charged particle accelerators is limited and presently they are mostly based on standard proton cyclotrons with energies in the 35–40 MeV range. A long list of candidate and emerging diagnostic and therapeutic radionuclei were proposed in literature, which are currently in research and development phase (including optimal production routes). In the frame of a systematic study we have investigated possible alternatives to low-medium energy proton production routes by using other light charged particles (d,^{3}He- and α-particle) up to 50 MeV and higher energy protons up to 80 MeV.

For investigation of production routes of medical radioisotopes with other light charged particles activation cross section enriched and natural targets of more than 50 elements were measured in international collaboration.

The deuteron induced reactions were investigated in more detail for production of ^{11}C, ^{13}N, ^{18}F, ^{44}Sc, ^{51}Cr , ^{52}Mn, ^{55}Co, ^{61}Cu, ^{62}Cu, ^{64}Cu, ^{67}Cu, ^{66}Ga, ^{67}Ga , ^{68}Ga, ^{75}Br, ^{76}Br, ^{77}Br, ^{72}As, ^{81}Rb, ^{82m}Rb, ^{90}Nb, ^{88}Y, ^{87}Y, ^{88}Zr, ^{89}Zr, ^{90}Y, ^{99m}Tc, ^{103}Pd, ^{110m}Ag, ^{111}Ag, ^{110m}In,^{111}In,^{113m}In, ^{114m}In, ^{117m}Sn, ^{123}I, ^{124}I, ^{139}Ce,^{140}Pr, ^{139}Pr,^{142}Pr, ^{143}Pr, ^{141}Nd, ^{149}Pm, ^{145}Sm, ^{153}Sm, ^{152}Tb, ^{155}Tb, ^{153}Gd, ^{161}Tb, ^{161}Ho,^{165}Er, ^{169}Er, ^{167}Tm,^{170}Tm, ^{166}Yb, ^{169}Yb, ^{177}Lu, ^{178m}Ta, ^{186}Re,^{192}Ir, ^{191}Pt,^{193}Pt, ^{195}Au, ^{198}Au, ^{199}Au, ^{192}Ir, ^{195m}Hg, ^{195g}Hg, ^{197m}Hg,^{197}Hg, ^{201}Tl.

The investigated reactions based on ^{3}*He bombardment* can be useful for production of ^{52}Mn, ^{55}Co, ^{60}Cu, ^{61}Cu, ^{62}Zn, ^{66}Ga, ^{67}Ga, ^{83}Sr, ^{82m}Rb, ^{103}Pd, ^{110m}I,^{117m}Sn, ^{118}Sb, ^{123}I, ^{124}I, ^{195m}Hg, ^{195g}Hg, ^{197m}Hg, ^{197}Hg, while *alpha particle* induced reactions were studied for production of the ^{38}K, ^{43}K, ^{52}Fe, ^{51}Cr, ^{55}Co, ^{60}Cu, ^{61}Cu, ^{67}Cu, ^{68}Ga, ^{71}Ge, ^{72}As, ^{82}Sr, ^{89}Zr, ^{97}Ru , ^{110m}In, ^{111}In, ^{114m}In, ^{117}Sn, ^{131}Cs, ^{167}Tm, ^{178m}Ta, ^{169}Yb, ^{172}Tm, ^{177}Lu, ^{195m}Au, ^{198g}Au, ^{199}Au, ^{211}At medical radioisotopes.

Higher energy proton (>40 MeV) data were obtained for production of ^{52}Fe, ^{51}Cr, ^{66}Ga, ^{67}Ga, ^{68}Ga, ^{64}Cu, ^{67}Cu, ^{82m}Rb, ^{83}Sr, ^{88}Zr, ^{88}Y, ^{93m}Mo, ^{110m}Ag, ^{131}Cs, ^{103}Pd, ^{110m}In, ^{111}In, ^{114m}In, ^{145}Sm, ^{167}Tm, ^{166}Yb, ^{169}Yb, ^{178m}Ta, ^{167}Tm, ^{169}Yb, ^{192}Ir, ^{191m}Pt,^{195m}Pt, ^{198g}Au medically relevant radioisotopes.

New additional experimental data will be presented and comparison with the standard proton reactions will be given to show when alternative particles or high energy proton beam can be considered.

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THE PRODUCTION OF RADIONUCLIDES FOR DIAGNOSTIC AND THERAPEUTIC APPLICATION IN NUCLEAR MEDICINE

Nicholas van der Meulen[1, 2], Christiaan Vermeulen[2], Roger Schibli[2, 3], Andreas Türler[1, 4], Ulli Köster[5], Cristina Müller[2]*

[1]Laboratory of Radiochemistry, Paul Scherrer Institute, Villigen-PSI, Switzerland, *e-mail: nick.vandermeulen@psi.ch
[2]Center for Radiopharmaceutical Sciences, Paul Scherrer Institute, Villigen-PSI, Switzerland
[3]Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland
[4]Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland
[5]Institut Laue-Langevin, Grenoble, France

Keyords: “matched pair”, radiochemical separation, ion exchange

The “matched pair” concept of radionuclide use is gaining in popularity, with one radionuclide utilized for imaging purposes, while another radionuclide of the same element used in higher doses for the treatment of the diagnosed tumour. This allows the radiolabelling conditions of the peptide in question to be consistent, as well as treating the tumour in the same area as being imaged. Paul Scherrer Institute (PSI) is concentrating its radionuclide production and radiopharmaceutical research on this principle.

Radionuclides used for diagnostic purposes (β^+-emitters for Positron Emission Tomography) are typically manufactured using cyclotrons (with the notable exception of ^{99}Tc), while radionuclides used for therapeutic purposes (β^--emitters and many α-emitters) are generally manufactured using research reactors. As a result, PSI collaborates with other facilities for neutron irradiation of target material.

Matched pairs under investigation at PSI include ^{44}Sc/^{47}Sc [1, 2] and ^{152}Tb/^{149,161}Tb [3], with development of chemical separations, as well as preclinical studies in this regard, ongoing.

^{44}Sc ($T_{1/2}$ = 3.97 h, β^+-emitter) is separated from its enriched Ca target material by dissolving the target in HCl and passing it through DGA extraction resin [1]. It is eluted and concentrated using a similar, smaller, resin column, such that the elution volume is low enough for direct radiolabelling capability. The product yielded up to 3 GBq ^{44}Sc, containing <1% ^{44m}Sc. A similar separation is utilized for the ^{47}Sc ($T_{1/2}$ = 3.35 d, β^--emitter) production from enriched ^{46}Ca target material, with yields up to 1 GBq radionuclically pure product being obtained from ~1 mg target material. These products have successfully been labelled to DOTA-peptides and, subsequently, injected into tumour-bearing mice [1, 2].

Mass-separated beams of ^{149}Tb ($T_{1/2}$ = 4.1 h, α-emitter) and ^{152}Tb ($T_{1/2}$ = 17.5 h, β^+-emitter), respectively, were implanted into Zn-coated Au foils. The Tb radionuclides were dissolved in HNO_3/NH_4NO_3, loaded onto a macroporous cation exchange resin and the Tb radionuclides eluted using dilute α-hydroxyisobutyric acid (α-HIBA). The separations yielded ~100 MBq ^{149}Tb and ~500 MBq ^{152}Tb, respectively, both >99% radionuclidically pure. A similar separation method was devised for ^{161}Tb, irradiated from Gd targets utilizing the $^{160}\text{Gd}(n,\gamma)^{161}\text{Gd}\rightarrow{}^{161}\text{Tb}$ nuclear reaction, yielding up to 15 GBq radionuclidically pure product [3]. Preclinical studies with these radionuclides are ongoing.

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Prompt gamma activation analysis

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PROMPT GAMMA-RAY ACTIVATION ANALYSIS FOR CERTIFICATION OF SULFUR IN FUEL OIL SRMS

Rick L. Paul

Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899 USA, e-mail: rick.paul@nist.gov

Keywords: prompt gamma-ray activation analysis, cold neutrons, thermal neutrons, analytical chemistry, sulfur, fuel oils, reference materials

Monitoring of sulfur levels in fossil fuels is of prime importance because of the environment impact from emissions. Mass spectrometric methods have been used at NIST in the certification of sulfur in residual fuel Standard Reference Materials (SRMs) at 0.1% to 4% levels, however a second independent method is required. The thermal neutron (TN) PGAA instrument located at beam port VT5 in the NIST Center for Neutron Research (NCNR) has long been used in the certification of major and minor elements in biologicals, agriculturals, and other highly hydrogenous materials, however this instrument does not have the sensitivity to accurately and routinely measure sulfur at <1%. Cold neutron (CN) PGAA offers improved sensitivity but has not been previously used at NIST for certification of elements in hydrogenous materials, due to the difficulty in calibration of element sensitivities. Element sensitivities in CNPGAA vary more sharply with both H concentration and geometry than in TNPGAA due to the added complication of neutron energy change within the sample. In order to improve both sensitivity and accuracy, a combination of CNPGAA and TNPGAA is being used. Sulfur/hydrogen mass fraction ratios for fuel oils are measured using the CNPGAA instrument on neutron guide NGD, which has 20 times the sensitivity for sulfur as the VT5 instrument, with mixtures of cysteine/urea/graphite and sodium sulfate/urea/graphite used as standards. The hydrogen mass fraction is then measured by TNPGAA using urea and tris(hydroxymethyl)-aminomethane as standards, and the sulfur mass fraction is then calculated using the two data sets. The detection limit is approximately 15 µg, with routine measurement of sulfur at mass fractions down to 0.1% or below possible with good counting statistics. The combination of instruments has the capability of improving detection limits and accuracy for certification of minor and trace elements in hydrogenous materials.

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FURTHER DEVELOPMENT OF IN-BEAM ACTIVATION ANALYSIS AT MLZ, GARCHING

*Zsolt Révay**, *Petra Kudejová*

Heinz Maier-Leibniz Zentrum, Technische Universität München, 85747 Garching, Germany, *e-mail: zsolt.revay@frm2.tum.de

Keywords: PGAA, gamma-ray and neutron shielding

In-beam activation analysis at MLZ, operated by the Technical University of Munich has been successfully tested and introduced for the analyses of different samples even with masses less than a milligram. The measurement consists of two parts: 1) a usual PGAA measurement which can partly be used as the irradiation for the next phase, 2) NAA with measuring the rest activity of the irradiated sample in the low-background counting chamber next to the PGAA instrument. However, the facility still needs more flexibility to make possible other types of measurements, too.

Recently, the shielding of the in-beam activation analysis facility has been redesigned, and by the time of the conference it will have been installed. The shielding concept has not changed; it is going to serve as a flexible set-up accommodating two detectors for occasional gamma-gamma coincidence measurements with variable sample-to-detector distances and a radiography camera for neutron-radiography-driven PGAA. The sample changer will accommodate 16 samples to enable the measurement of more samples in one batch which proved to be necessary since the high-flux irradiation is routinely available. The new sample holders will be made of thin aluminum frames, and they will be moved into the beam from a carousel placed above sample position.

The combination with radiography and detection with two detectors, also in coincidence mode, will add new features to the existing in-beam activation analysis capabilities. The planned second detector will be a planar or other low-energy detector with a much better energy resolution than the other one used for PGAA to provide the best possible separation of low-energy peaks. The gamma-gamma coincidence option is far from fully utilized in in-beam analyses, further investigations will be performed in this area. Radiography-driven PGAA will be useful for the investigation of complex samples, e.g. archeology objects.

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FAST NEUTRONS FOR PGAA APPLICATIONS

M. Rossbach[1]*, *E. Mauerhofer*[1], *Zs. Revay*[2]

[1]Institute for Energy and Climate Research, IEK-6, Nuclear Waste Management and Reactor Safety, Forschungszentrum Jülich GmbH, Germany, *e-mail: m.rossbach@fz-juelich.de
[2]Technische Universität München Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II), Germany, e-mail: zsolt.revay@frm2.tum.de

Keywords: fission neutrons, prompt gamma activation analysis, PGAA, inelastic neutron scattering

Fast neutrons, in contrast to thermal or cold neutrons, have been used for analytical purposes only exceptionally in the past. A systematic evaluation of their applicability for Prompt Gamma Activation Analysis (PGAA) was published in 1978 by Ahmed et al. [1]. However, with rising interest in fast reactors and increasing application of neutron generators for e.g. industrial process control or homeland security as well as for remote analytical investigations (prospecting, planetary science etc.) inelastic scattering reactions induced by MeV neutrons gain more attention. Being a threshold reaction, (n,n'γ) cross sections generally are weaker and do not scatter as much compared to (n,γ) of thermal reactions. A well collimated beam of relatively high-intensity fast neutrons is required for studying inelastic scattering PGAA. A beam (˜~10^8 cm^{-2} s^{-1}) of pure fission neutrons is provided at the Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II) at the TUM in Garching. A well shielded gamma-ray spectrometer was installed at the beam line SR10 (MedApp) and prompt gamma-ray spectra from pure element foils were taken and evaluated against the Demidov compilation [2–4]. Preliminary result show that energies and intensities of detected gamma rays match well for most elements, new gamma peaks have been recorded in the low and high energy range, neutron absorption in elements with high (n,γ) cross sections (B, Cd, Gd…) is not a problem, and some critical elements such as P can be more sensitively be analysed using fast neutrons compared to cold neutron PGAA.

A summary of experimental results using the fission neutron beam at FRM II for prompt gamma applications will be given together with relevant background information on the set-up of the facility and the spectrum evaluation so far.

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ALTERNATIVE BEAM STOP FOR MINIMIZING GAMMA-RAY AND FAST-NEUTRON BACKGROUND

Danyal Turkoglu[1], Greg Downing[1], Wangchun Chen[2,3], Dağıstan Şahin[2], Jeremy Cook[2]*

[1]Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899 USA, *e-mail: danyal.turkoglu@nist.gov
[2]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899 USA
[3]University of Maryland, College Park, MD 20742 USA

Keywords: prompt gamma ray activation analysis, cold neutrons, analytical chemistry, MCNP, instrument design

The new cold-neutron prompt gamma-ray activation analysis (CNPGAA) facility is operational at the NIST Center for Neutron Research. While awaiting an extension of the instrument space, a temporary design employs lithiated material (primarily ^{6}Li glass and secondarily ^{6}Li-containing polymer sheet) for neutron absorption within the flight tubes and sample chamber, resulting in low gamma-ray background since gamma-ray yields are negligible for ^{6}Li neutron absorption. However, the predominant ^{6}Li(n,α) reaction produces 2727-keV tritons, leading to triton-induced fast-neutron emission by ^{6}Li and ^{7}Li. In this setup, the close proximity of the ^{6}Li-glass beam stop to the high-purity germanium (HPGe) detector – combined with the high thermal-equivalent neutron flux (6.8×10^9 cm^{-2}s^{-1}) – leads to high rates of fast-neutron interaction with the HPGe detector. Consequently, the shielding was designed using Monte Carlo N-Particle (MCNP) simulations to incorporate borated polyethylene in the shielding to mitigate HPGe damage by fast neutrons. Candidate materials for a low gamma-ray background facility are typically limited to those with high ^{6}Li or ^{10}B content. While ^{10}B neutron capture produces 478-keV gamma rays, these are inconsequential with the beam stop sufficiently-far downstream from the sample and/or with judicious placement of lead (Pb) shielding. On the other hand, fast neutrons generated by ^{6}Li reactions are highly penetrating and require hydrogenous-shielding material for moderation before capture; thus, a gamma-ray spectrometer would require both gamma-ray and neutron shielding material for low background. In this work, we have considered alternative configurations for the beam stop such that fast-neutron background is reduced while maintaining low gamma-ray background. Possible configurations employing a borated beam stop downstream from the sample chamber have been modelled in MCNP to minimize background radiation. Most recently, we envisioned a novel beam-stop concept consisting of pressurized ^{3}He gas in a container with a thin-entrance window. The benefits of ^{3}He as a neutron absorber include: 1) high thermal-neutron absorption cross section (5331 barn), 2) high neutron absorption-to-scatter ratio, 3) no capture gamma-ray production, and 4) orders-of-magnitude lower (than ^{6}Li material) fast-neutron generation. The ^{3}He beam stop has the potential to reduce engineering and procurement of shielding while maximizing space for experimental equipment. We have conducted preliminary tests with an existing ^{3}He neutron-polarizer cell (containing 25 atm·cm of ^{3}He), which transmits less than 0.1% of the cold-neutron beam in MCNP simulations. While the fast-neutron interaction with the HPGe detector was reduced, the thick (~4 mm) specialized-composition glass entrance window to the cell increased gamma-ray background. Further design work will be conducted to realize an idealized ^{3}He module to serve as the beam stop.

Radiation chemistry

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RADIATION-INDUCED *IN-SITU* SYNTHESIS OF GOLD NANOSTRUCTURED MATERIALS

Z. I. Ali[1], *Weal H. Eisa*[2], *H. H. Saleh*[1], *G. A. Meligi*[3], *R. El-Sokary*[1]

[1]National Center for Radiation Research and Technology, Atomic Energy Authority P.O. Box 29 Nasr City, Cairo, Egypt
[2]Spectroscopy Department, Physics Division, National Research Center (NRC), Egypt
[3]Faculty of Science, Chemistry Department, Ain Shams University

Keywords: gold/polymer nanocomposites, irradiation, spectroscopic characterization, dye catalytic degradation

Gold nanoparticles were *in situ* synthesized via irradiation process, using PVA, (PVA:Cs), and (PVA:PAM) as host polymeric matrices. The effect of irradiation dose, polymer content, polymer combination $AgNo_3$, chitosan, poly acrylamide, and pH medium were studied. Gold nanoparticles (AuNPs) have spherical nanoparticles shape with different size ranging from 10–35 nm, which were characterized by ultraviolet-visible (UV-VIS) spectroscopy, X-ray spectroscopy and transmission electron microscopy. Fourior transform infrared spectroscopy (FTIR) shows the spectral shift together with reduced intensity of the -OH stretching vibration upon incorporation of the Au nanoparticles indicating the coordination between Au nanoparticles and the OH groups originating from the PVA chains. The synthesized gold nanoparticles have been successfully applied as a catalyst in the degradation of methyl orange and methylene blue by $NaBH_4$.

Acknowlegements
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SYNTHESIS OF CELLULOSE DERIVATIVE/ACRYLIC ACID SUPERABSORBENT HYDROGELS CROSSLINKED BY GAMMA IRRADIATION

Tamás Fekete[1, 2]*, *Judit Borsa*[3], *Erzsébet Takács*[1, 3], *László Wojnárovits*[1]

[1]Radiation Chemistry Department, Centre for Energy Research, Hungarian Academy of Sciences, Budapest, Hungary,
*e-mail: fekete.t@energia.mta.hu
[2]Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, Budapest, Hungary
[3]Óbuda University, Budapest, Hungary

Keywords: cellulose derivative, acrylic acid, hydrogel, crosslinking, gamma irradiation

Superabsorbent hydrogels have a wide array of potential applications due to their unique properties. While most commercially available superabsorbents are synthetic polymer-based, there is an increasing interest in replacing them with renewable materials, e.g. cellulose. Usually water-soluble derivatives are used to avoid the use of special solvents. Several different methods are available for gel formation.

In our work we prepared superabsorbent hydrogels from aqueous solutions of four cellulose derivatives (carboxymethylcellulose, methylcellulose, hydroxyethylcellulose and hydroxypropylcellulose). The samples were crosslinked by gamma-irradiation. We tried to improve the gelation by replacing part of the derivative with acrylic acid. The effect of various synthesis parameters such as the absorbed dose, solute concentration and acrylic acid ratio on the gel properties was determined. The degree of swelling and gel fraction was used to characterize the crosslinked samples. The gel composition was determined by FTIR-ATR spectroscopy, while SEM photographs were used to study the gel morphology. The effect of various parameters such as the pH and ionic strength of the swelling solution on the gel swelling was also investigated.

Gel formation occurred even in pure derivative solutions. Gel properties changed significantly with the absorbed dose and the solute concentration. Moreover, the derivative type and the molecular properties also had a major effect on the gel formation. The gelation required significantly milder synthesis conditions when acrylic acid was added to the solutions. Gels prepared from cellulose derivative/acrylic acid solutions had much higher gel fraction at the expense of lower water uptake. However, both gel properties could be improved compared to pure derivative gels in mild synthesis conditions. The addition acrylic acid proved to be most effective up to 10%. However, very high acrylic acid ratio (over 50%) had a negative impact on the gelation.

The swelling kinetics of gels was in-depth studied. The effect of the solvent properties depended on the derivative type and equilibrium water uptake. Moreover, the presence of acrylic acid also had a significant effect on the sensitivity to these parameters.

Acknowledgement
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THE CROSS-LINKED POLYMERIZATION OF POLYSTYRENE AND DIVINYL BENZENE WITHIN γ-IRRADIATION

Guangying Mu[1]*, Fangchao Wan*[1]*, Huan He*[1]*, Quanyao Zhu*[1]**, Meng Wang*[2]

[1]School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, P. R. China, *e-mail: cglamri@whut.edu.cn
[2]Institute of Fluid Physics, CAEP, Mianyang 621900, P. R. China

Keywords: γ-irradiation, cross-linked polymerization, polystyrene, divinyl benzene

The properties of thermosetting plastics are depended on not only the materials component but also cross-linked process. Regarding to the material system of polystyrene and divinyl benzene, the cross-linked curing process is controlled difficultly owing to the drastic heat release and huge volume shrinkage. In this paper, we report the method for controlling the cross-linked curing process by γ-irradiation. The products perform excellent mechanical strength. The cross-linked structures were characterized by the Fourier transform infrared spectroscopy (FT-IR) and Dynamic mechanical analysis (DMA). The results of FT-IR showed that, products possessed of the main structure of linear polystyrene macromolecules cross-linked by benzene rings provided by DVB. The mechanical properties showed close connection with dose rates and total irradiation doses of γ-ray. As the dose rate increased, the mechanical strength improved firstly and then dropt. The mechanical strength as a function with total dose showed the same change trend to the dose rate. The results of DMA showed that, glass transition temperature (T_g) and storage modulus (E′) of rubbery region both increased firstly and then reduced as the dose rate increased. The T_g and E′ both shifted to high values as the total dose increased. The crosslinking density of products was calculated by the storage modulus at the rubber region due to the theory of rubber elasticity. The calculated results showed that, crosslinking density increased as the dose rate rose from 10 Gy/min to 40 Gy/min, and then reduced from 40 Gy/min to 100 Gy/min. This trend was anastomotic to the changing of mechanical strength. It can be inferred that, the crosslinking of polystyrene and divinyl benzene was controlled by both radiation energy at unit time and the reaction time. Low dose rate can provide the sufficient time for chain segments motion, while the high dose rate is helpful to provide strong radiation energy for chain scission and combination. Moreover, the crosslinking density increased as the total dose increased, which indicated that the enhanced total dose was beneficial to improving the quantity of crosslinking junctions in the reaction system. However, the mechanical strength was not increased all along as the crosslinking density increased, which was due to that the stress was easier concentrated on the shortened chain segments as the crosslinking density increased. In summary, the cross-linked process of polystyrene and divinyl benzene can be controlled by adjusting the dose rate and the total radiation dose of γ-ray. The product synthesised with 40 Gy/min dose and 34 kGy total dose rate performs the optimal mechanical properties.

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•OH INDUCED OXIDATION OF PENICILLINS IN RELATION TO ADVANCED OXIDATION TECHNIQUES

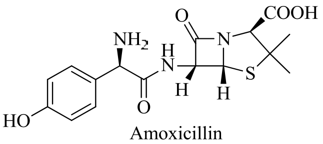
Laszlo Szabo[1, 2]*, *Tünde Toth*[2], *Gergely Racz*[1], *Tekla Engerhardt*[3], *Csilla Mohacsi-Farkas*[3],
Erzsebet Takacs[1], *Laszlo Wojnarovits*[1]

[1]Institute for Energy Security and Environmental Safety, Centre for Energy Research, Hungarian Academy of Sciences,
Konkoly-Thege Miklós út 29–33, H-1121 Budapest, Hungary, *e-mail: szabo.laszlo@energia.mta.hu
[2]Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Szent Gellért tér 4, H-1111 Budapest, Hungary, e-mail: john.taylor@microscopy.com
[3]Department of Microbiology and Biotechnology, Corvinus University of Budapest, H-1118 Budapest, Hungary,
e-mail: john.taylor@microscopy.com

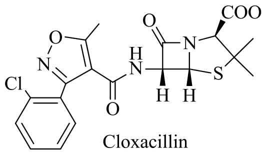
Keywords: antibiotic resistance, advanced oxidation, hydroxyl radical, bacterial susceptibility, penicillin

Antibiotics in general and penicillins in particular are hazardous water pollutants. Their presence in wastewater facilitates the spread of antibiotic resistance among several bacterial species that has a serious impact on human health. To eliminate the residual antimicrobial activity of wastewater implementation of advanced oxidation processes are recommended. These techniques are based on the high oxidation power of •OH that is *in situ* generated during the treatment.

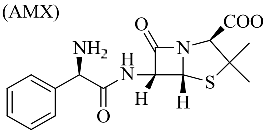
Advanced oxidation processes are promising technologies for removal of antibiotic residues from wastewater in terms of their high efficiency. However, recent studies have reported the remaining antibacterial activity of the products at early-stages of treatment on account of •OH reactions. The present study investigates the effect of such products of model β-lactams (amoxicillin, ampicillin, cloxacillin) on bacteria. Steady-state γ radiolysis techniques were applied to generate •OH in specific quantities.



Amoxicillin
(AMX)



Cloxacillin
(CLX)



Ampicillin
(AMP)

Several bioassays were performed at different •OH exposures to monitor the effects of the products on bacterial strains, including acute and chronic toxicity tests using *Vibrio fisheri,* and bacterial susceptibility tests using Gram positive *(Staphylococcus aureus*, *Bacillus subtilis)* and Gram negative *(Escherichia coli)* species. To find out the underlying reasons of the effects on these organisms final product analysis was performed. The drawback of advanced oxidation for bacteria will be clarified.

Radio- and nuclear analytical methods

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PORTABLE XRF SPECTROMETER USE FOR ARCHAEOMETRICAL STUDIES IN ROMANIA – A REVIEW

Bogdan Constantinescu

National Institute of Nuclear Physics & Engineering, Romania, e-mail: bconst@nipne.ro

Due to its mobility, portable X-Ray Fluorescence (pXRF) spectrometers are probably the most adequate elemental analyzer for archaeologists. pXRF analysis can be performed not only directly in museums or collections but even in archaeological sites, immediately artifacts are discovered. We report on some spectacular cases related to illegal excavations based on metal detectors in the area of Sarmizegetusa, the ancient Dacian capital, situated in an isolated mountain region (Orastie) in the heart of Transylvania. The analyzed artifacts – gold jewelry as one kilo each spiraled armbands, silver adornments as torques and brooches, gold and silver ancient coins as “Koson” and pseudo-Lysimachus staters, Thassos tetradrachms and Roman denarii – were recuperated by Romanian authorities from treasure hunters.

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ED-XRF FOR NON-DESTRUCTIVE ANALYSIS ON HIGH LEVEL NUCLEAR SAMPLE

Eric Esbelin, Valérie Boyer-Deslys, André Béres, Cédric Rivier*

CEA, Nuclear Energy Division, RadioChemistry & Processes Department, Analysis and Materials Metrology Laboratory, BP 17171,
30207 Bagnols-sur-Cèze Cedex, France, *e-mail: eric.esbelin@cea.fr

Keywords: ED-XRF, monochromator, actinides

High activity sample analyses represent a real challenge for the analyst due to the facilities and equipment needed. Radioprotection, waste and analytical effluent issues require very specific design for the equipment and generally lead to decreased performance compared to low activity sample analysis method.

In this context, X-ray fluorescence is particularly interesting as this technique requires no or reduced sample preparation and is non-destructive. In the ATALANTE facility at CEA Marcoule, this technique is widely used for the analysis of actinides in high activity samples.

The concentrations of the main actinides of interest (U, Np, Pu, Am and Cm) are determined by XRF in a hot cell equipped with a device dedicated specifically to actinide analyses via their L-line X-ray between 13 and 15 keV. In order to limit the counting rate of many radioactive emitters (X-ray and gamma emitters) in the analysis solution and the continuous spectrum, a graphite monochromator is placed between the sample and detector.

Commercial or free software packages currently available for processing X-ray spectra are designed for a specific instrument and/or do not take into account the special feature of our system, i.e. the presence of a monochromator. Therefore, we have developed a new X-ray analysis software for this particular system, taking matrix effect corrections into account.

In the phase of qualification of this new algorithm, many samples were analyzed by XRF and those with special matrices were also analyzed by other analytical techniques (alpha spectrometry, gamma spectrometry, ID-TIMS, ICP-AES, ICP-MS) to compare the results.

When the sample matrix can be properly described in software, this NDA device provides results with a good agreement with those of other analytical methods.

The description of this analytical device, a short presentation of theoretical model [1] and various examples on highly irradiated samples with large matrix effects will be presented during this talk.

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MÖSSBAUER STUDY OF BIOFILM FORMATION IN HYPOGENIC SPRING CAVES IN HUNGARY

Zoltán Homonnay[1], Erno Kuzmann[1], Krisztina Kovács, Anita Erős[2], Shiro Kubuki[3],*
Gyula Záray[1], Judit Mádl-Szőnyi[3]

[1]Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary, *e-mail: homonnay@caesar.elte.hu
[2]Institute of Chemistry, Tokyo Metropolitan University, Tokyo, Japan
[3]Department of Physical and Applied Geology, Eötvös Loránd University, Budapest, Hungary

Keywords: biofilms, Fe-bearing phases, hypogenic caves, Mössbauer spectroscopy

Budapest is often called “the capital of caves” because of abundant thermal spas fed by the largest natural underground thermal water system in Europe. The rock that hosts this aquifer system is Triassic carbonate. Interaction of this rock with water, especially with flowing water resulted in the formation of a complicated network of caves. This process is still on today. It is commonly thought that dissolution of calcium carbonate that is responsible for the formation of caves is due to the presence of carbon dioxide transforming insoluable carbonates into soluable hydrocarbonates. However, biofilms in which the metabolism of various microorganisms can produce acidic environment that also dissolves carbonates may present another mechanism to the evolution of cave systems.

The caves in Budapest belong to the group of hypogenic caves, with rather characteristic morphology and peculiar minerals. Recent speleogenetic theories, consider hypogenic karsts and caves as the manifestations of flowing groundwater [1]. Since flowing water can provide a permanent transport of nutrients for microorganisms, a possible biofilm assisted evolution of such caves is attracting more attention. Biofilm bacterial communities are definitely inhabiting the cave walls of the Buda Thermal Karst system.

The aim of the present work was to give qualitative and quantitative analysis of the iron containing phases showing up in the biofilms and in its nearest environment from different caves of Buda Thermal Karst.

^{57}Fe Mössbauer spectra of the biofilm samples were recorded in transmission geometry at 78K and at room temperature using ^{57}Co(Rh) source.

The analysis of the Mössbauer spectra of the biofilms revealed the presence goethite, hematite, ferrihydrite and siderite in various proportions.

The samples originating from different layers from beneath the biofilms contained only goethite. The common feature of this goethite was its superparamagnetism as deduced form low temperature Mössbauer runs. Nevertheless, the spectra that represent different layers the depth of which is assigned to the age of the particular layer showed marked difference in the distribution of internal magnetic field. This is most probably due to the different particle size distribution of goethite.

Possible correlation between the particle size/morphology of goethite, microbial activity and cave formation will be discussed.

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COMPARATION OF MULTI-ANALYTICAL TECHNIQUES FOR DETERMINATION OF RATIO OF ^{235}U/^{238}U ISOTOPES

Bangfa Ni, Caijin Xiao, Yonggang Yao, Long Hua, Xiangchun Jin, Pingsheng Wang*

Department of Nuclear Physics, China Institute of Atomic Energy, P.O. Box 275-50, Beijing, China, *e-mail: bfni@ciae.ac.cn

Keywords: neutron activation analysis, delayed neutron counting, k0-NAA, ^{235}U/^{238}U ratio

Determination of ^{235}U/^{238}U isotope ratio plays an important role in the nuclear fuel cycle, nuclear waste disposal, supervision and identification. In this article, a multi-analytical techniques such as relative NAA, k$_0$-NAA, delayed neutron counting are used to determination the ratios of ^{235}U/^{238}U isotopes through miniature neutron source reactor. For ^{235}U determination, the delayed neutron counting of ^{235}U fission neutron and decaying gamma of fission products of longer half-life have been employed as the indicators such as ^{103}Ru, ^{141}Ce, ^{143}Ce, Mo-99, Nd-147, etc. For the determination of ^{238}U, the products of ^{238}U (n,γ) ^{239}U (23.5 min, 74.7 keV) and ^{239}Np (56.5 h, 277.6 keV) are employed as the indicators. Different indicator combination is used for different quantitative calculation methods of ^{235}U/^{238}U. In this work, natural uranium, enriched uranium and their mixtures are used in the experiments of ^{235}U/^{238}U ratio. The results indicated that delayed neuron counting with the ^{239}U decay combination is suitable for fast determination ^{235}U/^{238}U ratio, and the ^{235}U products and ^{239}NP decay gamma combination is suitable for accurate ^{235}U/^{238}U ratio determination.

Radioanalytical methods of long-lived radionuclides

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METHOD DEVELOPMENT FOR THE DETERMINATION OF Pd-107 IN L/ILW LIQUID WASTES

Árpád Bihari[1], Zoltán Szűcs[1], Géza Horváth[2], Magdolna Mogyorósi[2], Béla Kovács[3], Tamás Pintér[4]*

[1]Hertelendi Laboratory of Environmental Studies, Institute for Nuclear Research, Hungarian Academy of Sciences, Debrecen, Hungary, *e-mail: bihari.arpad@atomki.mta.hu
[2]Isotoptech Zrt, Debrecen, Hungary, e-mail: horvathgeza@isotoptech.hu
[3]Institute of Food Science, Quality Assurance and Microbiology Centre for Agricultural Sciences and Engineering, University of Debrecen, Debrecen, Hungary, e-mail: kovacsb@agr.unideb.hu
[4]Paks Nuclear Power Plant, Paks, Hungary, e-mail: pinter@npp.hu

Keywords: Pd-107, DTM isotopes, separation techniques, ICP-MS

The low- and intermediate-level liquid wastes produced by the Paks Nuclear Power Plant contain many “difficult-to-measure” (DTM) radionuclides. Although their specific activity is low compared to the total (originating mostly from ^{60}Co,

^{134}Cs, ^{137}Cs, etc.), the reliable determination of these radionuclides is an important issue of nuclear waste management. ^{107}Pd ($T_{1/2} \approx 6.5\times10^6$ y) is the fission product of both ^{235}U (0.16%) and ^{239}Pu (3.3%). The separation technique being developed by us is based on the assumption that palladium, as an element of the platinum group, is in solid form in the highly alkaline matrix of the L/ILW liquid wastes to be qualified. Thus, it can be effectively pre-concentrated by filtering and acidic digestion has to be performed on the solid phase only. In case of ICP-MS measurements, ^{107}Pd has to be perfectly separated from Ag, which was achieved by the formation of water-soluble $K_2[PdCl_4]$ complex, while silver was removed as water-insoluble $AgCl_2$ precipitation. Detection limit of 1 Bq/dm^3 was achieved in case of most real L/ILW samples, depending on chemical efficiency.

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TRACE LEVEL DETERMINATION OF Pu ISOTOPES IN AUSTRALIAN SEDIMENTS

Megan Cook

National Research Centre for Environmental Toxicology, University of Queensland, 39 Kessels Road Coopers Plains QLD 4108, Australia, e-mail: megan.cook@uq.net.au

Keywords: plutonium, alpha spectrometry, Australia

Plutonium isotopes ^{239}Pu and ^{240}Pu are present in the global environment as contaminants, largely as a result of atmospheric nuclear weapons testing from the 1950s to the 1980s. Australia was designated as the location for the British nuclear weapons testing program from October 1952 to September 1958. This involved the detonation of 21 atmospheric tests in Australia and the Pacific releasing Pu isotopes into the regional environment and settling in the surface sediments of the State of Queensland. The objectives of this study are to analyse the trace amounts of Pu remaining in Queensland sediments; and investigate the major factors affecting the migration of Pu in this unique environment. Samples were gifted from the National Geochemical Survey of Australia and are accompanied by a large database of field, chemical and physical parameters. Each sample has been analysed for ^{239}Pu and ^{240}Pu using the techniques of fusion, co-precipitation, ion-specific resins and alpha spectrometry. A detection limit of 0.05 mBq/g has been achieved. The analytical results inform a decision-making process to investigate the factors affecting the migration of Pu isotopes in the unique Queensland environment. The investigation will involve a determination of sediment chemical and physical properties in correlation with location-specific variables.

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SEQUENTIAL SEPARATION AND DETERMINATION OF THORIUM AND URANIUM ISOTOPES IN SOIL SAMPLE WITH MICROTHENE-TOPO CHROMATOGRAPHIC COLUMN AND ALPHA-SPECTROMETRY

Guogang Jia

National Institute of Environmental Protection and Research, Via V. Brancati 48, 00144 Roma, Italy, e-mail: guogang.jia@anpa.it

Keywords: ^{238}U, ^{234}U, ^{235}U, ^{232}Th, ^{230}Th, ^{228}Th, soil, TOPO, alpha-spectrometry

A method for sequential separation and determination of uranium and thorium isotopes in environmental soil samples with a Microthene-TOPO (tri-octyl-phosphine oxide) column and alpha-spectrometry was developed. Soil samples in a platinum crucible were fused together with Na_2CO_3 and Na_2O_2 at 600 °C in a Muffle. Uranium and thorium were leached out with HCl and HNO_3, at the same time, some 40% HF was added to eliminate most of the silicates. At end some concentrated $HClO_4$ was added to the leaching solution to eliminate the residual HF through evaporation which could interfere the thorium determination. The mineralised or leaching solution in 2 M HNO_3 was passed through a Microthene-TOPO column to adsorb both uranium and thorium. After washing with 6 M HNO_3, thorium was first eluted with 2 M HCl and the eluent was evaporated to dryness. Thorium was transferred to an electrodeposition cell with a solution of 0.025 M $H_2C_2O_4$+0.15 M HNO_3 and electrodeposited on a stainless steel disc at pH 1.5. After further washing the column with 1 M HCl and 8 M HNO_3, uranium was directly eluted with a 0.025 M ammonium oxalate solution into an electrodeposition cell, and electrodeposited on a stainless steel disc. Both uranium and thorium isotopes on the discs are measured separately by alpha-spectrometry. The lower limits of detection of the method were 0.40 Bq kg^{-1} for ^{238}U and ^{234}U, 0.26 Bq kg^{-1} for ^{235}U, 0.27 Bq kg^{-1} for ^{232}Th, 0.44 Bq kg^{-1} for ^{230}Th and 2.0 Bq kg^{-1} for ^{228}Th if 0.5 g of soil were analyzed. In the technique, ^{232}U and ^{229}Th were used as yield tracers for uranium and thorium respectively. The quality control was carried out by determining the reference material (IAEA-326) supplied by the IAEA and the obtained results showed high accuracy and good precision. The advantage of the technique is that the usually tedious sample pre-treatment and mineralization was performed only once for the analyte of uranium and thorium. The direct uranium and thorium isotopic ratio analyses can provide very useful information in the studies of the contamination source terms, distributions, inventories, biological availability and ecological migration processes of the concerned radionuclides in the field of environmental protection, radiotoxicology, radioecology and geology.

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SELECTIVE ANALYSIS OF ^{210}Pb IN RIVER WATER SAMPLES WITH PLASTIC SCINTILLATION RESINS

Eloi Lluch[1], Javier Barreda[1], Alex Tarancón[1], Héctor Bagán[2], José Francisco García[1]

[1]Department of Analytical Chemistry, University of Barcelona, Martí I Franqués, 1-11, 08028, Barcelona, Spain,
e-mails: alex.tarancon@ub.edu, jfgarcia@ub.edu
[2] Department of Pure and Applied Biochemistry, Lund University, Getingevägen 60, hus II, 22100 SE, Lund, Sweden

Keywords: ^{210}Pb, waste reduction, PSresins, river water

^{210}Pb is a natural radionuclide belonging to the ^{238}U decay chain, which has become a radionuclide of significant importance in environmental sciences and in cultural heritage, since due to its half-life if 22.3 years, it is especially adequate for dating samples with less than 100 years. In such samples, with very low levels of activity, techniques with low detection limits (e.g. liquid scintillation or alpha spectroscopy) are usually used. However due to lack of selectivity of these techniques, the determination of ^{210}Pb requires from separation processes in order to remove the radioactive interferences from the matrix. These separation processes are usually time and reagent consuming and generate large amount of waste. One possibility to reduce time, reagents and avoid waste generation is the use of Plastic Scintillation Resins (PSresins). PSresin are Plastic Scintillation microspheres (PSm) of micrometric diameter coated with a selective extractant, which have the capability not only to retain the radionuclide but also to measure it due to its scintillating properties. Therefore, PSresins placed in a solid phase extraction (SPE) cartridge can be used to perform the separation and measurement in the same support avoiding by this way the steps of elution and sample preparation. In this sense, the aim of this paper is the development of method of analysis of ^{210}Pb based on the use of a PSresins selective to ^{210}Pb, which are packaged on a commercial SPE cartridge.

The work performed has been divided in three parts: the study of the measurement of ^{210}Pb and its daughters with PSm, the optimization of the coating of the PSm with a crown-ether and the conditions of separation using a SPE cartridge and finally the analysis of ^{210}Pb in river water samples. Results obtained show that detection efficiency was close to 50% when measuring only ^{210}Pb, since ^{210}Pb is a low-energy beta emitter, and 150% when equilibrium with 210Bi was reached. With regard to the optimization of the coating, different proportions of PSm and extractant were evaluated being the optimum ones those that have a 1:1/4 proportion. With these PSresins, separation of ^{210}Pb from ^{210}Bi and ^{210}Po can be performed selectively and with a recovery close to 90% in a 2.0M HNO_3 medium. The method developed was applied to the analysis of four different river waters from Catalonia (Spain) spiked with ^{210}Pb with deviations lower than 10%.

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RADON GAS ACTIVITY MEASUREMENTS IN THE FRAME OF AN INTERNATIONAL COMPARISON

Aurelian Luca, Maria Sahagia, Andrei Antohe, Mihail-Razvan Ioan, Leonardo Serbina, Constantin Ivan*

Horia Hulubei National Institute of Physics and Nuclear Engineering, IFIN-HH, Bucharest-Magurele, RO 077125, Romania,
*e-mail: aluca@nipne.ro

Keywords: ^{222}Rn, comparison, activity standardization, gamma-ray spectrometry

The radionuclide ^{222}Rn (radon) and its progeny represent the most important part of the natural radioactivity components contributing to the irradiation of the population. The accurate activity measurement of radon and the assurance of the international traceability and equivalence of the measurements is a problem of major concern for the worldwide radionuclide metrology community. Since 2010, at IFIN-HH, Romania, the Radionuclide Metrology Laboratory (LMR) has established a radon reference system, based on an original primary standardization method which allows the preparation of radon standard sources (gaseous or dissolved in liquid scintillator) and also the calibration of secondary standard installations, [1–3]. In order to validate the standardization method and assure the international metrological traceability and equivalence, LMR participated recently in the international comparison CCRI(II)-K2.Rn-222, organized in the frame of the International Committee for Weights and Measures, CIPM-CCRI(II)-Radionuclide Measurements; the pilot lab was CEA/LNE-LNHB, from Saclay, France. A cylindrical steel vial with ^{222}Rn gas in nitrogen atmosphere at 10^{-2} Pa, with a volume of about 105 cm^3 (sample ID GAZ3), was received at IFIN-HH. The purpose of the comparison was to determine the radon activity in the vial and its uncertainty, at the reference date July 1st, 2015, 12:00 h UTC. The radon was transferred from the GAZ3 vial in a LMR specific glass vial for gas and, from this one, into an ampoule with liquid scintillator solution (LS) for absolute activity measurement using the liquid scintillation counting method. Each step of the experimental procedure was carefully prepared and the quantitative transfer of radon was checked by using relative measurements performed with a high-resolution HPGe gamma-ray spectrometric system and a well-type ionization chamber CENTRONIC IG12/20A. Monte Carlo simulations were also performed to deduce the efficiency transfer factors for the steel vial. Because the comparison result is not yet published, the measured activity value of the vial GAZ3 is presented only relative to the activity of the LS ampoule used for transfer; the uncertainty budget of the radon activity is described. The experience of transferring radon gas between recipients at different pressures, during this comparison, will be useful to setup the operation mode of the future radon chamber which is under construction at IFIN-HH.

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SEQUENTIAL ANALYSES OF ACTINIDES IN SOIL AND SEDIMENT WITH TOTAL SAMPLE DISSOLUTION

Maoyi Luo[1, 2], Xiongxin Dai[1, 2], Yonggang Yang[1, 2], Lijuan Song[1, 2], Steffen Happel[3]*

[1]China Institute for Radiation Protection, Taiyuan, China, Country, *e-mail: luomaoyi414@gmail.com
[2]Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Suzhou, China
[3]TrisKem International, Bruz, France, e-mail: shappel@triskem.ca

Keywords: actinides, soil, sediment, fusion, sequential analyses

There is a growing demand for the determination of actinides in environmental and biological samples for environmental monitoring, radiological protection, and nuclear forensic reasons. Although numerous methods have been established for analyses of actinides in soil and sediment samples, many of them are very tedious and time consuming. Furthermore, some methods have used acid leaching to extract actinides from the soil and sediment matrices and refractory actinide materials may not be completely dissolved, which could lead to underestimation of the analytical results. A total sample dissolution method based on lithium metaborate fusion, followed by sequential column chromatographic separation, has been developed for the simultaneous determination of Pu, Np, Am, Cm isotopes by inductively coupled mass spectrometry (ICPMS) and alpha spectrometry. This method is reliable, easy for batch processing, and provides larger sample analysis throughput. The results of method optimization and validation are reported and discussed.

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RADIOANALYTICAL METHOD FOR THE SEPARATION OF U AND Pu APPLIED IN THE ANALYSIS OF SAFEGUARDS SWIPE SAMPLES IN IAEA ENVIRONMENTAL SAMPLE LABORATORY

Z. Macsik, B. Varga, S. Bulyha, A. Koepf, S. Konegger-Kappel, G. Stadelmann, K. Vogt

Environmental Sample Laboratory, Office of Safeguards Analytical Services, Department of Safeguards,
International Atomic Energy Agency, Austria

Environmental sampling was introduced in 1996 as one of a number of new IAEA safeguards measures that contribute to confirming the absence of undeclared nuclear material or nuclear activities. The collection of environmental samples at or near a nuclear site combined with ultrasensitive analytical techniques such as mass spectrometry, particle analysis and low level radiometric techniques can reveal signatures of past and current activities in locations where nuclear material is handled. Environmental sampling for safeguards is focused on the collection of swipe samples inside enrichment plants, in installations with hot cells and in other types of nuclear facilities, often in connection with complementary access activities under the additional protocol.

The radioanalytical procedure that is applied in the bulk analysis of environmental swipe samples for safeguards purposes is based on ion exchange and extraction chromatography. After the sample digestion and oxidation state adjustment the samples are loaded onto a stacked two-column system of AG MP-1M® anion exchange and UTEVA® extraction chromatographic columns. Uranium and Pu, respectively, are eluted from the separated UTEVA® and AG MP-M1® anion exchange columns followed by further purification of the separated fractions using a single column of AG MP-1M® anion exchange resin. The U and Pu amount and isotope ratios in the purified fractions are determined by single collector and multi collector ICP-MS.

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RAPID METHOD TO DETERMINE ACTINIDES AND SR-89/90 IN LIMESTONE AND MARBLE SAMPLES FOLLOWING A RADIOLOGICAL EMERGENCY

Sherrod Maxwell[1], *Ralf Sudowe*[2]

[1]Savannah River Environmental Laboratory, Aiken, SC, USA, e-mail: sherrod.maxwell@srs.gov
[2]University of Nevada Las Vegas, USA, e-mail: ralf.sudove@unlv.edu

Keywords: rapid method, fusion, actinides, strontium, fusion, limestone, marble

Limestone and marble have been used in many important buildings and monuments in the U.S, including the Pentagon, the Lincoln Memorial, the Washington Monument and the Empire State Building. If a radiological emergency such as a ‘dirty bomb” or nuclear accident occurs that impacts these types of buildings, there will be an urgent need for the rapid analysis of limestone and marble samples. The radiochemical measurements need to be rapid and reliable to support dose mitigation and environmental cleanup. It is very important to have reliable, high quality measurements to maintain the public trust. There is the potential for refractory particles to be present, so rugged sample digestion is needed. Recently, approximately 80% of participating laboratories failed to accurately determine uranium isotopes in soil samples in the U.S Department of Energy Mixed Analyte Performance Evaluation Program (MAPEP) Session 30, due to incomplete dissolution of refractory particles in the samples. Failing laboratories employed acid dissolution methods, including hydrofluoric acid, to recover uranium from the soil matrix. The failures illustrate the importance of rugged sample dissolution methods for the accurate measurement of analytes in the sample matrix. A new method for the determination of actinides and Sr-89/90 in limestone and marble samples has been developed that utilizes a rapid sodium hydroxide fusion to digest the sample. Following rapid pre-concentration steps, actinides and Sr-89/90 are separated using extraction chromatographic resins to collect and purify the radionuclides for assay. Challenges associated with the high calcium content in limestone and marble will be addressed. The advantages of sodium hydroxide fusion versus other fusion techniques will be discussed. This approach has a sample preparation time for limestone and marble samples of <4 hours.

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DETERMINATION OF ^{93}Zr IN NUCLEAR POWER PLANT WASTES: CRITICAL EVALUATION OF MEASUREMENTS

Szabolcs Osváth[1], *Nóra Vajda*[2], *Zsuzsa Molnár*[2], *Éva Kovács-Széles*[3], *Máté Halász*[4]

[1]National Public Health Center, National Research Directorate for Radiobiology and Radiohygiene, Anna utca 5,1221 Budapest, Hungary, e-mail: szabolcs.osvath@osski.hu

[2]RadAnal Ltd., Konkoly-Thege Miklós út 29–33, 1121 Budapest, Hungary, e-mails: vajdanor@gmail.com, molnarzs22@gmail.com

[3]Nuclear Security Department, Hungarian Academy of Science, Centre for Energy Research, Konkoly-Thege Miklós út 29–33, 1121 Budapest, Hungary, e-mail: eva.szeles@energia.mta.hu

[4]Budapest University of Technology and Economics, Institute of Nuclear Techniques, Műegyetem rakpart 9, 1111 Budapest, Hungary, e-mail: halasz.m@gmail.com

Keywords: zirconium-93, ICP-MS, nuclear power plant wastes

In thermal reactors, ^{93}Zr is produced by two processes: from ^{235}U by fission with ca. 6.3% yield and by neutron activation of stable ^{92}Zr which is a major component of the Zr cladding. Due to its long half-life (1.53×10^6 years), after 1000 years it is the second significant contributor (after ^{99}Tc) to the fission products activities of nuclear power plant wastes. As it is a pure β^--emitter ($E_{\beta,\max} = 60$ keV), chemical separation (typically liquid-liquid extraction using TBP or TTA, or ion exchange, or extraction chromatography using TRU, TEVA, UTEVA) is performed before measurement by LSC or ICP-MS.

The radioanalytical method developed and used in our laboratory for separation of ^{93}Zr consists of addition of carrier free ^{95}Zr tracer, sample destruction by repeated evaporations using concentrated acids, co-precipitation of $Fe(OH)_3/ZrO_2$, and separation of Zr on two consecutive UTEVA columns. Focal point of this separation is the complexing of F^--ions before loading the Zr containing sample on UTEVA resin. The zirconium sources were introduced in an ICP-MS.

When measuring ^{93}Zr by ICP-MS, isobaric (^{93}Nb, ^{93m}Nb, and ^{93}Mo) and polyatomic (e.g., ^{92}Zr^{1}H) interferences as well as abundance sensitivity due to ^{92}Zr and ^{94}Zr affect the results. Among these, the isobaric interference due to ^{93}Nb is critical, as niobium is always present in nuclear power plant wastes as the alloying component of zirconium, and ^{93}Nb is its only natural isotope.

In order to confirm the reliability of the analytical results, an activation model was developed to calculate the theoretical ratios of ^{93}Zr/^{93}Nb, ^{93}Zr/^{92}Zr and ^{93}Zr/^{94}Zr. The activation calculations for the fuel rod cladding and the assembly wrapper were performed with the MCNP5 general-purpose Monte Carlo code. A detailed model of a WWER-440 fuel assembly was built, and the reaction rates and fluxes were calculated in infinite lattice geometry with track length estimator tallies using the ENDF/B-VII.0 cross-section library. The specific activity of ^{93}Zr/Zr was calculated analytically by solving the corresponding nuclide chain equation.

The activity of ^{93}Zr in evaporator concentrate samples from a nuclear power plant equipped with WWER reactors was measured. Focusing on the separation of Zr from Nb, decontamination factors of Nb over Zr were determined. Using the activation model mentioned above, measured ^{93}Zr activities were critically evaluated.

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RADIOCHEMICAL SEPARATION OF LANTHANIDES AND AMERICIUM BY EXTRACTION CHROMATOGRAPY USING DGA RESIN

Dénes Párkányi[1], *László Szentmiklósi*[1], *Nóra Vajda*[2]

[1]Nuclear Analysis and Radiography Department, Centre for Energy Research, Hungarian Academy of Sciences,
e-mails: parkanyi.denes@energia.mta.hu, szentmiklosi.laszlo@energia.mta.hu
[2]Radanal Ltd., e-mail: vajdanor@gmail.com

Keywords: difficult-to-measure nuclides (DMN), lanthanides, americium, DGA resin

In the nuclear fuel cycle, several long-lived lanthanide and trivalent actinide isotopes such as ^{147}Pm (2,6 y), ^{151}Sm (90 y), ^{152}Eu (13 y), ^{154}Eu (9 y), ^{155}Eu (5 y) and ^{241}Am (432 y), ^{243}Cm (29 y), ^{244}Cm (18 y), respectively, are produced by fission or transmutation of the uranium fuel. These nuclides are usually generated at low quantities and/or they are pure alpha/beta emitters, therefore they are regarded as difficult-to-measure nuclides (DMN).

In order to develop efficient methods for the analysis of DMNs, an extraction chromatographic separation procedure was developed using N,N,N',N' tetraoctyl-diglycolamide resin (DGA is the registered trade mark of Triskem International) that is known to have extremely high capacity factors (k'>10^4) for trivalent lanthanides and actinides in concentrated mineral acid solutions.

Short-lived lanthanide isotopes with easy to measure gamma radiation, i.e. La-140, Ce-141, Nd-147, Pm-149, Sm-145, Sm-153, Eu-152, Eu-155, Gd-153, Tb-160 and Ho-166 were prepared by neutron activation of the stable lanthanide elements at the Budapest Research Reactor. Samples containing a mixture of lanthanides and Am-241 tracer were loaded on the DGA column from 3M HNO_3 followed by their sequential elution using various eluents (0.01–0.05M HNO_3 and 0.5–1.5 M HCl). Elution conditions (type and volume of eluent, flow rate, temperature) were optimized.

According to the results of the test experiments, chromatograms of several lanthanides and Am were obtained where “groups” of lanthanides such as La-Ce-Pr, Nd-Am, Pm, Sm, Eu-Gd, Tb-Dy-Ho, Er-Tm-Yb-Lu were well separated. Pm, Sm as well Am were separated from all lanthanides (the latter with the exception of Nd), the repeatability of the separations was confirmed. The separation procedures seem to be adequate for analytical applications. Separated lanthanide and actinide nuclides are to be detected by ICP-MS, alpha, beta and gamma spectrometry and the combination of thereof. Application examples will be presented.

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CHALLENGES AND STRATEGIES IN PLUTONIUM DETERMINATION FOR LARGE SIZE ENVIRONMENTAL SAMPLES

Jixin Qiao

Center for Nuclear Technology, Technical University of Denmark (DTU Nutech), DK-4000 Roskilde, Denmark

Determination of plutonium in environmental samples (e.g., soil, sediment, seaweed, seawater, etc.) is important for environmental monitoring, radiological risk assessment and radioecology studies. In most cases, the concentrations of plutonium isotopes are at low or ultralow levels ($<10^{-12}$ g/g or 10^{-12} g/L). Consequently, large sample size (>10 soil/sediment, >20 g seaweed, >100 L seawater) is typically needed to cope with sensitivity demands of either radiometric or mass spectrometric techniques. However, the adverse effects of massive matrix components and interfering radionuclides impose great challenges to achieve reliable and accurate analytical results.

During the past few years, several flow injection (FI)/sequential injection (SI) based analytical methods have been developed for plutonium environmental assay in Center for Nuclear Technology, Technical University of Denmark (DTU Nutech). Recently, more efforts are continuously devoted to improve the simplicity and applicability of these methods, especially for large size environmental samples. This paper gives an overview of analytical protocols developed for plutonium determination in DTU Nutech, and emphasizes challenges and strategies during the methodology development process. Moreover, recent improvement achieved by applying effective sample pre-treatment approaches and sophisticated automation techniques is also presented.

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ENVIRONMENTAL ^{129}I LEVEL, DISTRIBUTION AND SOURCE IN QINGHAI REGION OF CHINA

Dongxia Zhang[1], *Xiaolin Hou*[1, 2]

[1]SKLLQG, Shaanxi Key Laboratory of AMS Technology and Application, Xi´an AMS Center, Institute of Earth Environment, CAS, Xi'an 710061, China
[2]Center for Nuclear Technologies, Technical University of Denmark, Risø Campus, Roskilde 4000, Denmark

Keywords: long-lived radionuclide, AMS, nuclear environmental safety, soil, iodine

In this work, we collected surface soil samples (0–5 cm) in Qinghai region, and determined ^{127}I and ^{129}I in these samples using an effective chemical separation combined with a high sensitivity AMS measurement, in order to investigate ^{129}I level and distribution in Qinghai region, explore its sources in this region. The data is also useful for establishment ^{129}I environmental background in Qinghai region, and investigation on the impact of early human nuclear activities on the environment in the region.

The collected soil samples was dried, ground and sieve through a 200 mesh sieve. About 5 g ground soil samples was taken to a quartz boat, 1.0 kBq ^{125}I tracer was spiked for measurement of chemical yield. The boat with sample as put to a quartz working tube in a tube furnace for separation of iodine using combustion. The temperature of the furnace was gradually increased to 800 °C and kept for 1.5 hours under oxygen gas flow. The off gas from the working tube passed through a bubbler filled with 0.5 M NaOH–0.02 M $NaHSO_3$, liberated iodine from the sample was trapped in the solution in the bubbler. The entire combustion took about 3 hours. 3 ml of trap solution was taken to a plastic tube and measured using a gamma detector for ^{125}I, which was compared with the ^{125}I standard (the same amount of ^{125}I spike solution and diluted to 3 ml using the same trapping solution) for measurement of chemical yield of iodine during combustion. Chemical yield of 97–102% with average of 99% were obtained for soil samples. After measurement of ^{125}I, the solution is combined to remained trap solution. 1.0 ml trapped solution was taken and diluted 10 times using deionized water for measurement of ^{127}I using ICP-MS. To the remained solution, $NaHSO_3$ and 0.5 ml of ^{127}I carrier solution with a concentration of 2.0 mg/ml (prepared from a ^{129}I free iodine provided by Woodward company, USA, with a measured ^{129}I/^{127}I ratio less than 5×10^{-14}) were added, and pH was adjusted to 1–2 using HNO_3. After mixed, 1 ml of 1.0 mol/L $AgNO_3$ was added for precipitate iodine as AgI, which was separated by centrifuge. After dried, AgI precipitated was ground and mixed with niobium powder in a mass ratio of 1:5, which was then pressed in copper target holder. ^{129}I/^{127}I atomic ratio was measured using 3 MV accelerator mass spectrometry in Xi'an AMS Center. I^{5+} ion was selected for ^{129}I measurement. Procedure blanks were prepared using the same procedure as samples, the measured ^{129}I/^{127}I in the blanks are $(1–2)\times10^{-13}$, which is 2–3 orders of magnitude lower than that in samples.

More than 100 surface soil samples was analyzed, the results show that the concentrations of ^{127}I in Qinghai area are 0.75~16.8 µg/g (dry mass), average 4.72 µg/g, and agree with the literature values (0.5~40 µg/g); ^{129}I concentration are $(0.14\sim32.4)\times10^7$atmos/g, with an average of 6.61×10^7 atmos/g. An abnormally high value of 3.24×10^8 atmos/g was observed in the northeast of Qinghai, concentration of this might be associated with early nuclear activities in this regional; ^{129}I/^{127}I atomic ratios in all samples range $(0.9\sim102)\times10^{-10}$, with an average of 3.43×10^{-9}, which is higher than pre-nuclear level of 10^{-12} by 1–4 orders of magnitude, indicating that the surface environment in Qinghai region was significantly influenced by human activities.

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Pu CONTAMINATION IN THE SOILS OF GANSU PROVINCE IN NORTHWESTERN CHINA

Wenting Bu[1, 2, 3], *Qiuju Guo*[2], *Jian Zheng*[3], *Shigeo Uchida*[3]

[1]Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, Sichuan, 621900, China
[2]State Key Laboratory of Nuclear Physics and Technology, School of Physics, Peking University, Beijing, 100871, China, e-mail: qjguo@pku.edu.cn
[3]Research Center for Radiation Protection, National Institute of Radiological Sciences, Anagawa 4-9-1,
Inage, Chiba 263-8555, Japan, e-mail: jzheng@nirs.go.jp

Keywords: surface soil, $^{239+240}$Pu activity, ^{240}Pu/^{239}Pu atom ratio, Chinese nuclear test

The atmospheric nuclear test caused large amounts of Pu isotopes released into the environment. The contamination of Pu isotopes could be local, regional and global depending on the power of the explosion. From 1964 to 1980, 22 atmospheric nuclear tests took place in Chinese nuclear test site (Lop Nor). Investigating Pu contamination in the downwind areas from the nuclear test sites is important for radioactive assessment and radioactive source identification. Compared with other nuclear test sites, information about Pu isotopes from Chinese nuclear test site is rare.

In this work, Pu isotopes in soil samples from the Jiuquan region of Gansu province in northwestern China have been determined. The Jiuquan region is located in the downwind area from the Chinese nuclear test site. The $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in surface soils ranged from 0.025 to 0.892 mBq/g and from 0.080 to 0.193, respectively. The Pu activities and Pu inventories from different sampling sites varied significantly, suggesting that Pu contamination in this region was heterogeneous. The low ^{240}Pu/^{239}Pu atom ratio (<0.1), lower than that of global fallout observed in the soils revealed that Pu isotopes from this place were a combination of global fallout and regional fallout from the Chinese nuclear tests.

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FIRST SURVEY OF RADIOACTIVITY LEVELS IN ANGOLAN ADOBE DETERMINED BY GAMMA SPECTROMETRY

Judith Pena Dembo[1]*, *Péter Völgyesi*[1, 2], *Zsuzsanna Szabó*[3], *Zoltán Kis*[4], *Csaba Szabo*[1]

[1]Lithosphere Fluid Research Lab, Department of Petrology and Geochemistry, Institute of Geography and Earth Sciences, Eötvös University, Budapest, Hungary, *e-mail: judithpenadembo11@gmail.com
[2]Nuclear Security Department, Centre for Energy Research, Hungarian Academy of Sciences, Budapest, Hungary
[3]E-mail: zsszabo86@gmail.com
[4]Nuclear Analysis and Radiography Department, Centre for Energy Research, Hungarian Academy of Sciences, Budapest, Hungary

Keywords: environmental radioactivity, activity concentration, geological discrepancy, building material

Measurement of the environmental radioactivity in Angola is a novelty in spite of noticing a growing interest from all-over the world. This study therefore aims to investigate systematically the radioactivity of adobe, a widely used building material in Angola.

Sixty samples have been collected from three remote areas of the country with different geological background and climate. These were Cabinda in the North, Huambo in the central part and Menongue in the South. Activity concentrations for Ra-226 (assumed in secular equilibrium with U-238) and Th-232 as natural decay chain members and for K-40 have been determined by gamma spectrometry analysis. For this purpose an HPGe-detector-based acquisition system installed permanently in a low background chamber [1] was used.

The activity concentration results obtained for the separate areas are as follows (mean and sample range in Bq kg^{-1}): in *Cabinda* 32 (26-45) for Ra-226, 40 (36-49) for Th-232 and 50 (36-83) for K-40; in *Huambo* 69 (53-78) for Ra-226, 67 (39-84) for Th-232 and 80 (56-96) for K-40; in *Menongue* 25 (15-42) for Ra-226, 27 (21-32) for Th-232 and 52 (25-73) for K-40. According to the UNSCEAR 2000 Report [2] the average values in soil for radionuclides U-238, Th-232 and K-40 are 35, 30 and 400 Bq kg^{-1}, respectively. A comparison shows that the activity concentration of Ra-226 in Huambo is higher than the average; similarly, the value for Th-232 is also higher in both Huambo and Cabinda; whereas the value for K-40 is lower in all areas.

The importance of this survey comes from the fact that more than 30% of the Angolan population use adobe as building material. Therefore, results may have a social interest beside its scientific aspects and they will serve as reference for further studies.

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THE FATE OF PO-210 IN THE URBAN AIR

Magdalena Długosz-Lisiecka

Technical University of Lodz, Institute of Applied Radiation Chemistry, Wróblewskiego 15, 90-924 Łódź, Poland, e-mail: mdlugosz@mitr.p.lodz.pl

Keywords: polonium radiotoxicity, radiological hazard, aerosol residence time

The natural and artificial origins of the ^{210}Po radionuclide and its activity fluctuations in the air have been discussed. The main source of ^{210}Po in the lithosphere, atmosphere and oceans is the emanation and transport of one of the uranium daughters – gaseous radon from surface soil or sediments. Several research group hypothesis additional, anthropogenic origins as dominant ^{210}Po excess origins. The artificial sources of the ^{210}Po in the air are industrial processes, which are: fossil fuels combustion (gas, oil, coal and biomass), forest and bush fires, phosphoric acid production, sintering of ores, iron and steel industry and use of agricultural fertilizers. Technological activity and high temperature processes generate radioactive particles or flue gases and can effectively generate huge amount of fine and ultrafine particles with high disproportion between Po and Pb. Especially significant difference can be seen in activity distribution of fine and ultrafine particles. For ^{210}Po typical enhancement factor ranged from 30 to 200 and can reach over 5000 Bq/kg, while in coal samples occur only 20–30 Bq/kg. In technological temperature, higher than 1000 °C it is not possible to filter ^{210}Po out with regular ash recovery system. There is tendency to escape nuclides on the surface of fine and ultrafine particles, leading to an increased actively concentration with decreasing particle diameter.

The excess of ^{210}Po activity was found in lower tropospheric layer in central Poland. The annual activity release from coal power plant per GWe can occur even extreme level of 1 GBq. In local power plants the level of ^{210}Po release is definitely lower and equal several MBq Depend on type coal , technological temperature of burning average about 50% of ^{210}Po can be released in gaseous or ultrafine and fine particles with $d<1.5$ μm.

The difference between residence times calculation methods based on ^{210}Bi/^{210}Pb and ^{210}Po/^{210}Pb activity ratio should be attributed to the additional sources of ^{210}Po input to the atmosphere. Even up to 97% of the total ^{210}Po activity can be attributed to the additional its input.

The average values of ^{210}Po excess in air analyzed in Lodz city (Poland) show clear seasonal trend but low correlation with ^{210}Pb activity levels. Estimated seasonal change of the ^{210}Po excess is statistically significant. In the summer period the ^{210}Po/^{210}Pb activity ratio is much lower than in the winter period. The calculated additional ^{210}Po activity ranged from 8.8 to 42.46 μBq/m^3. The specific activity of ^{210}Po in Bq/g of the total suspended particles varies from 0.608 Bq/g for the winter to 0.257 Bq/g in the summer. These values significant exceed the measured specific activities of this radionuclide in soil 0.026 Bq/g. It may confirmed that observed excess of ^{210}Po in the winter period is coming from the source characteristic for this season like energetic coal or oil combustion typically used in central Poland region.

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COMBINED METHOD FOR THE FAST DETERMINATION OF PURE BETA EMITTING RADIOISOTOPES IN FOOD SAMPLES

Eva Kabai, Birgit Savkin, Isabell Mehlsam, Angela Poppitz-Spuhler*

Department SW Radiation Protection and the Environment, Federal Office for Radiation Protection, Ingolstädter Landstr. 1,
85764 Oberschleißheim, Germany, *e-mail: ekabai@bfs.de

Keywords: strontium, technetium, extraction chromatography, Sr-resin, TEVA-resin, LSC, food, milk

Fast radioanalytical methods are essential for a rapid response of decision makers. Beside the conventional methods, rapid methods for single isotopes determination are getting more and more widespread especially in view of the application in emergency situation. The combination of rapid single isotope specific methods with each other has the benefit to be even faster than analysing aliquots of the sample for each isotope individually.

In this work such a combined method was developed for the simultaneous determination of pure beta emitting radionuclides Sr-89/Sr-90 and Tc-99 in food samples. The method was tested on different sample matrices like milk and dairy products.

The combined method is a sequential method based on the precipitation of milk fat and proteins with trichloroacetic acid, followed by an anion exchange step for the separation of strontium from technetium. After this separation, the purification steps for strontium and technetium are done using Sr-resin and TEVA-resin, respectively. The typical chemical yields for the combined method are around 60% for both radionuclides. The whole determination takes around two working days. Therefore, it can be considered a fast combined method. The obtained detection limits for the combined method are as good as for the single isotope methods. Only extreme activity ratios could worsen the capability of the method.

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REMOVAL OF URANIUM(VI) AND THORIUM(IV) BY INSOLUBILIZED HUMIC ACID FROM AZRAQ SOIL IN JORDAN

Fawwaz Khalili, Alia'a Khalifa, Ghadeer Al-Banna*

Department of Chemistry, The University of Jordan, Amman – Jordan 11942, *e-mail: fkhalili@ju.edu.jo

Keywords: humic acid, insolubilized, adsorption, kinetic, thermodynamic, thorium(IV), uranium(VI)

Humic acid from Azraq soil in Jordan has been extracted and insolubilized. The sodium form of Insolubilized Azraq Humic Acid (INaAZHA) was characterized by Fourier transform infrared spectroscopy, elemental analysis, thermal gravimetric analysis, X-ray diffraction, scanning electron microscopy and differential scanning calorimetry. Adsorption of Th(IV) and U(VI) by INaAZHA was studied using batch technique at different temperatures (25.0, 35.0 and 45.0 °C) and at different pH values (1.00, 2.00 and 3.00); it was found that the uptake have increased with increasing pH and reached a maximum at pH = 3. The kinetic studies were done, and showed that the uptake increases with time until it reaches equilibrium in l5 hrs. These experiments fitted pseudo second-order kinetic model. A linearized form of the Langmuir, Freundlich and Dubinin–Radushkevich (D-R) adsorption isotherms were used to analyze the experimental equilibrium concentration data of Th(IV) and U(VI). The order for increasing adsorption capacity was as follows: Th(IV) > U(VI). The energy of adsorption process was calculated from the D-R and it was found that the adsorption is physisorption. Thermodynamic functions, $\Delta G°$, $\Delta H°$ and $\Delta S°$ were determined for each metal ion; the values of these functions for Th(IV) were found as: – 4.97 kJ/mol, 21.27 kJ/mol and 88.25 J/mol.K, and for U(VI) were found as: –5.05 kJ/mol, 5.47 kJ/mol, and 35.30 kJ/mol, respectively. The negative value of $\Delta G°$ indicates the degree of favorability of the adsorption process, while $\Delta H°$ values indicated that this process is endothermic. On the other hand, the process has positive entropy which means that the adsorption process increases the disorder of the system. Column experiment was used effectively for the determination of metal ion loading capacity. The uptake percent with the metal ions in column technique fall in the same order; Th(IV) > U(VI), where the uptake capacities in this technique of Th(IV) and U(VI) ions are 10.7 and 10.1 mg metal ion/g INaAZHA, respectively. Desorption studies were done using column experiments where (0.1 M), (0.5 M) and (1.0 M) HNO3 were used for elution and regeneration of the INaAZHA. The best percent recovery for Th(IV) and U(VI) ions were obtained when 1.0 M HNO3 was used.

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DECONTAMINATION OF RADIOACTIVE CONCRETE

Seung-Soo Kim, Gye-Nam Kim, Gyu-Seong Han, Jong-Won Choi*

Korea Atomic Energy Research Institute, Daejeon, Korea, *e-mail: nsskim@kaeri.re.kr

A great amount of uranium-contaminated (U-contaminated) concrete waste has been generated from the uranium conversion plant at KAERI. Thus its volume reduction is required for a reduction of the disposal amount. A practical decontamination process for U-contaminated concrete has been developed in this study. U-contaminated concrete pieces have to be decontaminated to below 1.0 Bq/g for the self-disposal of natural uranium.

The concrete waste is divided into three groups: one is a mortar block with epoxy generated from the floor surface of a laboratory whose radioactivity is high, another is a concrete block from the floor except the surface, having a lower radioactivity, and the last is a brick from the wall of a laboratory. The color of the wall brick surface contaminated with a high concentration of uranium was changed to yellow or brown. The colored surface was removed by a chisel in a glove box, and the radioactivity of the brick was then measured. The removal and measurement works were iterated until the radioactivity of the remaining block reached less than 1 Bq/g.

The mortar blocks coated with epoxy were directly burned for 15 minutes to remove the epoxy and binder. After burning, the removal of the surface and the measurement of the radioactivity were performed using the same decontamination method as for the bricks. Concrete blocks without epoxy were crushed to less than 30 mm in size, and the concrete pieces then sifted with a 1 mm pore-sized sieve. Concrete pieces larger than 1 mm were consecutively washed using a ball mill in order of clear recycle solution (around pH 1.0) and 1.0 M of fresh nitric acid. When the washed concrete pieces were washed with a small amount of tap water, the radioactivity of the concrete particles above 1 mm in size generally reached below 1.0 Bq/g. Concrete powder smaller than 1 mm and the murky solutions produced from the ball mill were put together into a rotary washing machine. The powder was washed in a pH 0.5–1.0 nitric acid solution for 6 hours. After removal of the supernatant, the remaining solution was centrifuged. The radioactivity of the dried solid was measured. When it was higher than 1 Bq/g, we used electrokinetic equipment for further continuous washing. The concrete powder reached 1 Bq/g within 10 days by the electokinetic equipment.

The supernatant produced from the washing process was adjusted to near pH 9 by adding CaO in order to precipitate the uranium. The precipitate was filtered using a filter pressure with a 25 μm pore size, and will be disposed of at a radioactive waste repository. To recycle this filtrate, sulfuric acid was added into the filtrate to form a $CaSO_4$ precipitate.

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RADIOCESIUM BEHAVIOR IN PONDS OF THE CLOSE PROXIMITY TO THE FUKUSHIMA DAI-ICHI NUCLEAR POWER PLANT

Alexei Konoplev, Yoshifumi Wakiyama, Kenji Nanba, Toshihiro Wada, Tsugiko Takase,*
Valentin Golosov, Mark Zheleznyak

Institute of Environmental Radioactivity, Fukushima University, Kanayagawa 1, Fukushima city, Fukushima Prefecture, 960-1296 Japan,
*e-mail: alexeikonoplev@gmail.com

Keywords: radiocesium, distribution, Fukushima, ponds, catchments

A major earthquake and devastating tsunami on 11 March 2011 caused a nuclear accident at the Fukushima Dai-ichi Nuclear Power Plant (FDNPP). As a result of the FDNPP accident, ^{134}Cs and ^{137}Cs deposited on the underlying surface in North-Western direction from the FDNPP. Mobility of radiocesium (r-Cs) of accidental origin in the aquatic environment is governed by the ratio of r-Cs chemical forms in fallout and site-specific environmental characteristics determining the rates of leaching, fixation/remobilization, as well as sorption-desorption of the mobile fraction. R-Cs in the environment is strongly bound to soil and sediment particles. This is due to high selective reversible sorption by micaceous clay minerals (illite, vermiculite etc.) and fixation.

The objective of this work is to study current dynamics of r-Cs in ponds/reservoirs within exclusion zone in the proximity to the FDNPP and to characterize r-Cs exchange between sediments and water column.

Field observations were carried out on four ponds (Inkyozaka, Suzuuchi, Funasawa and Kashiramori) and their catchments in the close proximity to the FDNPP – Okuma town. Water samples of 2 L volume were collected in the ponds three times during 2015 in duplicate and filtered in the laboratory using membrane filters of 0.45 μm pores. Filters and filtrates were assayed separately for ^{134}Cs and ^{137}Cs. Dissolved K^+, NH_4^+, Na^+, Ca^{2+}, Mg^{2+} in water samples were measured by ion chromatography, and stable $^{133}Cs^+$ was measured by ICP-MS. Soil samples were collected to a depth of 30 cm using a liner corer. The ^{137}Cs and ^{134}Cs activity concentrations were measured by gamma spectrometry using a high-purity germanium detector (HPGe) CANBERRA GC3018. The measurement time was set to ensure a statistical error not more than 5%.

Total r-Cs activity concentration in water of the ponds was found to be relatively high as compared with the rivers or large lakes in the area and was as high as 68 Bq/L for the most contaminated pond Suzuuchi. Activity concentration of particulate r-Cs in pond's water was found to be higher than that in the top soil of the catchment surrounding the pond and bottom sediments. *Kd* values in the ponds of Okuma town appeared relatively high (mostly in range 100–400 L/g) and comparable with *Kd*s observed for rivers and large lakes in Fukushima area. *Kd* values in Inkyozaka, Suzuuchi and Funasawa were quite stable during observation period, especially for Suzuuchi. At the same time, in Kashiramori *Kd* varies within an order of magnitude. The effective dispersion coefficients in the Fukushima soils were found to be relatively high (in range 2–10 cm^2/year) as compared to Chernobyl data. It is shown roles of K^+, NH_4^+ and $^{133}Cs^+$ in r-Cs remobilization are comparable, but their relative contributions in forming dissolved r-Cs concentration in water can vary with time.

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INTEGRATED CATCHMENT MODEL FOR PREDICTION OF RADIONUCLIDE RIVERINE TRANSPORT

Yan Lin[1], Raoul-Marie Couture[1], Daniel Butterfield[2], Martyn Futter[3], Luca Nizzetto[1], Knut Erik Tollefsen[1], Ole Christian Lind[4], Brit Salbu[4], Thorjorn Larssen[1]*

[1]Norwegian Institute for Water Research, 0349, Oslo, Norway, *e-mail: yan.lin@niva.no
[2]Enmosys, Glen Ellyn, IL 60138, USA, e-mail: dan.butterfield@gmail.com
[3]Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Uppsala, Sweden, e-mail: martyn.futter@slu.se
[4]Universitetstunet 3, 1430 Ås, Norway, e-mail: ole-christian.lind@nmbu.no

Keywords: riverine transport, virtual scenario, catchment model

After the Fukushima nuclear accident happened in 2011, the consequences following an accidental pulse contamination event raised once more much attention globally. Fast evaluation of the impacts following one such accident is urgently needed. A new synthesis model (INCA-RAD) was developed to integrate several feature of previous INCA models and adding the capability of simulating and predicting the transport and retention of radionuclides in river basins daily time step. INCA-RAD is applied at Vikedal catchment in Western Norway which is identified as a site to be affected by plume following a virtual UK nuclear accident. Test period is 5 years from 19.10.2008 to 14.01.2014 which is the worst case scenario identified by meteorological and deposition modelers. In the five year period, the bulk water column concentration of Cs-137 is between the 10^4–10^2 bq/m^3 order of magnitude. Sediment is gathering at bed of Vikedal Lake due to slowing down of water velocity. The radionuclides in sediment at the Lake reach therefore increases though the radionuclide in water column is decreasing.

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RADIOCHEMICAL ANALYSIS OF SAMPLE MATRICES ENCOUNTERED DURING THE EVALUATION OF POTENTIALLY CONTAMINATED SITES IN AUSTRIA

Eva Maria Lindner, Claudia Landstetter, Michael Zapletal, Christian Katzlberger*

Department of Radiation Protection and Radiochemistry, Austrian Agency for Health and Food Safety, Spargelfeldstr. 191, 1220 Wien, Austria,
*e-mail: eva-maria.lindner@ages.at

Keywords: soil samples, sequential digestion, radiochemical analysis, Ra-226, Ra-228, Pb-210, Po-210, U-238

Upon the discovery of radioactivity at the end of the 19th century several factories and institutes in Austria started to produce and process radioactive materials due to Austria's proximity and access to the Joachimsthal uranium mines. In a study carried out by the Austrian Agency for Health and Food Safety the premises of a former chemical factory were investigated. According to historical research the company, which was founded around 1890, used to process pitch blende residues (uranium ore residue) for the production of radium as well as monazite sands for the production of thorium and subsequent manufacturing of incandescent gas mantles. The site of the factory was situated next to a river and nowadays serves as a recreational area. The radiological survey found elevated levels of radioactivity and upon detailed examination of the soil samples, elevated activity concentrations of thorium, uranium and cerium.

Using the results and experience gained from the above mentioned investigation we attempted to develop a standardised screening procedure to aid the evaluation of potentially contaminated sites in the future. With the help of a standardised screening strategy on-site measurements are carried out and a sampling strategy is developed. Samples are then analysed through a combination of gamma-spectroscopy and radiochemical methods for the determination of natural radio-nuclides such as Ra-226, Ra-228, Pb-210, Po-210 and uranium. Methods were evaluated for the different sample matrices expected to be encountered at relevant locations, such as mud, soil, sediments and water (clear water as well as water containing colloids and suspended matter). On the basis of all the obtained results the prediction of an exposure scenario is possible.

Laboratory tests were carried out on ashed and non-ashed soil samples applying microwave digestion as well as wet digestion. Sequential acid digestion was performed using concentrated HNO3+H2O2, HCl and aqua regia followed by radio-chemical separation and analysis through liquid scintillation counting and ICP-MS. Satisfying chemical yields were achieved for the fractions digested with HNO3+H2O2 and aqua regia. More tests need to be performed to optimise the chemical yield of radium after digestion with HCl. A comparison of preliminary results with a long-term gamma-spectroscopic measurement showed a good correlation between the activity concentrations of different natural radionuclides.

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RADIOLOGICAL AND CHEMICAL TOXICITY RISKS OF URANIUM IN GROUNDWATER BASED-DRINKING AT GOSA AND LUGBE AREA OF ABUJA, NORTH CENTRAL NIGERIA

Omeje Maxwell[1, 2], Husin Wagiran[2], Aizebeokhai Philips Ahzegbobor[1], E. S. Joel[1], Olusegun Adewoyin[1], Kayode Olusola[1]*

[1]Department of Physics, College of Science and Technology, Covenant University, P.M.B. Ota, Ogun State, Nigeria,
e-mail: Maxwell.omeje@covenantuniversity.edu.ng
[2]Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310, Johor, Malayisa, e-mail: husin@utm.my

Keywords: Abuja, radionuclides, toxicity risk, radiological risk

Inadequate public water supply by the Water Board in Abuja has forced the inhabitants to source for groundwater as the only alternative without radio-toxicity risk concern. The radiological cancer and Chemical toxicity risks of uranium in Gosa and Lugbe groundwater based-drinking water samples were measured and compared with Water Board and hand-dug well water samples from the same area using inductively coupled plasma mass spectrometry (ICP-MS).The highest radiological risks for cancer mortality and morbidity were found to be low, with highest values of 1.03×10^7 and 1.57×10^7 obtained from Lugbe borehole. The chemical toxicity risk of ^{238}U in drinking water over a life time consumption has a mean value of 4.0×10^3 μg kg^{-1} day^{-1} with highest value of 6.0×10^{-3} μg kg^{-1} day^{-1} obtained from

Lugbe boreholes. Significantly, this study inferred that the ^{238}U concentrations reported in groundwater based-drinking originate from granitic strata induced by denudation and tectonic events in the area. The radiological and chemical toxicity risks values were far below the standard recommended by International Committee on Radiological Protection, World Health Organization and United State Environmental Protection Agency. Results of these measurements could be of importance in radio-epidemiological assessment of uranium induced cancer in the population of the inhabitants of Abuja.

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CUCURBITURIL MACROCYCLES FOR THE COMPLEXATION OF RADIOCESIUM IN THE CONTAMINATED ENVIRONMENT

Fabio Pichierri

Department of Applied Chemistry, Tohoku University, Sendai, Japan, e-mail: fabio@che.tohoku.ac.jp

Keywords: Cs-137, ion sensing, cucurbituril, computational chemistry, molecular design

Computational chemistry methods in combination to crystallographic databases are powerful tools for studying the complexation of radionuclides by artificial macrocycles. In this regard, we have recently investigated the interaction of hydrated cesium ions with cucurbituril, CB[6], a pumpkin-shaped macrocycle with the ability to coordinate alkali metal ions through its carbonyl-laced portals [1]. According to the results of our density functional theory (DFT) calculations, and important aspect of the complexation process is concerned with the partial dehydration of the $Cs^+(aq)$ ion which loses three or four water molecules in order to coordinate the carbonyl groups of CB[6]. Since the Cs^+-OH_2 bond is weaker than the corresponding M^+-OH_2 (M = Li-Rb) bonds, the complexation of radiocesium is favoured especially when the soil is contaminated by this specific metal cation.

One of the problems encountered so far, however, is concerned with the low selectivity of the CB[6] macrocycle towards cesium ion binding. It would be therefore important to introduce specific chemical groups (i.e. substituents) into the macrocycle so as to increase its selectivity towards the cesium ion. One possibility is offered by the introduction of aromatic moieties which may enhance the selectivity through the formation of Cs×p interactions. In this contribution we will discuss about the molecular structures and binding abilities of several derivatives of the CB[6] macrocycle as obtained from our DFT calculations. It is hoped that the information thus obtained would be useful in the design of highly-selective receptors for the capture of radionuclides in contaminated environments.

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ACTIONS FOR REMEDIATION IN CASES WITH LARGE CONCENTRATION OF RADON INDOOR

Alejandro Martín Sánchez[1], *María José Nuevo*[2]

[1]Department of Physics, University of Extremadura, Elvas Av. w/n, 06006 Badajoz, Spain, e-mail: ams@unex.es
[2]Department of Physics, University of Extremadura, Elvas Av. w/n, 06006 Badajoz, Spain, e-mail: maria@unex.es

Keywords: radon concentration indoor, remedial actions, case studies

Remedial actions are totally necessary in environment where high radon concentrations have been detected. In an initial survey about measurements of indoor radon concentration in working places performed in the region of Extremadura (Spain) several sites were detected as having high radon concentrations. Generally, these sites were placed in zones where the natural background radiation was also high. In this way, a deeper study seemed advisable on the affected zones, performing surveillance and taking remedial actions when necessary.

A project started proposing remedial actions. Principal proposed actions include ventilation (when possible), architectonical actuations, or limiting the time of residence of the people working in the exposed areas (when no other actions can be performed). Several examples were studied, analyzing each case and the effects that the proposed actions caused on the changes in the indoor radon concentrations. Studied sites include caves, cellars, historical buildings, hotels or museums. To facilitate the implementation of the existing rules and legislation, it was intended to design a protocol for places with high concentration of radon. This plan includes the study of seasonal variations, dose estimations, and the proposed remedial actions.The study was enlarged to include also dwellings.

Several case studies were performed. The main objective of this project was to carry out a comprehensive study of those places where great radon concentrations were found in the past. As a part of this work, control and monitoring of remedial actions were undertaken, analysing the efficiency of the proposed methods and even proposing new actions when necessary, always in order to limit the dose received by users (inhabitants or workers).

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DETERMINATION OF LEVELS OF NATURALLY OCCURRING RADIOACTIVE MATERIALS IN LAGOON SAMPLES CONTAINING PRODUCED WATER FROM THE MINAGISH OIL FIELD IN THE STATE OF KUWAIT

Hasan Shams

University of Surrey Department of Physics, United Kingdom, e-mail: hs00174@surrey.ac.uk

An evaluation of the activity concentration associated with both naturally occurring and anthropogenic radionuclides has been undertaken as part of a systematic study to provide a radiological map of a produced water lagoon located in the Minagish oil field in the south west of the State of Kuwait. The lagoon contains material from the discharge of produced water which is a by-product of oil production in the region. The lagoon samples have been prepared and placed into sealed, marinelli beakers for a full gamma-ray spectrometric analysis using a high-resolution, low-background, high-purity germanium detection systems. Of particular interest are the calculation of the activity concentrations associated with members of the decay chains following decays of the primordial radionuclides of the ^{238}U chain (^{226}Ra, ^{214}Pb, ^{214}Bi) and the ^{232}Th chain (^{228}Ac, ^{212}Pb, ^{208}Ti). The paper presents an overview summary of the experimental samples which have been analyzed to date.

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DETERMINATION OF CONDITIONAL STABILITY CONSTANTS FOR CO^{2+} WITH HUMIC ACID USING HUMIC ACID GRAFTED ON SILICA GEL

Gyula Szabó[1], Szabolcs Osváth[1], Péter Rell[1], Hanna E. Solt[2], Brian Powell[3]

[1]National Public Health Center, National Research Directorate for Radiobiology and Radiohygiene, PO Box 101, H-1775 Budapest, Hungary, e-mails: szabogy@osski.hu, osvath.szabolcs@osski.hu, rell.peter@osski.hu
[2]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2, H-1117 Budapest, Hungary, e-mail: solt.hanna@ttk.mta.hu
[3]Environmental Engineering and Earth Sciences, L. G. Rich Environmental Laboratory, Clemson University, 342 Computer Ct. Anderson, SC 29625, USA, e-mail: bpowell@clemson.edu

Keywords: ^{60}Co, humic acid, complex stability constant

Cobalt remains among the most investigated environmental contaminant. The anthropogenic contamination of terrestrial environment by Co arises mainly from mining and industrial activities. The environmental fate of Co is also of broad interest due to the discharge of ^{60}Co to riverine system from nuclear reactors and groundwater through inappropriate disposal or leakage from nuclear waste repository.

It is now well established that humic substances form complexes with a wide variety of metal ions but the nature of the complexation by these biogeopolymers remains poorly understood. Humic acids occur in solution in environmental aqueous phases, as colloids and sorbed on to the surfaces of environmental particles. Investigations with metal ions verify that various forms of humic acids are important components in the environmental behaviour of many toxic metals and radionuclides and determine their migrations in the environment.

This account will report the preparation of chemically bond humic acid on silica gel to model the surface bound or colloid humic matter. This solid humic acid was characterized by diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS). We also studied the interaction of humic acid chemically immobilised on silica gel, with Co(II) at different pH by titrating of the suspended materials in 0.1 M ionic solutions using ^{60}Co(II) as a tracer. The binding kinetics of Co(II) with humic acid have been investigated. The cobalt-humic acid stability constants were obtained from the results of latter experiments by using charge neutralisation-model, kinetic experimental data and non-linear regression of binding isotherms. The results have been interpreted in terms of complexes having 1:1 stoichiometry.

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ARTIFICIAL AND NATURAL RADIONUCLIDES IN ANTARCTIC BIOTA

Katarzyna M. Szufa[1], Jerzy W. Mietelski[1], Maria A. Olech[2, 3]*

[1]The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, E. Radzikowskiego 152,
31-342 Cracow, Poland, *e-mail: katarzyna.szufa@ifj.edu.pl
[2]Institute of Botany, Jagiellonian University, Zdzisław Czeppe Department of Polar Research and Documentation, Kopernika 27,
31-501 Cracow, Poland
[3]Institute of Biochemistry and Biophysics, Polish Academy of Sciences, Department of Antarctic Biology, Ustrzycka 10/12,
02-141 Warsaw, Poland

Keywords: Antarctica, artificial radionuclides, natural radioactivity, biota

Antarctic region is thought to be most clear and untouched by mankind. Knowledge about accumulation of natural and artificial radionuclides is crucial for radiological protection of southern polar environment. Despite the vast majority of nuclear weapons tests took place on northern hemisphere from 1957 to 1963 it is possible to detect radioactive contamination on territories around the South Pole (mostly radioisotopes of americium, caesium, strontium, plutonium). Moreover in 1964, an accident of American satellite energized by an on-board plutonium system SNAP-9A made up additional plutonium contamination. Even though there are numerous research stations in Antarctica where a various environmental studies are carried out accumulation of natural and artificial radionuclides has not been explored enough so far.

In our research we examined a number of biotic representatives like mosses, lichens, algae, seals, birds etc. from King George Island and several Antarctic continental areas to find radioactive nuclides, both natural (^{40}K, ^{210}Pb, ^{230,232}Th, ^{234,238}U) and artificial (^{241}Am, ^{137}C, ^{238,239,240}Pu, ^{90}Sr). Materials for analysis were collected between 2005 and 2009. Concentrations of potassium, lead and caesium were determined by high resolution low-background gamma-ray spectrometer with an HPGe detector, strontium by Liquid Scintillation Counter and other radioisotopes by alpha spectrometers with silicon detectors. Alpha and beta emitting radionuclides where separated with radiochemical techniques before spectrometric measurements. No caesium where found in marine organism while plutonium was revealed in almost all investigated samples. Due to plutonium content origins of contamination may by discovered through calculating ^{238}Pu/$^{239+240}$Pu activity concentration ratio. Furthermore estimation of annual doses from natural and artificial isotopes received by examined organisms may be performed.

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SPECTROSCOPIC SCREENING FOR THE SPECIATION OF EUROPIUM AND CURIUM IN THE GASTROINTESTINAL TRACT

Claudia Wilke, Astrid Barkleit, Thorsten Stumpf*

Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328 Dresden, Germany,
e-mail: c.wilke@hzdr.de

Keywords: body fluids, digestive system, lanthanides, actinides, europium, curium, TRLFS

Lanthanide and actinide elements are exogenous metals, which have no essential role in normal biochemistry. Actinides (An) are radioactive elements and are used in nuclear reactors and weapons, while lanthanides (Ln) have a variety of practical applications, e.g., as catalysts or dopants in laser materials. Through different processes these heavy metals could be potentially released into the environment where they could be further incorporated into the food chain. Because of their potential chemical- and radiotoxicity, it is important to understand their chemical and biological behavior in the human body. This study focuses particularly on the biochemical behavior of Ln(III) and An(III) in the human gastrointestinal tract. To this end, a spectroscopic screening was performed for Eu(III), as a representative of Ln(III) and An(III), by time-resolved laser-induced fluorescence spectroscopy (TRLFS) to identify their possible binding partners in the human gastrointestinal system simulated by using an *in vitro* digestion model [1, 2]. This model is the basis of an international unified bioaccessibility protocol.

The first experiments were performed at room temperature with dissolved 1×10^{-5} M Eu(III) in single constituents and different mixtures of the digestive juices (saliva, gastric, pancreatic and bile juice). For the saliva sample, the TRLFS spectra indicate a strong complex formation of Eu(III) with inorganic ligands, especially with carbonate, phosphate and sulfate, also calcium as counter ion shows an influence on the complexation. The proteins amylase and mucin are likely to be minor binding partners for Eu(III). Due to the acidic conditions in the stomach Eu(III) is expected to be present primarily as aquo species. In contrast to saliva the Eu(III) speciation in the pancreatic juice is influenced by different proteins. Strong complexation of Eu(III) was indicated with the glycoprotein mucin, which is part of the mucosa of the gastrointestinal tract [3]. The inorganic ions such as carbonate, phosphate and calcium are also involved in the complexation but their contribution is likely to be moderate. The interpretation of the luminescence spectra in the bile juice is not straightforward due to the complexity of the bile system which is composed of many ingredients like electrolytes, proteins, bile acids and alcohols and decomposition products [3]. Both inorganic and organic constituents could contribute the complexation with Eu(III). The measurements were also carried out for Cm(III) and at body temperature (37 °C). Based on the obtained results, the next step of this study will focus on the intestine, primary on mucin as a main binding ligand.

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URANIUM ISOTOPES IN GREEK RIVERS

Dimitrios C. Xarchoulakos, Konstantina Kehagia, Konstantinos Potiriadis*

Radiochemistry Laboratory, Department of Environmental Radioactivity Monitoring, Greek Atomic Energy Commission,
*e-mail: dimitris.xarchoulakos@eeae.gr

Keywords: ^{238}U, ^{234}U, Greek rivers, alpha spectrometry

A uranium isotopes study has been carried out in river waters all over Greece, because surface waters play an essential role in the migration and redistribution of radionuclides in the earth crust.

Uranium is a primordial radioactive element that is widely abundant at the environment. Furthermore, the ^{234}U/^{238}U activity ratio provides information about the mechanisms and processes of uranium transport and origin.

Various studies in river samples have been carried out, showing that the activity concentration of uranium isotopes depends on several environmental and physicochemical factors [1].

The aim of the present study is the level estimation of ^{238}U and ^{234}U to the majority of the Greek rivers. Fifteen samples for the year 2014 and twenty samples for the year 2015 were collected *(Fig.1)*.

Fig. 1. Sampling points of the examined Rivers

Each sample was spiked with ^{232}U tracer. The separation of uranium was performed by anion exchange and the source preparation via electrodeposition. The source was measured by a-spectrometry [2].

^{238}U average values for 2014 samples, ranged from 2.14 to 71.02 mBq/L and the ^{234}U/^{238}U ratio ranged from 1.10 to 2.04. Respectively, the ^{238}U mean values for 2015 samples ranged from 2.50 to 52.57 mBq/L and the ^{234}U/^{238}U ratio ranged from 1.10 to 1.83. The ^{234}U/^{238}U ratios that are greater than 1 can be attributed to the increased rate of ^{234}U removal [3] and the rock type of the examined sampling points [4, 5].

Taking into account the measurement results of the investigated waters, the following conclusions can be drawn:

- ^{238}U is found in a wide range of concentrations in the river waters under investigation.
- Radioactive disequilibrium is found in ^{234}U/^{238}U.
- The activity concentrations of ^{238}U in the years 2014 and 2015 are in the most of the rivers quite comparable. There is an exception in some river waters, which can be attributed to the different weather conditions in the above mentioned years.
- The activity concentration values of this study are comparable with international values.

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A RAPID METHOD FOR RADIO-STRONTIUM IN SOIL SAMPLES

Yonggang Yang[1, 2]**, *Xiongxin Dai*[1, 2], *Maoyi Luo*[1, 2], *Lijuan Song*[1, 2], *Steffen Happel*[3]

[1]China Institute for Radiation Protection, Taiyuan, China, *e-mail: yangyonggang1123@163.com
[2]Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Suzhou, China, e-mail: daixx@yahoo.com
[3]Triskem International, France, e-mail: shappel@triskem.ca

Keywords: TDCR Cherenkov counting, radio-strontium, yttrium-90, soil samples

A rapid method for the determination of radio-strontium in soil has been developed. In this method, radio-strontium in soil is leached out using concentrated acid after sample ashing. The strontium/yttrium are then preconcentrated with a mixed hydrous titanium oxide (HTiO)/calcium carbonate co-precipitation, followed by a rapid column chromatographic separation using stacked Sr-Resin and DGA cartridges. After splitting the cartridges, the Sr and Y are stripped off the Sr-Resin and DGA resin, respectively. Strontium-89/90 in the Sr eluate are counted by the triple-to-double coincidence ratio (TDCR) Cherenkov counting followed by liquid scintillation (LS) counting using a Hidex 300SLL LS counter, and yttrium-90 in the Y eluate is measured by TDCR Cherenkov counting. This method allows simultaneous determination of Sr-89/90 with no need of waiting for several days to recount the growth of ^{90}Y in the Sr counting sample. The method is suitable for quick measurement of radio-strontium in soil samples in the event of radiological/nuclear emergency.

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RADIOACTIVITY IN THE BALTIC SEA AS AN ELEMENT OF THE MARINE ENVIRONMENT STATUS ASSESSMENT

Tamara Zalewska[1]*, *Maria Suplińska*[2], *Anna Apanel*[1], *Michał Saniewski*[1]

[1]Institute of Meteorology and Water Management – National Research Institute, Maritime Branch, Waszyngtona 42, 81-198 Gdynia, Poland, *e-mail: tamara.zalewska@imgw.pl
[2]Central Laboratory for Radiological Protection, Konwaliowa 7, Warsaw, Poland, e-mail: msuplinska@imgw.pl

Keywords: ^{137}Cs, ^{90}Sr, Baltic Sea, environment status assessment

At present, environmental protection and the specific measures, including those of legal nature in order to improve its condition and to preserve it in the least altered form are getting increasing public interest. Taking into account the ecological objectives on hazardous substances stated by the HELCOM Baltic Sea Action Plan (the first in the world regional programme concerning protection of marine environment) and the requirements of Marine Strategy Framework Directive (Directive 2008/56/EC) a critical set of indicators so-called core indicators that are needed to regularly assess the status of the Baltic Sea marine environment against targets that reflect good environmental status have been established. Radioactivity is one of the elements influencing the final status of the environment with respect to hazardous substances, hence ^{137}Cs in fish and surface water was recommended as a core indicator for radioactive substances.

The contemporary level of anthropogenic radioactivity in the Baltic Sea results mainly from the distribution of radioactive isotopes – ^{137}Cs and ^{90}Sr in seawater, marine sediments and biota. The main input sources of these isotopes to the marine environment were the Chernobyl accident in 1986 and the tests of nuclear weapons carried out in 1950s and 1960s. The activity concentration of ^{137}Cs in seawater is decreasing after having reached the maximum in 1991 (101 Bq m^{-3}), and the major processes involved are the radioactive decay, bioaccumulation together with sedimentation and water exchange with the North Sea. In 2014, the mean concentration of ^{137}Cs in seawater of the southern Baltic Sea was 27.3 Bq m^{-3}, and that of ^{90}Sr – 6.6 Bq m^{-3}. The activity of ^{137}Cs in commercial fish closely follows the situation in seawater. In 2013, the mean concentration of radioactive cesium in herring *(Clupea harnegus)* was 3.7 Bq kg^{-1} w.w., in cod (*Gadus morhua*) – 4.7 Bq kg^{-1} w.w., flounder (*Platichthys flesus*) – 3.4 Bq kg^{-1} w.w. and in sprat (*Spratus spratus*) – 3.9 Bq kg^{-1} w.w. Activity concentrations of ^{90}Sr in the same species were much more diversified: herring – 0.02 Bq kg^{-1} w.w., cod – 0.15 Bq kg^{-1} w.w., flounder – 0.16 Bq kg^{-1} w.w. and sprat – 0.03 Bq kg^{-1} w.w.

Data on the current concentration of ^{137}Cs in selected matrices related to the target values defining the boundary between good and inadequate environmental conditions, allow an assessment of the state of marine areas in terms of contamination by radioactive substances. In the southern Baltic Sea good environmental status (GES) was not achieved for any of the assessed ecosystem elements: herring, flounder and seawater.

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PRESIGNAL SIGNATURE OF RADON (RN^{222}) FOR SEISMIC EVENTS

Maria Zoran[1]*, *Dan Savastru*[1], *Doru Mateciuc*[2]

[1]Department of Environmental Satellite Remote Sensing, National Institute of R&D for Optoelectronics, Bucharest – Magurele, Atomistilor Street 409, Romania, *e-mail: maria@dnt.ro

[2]Department of Lithospheric Research, National Institute of R&D for Earth Physics, Bucharest – Magurele, Calugareni Street 12, Romania, e-mail: dmateciuc@infp.ro

Keywords: solid state nuclear track detectors, radon anomalies, seismic precursors, seismic hazard, Vrancea, Romania

Research on earthquake-related presignal radon (Rn^{222}) monitoring has gained enormous attention during last decades. Anomalous behaviour of radon in air, soil and groundwater can be used as a reliable precursor for an impending earthquake. While earthquake forecasting is a controversial issue, earthquake prediction research has greatly increased our understanding of earthquake source mechanisms, the structural complexities of active geotectonic fault zones, and the earthquake recurrence interval, expected at a given location. Rock microfracturing in the Earth's crust preceding a seismic rupture may cause local surface deformation fields, rock dislocations, charged particle generation and motion, electrical conductivity changes, radon and other gases emission, fluid diffusion, electrokinetic, piezomagnetic and piezoelectric effects as well as climate fluctuations. Space-time anomalies of radon gas emitted in underground water, soil and near the ground air weeks to days in the epicentral areas can be associated with the strain stress changes that occurred before the occurrence of medium and strong earthquakes. This paper presents some results of continuous monitoring of radon in air near the ground in Vrancea seismic area, Romania and investigates temporal variations of radon concentration levels in air near or in the ground by the use of short term (ten days exposure time) solid state nuclear track detectors (SSNTD) CR-39. Radon in air monitoring together with seismic activity and meteorological parameters were performed at seismic stations Plostina (Vrancea), Cheia (Muntele Rosu Observatory) and Bucharest Magurele, Romania. Radon anomalies along with meteorological parameters were found to be statistically significant for the seismic events within the moment magnitudes $M_w > 5.0$ and epicentral distances of 15–200 km from the monitoring station. The frequent positive and negative anomalies with constant environmental perturbation indicate the opening and closing of micro cracks within the volume of dilatancy by strain stress energy. The spike-like and sharp peak anomalies were recorded before, during and after earthquakes occurred in the area. The variations of radon in air above the ground concentrations were found to be correlated with seismic activities in the Vrancea area. The correlation between radon level and meteorological parameters was also discussed.

Radiolabeled compounds and radiopharmaceuticals

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CHARACTERIZATION OF GIRENTUXIMAB-DOTA CONJUGATES FOR LABELLING WITH THERAPEUTIC RADIONUCLIDES

Tais Basaco[1, 2], Stefanie Pektor[3], Niurka Meneses[2], Josue Moreno[1], Matthias Miederer[3], Andreas Türler[1, 2]*

[1]Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, Switzerland, *e-mail: tais.basaco@dcb.unibe.ch
[2]Department of Chemistry and Biochemistry, Paul Scherrer Institute, Villigen PSI, Switzerland
[3]Department of Nuclear Medicine, Johannes Gutenberg-University of Mainz, Langenbeckstr. 1, Germany

Keywords: radioimuntherapy, DOTA-Girentuximab conjugates, liquid chromatography–mass spectrometry, ^{177}Lu-radioconjugates

Girentuximab (cG250) is a chimeric monoclonal antibody (mAb) reactive with the CAIX antigen, overexpressed on the cell surface of most (>90%) clear cell carcinomas (RCCs) being a potential candidate for radioimmunotherapy of RCCs. The goals of this study are to conjugate G250 native antibody with the bifunctional chelating agent DOTA (1,4,7,10-Tetraazacyclododecane-N,N',N'',N'''-tetraacetic acid) via a benzyl-thiocyano group as a linker (p-SCN-βn-DOTA), characterize the conjugates by mass spectrometry (LC/MS-MS) and evaluate the immunoreactivity of the bioconjugates. DOTA-G250 conjugates were prepared and purified by membrane centrifugation. The conjugates were analyzed by size exclusion chromatography (SE-HPLC) and by infusion on LC/MS-MS to determine exact mass. The conjugates were characterized by electrophoresis using 12.5% acrylamide gels and sodium dodecyl sulphate (SDS-PAGE). After, they were digested with trypsin and injected on LC/MS-MS using high collision dissociation (HCD) and electron transfer dissociation (ETD) to identify the potential modified peptides. The conjugates were labeled with ^{177}Lu in sodium acetate buffer pH = 5.5–7 at 37 °C. The immunoreactivity was evaluated in CAIX negative (SKRC-18) and CAIX positive (SKRC-52). The protein conjugation and purification was proved by the HPLC comparing the position of the peak for DOTA-G250 with the peak of native G250. In addition, on the SDS-PAGE chromatograms the conjugate zones, as expected, were broader and shifted to higher molecular weight compared to the native zones. The ratio of DOTA molecules per molecule of mAb ranged from 2 to 6 in different conjugates based on the information from the mass spectra and SDS-PAGE chromatogram of the light chains (LH). In the case of the heavy chain (HC), the ratio was higher but it could not be exactly measured by intact mass due to the high heterogeneity. The peptide sequence coverage in the conjugates was 98% and 92% for the LC and HC, respectively and potential DOTA modification sites were identified. The conjugates were labelled with ^{177}Lu obtained >95% of radiochemical yield. High specific activities (12 MBq/µg) were reached with this type of conjugates. The radioconstructs with highest specific activity were not stabilized in presence of sodium ascorbate post labeling. The binding to cells was higher in the type of conjugates with less DOTA.

In a further stage of the work, it is intended to label the DOTA-G250 conjugates with, ^{225}Ac and evaluate the properties of the labelled constructs *in vitro* and *in vivo*.

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SYNTHESIS AND *IN VIVO* EVALUATION OF (R)-(+)- AND (S)-(–)-^{18}F-LABELED 2-ARYLBENZOHETEROCYCLIC DERIVATIVES FOR PET MAPPING OF β-AMYLOID PLAQUES

Mengchao Cui[1], Yanping Yang[1], Xuedan Wang[1], Hualong Fu[1], Jinming Zhang[2], Xiaojun Zhang[2], Boli Liu[1]*

[1]Key Laboratory of Radiopharmaceuticals, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing, China,
*e-mail: cmc@bnu.edu.cn
[2]Department of Nuclear Medicine, Chinese PLA General Hospital, Beijing, China, e-mail: zhangjm301@163.com

Keywords: β-amyloid, enantiopure, 2-arylbenzoheterocyclic, PET

In pursuit of reducing lipophilicity and enhancing signal-to-noise ratio of radiotracers targeting A*β* plaques in AD brains, three pairs of enantiopure (*R*)- and (*S*)-^{18}F-labeled 2-arylbenzoheterocyclic derivatives were designed, synthesized and evaluated. In biodistribution studies, all the (*S*)-enantiomers exhibited dramatically improved clearance profiles with several-fold higher brain$_{2\ \mathrm{min}}$/brian$_{60\ \mathrm{min}}$ ratio than the (*R*)-enantiomers, and this phenomenon was further investigated by *in vivo* metabolism studies. The most potent probe, (*S*)-[^{18}F]**28**, exhibited a combination of high binding affinity to A*β* aggregates (K_i = 15.5 ± 3.2), high initial brain uptake (9.46% ID/g at 2 min), fast clearance from normal brain tissue ($\text{brain}_{2\,\text{min}}/\text{brian}_{60\,\text{min}}$ ratio = 27.8), and satisfactory *in vivo* biostability in the brain (80% of intact form at 30 min). (*S*)-[^{18}F]**28** clearly labeled A*β* plaques in *in vitro* autoradiography of postmortem AD patients and Tg mice brain sections. *Ex vivo* autoradiography in Tg mouse further demonstrated that (*S*)-[^{18}F]**28** did penetrate the intact BBB and specifically bind to A*β* plaques *in vivo.* Finally, a direct comparison of PET/CT scans in rhesus monkeys between (*S*)-[^{18}F]**28** and [^{18}F]AV45 were performed. (*S*)-[^{18}F]**28** displayed about two folds clearance rate and lower white matter uptake in the monkey brain than [^{18}F]AV45. Overall, (*S*)-[^{18}F]**28** may be a potential PET probe for imaging A*β* plaques in AD brains, and further PET studies in human were currently onder way.

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SEMI-AUTOMATED SYSTEM FOR PURIFICATION, CONENTRATING AND LABELING OF ^{68}Ga-RADIOPHARMACA FOR PRECLINICAL APPLICATION

Erik de Blois, Rory de Zanger, Max van Peski, Ho Sze Chan, Wouter Breeman*

Department of Nuclear Medicine, Erasmus MC, Wytemaweg 12, the Netherlands, *e-mail: r.deblois@erasmusmc.nl

Keywords: ^{68}Ga-generator, preclinical application, imaging

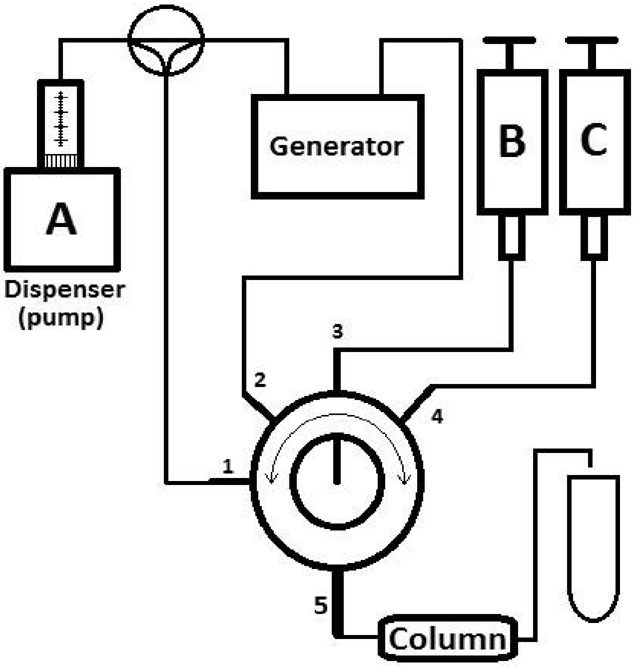

Fig. 1. Schematic of NaCl based purification of ^{68}Ga eluate to make ready to use high concentrated ^{68}Ga suitable for direct radiolabelling. A: 0.1 M HCl for eluting generator. B: 1 mL Syringe with 0.5 mL of 5 M NaCl (spiked with HCl) for desorption of ^{68}Ga. C: 10 mL Syringe with air to empty column before elution of ^{68}Ga

Introduction: Nowadays ^{68}Ga-radiopharmaca have become more common in the field of Nuclear Medicine to visualize receptor-mediated processes. In contrast to straightforward labelling-procedures for these clinical applications, preclinical application are hampered for reasons like low volume-activity, volume, high osmolality high specific activity. Therefore we developed a semi-automatic system specifically to overcome these problems *(Fig. 1)*.

Objectives: Obtain within 20 minutes, applicable amounts of ^{68}Ga labelled peptide (20–30 MBq/nmol) for preclinical application such as imaging. In contrast to human application (e.g. 35 nmoles/ 150 MBq/ 9 mL at ~300 mosmol), specification for mice injection are 0.2 nmoles/5 MBq in ≤0.2 mL ~300 mosmol. The here described system was investigated by using a 9–12 month old clinical grade ^{68}Ga-generator (EZAG) originally containing 1110 MBq (now 200–300 MBq), which is too low for clinical applications.

Methods and materials: NaCl based method (Muller et al., 2012) and was implemented in low volume PEEK system (tubing 0.03 inch) *(Fig. 1).* Bio-Safe column (PEEK-2.1 × 300 mm – 2 µm filter frits – total volume 173 µL, Triskem) was filled with PSH resin (50 mg, cation) and connected to 6-way manual valve (Inacom instruments). ^{68}Ga was trapped on the column (position 2) by eluting ^{68}Ga-generator with 6 mL 0.1 M HCl. Valve was switched (position 4) and flushed with 10 mL of air to empty PEEK tubing and PSH column. Valve was switched to position 3 and content of syringe B (see *Fig. 1*) was used to desorb ^{68}Ga from the resin. 0.2 mL was collected, aliquot was taken (0.1 mL), buffer (<0.050 mL of 0.5 M sodium acetate pH 5) was manually added to adjust pH to 3.5. DOTA-TATE was used as a peptide model. Radiolabelling was performed after addition of DOTA-TATE (4.8–7.2 nmoles) and heated for 5 min 80 °C.

Results: >60% (120–180 MBq) of ^{68}Ga activity was desorbed from PSH column and collected in <0.2 mL. ^{68}Ga could be labelled with DOTA-TATE at high incorporation (ITLC) and radiochemical purity (HPLC). After radiolabelling, peptide could be diluted to physiological conditions to required condition (200 pmoles/5 MBq in ≤0.2 mL ~300 mosmol) which is suitable for intravenous mice injection.

Conclusions: With here described system low activity containing ^{68}Ga-generator could be used to label DOTA-peptide in preclinical applicable amounts and within 20 minutes.

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THE METALLOBIOCHEMISTRY OF ULTRATRACE LEVELS OF TECHNETIUM-99 IN THE RAT

Flavia Groppi[1], Simone Manenti[1], Mauro L. Bonardi[1], Enrico Sabbioni[1, 2]*

[1]LASA, Università degli Studi di Milano and INFN-Milano, via F.lli Cervi 201, I-20090 Segrate, MI, Italy, *e-mail: flavia.groppi@mi.infn.it
[2]CeSI, Aging Research Center, "G. d'Annunzio" University Foundation, 66100 Chieti, Italy

Keywords: nuclear medicine, radioactive waste, Tc-99g, pertechnetate

Technetium-99 (^{99}Tc) is a radioactive metal originated by natural spontaneous fission of ^{238}U. Although it has no significant industrial use, not negligible amounts of this radioelement are produced as fission product in nuclear reactors for energy production, being present in fuel reprocessing plants and in facilities that treat or store radioactive waste, in which represents the largest fraction of the total long-lived radiation emissions. In addition, its short-lived parent, ^{99m}Tc ($t_{1/2}$ = 6 h), produced by ^{99}Mo/^{99m}Tc cow, is widely used for medical diagnostic purposes. In recent years there was a worldwide shortage of ^{99}Mo/^{99m}Tc system that boosted the interest in verifying alternative way of production of ^{99m}Tc by cyclotron via ^{100}Mo(p,2n)^{99m}Tc nuclear reaction. The ^{99}Tc from ^{99m}Tc decay must be assessed in the patient dosimetry. In addition, ^{99m}Tc is recently used for the radiolabelling of chitosan nanoparticles. Consequently, ^{99}Tc is also present in hospitals, academic institutions and research establishments. Although a huge amount of literature is existing on concentrations and accumulation of ^{99}Tc in different environmental compartments, much less is still today known about its metabolic patterns in mammals. In this context, the characteristics of ^{99}Tc such as a long half-life ($t_{1/2} = 2.1\times10^5$ a) and consequently a poor specific radioactivity (A_S = 630 kBq/mg) as well as the pure β-nature of the emitted radiation, make very difficult its direct use for studies on metabolic fate of environmental doses in tissues, subcellular fractions and biomolecules of mammalian systems. On the other hands the short half-life of ^{99m}Tc makes it not suitable for such metallobiochemical experiments at medium term exposure. In this work, we studied the metabolic patterns of ultratrace levels of Tc in rats by using ^{95m}Tc radiotracer ($t_{1/2}$ = 60 d, E_g = 204 keV), that was prepared by cyclotron irradiation on natural Mo target via ^{nat}Mo(p,xn)^{95m}Tc nuclear reaction and separated radiochemically in the form of oxyanion $^{95m}TcO_4^-$ (A_S = 840 MBq/mg). Groups of feeded and non feeded animals received orally 2.33 ng ^{95m}Tc/rat as pertechtenate. At 4 h post-exposure the radioactivity in tissues of the non feeded group was significantly higher compared to that of the feeded animals, stomach, thyroid, skin, fat, intestine, kidney and liver having the highest percentage of the dose administered. In the blood the radioactivity was mainly present in the plasma in association with proteins and biomolecules with low molecular weight. In feeding rats after 1, 2, 4, 8 and 15 d, ^{95m}Tc, retained in the tissues, gradually decreased being <1% of the dose administered at 15 d, suggesting a short biological half-life of the radioelement in rats. A rapid elimination of ^{95m}Tc occurred in the first 2 d, the main route of excretion being via feces. In the liver, kidney and spleen, nuclei and mitochondria were the cellular organelles retaining the major fraction of the cellular radioactivity. Gel filtration of the ^{95m}Tc-cytosol showed that the radioelement was present in association with two biochemical pools being eluted as two main peaks corresponding to high and low molecular weight components.

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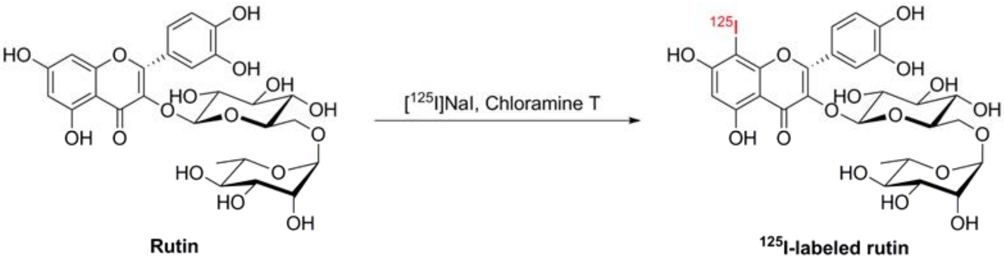
EFFICIENT RADIOSYNTHESIS OF ^{125}I-LABELED RUTIN FOR BIODISTRIBUTION STUDY OF RUTIN

Jongho Jeon[1, 2], Mi Hee Choi[1], Jung Ae Kang[1], Ha Eun Shim[1], You Ree Nam[1], Hye Rim Kim[1],*
Dae Seong Choi[1], Sang Hyun Park[1, 2], Beom-Su Jang[1, 2]

[1]Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongeup 580-185, Republic of Korea,
*e-mail: jeonj@kaeri.re.kr
[2]Department of Radiation Biotechnology and Applied Radioisotope Science, Korea University of Science and Technology, Daejeon 305-350, Republic of Korea

Keywords: rutin, radiolabeling, ^{125}I, biodistribution, SPECT/CT

The purpose of this research is to synthesize radiolabeled rutin for biodistribution study and *in vivo* SPECT/CT image of rutin. An optimized labeling condition provided ^{125}I-labeled product with 53.5% of radiochemical yield and >99% of radiochemical purity *(Scheme 1)*. A weak acidic condition (pH = 4–5) and short reaction time (<3 min) were key factors to provide high radiochemical yield and to minimize impurities during the labeling reaction. Radioiodine labeled rutin was orally administered to normal ICR mice and biodistribution data and images were obtained using SPECT/CT imaging system *(Fig. 1)*. *Ex vivo* biodistribution study showed that most of ^{125}I-labeled rutin was initially found in the stomach and small intestine and a portion of the product was then distributed in internal organs such as liver, spleen and kidneys. While intravenously injected ^{125}I-labeled rutin was accumulated in liver and then a large part of it was transferred to small intestine. The present results provide an efficient radiolabeling method of flavonoid glycoside as well as quantitative organ distribution of orally administered and intravenously injected rutin.



Scheme 1. Radiolabeling of rutin using ^{125}I, radiochemical yield = 53.5 ± 7.5% (n = 4)

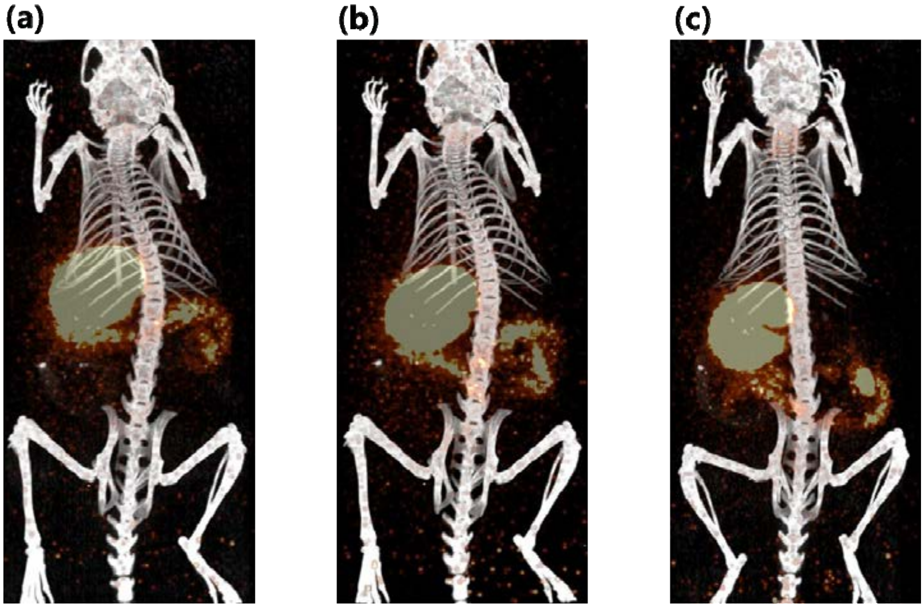


Fig. 1. SPECT/CT images of orally administered ^{125}I-labeled rutin.
(a) 1 h post administration (b) 2 h post administration (c) 4 h post administration

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RADIOIMMUNOCHEMICAL STUDIES TO DEVELOPMENT OF SOLID PHASE RADIOIMMUNOASSAY SYSTEM USING COATED BEADS FOR THE ASSESSMENT OF HUMAN CHORIONIC GONADOTROPIN

Kh. M. Sallam, A. S. A. El-Bayoumy, N. L. Mehny*

Labeled Compounds Department, Hot Labs Center, Egyptian Atomic Energy, Cairo, Egypt, *e-mail: drkhaledsallam@yahoo.com

Keywords: radioimmunoassay, B-HCG, normal rabbit serum, bovine serum, polyclonal antibody, oxidizing agents

A method has been developed for immobilization of prepared human chorionic gonadotropin (B-HCG) antisera on fresh plastic beads through an immunochemical bridge. This type of immobilization has been shown to be more consistent than direct adsorption on plastic. Such immunochemically coated antisera on plastic beads has been used in the development of a non centrifugation radioimmunoassay. In addition to the preparation of ^{125}I-BHCG using different oxidizing agents was carried out. The solid phase RIA assay system has been found to be technically as sound as the conventional method.

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RADIOLABELING OF MELATONIN USING DIFFERENT OXIDIZING AGENTS FOR IMMUNOASSAY PURPOSE

Kh. M. Sallam, A. S. A. El-Bayoumy, N. Farouk*

Labeled Compounds Department, Hot Labs Center, Atomic Energy Authority, P.O. Box 13759, Cairo, Egypt, *e-mail: drkhaledsallam@yahoo.com

Keywords: melatonin, ^{125}I-melatonin, oxidizing agents, polyclonal antibody

A specific and sensitive double antibody radioimmunoassay for melatonin (Nacetyl-5-methoxytryptamine) has been developed utilizing N-3-(4-hydroxyphenyl)-propionyl-5-methoxytryptamine for radioiodination using different oxidizing agents. Also utilizing rabbit antisera to a bovine serum albumin conjugate of N-succinyl-5-methoxytryptamine using four rabbits was carried out. Optimization of RIA kit was carried out followed by validation tests. Serum samples with melatonin concentrations of 700 pg/ml, 350 pg/ml and 100 pg/ml had intra-assay coefficients of variation of 8.7%, 9.4%, and 11.2%, respectively. The respective inter-assay coefficients of variation were 12.1%, 12.5%, and 13.2%.

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SEPARATION AND PURIFICATION OF TECHNETIUM-99m FROM MOLYBDENUM-99 PRODUCED BY ELECTRON LINEAR ACCELERATOR

Katsuyoshi Tatenuma[1], Yumi Suzuki[1], Akira Tsuguchi[1], Atsushi Tanaka[1], Takahiro Tadokoro[2], Yuko Kani[2], Yasumasa Morikawa[3], Asaki Yamamoto[3], Shun Sekimoto[4], Tsutomu Ohtsuki[4]*

[1]Kaken Inc, Mito, Japan
[2]Hitachi, Ltd., Hitachi, Japan
[3]FUJIFILM RI Pharma Co., Ltd., Sammu, Japan
[4]Kyoto University Research Reactor Institute, 2-1010, Asashiro-Nishi, Kumatori, Sen-nan, Osaka 5900494, Japan,
*e-mail: sekimoto@rri.kyoto-u.ac.jp

Keywords: electron linear accelerator, Tc-99m, Mo-99, Tc-99m master milker, Tc-99m generator

Shortage in supply of Mo-99 resulting from the shutdown of reactors for its production can be a global issue. Recently, therefore, production of Mo-99 by using an accelerator has been investigated in Japan. We have also launched the development of new complex system for production of Mo-99 by using an electron linear accelerator and subsequent separation system of Tc-99m. In our previous experiments, Mo-100 oxide powder was irradiated with bremsstrahlung photons generated using the electron linear accelerator in Research Reactor Institute, Kyoto University (KUR-Linac), and we confirmed that Mo-99 was successfully produced [1].

In this study, separation and purification method of Tc-99m generated from Mo-99 was applied to Mo-99 produced in KUR-Linac. The milker method from Mo-99 to Tc-99m is able to generate an enormous amount of Tc-99m (1.8E+13 Bq in maximum) as the practical application stage for generation of high-purity and concentration Tc-99m solution, even though the specific activity of Mo-99 as a source material is low (1.8–3.7E+10 Bq/g Mo) [2]. Additionally, it is found that the NAC (Nanosize Alumina Coagulated) type of column for adsorption of Mo-99 was a powerful tool as the Tc-99m generator. The detail of Tc-99m separation system will be discussed in the presentation.

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TECHNETIUM-99m LABELED MULTIVALENT GALACTOSYL DENDRIMER FOR HEPATIC ASGP RECEPTOR IMAGING

Wenjiang Yang[1, 2]**, Jingquan Xue*[1, 2]*, Jianjun Wang*[1, 2]*, Yanhua Zhang*[1, 2]*, Yu Liu*[1, 2]

[1]Division of Nuclear Technology and Applications, Institute of High Energy Physics, Chinese Academy of Sciences , Beijing 100049, China, *e-mail: yangwj@ihep.ac.cn

[2]Beijing Engineering Research Center of Radiographic Techniques and Equipment, Beijing 100049, China

Keywords: ^{99m}Tc, ASGP, liver imaging, dendrimer, SPECT

Accurate assessment of liver function could be useful for guiding treatment and evaluating prognostic factors. Radiolabeled ASGPr (asialoglycoprotein receptor) probes can provide a noninvasive, sensitive and accurate way to estimate liver function. In this study, the novel ASGPr probes are prepared by radiolabeled multivalent galactosyl dendritic probe with ^{99m}Tc and studied with microSPECT imaging in SD rats.

Radiosynthesis: The multivalent galactosyl dendritic precursor G2-4La-HYNIC was labeled with ^{99m}Tc using tricine as coligand. The labeling yield was greater than 95%. After rapid purified with HiTrap desalting column, the radiochemical purity of ^{99m}Tc[G2-4La-HYNIC](tricine)$_2$ was above 99% as determined by TLC and radio-HPLC.

Biodistribution: ^{99m}Tc[G2-4La-HYNIC](tricine)$_2$ (about 0.185 MBq, 10^{-9}mol/kg) was injected into mice through the tail vein. ^{99m}Tc[G2-4La-HYNIC](tricine)$_2$ had rapid liver accumulation with good retention. The initial liver uptake is 32.2±4.2% %ID/g at 10 min after injection (n = 5). At 30 and 120 min post-injection time the liver uptake were 32.3±2.2 %ID/g and 30.6±3.9 %ID/g, respectively. The blood and kidney showed relatively low activity. When using GSA as inhibitor, the liver uptake was decreased significantly ($P<0.01$). The results of biodistribution showed that the ^{99m}Tc[G2-4La-HYNIC](tricine)$_2$ has high affinity with the ASGP receptor, and its uptake in the liver via receptor-mediated.

Dynamic SPECT imaging: Data were acquired using a small animal SPECT/CT scanner, which was developed by the IHEP, CAS. An one-hour dynamic scan of SD rat was conducted immediately after injected via the tail vein with 37 MBq of ^{99m}Tc[G2-4La-HYNIC](tricine)$_2$ (1.3×10^{-8} mol/kg). ROI were drawn on the heart, liver, and kidneys and the time activity curves were calculated for these regions. The liver uptake in rats peaked within 10 min after injection, while the radioactivity in the blood was decreased rapidly. A part of radioactivity was metabolized via the kidneys. About 4 min to reach the peak, then quickly washout from kidneys. The blocking study was performed by pre-injected free GSA five minutes before intravenously injected of the radiotracer. The results showed that the radioactivity level in the liver was significantly reduced and retained within 1 h. After blocking, the unbounded tracer could rapid clear through the kidney. The ^{99m}Tc[G2-4La-HYNIC](tricine)$_2$ had a short circulation time in bloodstream which could reduce the level of radioactivity in the hepatic blood pool and other vascularized organs.

Conclusions: ^{99m}Tc[G2-4La-HYNIC](tricine)$_2$ was prepared with high radiochemical yield. Biodistribution and imaging studies demonstrated hepatic targeting and rapid blood clearance for this tracer. The promising biological properties affords potential applications for assessment of hepatocyte function in the future.

Acknowledgement

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INVESTIGATION OF ANTICANCEROGENIC EFFECTS OF RADIOIODINATED INDOLE3CARBINOL AND PLGA ENCAPSULATED INDOLE3CARBINOL COMPOUNDS UTILIZING *IN VITRO* METHODS

Gorkem Yildiz, F. Zumrut Biber Muftuler, Ayfer Yurt Kilcar, Volkan Tekin, E. Ilker Medine, Ozge Kozgus Guldu

Institute of Nuclear Sciences, Ege University, Bornova-Izmir 35100, Turkey, e-mails: gorkem_3219@hotmail.com, fazilet.zumrut.biber@gmail.com, ayferyurt@yahoo.com, volkantekin@windowslive.com, ilkermedine@gmail.com, ozgekzgs@gmail.com

Keywords: indole3carbinol (I3C), cruciferous vegetables, PLGA, ^{131}I, cell culture, cytotoxicity, anticancerogenic effects, MCF-7, Caco-2, PC3 cells

Recently, use of natural products has gained more importance and recent studies emphasized that consuming cruciferous vegetables (broccoli, brussel sprout, cauliflower, collard greens and curly kale) lowers cancer risk. In the literature, there are a lot of studies which are showed that indole3carbinol (I3C) and metabolic ingredients of cruciferous vegetables provide antitumor activity against many cancer types including breast, prostate and colon cancer.

In present study, radioiodination and encapsulation with poly lactic-co-glycolic acid (PLGA) of I3C has been performed. Anticancerogenic effects of I3C and PLGA encapsulated I3C (I3C-PLGA) have been investigated utilizing *in vitro* methods.

Nanoparticles containing biodegradable and biocompatible polymers such as PLGA have been widely used and important research subject about pharmaceutical carriers. Their main usages in medical science contain being a carrier for drug, genes and antigens as well as *in vitro* studies. In this study, quality control of I3C and I3C-PLGA has been performed with High Performance Liquid Chromatography (HPLC) and structural analysis of ^{127}I-I3C has been verified using Nuclear Magnetic Resonance (NMR). I3C and I3C-PLGA compounds have been radiolabelled in high yields with ^{131}I [(^{131}I-I3C), (^{131}I-I3C-PLGA)] which is widely used for diagnosis and treatment in nuclear medicine. Quality control studies of radioiodinated compounds have been determined using Thin Layer Radio-Chromatography (TLRC) while anticancerogenic effects have been studied on breast adenocarcinoma epithelial (MCF-7), colon adenocarcinoma epithelial (Caco-2), prostate carcinoma epithelial (PC3) cells.

All experimental results demonstrated that radioiodinated compounds are promising in order to be used in nuclear medicine as well as present study contributed previously reported studies.

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INVESTIGATION OF ^{99m}Tc LABELLED PLUMBAGIN VIA ER DEPENDENT EXAMINATION AGAINST BREAST CANCER CELLS AND COMPARISON WITH PLGA ENCAPSULATED FORM

Ayfer Yurt Kilcar, Volkan Tekin, F. Zumrut Biber Muftuler, E. Ilker Medine

Institute of Nuclear Sciences, Ege University, Bornova-Izmir 35100, Turkey, e-mails: ayferyurt@yahoo.com, volkantekin@windowslive.com, fazilet.zumrut.biber@gmail.com, ilkermedine@gmail.com

Keywords: plumbagin, PLGA encapsulation, radiolabeling, ^{99m}Tc, breast cancer cells, estrogen receptor dependency

Plant origin products having anticancer properties gain importance because of cancer prevalent. Within the cancer types, breast cancer is second at the causes of death in women. Because of the heterogeneity of breast cancer is main roadblock at the diagnosis and targeted therapy, mainly researchers are focused on studies willing to add novel advances in detection and treatment of breast cancer. Although estrogen receptor (ER) expression is closely associated with the biology of breast carcinoma, little is known about mechanisms which control ER expression. The expression of ER plays a central role in the biology of breast cancer. This means that ER specifity of any agent has a noteworthy significance.

Plumbagin (PL) which is naturally present in *Plumbago zeylanica* has been used in Indian medicine since the ancient time. It is reported that PL exhibited anticancer and antiproliferation properties on a variety of cell lines and animal models. Recently; investigation of the potential and mechanism of PL on various cancer types and diseases gained great importance because of the biological activities of PL including antitumor activity. In several studies it is seen that PL has inhibitory effect on various cancer cells such as prostate, ovarian etc. However, ER dependent data of PL on breast cancer cells were missed.

In current study, ER dependent diagnosis potential of PL is investigated by labelling with ^{99m}Tc and *in vitro* studies (cytotoxicity and incorporation assays) on ER positive (MCF-7) and negative (MDA-MB-231) adenocarcinoma cells. Additionally, poly (D,L-lactide)-co-gly-colide (PLGA) encapsulation of PL (PL-PLGA) is carried out to reduce toxicity of PL. Also, effect of encapsulation on its potential is investigated.

Consequently, PL and PL-PLGA were labelled with ^{99m}Tc (^{99m}Tc-PL and ^{99m}Tc-PL-PLGA) in yields over 95%. ^{99m}Tc-PL-PLGA was more stable than ^{99m}Tc-PL. Both labelled compounds were hydrophilic; ^{99m}Tc-PL-PLGA was more hydrophilic. Cytotoxicity assays were confirmed that PLGA encapsulation was eliminated the toxicity of PL. ^{99m}Tc alone has no important incorporation on adenocarcinoma cells, the incorporation percent of ^{99m}Tc-PL and ^{99m}Tc-PL-PLGA increased in an ER dependent manner. Both of the labelled compounds have ER specificity. It is seen that ^{99m}Tc-PL-PLGA has considerably high ER dependent incorporation efficiency than ^{99m}Tc-PL.

To sum up, PLGA encapsulation effected positively on properties of PL; reduced toxicity, increased stability and ER specifity. A promising agent for the diagnosis of ER+ breast cancer is suggested.

Radionuclide separation

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REMOVAL OF ^{226}Ra FROM AQUEOUS MEDIA AND ITS THERMODYNAMICS AND KINETICS

Sema Akyil Erenturk[1], *Aysun Kilincarslan Kaygun*[2]

[1]Energy Institute, Istanbul Technical University, 34469 Maslak, Turkey, e-mail: erenturk@itu.edu.tr
[2]Cekmece Nuclear Research and Training Center, Yarimburgaz Mah. Nukleer Arastirma Merkezi Yolu, 34303 Kucukcekmece-Istanbul/Turkey, e-mail: aykilincar@yahoo.com

Keywords: adsorption, radium-226, aqueous media, isotherms, thermodynamic, kinetic

Several radionuclides can be found in aquatic environment, both naturally occurring and anthropogenic. Their concentrations are variable and depend on the nature of the aquifer rock type sand the prevailing lithology. Preconcentration and separation processes based on adsorption processes are important in nuclear technology, industry, medicine and daily life. Adsorption of radioactive elements onto various solids is important in purification process, environmental contamination and separation and preconcentration of elements. Many organic and inorganic adsorbents are used treatment of radioactive and industrial wastes. The composite adsorbents are very special class of adsorbents, developed to improve the processes of separation, concentration or removal of metal ions from solutions. They have attracted attention as adsorber materials in recent year.

In this study, the composite adsorbent as granule were prepared by mixing of poliacrylonitrile (PAN) and clinoptilolite that is a natural zeolite in specific conditions. The prepared composite adsorbent was used for investigating the adsorption behaviour of ^{226}Ra. Adsorption of ^{226}Ra was studied in column system. The effective parameters such as pH of the solution, contact time in column and temperature of solution for adsorption behaviour of ^{226}Ra were studied. Adsorption yield of ^{226}Ra on composite adsorbent from aqueous solution in optimum conditions were determined as 98.73±0.59% at pH 5.0 for 30 °C in a short time. The applications of the isotherm models such as Langmuir, Freundlich, Dubinin–Radushkevich (D–R) isotherms have been studied to evaluated adsorption characteristics of ^{226}Ra onto composite adsorbent. It was found that the processes for ^{226}Ra were exothermic. The thermodynamic parameters such as free energy (DG°), enthalpy of adsorption (DH°) and entropy (DS°) were calculated. Adsorption kinetics of the radium were also studied.

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URANIUM RECOVERY FROM SIMULATED ^{99}Mo PRODUCTION WASTE USING NON-DISPERSIVE MEMBRANE BASED SOLVENT EXTRACTION

Maretha Fourie[1, 2]*, *Willie C. M. H. Meyer*[1, 3], *Derik J. van der Westhuizen*[2], *Henning M. Krieg*[2]

[1]South African Nuclear Energy Corporation SOC Ltd (Necsa), Elias Motsoaledi Street, R104 Pelindaba, P.O. Box 582, Pretoria 0001, South Africa, *e-mail: maretha.fourie@necsa.co.za
[2]Chemical Resource Beneficiation, North-West University, Potchefstroom campus, Private Bag X6001, Potchefstroom 2531, South Africa, e-mail: 20122950@nwu.ac.za
[3]Centre for Applied Radiation Science and Technology, North-West University, Mafikeng campus, Private Bag X2046, Mmabatho 2735, South Africa, e-mail: willie.meyer@necsa.co.za

Keywords: uranium, tributyl phosphate, fission products, acetohydroxamic acid, membrane based solvent extraction, ^{99}Mo

Dispersive solvent extraction and non-dispersive membrane based solvent extraction (MBSX) was investigated for uranium (U) recovery from waste containing nitric acid (HNO_3), acetohydroxamic acid (AHA) and a unique matrix of fission product surrogates present in ^{99}Mo production residue, with tributyl phosphate (TBP) as extractant. Similar U(VI) extraction results (95% with [U(VI)] = 7500 mg L^{-1}) were obtained for both MBSX and dispersive contacting methods and no significant amount of fission products were extracted. AHA did not significantly influence U(VI) or fission product extraction. With MBSX, U(VI) was stripped almost completely from TBP in a single stage using 0.5 M ammonium carbonate ($(NH_4)_2CO_3$), compared to traditional dilute HNO_3 with which complete U(VI) recovery (in a single stage) was not possible. MBSX has been established as a promising technique for U(VI) recovery from a simulated HNO_3 waste stream generated during ^{99}Mo production. Complete U(VI) extraction and stripping in a single membrane contactor may be achieved when using a dispersion liquid membrane (DLM) configuration.

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THE EFFECT OF NITRIC ACID CONCENTRATION ON HIGHER VALENCE AMERICIUM REDUCTION KINETICS

Travis S. Grimes, Bruce J. Mincher*

Aqueous Separations and Radiochemistry, Idaho National Laboratory, 2525 Fremont Ave, Idaho Falls, ID, 83401, USA,
*e-mail: Travis.Grimes@inl.gov

Keywords: americium oxidation, actinide separation, reduction kinetics

Numerous solvent extraction processes have been proposed in an attempt to fully close the nuclear fuel cycle and incorporate recycling of the reusable materials. One common component among the industrially relevant separations systems is the oxidation state manipulation of Pu and Np. Recent efforts to streamline the processes necessary to recycle used nuclear fuel have included oxidizing americium, one of the minor actinides found in the fuel after irradiation. Oxidizing Am(III) to Am(VI) would simplify used fuel recycling by incorporating a group actinide decontamination where U, Pu, Np, and Am are co-extracted in one step and then selectively back extracted into appropriate product streams. Americium(III) oxidation to Am(VI) is easily achieved in high nitric acid medium using the powerful oxidant sodium bismuthate. This process is represented in the following equation:

$$2Am^{3+}+3BiO_3^{-}+10H^{+} \rightarrow 2AmO_2^{2+}+3Bi^{3+}+5H_2O \quad (1)$$

This type of process would require a complete understanding of not only Am(III) oxidation to Am(VI) but also subsequent reduction of the Am(VI) back to Am(III). For this system, the auto reduction rates for Am(VI) to Am(V) and Am(III) are complicated by secondary reactions with radiolysis products produced by the Americium's alpha decay. Another complicating factor which could affect the Am(VI) reduction kinetics include disproportionation reactions in higher acid media. The goal of this project is to monitor the reduction of Am(VI) to Am(V) and Am(III) and determine the kinetic reaction rates, the kinetic reaction orders, and the simultaneous secondary reaction mechanisms. It is envisioned the layers of complexity associated with these types of kinetics can be peeled back and a deeper fundamental understanding of Am(VI) reduction in the presence of higher concentrations of nitric acid and americium metal ions and can be obtained.

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EVIDENCE FOR THE PREDOMINANCE IN AQUEOUS SOLUTIONS OF A MIXED TRIHALOGEN SPECIES, AtIBr⁻: A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY

Ning Guo, Dumitru-Claudiu Sergentu, David Teze, Rémi Maurice, Julie Champion,
Nicolas Galland, Gilles Montavon*

SUBATECH, UMR CNRS 6457, IN2P3, Université de Nantes, Ecole des Mines de Nantes, 4 rue A. Kastler, 44307 Nantes, France,
*e-mail: ning.guo@subatech.in2p3.fr.

Keywords: astatine, mixed trihalogens, extraction methods, density functional theory

Astatine-211 is a promising therapeutic agent for nuclear medicine [1, 2]. Indeed, the radioactive properties of this alpha emitter At-211 make it an effective candidate for targeted alpha therapy, in which it must be bound to adequate targeting agents. Although this fact has triggered many investigations in the last two decades, the basic physical and chemical properties of astatine are still poorly known [3]. Actually, studying the chemical properties of astatine species is particularly difficult since one can only work at ultra-trace concentrations (typically 10^{-11} to 10^{-15} mol×L^{-1}). Therefore, no spectroscopic tool can be used to identify astatine species. The firm identification of such species thus requires combining the outcomes of experiments and computations, for instance based on density functional theory [4–6]. In previous studies, stable At^{+} and AtO^{+} species were identified in acidic and non-complexing aqueous media, which indicates a more "metallic" character of At, compared to the other halogens [7]. At^{+} can form some complexes of the AtX and AtX_2^{-} types (with X = Cl, Br), for which the complexation constants can be determined from the modeling of liquid/liquid extraction curves [4].

In this work, we determine the complexation constants corresponding to the AtI and AtI_2^{-} species with the same methodology, and show that a new species can be formed in solutions containing both Br^- and I^- ions, with an associated complexation constant of 7.5±0.2 (in Log). By comparing this value to computed ones, we identify this species as being $AtIBr^-$, a mixed trihalogen anion. To the best of our knowledge, it is the first time that such a trihalogen species is found stable in solution, and can be even predominant.

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AN IMPROVEMENT IN THE PRETREATING TECHNIQUE FOR DETERMINING RADIONUCLIDES IN SEAWATER

Jianhua He, Yiliang Li, Dekun Huang, Feng Lin, Wu Men, Wen Yu

Third Institute of Oceanography, State Oceanic Administration, Xiamen, 361005, China

Keywords: radionuclides, pretreatment, equipment

An integrated equipment was developed in order to faster the precipitation and filtration process during the analysis of radionuclides, such as Cesium, Strontium, Cobalt, Thorium, Radium, etc., in large volume seawater. The solution could be filtrated immediately, without waiting for settlement, after the reaction and radioactive equilibrium with this equipment, that will Improve pretreatment efficiency dozens of times from several days to less than one hours. Also this equipment is suitable for operation onboard.

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A STUDY ON SALT SEPARATION WITH HIGH THROUGHPUT FROM URANIUM DEPOSITS

S. W. Kwon, J. H. Jeung, S. B. Park, S. W. Paik, D. H. Ahn*

Korea Atomic Energy Research Institute, 989-111 Daedukdaero, Yuseong, Daejeon, 305-353, Korea, *e-mail: swkwon@kaeri.re.kr

Keywords: electrorefining, pyroprocess, high throughput, salt distillation

Pyroprocessing has been developed for the recovery of actinide elements from spent fuel due to its advantages of a compactness, a nuclear proliferation resistance, and a reduction of a secondary waste generation. The solid cathode processing is necessary to separate the salt from the cathode for the preparation of the uranium ingot with a high purity. It is indispensable to increase a throughput of the salt removal process from uranium deposits which is generated on the solid cathode of electro-refiner in pyroprocess. In this study, it was studied on the development of the salt distiller with high throughput for the separation of adhered salt in the uranium deposits generated from the electro-refiner. Some concepts such as a liquid salt separation prior to salt distillation and a porous crucible system were proposed for the enlargement of the throughput. The feasibility of the concepts was examined by the salt separation experiments. The amount of salt to be distilled could be reduced by the liquid salt separation prior to the salt distillation. The residual salt remained in the deposits after the liquid salt separation was successfully removed further by the vacuum distil-

lation. A porous crucible system was introduced for the successful liquid salt separation. Two step weight reductions took place in the porous crucible, whereas the salt weight reduced only at high temperature by distillation in a nonporous crucible. The first weight reduction was caused by the liquid salt penetrated out through the perforated crucible during the temperature elevation until the distillation temperature. After the liquid salt flew out through the perforated crucible by gravity, the weight was kept constant until the salt evaporation temperature. Besides the porous crucible, the concept of multiple crucibles was also proposed. Multilayer crucibles have a benefit to expand the evaporation surface area. It could be concluded that the multilayer porous crucible system is an effective way for the achievement of a high throughput performance in the salt separation process because the liquid salt of the uranium deposits can be separated during temperature elevation for the distillation and high surface area for salt evaporation.

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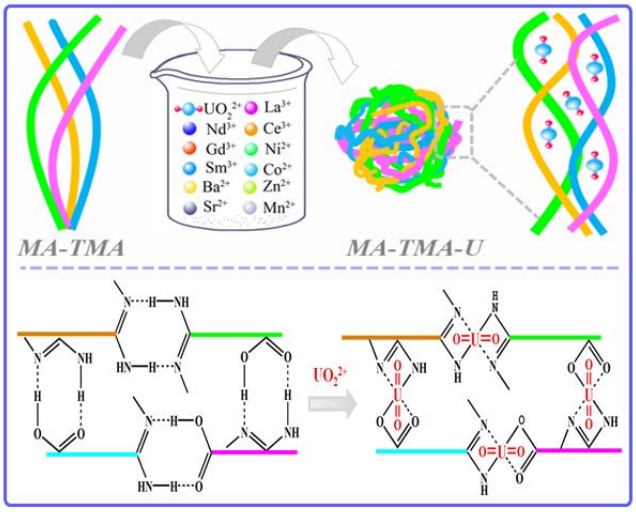
AN ADAPTIVE SUPRAMOLECULAR ORGANIC FRAMEWORK FOR HIGHLY EFFICIENT SEPARATION OF URANIUM VIA *IN SITU* INDUCED FIT MECHANISM

Bo Li, Chiyao Bai, Shuang Zhang, Xiaosheng Zhao, Lei Wang, Yang Li, Kuan Ding, Xi Shu, Shoujian Li, Lijian Ma

College of Chemistry, Sichuan University, Key Laboratory of Radiation Physics & Technology (Sichuan University), Ministry of Education, Chengdu 610064, P. R. China, e-mail: sjli000616@scu.edu.cn

Uranium is one of the most important source materials for nuclear energy industry. Thus, separation and recovery of uranium from various uranium-containing aqueous systems are of great scientific and practical significance. In the present work, on the basis of the unusual coordination structure of UO_2^{2+} [1] combined with the adaptive nature of supramolecular organic frameworks (SOFs) [2, 3], we designed and prepared a novel SOF-based SPE adsorbent (MA-TMA) using N-donor-containing melamine (MA) and O-donor-containing trimesic acid (TMA) as bifunctional building blocks mutually linked via hydrogen bonds. The as-prepared MA-TMA, with rich N-/N- and N-/O-heterocyclic structure throughout its framework, provide accessible coordination geometry and/or ligand environment for uranyl ion, which builds the crucial structural basis for the pre-organized adaptive frameworks closely related to the "induced-fit" and selective recognition of uranyl ion. The main results are as follows: 1) The highest selectivity of 92%, so far unreported, and a considerable capacity of 324 mg g^{-1} for uranium adsorption by MA-TMA are observed in a weak acidic multi-cation solution (pH 2.5), accompanying with a distribution coefficient K_d value of 16000 mL g^{-1}, 100-fold or more over other 11 competitive cations; 2) MA-TMA could reach its limiting saturation capacity of 1028 mg g^{-1} at pH 4.5 in pure-U(VI) solution; 3) Noteworthily, the morphology of MA-TMA changed from the ribbon-like structure in nano-diameter before adsorption into the aggregated granules with a size of tens of microns after adsorption, which would be much more favorable for subsequent solid-liquid separation. Furthermore, possible mechanisms for the selective recognition of uranyl is explored based on experimental characterization and chemical rationale *(Scheme 1)*.



Scheme 1. Possible mechanism of uranium extraction by MA-TMA

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MICRO-CHROMATOGRAPHIC SYSTEMS FOR RADIOCHEMISTRY: AN ORGANIC MONOLITH FOR THE SEPARATION U/EU

Marion Losno[1], Ivan Ferrante[2], Stéphanie Descroix[2], Clarisse Mariet[1]

[1]CEA,DPC,SEARS,LANIE, French Alternative Energies and Atomic Energy Commission, Saclay, France,
e-mails: marion.losno@cea.fr, clarisse.mariet@cea.fr
[2]MMBM Group, Institut Curie Research Center, CNRS UMR 168, Paris, France

Keywords: microfluidics, centrifugal platform, Lab-on-CD, porous polymer monolith, chemical functionalization, anion-exchanger, nuclear spent fuel

The use of a centrifugal microfluidic platform is an alternative to classical chromatographic procedures for radiochemistry. The original design of the microfluidic platform has been thought to fasten and simplify the prototyping process with the use of a circular platform integrating four rectangular microchips made of thermoplastic. The microchips, dedicated to anion-exchange chromatographic separations, integrate a localized monolithic stationary phase as well as injection and collection reservoirs. An ion-exchange support with respect to the *in-situ* light-addressable process of elaboration is specifically designed to be incorporated as radiochemical sample preparation module in microsystem devices.

Since their introduction in the early 1990s polymethacrylate monoliths have emerged as a powerful alternative for microscale separations or sample treatment. Their relatively simple implementation in columns with small internal diameters makes them particularly attractive for the new chromatographic challenges of complex matrices analysis and on-chip separations. Despite their relatively poor ion-exchange capacity due to their highly porous structure, their use as anion exchangers is of large interest for nuclear analysis as numerous separations are based on this process.

A photopolymerized poly(ethylene glycol dimethacrylate-co-allyl methacrylate) monolith has been synthesized. It was then functionalized via a photografting process based on the ene-thiol click chemistry to give anion exchange properties to the monolith. The stationary phase has been optimized to improve its chromatographic performances especially regarding anion exchange chromatography. Synthesis and chromatographic results obtained with this monolith at macro scale and in COC micro-devices will be presented and discuss in term of reproducibility and robustness. Application to analysis of nuclear material will be presented.

Thanks to their unique "easy-to-use" features, centrifugal microfluidic platforms are potential successful candidates for the downscaling of chromatographic separation and especially in the case of radioactive samples. Automation, multiplexing, easy integration in glove-boxes environment and low cost of maintenance are some advantages of the development of centrifugal microfluidic devices. Moreover the low amount of sample needed for the analysis allows the decrease of volume of effluents and the exposition of the operators to radiations during the analysis.

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CERN-MEDICIS (MEDICAL ISOTOPES COLLECTED FROM ISOLDE): A NEW FACILITY

Y. Martinez[1, 2], T. Stora[2], T. E. Cocolios[1]; for the CERN-MEDICIS collaboration

[1]KU Leuven, Instituut voor Kern- en Stralingsfysica, 3001 Leuven, Belgium, e-mails: yiselmp@cern.ch, thomas.cocolios@fys.kuleuven.be
[2]CERN, CERN, CH-1211 Geneva 23, Switzerland, e-mail: thierry.stora@cern.ch

Keywords: CERN-MEDICIS, ISOLDE, CERN, radioisotope, targeted alpha therapy (TAT), cancer, PET, imaging

The CERN-MEDICIS laboratory is located in an extension of the CERN-ISOLDE radioactive ion beam facility in Geneva, Switzerland. Since more than 80% of the proton beams passes through the ISOLDE targets without interacting, the MEDICIS targets can be placed right after to produce secondary radioactive isotopes and benefit from the otherwise lost beam.

With the development of the facility, many innovative radioisotopes will become available for offline research. Applications in fundamental studies in cancer research and new imaging and treatment protocols in cell and animal models will follow. On a weekly basis, 500 MBq isotope batches, purified by electromagnetic mass separation combined with chemical methods can be collected. Also, within the project and thanks to the expertise of JRC-ITU to build ^{225}Ac/^{213}Bi generators for targeted alpha therapy trials, a proposal to test beam intensities of ^{225}Fr/Ra achieved with UC_x and ThC_x targets at ISOLDE has been approved. These beams are foreseen as an alternative way to produce the ^{225}Ac isotopes needed for this generator. These tests will start with the first ISOLDE beams in 2016.

A dedicated facility at CERN for the production of innovative isotopes, by joining forces with leading institutes in life and medical sciences is an exciting prospect for this scientific program in the coming years. The facility will be nearing completion in 2016. The results of tests with activation of an UC_x target will be reported.

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EXPERIMENTAL AND MODELING STUDY OF FISSION PRODUCTS EXTRACTION WITH N,N-DIALKYLAMIDES

P. Moeyaert[1], C. Sorel[1], J.-F. Dufrêche[2], M. Miguirditchian[1]*

[1]French Alternative Energies and Atomic Energy Commission, CEA, Nuclear Energy Division, Radio Chemistry & Processes Department, DRCP, BP 17171, F-30207 Bagnols sur Cèze, France, *e-mail: pauline.moeyaert@cea.fr

[2]Institut de Chimie Séparative de Marcoule, Université de Montpellier 2, UMR 5257 CEA / CNRS / UM2 / ENSCM BP 17171, F-30207 Bagnols sur Cèze cedex, France

Keywords: solvent extraction, fission products, N,N-dialkylamides, TBP, modeling

In the framework of the development of Generation IV reactors, new solvent extraction processes are under development for the reprocessing of spent nuclear fuels. N,N-dialkylamides demonstrated their potentiality in the recovery and recycling of fissile materials, plutonium and uranium, as an alternative to TBP. New investigations have been recently undertaken with N,N-dialkylamides to develop an innovative solvent extraction process devoted to plutonium and uranium separation. If uranium extraction with N,N-dialkylamides has been already intensively studied during the last decades, the extraction of fission products by N,N-dialkylamides remains poorly investigated. Among the fission products present in the spent fuel, ruthenium and technetium exhibit a singular behaviour in reprocessing operations performed by solvent extraction. Batch experiments were performed to study their behaviour towards their extraction by N,N-dialkylamides and to determine extraction isotherms. All extraction experiments were performed at 25 °C by contacting N,N-dialkylamides diluted in TPH with aqueous solutions of Tc or Ru spiked with ^{99m}Tc or ^{106}Ru respectively, at different nitric acid concentrations (from 0.1 to 6 M) and different uranium concentrations (from 0 to 200 $g.L^{-1}$). In order to understand and simulate the behaviour of Tc and Ru in the solvent extraction process, computational calculations were performed. Experimental distribution ratios of technetium(VII) and ruthenium(III) were described with a physicochemical model based on the application of the mass action law on each extraction equilibrium and assumptions about the stoichiometry of the complexes formed in organic phase. Deviations from ideality in aqueous phase were estimated by calculating the activity coefficient of each component according to the “simple solutions”. These models were then validated by comparing experimental and calculated organic concentrations. In addition, speciation studies – including EXAFS and ESI-MS experiments – were performed to confirm the stoichiometries of the complexes supposed in organic phase to model correctly the experimental isotherms. Finally, these results were compared with data obtained with the TBP solvent currently used in the PUREX process in order to compare both solvents towards fission products extraction.

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SEPARATION OF ^{230}Pa FROM RADIONUCLIDES GENERATED IN NATURAL THORIUM IRRADIATED BY PROTONS

Valentina Ostapenko[1, 2]*, *Aleksandr Vasiliev*[1, 2], *Elena Lapshina*[2], *Stanislav Ermolaev*[2], *Boris Zhuikov*[2], *Stepan Kalmykov*[1]

[1]Chemistry Department, Lomonosov Moscow State University, Leninskie Gory 1, 119991, Russia, *e-mail: ostapenkochem@gmail.com
[2]Institute for Nuclear Research of Russian Academy of Sciences, 60th October Anniversary Prospect, 7a, Moscow 117312, Russia

Keywords: ^{230}Pa, ^{230}U, irradiated thorium target, separation of radionuclides

^{230}U ($t_{1/2}$ = 20.8 days) and its daughter ^{226}Th ($t_{1/2}$ = 31 min) are promising radionuclides for application in targeted alpha-therapy. ^{230}U is a daughter radionuclide of ^{230}Pa which may be produced from natural thorium irradiated with medium-energy protons via nuclear reaction ^{232}Th(p,3n)^{230}Pa. Other α-emitters such as ^{225}Ac and ^{223}Ra, as well as a great number of fission and spallation products are also generated in a thorium target. Isolation of medicine-applicable ^{225}Ac and ^{223}Ra from the thorium target was described earlier [1, 2]. The aim of this work is isolation of ^{230}Pa in parallel with ^{225}Ac.

Targets of ^{232}Th were 40–60 µm thickness and 100–300 mg weight. Foils were irradiated at the INR linear accelerator by a beam of protons with energy of 110 MeV and a current of about 5 mA. Irradiated thorium was dissolved in 6 M HCl with small addition of concentrated HNO_3. Isolation of ^{230}Pa was carried by liquid-liquid extraction and chromatography.

The extraction of protactinium by methyl-isobutyl ketone from HCl solutions was studied in concentration range from 3 to 7 M HCl. The optimum concentration for the extraction of protactinium was 5 M HCl. However, ^{95}Nb, ^{103}Ru, ^{126}Sb were also extracted with ^{230}Pa. Organic phase was washed with mix 4% $H_2C_2O_4$ – 5 M HCl for removing traces of ^{95}Nb. Then ^{230}Pa was re-extracted from the organic phase with 8% $H_2C_2O_4$. Finally ^{230}Pa was separated from ^{126}Sb on AG 1×8 (anion exchange resin) using 3M HCl. As a result, the overall chemical yield of ^{230}Pa was 95% and radionuclide impurities below 0.5%. The obtained ^{230}Pa can be used as a source of ^{230}U for a ^{230}U/^{226}Th generator.

Acknowledgement

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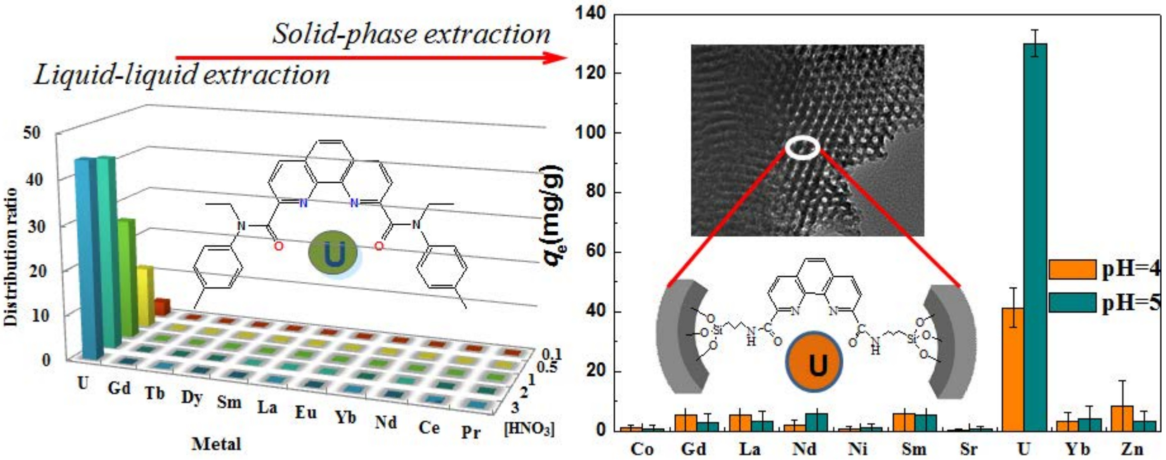
PHENANTHROLINE-BASED TETRADENTATE LIGAND FOR SELECTIVE U(VI) CAPTURE: FROM LIQUID-LIQUID EXTRACTION TO SOLID-PHASE EXTRACTION

Li-Yong Yuan[1], *Lin Zhu*[1], *Xin-Rui Zhang*[1], *Zhi-Fang Chai*[1, 2], *Wei-Qun Shi*[1]

[1]Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China, e-mail: shiwq@ihep.ac.cn
[2]School of Radiological & Interdisciplinary Sciences, Soochow University, Suzhou 215123, China

A phenanthroline-based tetradentate ligand with hard–soft donors combined in the same molecule, N,N-diethyl-N,N'-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen), was designed and synthesized for the aim of selective extraction towards actinides over lanthanides. In liqiud-liqiud extraction, the extraction behaviors of U(VI) by Et-Tol-DAPhen in 3-nitrobenzotrifluoride diluents were investigated in detail. It was found that the extraction shows fast kinetics of less than 5 min, high extraction capacity, acidity and nitrate ion concentration dependency, and excellent selectivity towards U(VI) over lanthanides. Stripping experiments indicated that a back extraction efficiency of almost 100% could be achieved via only one stage operation using 5% Na_2CO_3 solution. In solid-phase extraction, a novel mesoporous sorbent, KIT-6-DAPhen, was fabricated by covalently grafting phenanthrolineamide groups onto a large pore three-dimensional cubic silica (KIT-6) support, and was used as sorbents for selective U(VI) capure from aqueous solution. From the fast sorption kinetics of less than 2 h, the superior sorption capacity of 328 mg/g to most of the existing functionalized mesoporous silicas, and desirable selectivity for U(VI) ions over a range of competing metal ions, it is concluded that that KIT-6-DAPhen is indeed an efficient and feasible sorbent for U(VI) uptake from aqueous solution. Density functional theory (DFT) calculation combined with FTIR and EXAFS characterization was performed to understand the U(VI) sorption mode onto KIT-6-DAPhen, which indicated that U(VI) ions were sorbed in hydroxide complexes form by the phenanthrolineamide groups, and no sorption of nitrate ions as both counter ions and chelating agent occurred. This work promises to provide new data for assessing the feasibility of Et-Tol-DAPhen, as well as other new ligand with hard–soft donors combined in the same molecule, applied in the group separation of actinides over lanthanides.



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Short presentations

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TOWARDS AN AUTOMATIC PROCEDURE FOR THE PRODUCTION OF ASTATINATED RADIOPHARMACEUTICALS

Emma Aneheim[1]*, Sture Lindegren*[1]*, Holger Jensen*[2]

[1]Targeted Alpha Therapy group, Department of Radiation Physics, Sahlgrenska Academy at University of Gothenburg,
SE41345 Gothenburg, Sweden
[2]PET and Cyclotron Unit, KF-3982, Copenhagen University Hospital, DK 2100, Copenhagen, Denmark

Keywords: astatine, automation, antibody labeling

In recent time targeted radiotherapy of cancer tumors have gained an increasing interest. For microscopic tumors or single cancer cells, alpha therapy is especially interesting due to the high LET of the alpha particles. One promising nuclide for targeted alpha therapy is ^{211}At. ^{211}At decays with 100% alpha-emission along two different branches and has a half-life of 7.2 hours. The Targeted Alpha Therapy group at Sahlgrenska Academy in Sweden has been performing research regarding alpha therapy using astatine and monoclonal antibodies for intraperitoneal treatment of disseminated ovarian cancer for over fifteen years. The research has been taken from bench to bedside including a number of preclinical studies and a phase I clinical trial on nine patients with recurrent ovarian cancer. However, to be able to move forward towards future phase II/III studies, the current manual synthesis of the radiolabeled antibodies would benefit from being automated. In this work such an automation has been performed and evaluated.

The automation has been performed by adapting a commercially available radiopharmaceutical module from Scintomics Gmbh (Hot Box III) to not only perform labeling but to also automatically produce astatine from irradiated target material. The ^{211}At used is produced in a cyclotron (at Copenhagen University Hospital) by alpha particle activation of ^{209}Bi through the reaction ^{209}Bi(α, 2n)^{211}At. This is facilitated using ca 30 MeV alpha particles. The commercially available monoclonal antibody Trastuzumab has been used for labeling and a SKOV3 cell line to investigate maintained immunoreactivity after the automatic labeling procedure.

Purified monoclonal antibodies labeled with astatine have been automatically produced from irradiated target material with reasonable yield using the novel equipment. The automatic astatine distillation procedure has been found to be able to deliver astatine to the synthesis with high yield. This has also been demonstrated to be possible using different types of chemical astatine delivery systems. The product has been shown to be radiochemically pure and to maintain its immunoreactivity throughout the process. These results have been obtained after modifications of the manual synthesis and distillation processes as well as an extensive equipment development.

This work has shown that it is possible to produce astatinated radiopharmaceuticals such as labeled monoclonal antibodies from irradiated target material using a custom made automatic system integrating labeling with a commercial module and astatine distillation.

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RADICHEMICAL DISTRIBUTION OF HAZARDOUS NATURAL RADIONUCLIDES DURING MONAZITE MINERAL PROCESSING

Mostafa M. Hamed, M. A. Hilal, E. H. Borai

Hot Laboratories and Waste Management Center, Atomic Energy Authority, P.O. Box 13759, Cairo, Egypt

Keywords: low-grade monazite natural radionuclides, radium, thorium, annual effective dose

It is very important to calculate the radioactivity concentration for low-grade monazite ore (50%) and different other materials produced as results of chemical processing stages to avoid the risk to workers. Chemical processing of low-grade monazite pass through different stages, washing by hydrochloric acid and digested with sulfuric acid and influence of pH on the precipitation of rare earth elements has been studied. The radioactivity concentrations of ^{238}U(^{226}Ra) and ^{232}Th as well as ^{40}K were calculated in crude low-grade ore and found to be 54435±3138, 442105±29200 and 5841±345Bq/kg, respectively. These values are greatly higher than the exempt levels 25 Bq/kg. After chemical digestion of the ore, the results demonstrated that un-reacted material contains significant radioactivity reached to approximately 8, 13 and 23% for ^{238}U, ^{232}Th and ^{40}K, respectively. The results show that 60% of ^{232}Th are located in the digested white slurry with small portions of ^{238}U and ^{40}K. Most of ^{238}U radioactivity is extracted in the green phosphoric acid which produced from conversion of P_2O_5 by H_2SO_4 into phosphoric acid. The average values of the Ra_{eq} for monazite ore, un-reacted black precipitate, weight precipitate, brown precipitate and crystalline material samples were calculated and found to be 687095±44921, 85068±5339, 388381±22088, 313046±17923 and 4531±338 Bq/kg, respectively. The calculated values of Ra_{eq} are higher than the average world value (it must be less than 370 Bq/kg). Finally the external hazardous, internal hazardous and $I_{\gamma r}$ must be less than unity. This means that specific radiation protection program must be applied and implemented during monazite processing.

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INTERCOMPARISON NaI(Tl) AND HPGe SPECTROMETRY TO STUDIES OF NATURAL RADIOACTIVITY ON GEOLOGICAL SAMPLES

Nguyen Quoc Hung, Tran Thien Thanh, Huynh Dinh Chuong, Chau Van Tao*

Department of Nuclear Physics, Faculty of Physics and Engineering Physics, VNUHCM-University of Science, 227, Nguyen Van Cu Street, District 5, Ho Chi Minh city, Vietnam, *e-mail: ttthanh@hcmus.edu.vn

Keywords: efficiency calibration, environment measurement, NaI(Tl) detector, HPGe detector.

Gamma spectrometry with NaI(Tl) detector is a well-developed and consolidated method for measurements of the naturally occurring terrestrial gamma radiation of ^{40}K and the decay series of ^{232}Th and ^{238}U have broadly been used from mineral exploration to environmental radiation monitoring providing quantitative information. It has a high detection and can work in condition of room temperature. The concentration of ^{238}U and ^{232}Th are then evaluated detecting the

γ-rays produced by ^{214}Bi (1764.5keV) and ^{208}Tl (2614.5keV) respectively.

In the first step, the kit standard samples (RGK, RGTh and RGU) have been used to experimentally calibrate the efficiency of the NaI(Tl) detector for volume sources on end-cap detector. The geological samples were collected from an environment on Vietnam by Southern geological mapping division and the activities of radionuclides in the geological sample have been determined using NaI(Tl) detector.

In parallel, the results of *in situ* γ spectra using NaI(Tl) detector have been compared with the laboratory measurements by using HPGe detectors on geological samples.

Based on these results, the natural activity of sample is determined with a maximum deviation of NaI(Tl) and HPGe spectrometry of about 6%. The reveal some discrepancies that are discussed.

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LIQUID SCINTILLATION COUNTING METHODLOGY FOR ^{99}Tc ANALSYIS IN VARIOUS AQUEOUS MATRICES

Mumtaz Khan[1]*, *Wooyong Um*[1, 2]

[1]Nuclear Environment Laboratory, Division of Advance Nuclear Engineering, Pohang University of Science and Technology, Pohang, South Korea, *e-mail: mumtazkhan03@postech.ac.kr
[2]Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, Washington 99354, USA, e-mail: wooyong.um@pnnl.gov

Keywords: liquid scintillation counting, Ultima Gold, Ultima Gold LLT, ^{99g}Tc

Current work presented a unique approach for liquid scintillation counting (LSC) analysis of single-radionuclide samples containing appreciable organic or inorganic quench for deionized water, tap water, groundwater, seawater, and urine samples. Analytical parameters were measured in the presence of various quench impurities including 1.9 to 11,900 ppm dissolved solids and nitromethane using liquid scintillation counter. Counting efficiency was found to be 91.66% for Ultima Gold LLT (ULG-LLT) and Ultima Gold (ULG). Relative error in spiked ^{99g}Tc samples was ±3.98% in ULG and ULG-LLT cocktails. Minimum detectable activity was determined to be 25.3 mBq and 22.7 mBq for ULG-LLT and ULG cocktails, respectively. A pre-concentration factor of 1000 was achieved at 100 ˚C for 100% chemical recovery. Current method facilitates to select cocktail according to matrices chemistry of the ^{99g}Tc sample. The method has more sensitivity than previous reports and a range of matrices can be analysed.

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A PRELIMILARY INVETIGATION OF STABLE CARBON AND NITROGEN ISOTOPE VALUES IN TAIWAN MILK

Chuan-Pin Lee[1]*, *Ming-Chee Wu*[1], *Jih-Tay Hsu*[2], *Sung-Yun Lin*[3], *Yu-Lin Tu*[1], *Lin-Chen Kang*[1], *Chun-Hua Pan*[1]

[1]Department of Earth Sciences, National Cheng Kung University, Address1, University Road, Tainan City, 70101, Taiwan, *e-mail: cplee@mail.ncku.edu.tw
[2]Department of Animal Science and Technology, National Taiwan University, Taipei, 10673, Taiwan
[3]Technical Service Center, National Animal Industry Foundation, Ping-Tung, 900, Taiwan

Keywords: carbon, nitrogen, milk, argillite, granite

The aim of this study was to investigate the distribution of δ^{13}C and δ^{15}N of bulk milk in Taiwan. A total of 25 domestic milk samples and 8 commercial milks from several countries (Australia, New Zealand, Italy, U.S, Japan) in Taiwan supermarket were collected and analysed by a Stable Isotope Ratio Mass spectrometer connected by Elemental Analyser. Principal carbon and nitrogen component analysis showed a similar result between domestic and international milk samples after freeze-drying. It is found that δ^{13}C and δ^{15}N in domestic samples could be easily discriminated between Australia and New Zealand due to different feeding ways. Therefore, the isotopic composition of milk samples may be utilized as a good biomarker in commercial milks that conveys reliable isotopic information to track milk to their regional origin.

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POLONIUM ^{210}Po AND RADIOLEAD ^{210}Pb IN CALCIUM AND MAGNESIUM SUPPLEMENTS

Dagmara I. Strumińska-Parulska, Bogdan Skwarzec

University of Gdańsk, Faculty of Chemistry, Environmental Chemistry and Radiochemistry Chair, Wita Stwosza 63, 80-952 Gdańsk, Poland

Polonium ^{210}Po ($T_{1/2}$ = 138.376 days) and radiolead ^{210}Pb ($T_{1/2}$ = 22.2 years) appear at the end of the decay-chain of uranium ^{238}U and are radio-ecologically interesting natural elements to investigate due to their high radiotoxic characteristics. These radionuclides are introduced into the biosphere through various routes of terrestrial and marine radioecological pathways and are continuously deposited from the atmosphere in association with aerosols. Both ^{210}Po and ^{210}Pb radionuclides are, together with radon, the natural radioactive material delivering the highest natural dose to living organisms.

The aim of the study was: activities determination of polonium ^{210}Po and radiolead ^{210}Pb in 17 popular calcium and magnesium supplements for adults. The research material covered different mineral (calcium carbonate, dolomite, chalk, marine shells) and organic calcium compounds (calcium lactate, gluconate, pantothenate and diglycinate).

The study showed ^{210}Po and ^{210}Pb were present in analyzed calcium and magnesium supplements and could be an additional source of ^{210}Po and ^{210}Pb for the consumers. The values of ^{210}Po and ^{210}Pb activities concentration in analyzed Ca pharmaceutics ranged from 0.07 to 3.88 and 0.08 to 2.97 $mBq \cdot g^{-1}$ respectively, and the maximum annual effective radiation dose from RDI value of 1 g of Ca consumption was calculated at 12.7 µSv from ^{210}Po and 5.57 µSv from ^{210}Pb. The values of ^{210}Po and ^{210}Pb activities concentration in analyzed Mg pharmaceutics ranged from 0.020 to 3.84 $mBq \cdot g^{-1}$ and from 0.02 to 3.85 $mBq \cdot g^{-1}$ respectively, and the maximum annual effective radiation dose from 400 mg of Mg consumption was calculated at 3.38 µSv from^{210}Po and 2.3 µSv from ^{210}Pb.

Inorganic samples were richer in ^{210}Po in comparison to organic. Also natural origin supplements, especially those made from sedimentary rocks, were richer in polonium and radiolead in comparison to the rest of analyzed samples.

Acknowledgement

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A PROCEDURE TO ESTIMATE THICKNESS OF INNER DEAD-LAYER OF N TYPE HPGe DETECTOR USING MCNP CODE

Tran Thien Thanh, Huynh Dinh Chuong, Le Thi Ngoc Tran, Nguyen Quoc Hung*

Department of Nuclear Physics, Faculty of Physics and Engineering Physics, VNUHCM-University of Science, 227, Nguyen Van Cu Street, District 5, Ho Chi Minh city, Vietnam, *e-mail: ttthanh@hcmus.edu.vn

Keywords: HPGe detector, gamma spectrometry, optimised detector model, dead-layer, MCNP code, detection efficiency

Nowadays, HPGe detectors are commonly used for gamma spectrometer, mainly because of its high resolution, that can applied for the analysis of radioisotopes in environment or radioactive waste. The accurate results of analysis can only be achieved when detection efficiency of HPGe detector is known exactly. Monte Carlo simulation has been widely used for full-energy peak efficiency (FEPE) calculation of HPGe detectors.

The main purpose of this paper is to improve the reliability and the accuracy of the FEPE values calculated by the Monte Carlo simulation for gamma spectrometry. It is necessary to determine exactly the characteristic parameters of the spectrometer, especially the geometry of the HPGe detector. For N type HPGe detector, the thickness of inner dead-layer is an important parameter which affects significantly FEPE values. However, it is difficult to determine the thickness of inner dead-layer by the experimental method. So, a procedure to estimate the thickness of inner dead-layer of N type HPGe detector using MCNP code is presented.

In this work, a model of gamma spectrometer, which includes a N-type coaxial HPGe detector, source support and shielding chamber, is constructed detailed by MCNP5 code. The shape and dimensions of HPGe detector are determined by the radiography to characterize accurately geometry for Monte Carlo simulation. In there, the rounded parts at front corners and hole bottom of Germanium crystal are carefully attended. Experimental measurements and simulations are carried out with standard point sources: ^{54}Mn, ^{57}Co, ^{60}Co, ^{88}Y, ^{109}Cd, ^{134}Cs, ^{137}Cs, ^{152}Eu at distance 5 and 10 cm from source to detector. Experimental efficiencies are corrected summing coincidence effect by ETNA software. The adjustment of Lithium inner-dead layer thickness is performed in order to obtain relative deviation below 2% between experimental efficiency and simulated efficiency with energies into range 88-1836 keV.

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FLUORESCENT TPE-BASED SENSOR FOR URANIUM RECOGNITION WITH AIE CHARACTERISTICS

Jun Wen, Sheng Hu, Xiaolin Wang*

Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, 621900, Sichuan Province, China,
*e-mail: junwen@caep.cn

Uranium is a representative element of an actinide metal that has naturally radioactivity and widely distributed in the environment [1]. Uranium is one of the main fuel in nuclear energy generation, and it also has been used in nuclear weapons [2]. With the growing human demand for nuclear energy, the worldwide uranium consumption is continuous increasing. For uranium, the most stable and common ionic form is appears as a complex of the uranyl ion (UO_2^{2+}), because uranyl is water soluble, it is readily migrated to environment. Unfortunately, uranium is radioactive and chemically toxic, it was reported that human exposure to uranium could give rise to lung cancer, urinary system disease and genetic diseases.

Considering the widespread use of uranium and its toxic properties, the development and improvement of analysis methods for the determination of uranium are vital. Therefore, many techniques have been used for the determination of uranium. Among these analysis methods, fluorescence detection is a simple, rapid, highly selective, and low-cost method for metal ion determination. However, only few reports on the application of this technique to uranium ion analysis have been published [3, 4].

Herein, 2-(4, 5-dihydrothiazol-2-yl) phenol containing TPE derivative is synthesized and it optical properties are investigated. This molecular can function as "turn-off" fluorescent chemosensors for uranyl ions in aqueous solution. Uranyl can be detected by the naked eye a owing to the AIE phenomenon. The sensor showed high selectivity for uranyl compared to all other metals tested, and this recognition displayed good anti-interference qualities. This sensor has potential applications in environmental systems for uranyl ion detection.

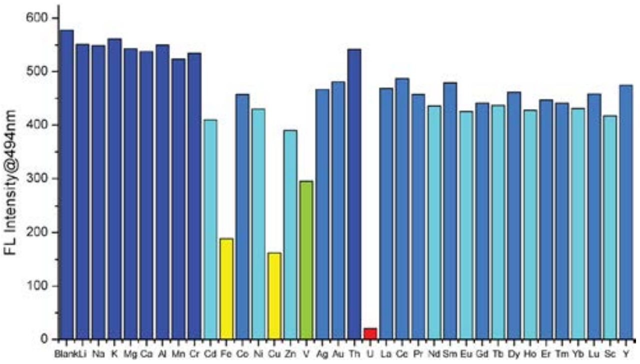

Fig. 1. Column diagrams of the fluorescence intensity of TPE-T+M^{n+} at 494 nm. TPE-T (10 mm) at a f_w of 95 % upon the addition of 2 equivalent of metal ions

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CAEN ELECTRONIC INSTRUMENTATION FOR PHYSICS EXPERIMENTS

Gianni Di Maio

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OVERVIEW OVER SOME RECENTLY DEVELOPED EXTRACTIONCHROMATOGRAPHIC RESINS AND THEIR APPLICATION IN RADIOANALYSIS AND RADIONUCLIDE PRODUCTION

Steffen Happel, Carina Dirks, Aude Bombard*

TrisKem International, 3 Rue des Champs Géons ZAC de, L'Éperon, 35170 Bruz, France, e-mail: shappel@triskem.fr

Keywords: extraction chromatography, decommissioning, radionuclide production, environmental monitoring

An overview will be given over some recently developed, commercially available extraction chromatographic resins and their respective application in environmental monitoring, decommissioning and the production of radionuclides.

Examples shown will include amongst others:

- TBP Resin and its use for Sn-126 determination in decommissioning samples, as well as its use for the separation of Sn from large amounts of Cd (e.g. for production of Sn-117m) [1]

- TK100 and TK101 Resins, both finding use in the direct concentration and separation of Sr, Pb respectively, from water samples at pH 2–7, thus eliminating the need for preconcentration steps. Special focus will be placed on the rapid determination of Sr-89/90 in emergency water samples using TK100 Resin and the direct determination of Pb-210 from up to 5L samples using TK101 Resin discs [2]
- ZR Resin for the separation of Zr, Ti and Ge from their respective target materials for use in radiopharmaceutical applications [3]

References

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[3] Dirks et al.: On the development and characterisation of an hydroxamate based extraction chromatographic resin, poster presented at the 2016 RRM conference, October 25th–30th, Iowa city, IA, USA

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ADVANCES IN DETECTOR READOUT ELECTRONICS FOR NUCLEAR SPECTROSCOPY

Wolfgang Hennig

XIA LLC, 31057 Genstar Road, Hayward, CA 94555, USA, e-mail: whennig@xia.com

XIA LLC produces advanced X-ray and gamma-ray digital signal processing electronics and related instruments with applications in research and industry. Generally speaking, our instruments fall into three broad categories – supporting X-ray detectors, gamma-ray detectors, and ultra-low background counting. Our DXP X-ray detector electronics span the spectrum from low cost OEM cards for handheld and benchtop applications to modular PXI systems and standalone units for ultra-high rate spectroscopy at synchrotrons and elsewhere. Our DGF gamma-ray detector electronics cover an ever wider range of research applications from pulse shape analysis using high speed scintillators to very high energy resolution HPGe spectrometry, to coincidence data collection in large nuclear physics detector arrays. Our ultra-low background instrumentation combines anticoincidence and pulse shape analysis to reliably count samples producing only a few counts per day.

Continuous improvements in digital processing components allow the design of data acquisition modules with ever more channels, higher digitization rates, and higher throughput. Our presentation will give an overview of XIA's latest electronics and their use in a variety of nuclear physics applications. Special focus will be on the recently introduced FalconX ultra-high rate X-ray processor and the Pixie-4 Express gamma-ray processor.

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NUCLEAR MEASUREMENT SOLUTIONS OF GAMMA TECHNICAL CORPORATION

János Petrányi

Gamma Technical Corporation, Illatos út 9, 1097 Budapest, Hungary, e-mail: petranyi@gammatech.hu

Keywords: nuclear measurement techniques, scintillation, radiation monitoring, measuring instruments

It is my great pleasure to introduce the activity and product line of our company. Gamma Technical Corporation was founded in 1920 and has been developing and manufacturing radiation measuring instruments for more than 50 years. Our company has always been involved in R&D of innovative technologies. Today we offer unique solutions in the field of radiation detection, measurement and identification such as portable, shielded activity measuring instruments, radiological food tester, complex building monitoring, onboard radiation reconnaissance systems and radiation portal monitors. We manufacture highly customizable intelligent scintillation probes with integrated analyser and a wide range of scintillation crystals for various radiation counting and spectrometry tasks, based on our own crystal-rowing facility, including sandwich scintillators for the simultaneous measurement of different kinds of radiation. Our portfolio also includes handheld and fixed radiation measuring devices, which are designed to withstand harsh environmental conditions due to their rugged, military construction. We can provide complete instrumentation for nuclear measurement, research and education. Measuring systems, including intelligent nuclear detector(s), lead shielding, displaying and analytical software are available for a wide range of applications. Gamma offers complex monitoring stations for both outdoor and indoor use, customized for area, building, region or countrywide scale monitoring, radioactive emission monitoring, air or water quality surveillance purposes.

Our main products in the field of nuclear measurement:
- GM tube based radiation measuring instruments,
- scintillation crystals and detectors,
- radiation portal monitors,
- radioactive particle monitoring systems,
- local and countrywide monitoring and early warning systems,
- radiation reconnaissance devices,
- radioactive emission monitoring systems,
- meteorological instruments,
- respiratory protective equipment.

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PHYSICS, NO NUMEROLOGY

Wolfram Westmeier, Klaus Siemon

Gesellschaft für Kernspektrometrie mbH, D-35085 Ebsdorfergrund, Germany

Keywords: nuclear spectrometry, physics of interaction, peak-shapes, baseline, resolution, tailing, spectrum analysis

There is no reason to assume simple mathematically defined functions that shall describe the shape of peaks in photon or particle spectra, or the course of the baseline, i.e. the background under a peak or multiplet, or the tailing function(s) to a peak. One can deduce the characteristic shape of these spectral properties from the physics of interactions of a photon or particle between emission and complete registration. The description of these interactions leads to the physics-oriented shape description which can be mathematically formulated and solved. For proper application of the method one also has to include the propagation and handling of electronic signals in the description.

This method of physics-oriented spectrum analysis is applied to the analysis of spectra from scintillation detectors (e.g. NaI(Tl), LaBr3(Ce), CeBr3, BGO, CsI, others), high resolution photon semiconductors (e.g. HPGe, CZT, CdTe) and from alpha-particle detectors [1].

Examples will be shown of spectrum analyses with the spectrum analysis programs SODIGAM (scintillator spectra, also good for X-ray spectra from proportional counters), GAMMA-W (high-resolution gamma-ray spectra from HPGe and Ge(Li) detectors) and ALPS (alpha particle spectra from Si-semiconductors and gridded ionisation chambers).

As an example for the resolving power of physics-oriented analyses the figure shows an alpha spectrum measured with a Si-semiconductor detector from a sample of granite powder. All peaks from the complete decay chains of ^{238}U and ^{232}Th are analysed and quantified to better than ±25%. Thus, one can now make nuclide-specific alpha spectrometry but without time-consuming and expensive chemistry!

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POSTER PRESENTATIONS

Actinide analytical chemistry

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GCMS ANALYSIS OF ORGANIC COMPOUNDS ON PLUTONIUM

Paul Heads, Chris Poile, Pam Thompson*

Department of Nuclear Analytical Science, AWE, Aldermaston, Reading, RG7 4PR, England, *e-mail: Paul.heads@awe.co.uk

Keywords: GCMS, plutonium

The actinides analysis facility at AWE performs a wide range of chemical analysis in support of all aspects of AWE's programmes involving actinide material. This mostly consists of elemental and isotopic analysis of the actinide material, but can also include analysis of remnant material from the manufacturing process.

During the milling of plutonium swarf is produced and collected at the bottom of the lathe, along with any machining grease. This organic material and swarf is then processed and the plutonium material is reclaimed and put back into the manufacturing process. GCMS analysis of the plutonium swarf can give analytical information about the manufacturing process, and what organic compounds were used. Sampling in this instance has been performed using SPME headspace and liquid immersion techniques. The resulting samples were then analysed by GCMS, on a unique instrument that has been modified to fit an auto-sampler and injection port into a fume cupboard for the analysis of contaminated samples.

SPME sampling was performed with an infield headspace sampler, and a fibre consisting of divinylbenzene/carboxen/polydimethylsiloxane. Liquid immersion sampling is performed with DCM. The results from the SPME headspace analysis will be discussed, along with the effectiveness of this technique. The results from the liquid immersion technique will also be discussed, and a comparison of the two techniques will be considered for future analysis.

The final results taken from the mass spectra show good agreement with common lubricants used in machining processes. This work is part of on-going compatibility analysis with the production process and demonstrates the ability to identify organic impurities on metal samples. This ability to analyse highly radioactive plutonium samples by GCMS is a unique capability to AWE.

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DEVELOPMENT OF AN ANALYTICAL PROCEDURE FOR THE SIMULTANEOUS DETERMINATION OF Np AND Pu IN CLAY SAMPLES

T. Renz[1, 2], M. Plaschke[1], F. Quinto[1], M. Lagos[1], A. Bauer[1], H. Taubald[2], H. Geckeis[1]*

[1]Institut für Nukleare Entsorgung, Karlsruher Institut für Technologie, Hermann-von-Helmholtz-Platz 1,
76344 Eggenstein-Leopoldshafen, Germany, *e-mail: markus.plaschke@kit.edu
[2]Universität Tübingen, Isotopengeochemie, Wilhelmstraße 56, 72074 Tübingen, Germany

Keywords: nuclear waste disposal, clay, mass spectrometry

The actinides ^{237}Np and Pu are among the most important contributors to the long-term radiotoxicity of nuclear waste. Clay or clay-rich materials are considered in many countries as potential host rocks for the long-term, safe and at-depth disposal of high-level nuclear waste, as well as serving as major technical constituents in repository systems. We present an analytical procedure for the simultaneous determination of Np and Pu isotopes in clay (or clay-rich) samples using ICP-MS. For the determination of ^{237}Np a long-lived isotope pure enough to serve as isotopic yield tracer is not available. Therefore, we investigated the suitability of a Pu isotope as potential non-isotopic yield tracer for the determination of ^{237}Np on the basis of a previous study [1]. Clay samples are spiked with standard solutions of ^{242}Pu and ^{237}Np. Our analytical procedure includes the following steps:

a) leaching of the actinides from the spiked clay samples,
b) redox adjustments of Np and Pu,
c) pre-concentration of Np and Pu using iron hydroxide co-precipitation,
d) redox adjustment of Pu prior to the column separation,
e) chromatographic co-extraction of Pu and Np from the sample matrix and
f) determination of the actinides using ICP-MS.

The procedure is successfully applied to montmorrilonite and illite clay samples up to 1g sample size. High chemical yields with values between 80 and 90% were obtained for both nuclides. The suitability of a Pu isotope as non-isotopic tracer for determination of ^{237}Np is indicated by the chemical yield ratios of the two nuclides (yield$_{Np}$/yield$_{Pu}$). Values close to one were obtained evidencing identical behaviour of the two nuclides during the procedure. It turned out that accurate pH adjustment during the reductive co-precipitation (step c) and short processing times (steps b–d) are crucial steps in order to obtain high chemical yields and yield ratios close to one.

The presented method is particularly developed with regard to ultra-trace level determinations using accelerator mass spectrometry (AMS). Future applications are in the investigation of global fallout actinides in environmental clay-rich materials (e.g., at potential repository sites) and the diffusion behavior of actinides in compacted clay liners used as technical barriers in nuclear waste repositories.

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THORIUM-INDUCED VESICULAR SELF-ASSEMBLIES BASED ON PILLAR[5]ARENE OXIMES

*Xiangyang Yuan, Yiming Jia, Quan Gan, Lihua Yuan, Wen Feng**

Institute of Nuclear Science and Technology, Key Laboratory for Radiation Physics and Technology of Ministry of Education,
College of Chemistry, Sichuan University, Chengdu 610064, China, *e-mail: wfeng9510@scu.edun.cn

Keywords: pillar[5]arene oxime, thorium(IV) ion, self-assembly

Preorganization of chelating groups on pillararenes often leads to unique properties [1]. A novel pillar[5]arene-based benzaldehyde oxime (P5ABO) 1 has been synthesised. This preorganized host showed preferential recognition of Th^{4+} over all eight lanthanide metal ions tested in acetonitrile solution. The selective complexation was investigated by UV-vis spectroscopy and ^{1}H NMR technique. Of great interest is the observation that the P5ABO experiences a strong Th^{4+}-induced aggregation. Exploration of the resultant self-assemblies by scanning electron microscopy, transmission electron microscopy and atomic force microscopy revealed the formation of vesicular architectures in acetone-water solution. Notably, the size of vesicles was fond to be water-acetone ratio dependent. Successful encapsulation of rhodamine dye suggested the potential of using metal-containing pillar[5]arene-based complexes for constructing vesicles for enclosing guest molecules.

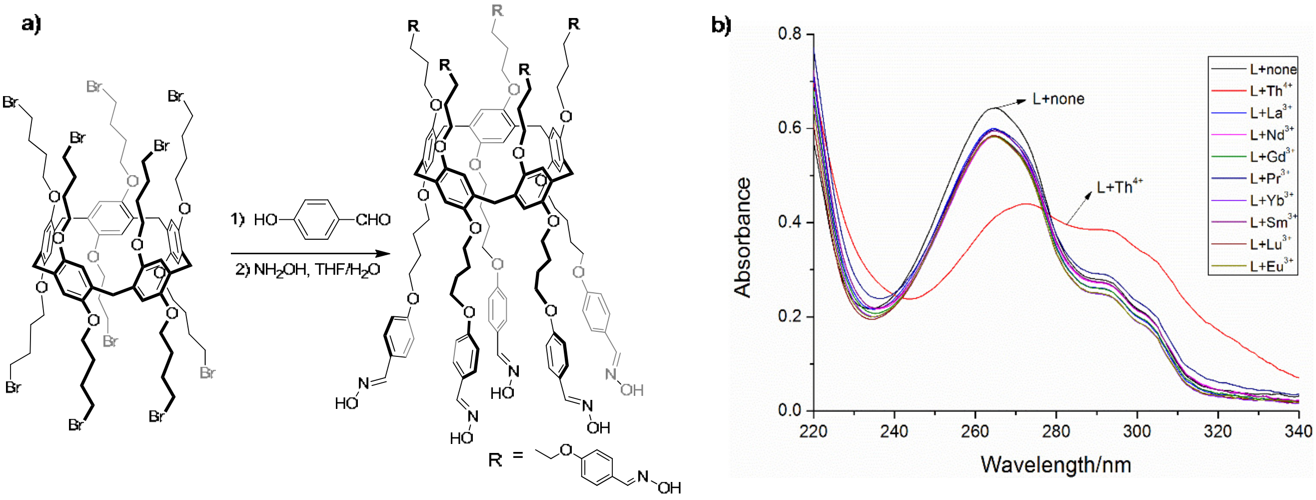

Fig. 1. Synthesis route of pillar[5]arene-based benzaldehyde oxime 1 a) and its UV-Vis absorption spectra of 1 in the presence of various metal salts in CH_3CN b)

Acknowledgements

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Advances in radiochemistry supporting the nuclear fuel cycle

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DETERMINATION OF DIFFICULT TO MEASURE RADIONUCLIDES IN REACTOR COMPONENTS AND FUEL ASSEMBLIES

Boris Remenec[1], *Silvia Dulanská*[2], *Ľubomír Mátel*[2], *Gabriela Wallová*[3]

[1]Radiation Protection SE-EBO, 919 31 Jaslovske Bohunice, Slovakia, e-mail: boris.remenec@gmail.com
[2]Department of Nuclear Chemistry, PriF UK, Comenius University, Mlynská dolina, Ilkovičova 6, 842 12 Bratislava, Slovakia, e-mail: dulanskas@gmail.com
[3]Water Research Institute, Slovak National Water Reference Laboratory, Department of Radiochemical Methods, Nábr.arm.gen.L.Svobodu 5, 812 49 Bratislava, e-mail: gabriela.wallova@gmail.com

Keywords: NPP decommissioning, radioactive waste characterization, radionuclide analysis

The NPP V1 (Slovakia) is decommissioned now and activity of radionuclides has to be measured for estimation of the total inventory of radioactivity. It is assumed that the majority of the activity is induced activity. Construction and internal parts of the reactor and fuel such as: pressure vessel, RPV internal cladding, control rod connection rod, control rod neutron absorbers, shielding elements, protective tubes unit, core barrel, neutron in-core measurement channels were analyzed. Activity concentrations of ^{60}Co, ^{55}Fe, ^{63,59}Ni, ^{90}Sr, ^{99}Tc, ^{93}Mo, ^{94}Nb, transuranic elements were determined. The most dominant radionuclides were ^{55}Fe, ^{60}Co, ^{63}Ni which together represent more than 99% of the total activity. Fission elements were not found in all analyzed samples. The activity concentrations of radionuclides varied from type of analyzed material, exposure time to neutrons and intensity of neutron flux. The highest activity was measured in the control rod connection rod and shielding element from fuel assemblies and RPV internal cladding from construction material samples. These samples were exposed to neutrons for the longest time and with the highest neutron flux. The presented results were used for calculation of scaling factors for characterization of the activated components of NPP V1.

Mass spectometry

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CONFIDENCE LEVELS FOR CATEGORIZING URANIUM MATERIALS BY INDUCTIVELY COUPLED PLASMA MASS-SPECTROMETRY (ICP-MS) WITHOUT CLEAN-ROOM FACILITIES

Tiong Ling Ying Diane[1], *Pong Boon Kin*[2], *Richard D. Webster*[3]

[1]School of Physical and Mathematical Sciences, Chemistry and Biological Sciences, Nanyang Technological University, 21 Nanyang link SPMS-CBC-02-01, Singapore 637371, e-mail: ltiong001@e.ntu.edu.sg
[2]DSO National Laboratories, 11 Stockport Road, Singapore 117605
[3]School of Physical and Mathematical Sciences, Chemistry and Biological Sciences, Nanyang Technological University, 21 Nanyang link SPMS-CBC-02-01, Singapore 637371

Keywords: ICP-MS, uranium, GUM, uncertainty measurement

The enrichment level of ^{235}U isotopes can be used to categorize uranium materials, which may be critical for determining their intended uses. In the event of emergency nuclear power and radiation incidents, confidence levels of reported concentrations and isotopic abundances are essential, as these are critical information for decision making. Therefore, it is important to have the capability for measuring uranium samples with accuracy and precision. As uranium is ubiquitous in the environment, sample preparation for uranium analysis is typically performed in a clean-room facility to avoid contamination of samples. However, it can be recognized that clean-room facilities are not always available to laboratories, particular for on-site analysis. Hence, the aim of this work is to evaluate the limitations of uranium analysis using a quadrupole ICP-MS in the absence of a clean-room facility. The Guide to expression of Uncertainty in Measurement (GUM) was used to calculate the expanded uncertainties associated with the amount of uranium (ng) and ^{235}U enrichment in the sample. The analytical method for sample preparation involved sample dissolution using $LiBO_2$ fusion, followed by extraction of uranium by UTEVA resins. An Agilent 7700× quadrupole ICP-MS was used to measure m/z 235 and 238. ^{233}U was used as an internal reference for quantifying the uranium isotopes. One of the sources of natural uranium contamination during sample preparation has been identified in this presented work; Ashless grade Whatman filters minimizes the amount of natural contamination of uranium which improves the detection limit of the current sample dissolution method.

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DEVELOPING THE METHOD FOR DIRECT DETERMINATION OF Pu-239 BY ICP-MS IN ACID SOLUTIONS AFTER SOIL DIGESTION

Dmitriy Zheltov, Alexander Bychenko, Mariya Edomskaya, Pavel Kharkin,*
Galina Gluchshenko, Lyudmila Matiyenko

Center of Complex Environment Research, Institute of Nuclear Physics, Ibragimov St. 1, Almaty, 050032, Republic of Kazakhstan,
*e-mail: zheltovda@gmail.com.

Keywords: plutonium, ICP-MS, matrix effect, matrix coefficient, matrix correction

The method for direct mass-spectrometric determination of ^{239}Pu in the acid solutions after soil digestion was developed *(Fig. 1)*. A Perkin Elmer SCIEX ELAN-9000 quadrupole-based ICP-MS instrument was used. The detection limit of the method for a 3 g soil sample taken up in 100 ml of 3 mol l^{-1} nitric acid is 10 Bq kg^{-1} of ^{239}Pu.

It was found that the significant matrix effects was observed during mass-spectrometric measurements of ^{239}Pu in the acid digestion solutions. The matrix coefficients for ^{238}U and ^{239}Pu were experimentally found. The range of the matrix coefficients for ^{238}U and ^{239}Pu was from 3.5 to 9, which indicates a high content of the matrix elements. It is shown that the matrix coefficient of ^{238}U statistically insignificantly different from the matrix coefficient of ^{239}Pu.

For matrix correction of ^{239}Pu direct measurement result it is proposed to use internal standardization by ^{238}U isotope. A calibration of the mass spectrometer was performed by the ^{238}U standard additive.

The plutonium content in 24 soil samples from the Semipalatinsk Test Site (STS) was estimated in accordance with the procedure in *Fig. 1*. The range of the ^{239}Pu specific activity was from 5.7 to 362 kBq kg^{-1}. The comparison of the obtained ICP-MS results with the $^{(239+240)}$Pu alpha-measurement results, calculated for the specific activity of ^{239}Pu using the atomic ratio of ^{239}Pu/^{240}Pu for weapon plutonium has shown the satisfactory convergence (≤40%).

The developed method is used in the Institute of Nuclear Physics for the express analysis of the plutonium high level soil samples from the STS, for sorting the soil samples by the contamination level and as the alternative method of ^{239}Pu determination in the soil.

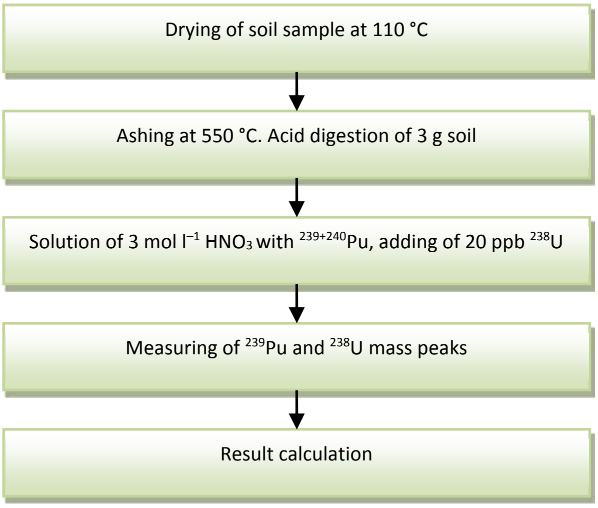

Fig. 1. Procedure of ^{239}Pu direct determination in soil digestion solution by ICP-MS

Neutron activation analysis

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DETERMINATION OF k_0 AND Q_0 FOR ^{113}In(n,γ)^{114m}In REACTION WITH COVARIANCE ANALYSIS

Lívia F. Barros, Mauro S. Dias, Marina F. Koskinas, Ione M. Yamazaki, Renato Semmler, Rafael V. Ribeiro

Laboratório de Metrologia Nuclear (Nuclear Metrology Laboratory – LMN), Centro do Reator de Pesquisas (Research Reactor Center – CRPq), Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP), São Paulo, Brazil,
e-mails: liviabarros4@gmail.com, msdias@ipen.br, koskinas@ipen.br, yamazaki@ipen.br, rsemmler@ipen.br, rafaelvanhoz@outlook.com

Keywords: k_0, Q_0, Neutron Activation Analysis, covariance analysis

The use of k_0 *Method* for quantitative reactor Neutron Activation Analysis (NAA) is a well-known technique for determining multi-element concentrations in different materials. In order to achieve good results, there is a continuing need for improving the accuracy of k_0 and Q_0 parameters for several neutron capture reactions. ^{113}In(n,γ)^{114m}In reaction can be considered particularly interesting because k_0 and Q_0 discrepancies appear in the literature. This fact motivated the present work which is focused on the measurement of k_0 and Q_0 values for this reaction with the purpose of improving the existing data catalogues. The irradiations were performed near the core of the IEA-R1 4.5 MW swimming-pool nuclear research reactor of the Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP – Nuclear and Energy Research Institute), in São Paulo, Brazil. The distribution of epithermal neutron flux α in the IEA-R1 is close to zero at the chosen irradiation position, which favors to obtain Q_0 accurately. Two irradiations were carried out in sequence using two sets of samples: the first with a cadmium cover around the samples and the second without. The activity measurements were carried out in an HPGe gamma-ray spectrometer. Standard sources of ^{152}Eu, ^{133}Ba, ^{60}Co and ^{137}Cs supplied by the IAEA were used in order to obtain the HPGe gamma-ray peak efficiency as a function of the energy. The covariance matrix methodology was applied to all uncertainties involved. The final values for k_0 and Q_0 were compared with the literature.

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USE OF INAA IN THE HOMOGENEITY EVALUATION OF A BOVINE KIDNEY CANDIDATE REFERENCE MATERIAL

Liliana Castro, Edson G. Moreira, Marina B. A. Vasconcellos*

Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP, Av. Prof. Lineu Prestes 2242, São Paulo, Brasil, *e-mail: lcastroesnal@usp.br

Keywords: reference material, meat products, bovine kidney, homogeneity assessment, Neutron Activation Analysis, Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA)

Evaluation of the homogeneity is a critical step in the preparation process of reference materials. The batch of material must be sufficiently homogeneous for the intended use and this must be reflected in the value assigned to the material uncertainty and by the minimum amount of sample for which the assigned values and their uncertainties are valid. To ensure the representativeness of the value assigned to the certificate parameters and their uncertainties, the assessment of the homogeneity of the material must be performed very carefully.

The present study describes the use of Instrumental Neutron Activation Analysis, INAA, for the homogeneity evaluation of a bovine kidney candidate reference material.

The mass fractions of some inorganic constituents (As, Co, Cr, Fe, K, Na, Se and Zn) were determined to evaluate the between and within bottle homogeneity, as well as the minimum amount of sample. For the between bottle homogeneity assessment the determinations were performed in ten bottles from the total batch of 176, chosen using a random stratified scheme. For the evaluation of the within bottle homogeneity and the minimum amount of sample one bottle was chosen, also using a random scheme.

Statistical analysis of the results was performed using Analysis of Variance (ANOVA) and multivariate techniques such as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were applied as complementary techniques.

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DETERMINATION OF THE NEUTRON CAPTURE CROSS-SECTION OF ^{232}Th INDUCED BY D-D/D-T NEUTRONS USING THE NEUTRON ACTIVATION METHOD

Lan Chang-lin, Xie Bao-lin, Zhang Yi, Peng Meng, Yao Ze-en, Kong Xiang-zhong

School of Nuclear Science and Technology, Lanzhou University, Gansu Provence 730000, China, e-mail: lanchl@lzu.edu.cn

Keywords: ^{232}Th(n, γ)^{233}Th reaction, capture cross-section, neutron activation method

Abstract: The ^{232}Th(n, γ)^{233}Th neutron capture reaction cross-sections at average neutron energies of 2.5±0.3 MeV and 14.8±0.2 MeV from the D-D/D-T neutron generator have been measurement using the activation method. The neutron flux was determined using the monitor reaction ^{58}Ni(n,p)^{58}Co or ^{27}Al(n,α)^{24}Na. Induced gamma-ray activities were measured using a low background gamma ray spectrometer equipped with a high resolution HPGe detector. The experimentally determined cross-sections were compared with the literature data, evaluated data of ENDF/B-VII, JENDL-4.0, CENDL-3.1 and JEFF-3.1. The Excitation functions of ^{232}Th(n,γ) reaction were also calculated theoretically using the TALYS 1.6 computer code. The new results measured in this work are useful for verifying the accuracy of nuclear models used in the data evaluations and practical applications.

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BOX-COX TRANSFORMATION ON DATASET FROM COMPOSITIONAL STUDIES OF ARCHAEOLOGICAL POTTERIES

José Osman dos Santos[1], Casimiro Sepulveda Munita[2], José Espinola da Silva[1], Michel Santana Reis[3]*

[1]Coordenação de Física, Instituto Federal de Sergipe – Campus Lagarto, CEP 49055-660, Sergipe, Brazil, *e-mail: osmansantos@ig.com.br
[2]Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP. C.P. 11049 CEP 05422-970, São Paulo, SP, Brasil, e-mail: camunita@ipen.br
[3]Aluno Bolsista do PFRH 127B, Instituto Federal de Sergipe – Campus Lagarto, CEP 49055-660, Sergipe, Brazil,
e-mail: joseespinoladasilvajr@uol.com.br

Keywords: INAA, archaeometry, multivariate statistics

In many archaeometric studies to determine the provenance of potteries by means of the elemental composition the normality is assumed to be desirable. The non-normality and non-normality features of geochemical variables provide a challenge for parametric statistical analyses since normality of datasets is required by many multivariate statistical methods such as principal components, canonical correlation, discriminant analyses and MANOVA. In many published examples of the use of multivariate methods to archaeometry studies, it is neglected that geochemical data almost never follow a multivariate normal distribution. Here, a geochemical dataset was obtained by means of Instrumental Neutron Activation Analysis (INAA) of archaeological potteries from Xingó, Sergipe State – Brazil which was used to demonstrate that in provenance studies, data as rule, shows neither a multivariate normal nor multivariate lognormal distribution. In this work, 50 ceramic fragments and 1 clay sample from Justino site were analyzed by means of INAA: Cemetery B (25), Cemetery C (25) and one clay sample collected near to Justino site. Eleven elements (Na, Lu, Yb, La, Th, Cr, Cs, Sc, Fe, Eu and Hf) were used for the interpretation of the results. A logarithmic transformation did not produce a multivariate normal distribution and it was necessary an optimal method of transformation for the raw data, which is a powerful method of Box-Cox transformation to dataset closer to multivariate normality. To statistical interpretation, this paper presents the MNV package from R Software, which can be used to test multivariate normality by using of measures of multivariate skewness and kurtosis of Mardia. When the multivariate normality test was disapproved, then the data was nearly normalized be means of Box-Cox or logarithmic transformation both marginally and jointly on the variables. In this paper, we have selected the parameter of the Box-Cox transformation by using of Akaike's information Criterion (AIC). Find transformation to normalize data by means of Box-Cox transformation, the significance between compositional groups of pottery specimens from Justino archaeological site could be tested by Hotelling's T^2 statistics (at 5% significance), which is the multivariate equivalent of the Student's t-statistics.

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STATE-OF-THE-ART OF NEUTRON ACTIVATION ANALYSIS AT THE REACTOR IBR-2 OF JOINT INSTITUTE FOR NUCLEAR RESEARCH IN DUBNA, RUSSIA

Marina Frontasyeva, Sergey Pavlov*

Department of Neutron Activation Analysis and Applied Research, Division of Nuclear Physics, Frank Laboratory of Neutron Physics,
Joint Institute for Nuclear Research, str. Joliot-Curie, 6, Dubna, 141980, Moscow Region, Russian Federation, *e-mail: marina@nf.jinr.ru

Keywords: automation of neutron activation analysis, monitoring of atmospheric deposition of heavy metals and radionuclides, monitoring aquatic ecosystem, bionanotechnology, medicinal plants, cosmic dust, microscopy, radioecology

The history of the development of neutron activation analysis in the Laboratory of Neutron Physics at Joint Institute for Nuclear Research is briefly outlined. Created under initiative of Academician I.M. Frank in the 1960s a small group now turned into a large international team involved in projects in the framework of programs coordinated and supported by IAEA, the European Union, the Russian Fund for Basic Research, as well as grants of Plenipotentiaries of JINR Member States. Modernization of the pneumatic system, recently equipped with three automatic sample changers, and created NAA database to automate the measurement and processing of gamma spectra of induced radionuclides are described. Experience in the life sciences and materials science is summarized. Examples are given of projects related to the monitoring of atmospheric deposition of heavy metals and radionuclides carried out in the framework of the United Nations Program on Long-Range Transboundary Air Pollution in Europe (UNECE ICP Vegetation), a project to assess the state of the environment in Egypt, based on the analysis of soil and the sediment basin of the river Nile, as well as project on monitoring trace elements in aquatic ecosystem in the Western Cape, South Africa (Mussel Watch Program), etc. In combination with microscopy, the synthesis of nanoparticles of various metals via biotechnology is studied. Our investigations on applying NAA to solve the problem of industrial wastewater treatment were twice awarded Gold Medals by the European Union, in 2013 and 2015. New areas of research – study of natural medicinal plants and search for cosmic dust in natural planchettes (Arctic and Antarctic mosses, Siberian peat bog cores, etc.) – reflect the public and scientific interest in these topics. Future extensions of the department's research will be connected with the development of radioecological studies using precision gamma-spectrometry and the creation of a low-background laboratory for carrying out measurements of natural and anthropogenic radioactivity.

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NEUTRON ACTIVATION ANALYSIS USING A MODIFIED ABSOLUTE CALIBRATION METHOD

Chun-Kai Huang[1], Wen-Chyi Tsai[2], Shiang-Huei Jiang[1, 2]*

[1]Institute of Nuclear Engineering and Science, National Tsing Hua University, Hsinchu 30013, Taiwan, *e-mail: ckhuang.taiwan@gmail.com
[2]Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013 Taiwan

Keywords: Neutron Activation Analysis, MCNPX, THOR

Although the direct comparator method of NAA is the most popular and accurate method, a calibrator containing a known amount of the element(s) of interest needs to be irradiated together with the unknown sample. For the absolute calibration method of NAA, the mass of an element measured is determined by directly applying the measurement equation of NAA, i.e., can be derived from the net counts in the corresponding peak of the measured gamma-ray spectrum. The key point and meanwhile the most difficult thing in the absolute calibration method is the determination of the reaction rate per atom, which depends complicatedly on the characteristics including the intensity as well as the energy and angular distributions of the irradiation neutron field. In this work we conducted NAA by using the BNCT beam at THOR to irradiate the test sample located along the center axis at a depth of 2 cm, where the thermal neutron fluence rate is the maximum, of a $20 \times 20 \times 20$ cm^3 PMMA phantom directly contacting the beam exit. Simplicity and convenience are our emphases and high degree of accuracy is not our pursuit. Accordingly, we chose absolute calibration method for analysis to avoid the necessity of the preparation of calibrators containing a known amount of

the element(s) of interest, which is sometimes not easy to achieve. In our BNCT beam an equivalent surface source has been well-characterized with space, energy and angular distributions and a process of verification and validation has been made. Therefore, the reaction rate per atom of any interest element in the sample at the irradiation position for a specific source strength, i.e., reactor power, can be calculated by using MCNPX Monte Carlo code. In addition, there is an on-line neutron monitoring system consisting of three miniature fission chambers installed in our BNCT beam, which was well-calibrated in terms of source strength per cps of neutron monitors. The NAA method applied in our BNCT beam, for which the reaction rate per atom of the interest element is derived from a Monte Carlo code calculation and the effect caused by time-dependent neutron fluence rate is precisely corrected, is called by us the modified absolute calibration method. By using this modified absolute calibration method proposed in this work, we have conducted three NAAs. The first NAA was for an alloy foil of Mn (88%) and Ni (12%) with a diameter of 12 mm and 0.1 mm in thickness. The measured weight percent of Mn and Ni were agreed very well with the specification of the sample. The second one was for a CaF_2:Mn TLD with dimensions of $3.2\times3.2\times0.89$ mm^3. The weight percent of Mn was determined to be 1.6% agreed very well with the data measured by the direct comparator method. The third one was for a test sample of stainless steel (SS304) with a weight of 741.9 mg. The compositions of Cr, Ni, and Mn were determined to be 18.44%, 10.0%, and 0.88%, respectively, which fell in the ranges of 17.5–20%, 8–11% and <2% of the specification of SS304. In addition, 0.25% of Co was found in the test sample.

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DETERMINATION OF VANADIUM IN TITANATE-BASED FERROELECTRICS BY INAA WITH DISCRIMINATING GAMMA-RAY SPECTROMETRY

Jan Kameník[1], Kateřina Dragounová[2], Jan Kučera[1], Zdeněk Bryknar[2],
Vladimir A. Trepakov[3], Vladimír Strunga[1]

[1]Nuclear Physics Institute of the Czech Academy of Sciences, Řež 130, 250 68 Řež, Czech Republic,
e-mails: kamenik@ujf.cas.cz, kucera@ujf.cas.cz, strunga@ujf.cas.cz
[2]Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Trojanova 13, 120 00 Prague, Czech Republic,
e-mails: katerina.dragounova@fjfi.cvut.cz, zdenek.bryknar@fjfi.cvut.cz
[3]Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, 182 21 Prague, Czech Republic, e-mail: trevl@fzu.cz

Keywords: ferroelectrics, vanadium, INAA

Crystals of incipient ferroelectric strontium titanate ($SrTiO_3$) and ferroelectric barium titanate ($BaTiO_3$) are model representatives of highly polarizable ABO_3 perovskite-type oxides. They are applied in a wide range of components in various devices due to their exceptional functional properties that can be tailored by suitable admixtures. At the same time they are extremely sensitive to a very low content of specific impurities. In this context study of behaviour of polyvalent transition metals with 3d valence electrons (e.g., vanadium), which strongly influence the charge transport and photorefraction properties of these crystals, is of great interest. This paper describes determination of vanadium in $SrTiO_3$ and $BaTiO_3$ crystals using instrumental neutron activation analysis (INAA). Vanadium is determined in INAA with a low limit of detection (LOD) by counting of the 1434.06 keV gamma line of short-lived ^{52}V (half-live $T_{1/2}$ 3.74 min). However, the activity formed by activation of crystal matrix elements Sr, Ba, and Ti with thermal neutrons dictates counting of samples at large distance from the detector thus deteriorating the LOD of vanadium. We have been investigating application of shielding foils for suppression of the radiation from products of activated matrix elements while still leaving enough gamma radiation of ^{52}V for detection. A series of measurements was conducted with aluminium, copper, and lead foils of various thickness and a calibration ^{152}Eu source. A lead foil of 5 mm thickness was found to be the most suitable for the given purpose and was later used in a model experiment with irradiated BaTiV and SrTiV mixtures. The procedure with the foil allowed counting of the sample at much closer distance from the detector and led to improving the LOD of vanadium by a factor of two. The procedure was then used for analysis of two real ferroelectric crystals with mass of about 75 mg. Standard reference material SRM 1648 Urban Particulate Matter (NIST) was used as the control material.

The study was performed within CANAM infrastructure (MEYS project no. LM2011019).

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ANALYSIS OF ARISTOLOCHIA LONGA MEDICINAL PLANT FROM ALGERIA

Z. Lamari[1]*, *R. Larbi*[1], *H. Neggache*[2]

[1]Department Recherche, Comena, Bp43 Centre de Recherche Nucleaire de Draria, Algerie, *e-mail: zohralamari@yahoo.fr
[2]Département Application Nucléaire, Alger, Algerie

Keywords: medicinal plants, trace element, biological effects, INAA

Neutron activation analysis was applied to assess trace element concentrations in Aristolochia Longa, Bereztam is the common name, medicinal plant widely used in traditional medicine in Algeria, Morocco and forbidden in several countries. The Cr, Na, La, K, Br, As, Sb have been quantified by long irradiation time with thermal and epithermal flux of 3.98 E13 n / cm^2 / s and 1.49 E12 n / cm^2 / s respectively. This irradiation was performed in the core of NUR Algerian Reactor. Certified reference materials SDM-2TM lake sediment was used for the elemental quantification, the IAEA –V10 Hay Powder and IAEA –SL1 Lake Sediment were analyzed for quality of the analytical results.

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RARE EARTH ELEMENTS CONTENT AND LEACHABILITY IN COAL FLY ASH FROM FIGUEIRA COAL POWER PLANT

Camila Neves Lange, Marina Beatriz Agostini Vasconcellos, Ana Maria Graciano Figueiredo,
Iara Maria Carneiro de Camargo, Liliana Castro, Regina Beck Ticcianeli

Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP), São Paulo, SP, Brazil, e-mail: clange@usp.br

Keywords: REEs, leaching, fly ash, coal

On the last couple of years, Brazilian southeast region has faced a serious drought and hydroelectricity is the main source of power in this country portion. Because of that, coal power plants have been operating in their maximum capacity and have enhanced the production of coal fly ash (CFA) in Brazil. Several studies on its reutilization have been conducted and its chemical characterization is important to point new uses and to improve the existing ones. Recently, CFA has been considered as source of rare earth elements (REEs) and the offspring of this new use of this industrial waste has intensified the number of studies on determination of REEs content and leachability, since dilute acid dissolution has been pointed as a possible alternative of extraction of these elements from CFA. The aim of this study was to evaluate REEs content in coal fly ash from Figueira Power Plant, located at Paraná State, Brazil. Besides that, CFA were leached with a dilute solution composed of HNO_3 and H_2SO_4 (pH = 4.5) over 168 and 336 days. The REEs content was analysed on ashes before and after leaching by Instrumental Neutron Activation Analysis (INAA) and evaluated by statistical tools, such as analysis of variance (ANOVA) and principal component analysis (PCA). The content obtained for non leached ash was compared with those present in commercial REEs ores, such as monazite and bastnaesite, for future commercial purpose.

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SOIL TRACE ELEMENT STATUS IN AN IMPOUDED VEHICLES SCRAPYARD

Camila Neves Lange[1], *Ana Maria Graciano Figueiredo*[1], *Jacinta Enzweiler*[2]

[1]Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP), São Paulo, SP, Brazil, e-mails: clange@usp.br, anamaria@ipen.br
[2]Instituto de Geociências, Universidade Estadual de Campinas (UNICAMP), Campinas, SP, Brazil, e-mail: jacinta@ige.unicamp.br

Keywords: metals, impounded vehicles scrapyard, soil

The number of motor vehicles has increased by 118% over the past decade in Brazil, which is transforming urban space regarding mobility, parking and disposal capacity of these vehicles. Impounded vehicle scrapyard overcrowding has become a challenge in many Brazilian regions. This now is considered a potential risk to soil quality, since vehicles are

usually parked directly on the topsoil. The aim of this study was to evaluate topsoil samples from a scrapyard of impounded vehicles for Potentially Toxic Elements (PTEs), like As, Co, Cr, Cu, Mo, Ni, Pb, and Zn, and rare-earths. The area of study is in Ribeirão Pires, São Paulo, Brazil. For this purpose, forty samples were analysed by Instrumental Neutron Activation Analysis (INAA) and X-Ray Fluorescence Spectrometry (XRF). The obtained values were compared with literature data from Brazil and other regions around the world, as so with recommended values from environmental regulatory agencies. Some soil-geochemical variables [including pH, organic matter (OM), cation exchange capacity (CEC)], and texture (e.g. clay, silt and sand content) were used to interpret the behaviour of the studied elements in the soil. The PTEs contents ranged as follows: As (<3–15 mg kg^{-1}), Co (2–30 mg kg^{-1}), Cr (7–183 mg kg^{-1}), Cu (3–73 mg kg^{-1}), Mo (<1–6 mg kg^{-1}), Ni (<3–38 mg kg^{-1}), Pb (23–211 mg kg^{-1}) and Zn (18–352 mg kg^{-1}). In some hotspots, PTEs content exceeded continental crust and also international recommended values. The normalization of the rare-earth data by the Post-Archean Average Australian Shale (PAAS) indicated high anomalous values of Ce in some points that may suggest an anthropogenic source, such as vehicle exhaust catalysts (VEC). Total contents of PTEs rank in the following order: Cr>Zn>Pb>Cu>Ni>As>Co>Mo. This is the first study in scrapyards of impounded vehicles in Brazil. The results may be used to monitor soil contamination in these sites and for more effective environmental management.

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NEUTRON AND PHOTON ACTIVATION ANALYSES IN GEOCHEMICAL CHARACTERIZATION OF LIBYAN DESERT GLASS

Jiří Mizera, Zdeněk Řanda, Ivana Krausová

Nuclear Physics Institute, The Czech Academy of Sciences, Hlavní 130, 250 68 Řež, Czech Republic,
e-mails: mizera@ujf.cas.cz, randa@ujf.cas.cz, krausova@ujf.cas.cz

Keywords: INAA, IPAA, Libyan Desert Glass, tektite, Kebira Crater

Nine samples of Libyan Desert Glass (LDG) have been analyzed using instrumental neutron activation analysis (INAA) in various analytical modes (short and long time irradiation, epithermal) and photon activation analysis (IPAA). Elemental composition of LDG points to quartz sand as a main component of the parent materials, with admixture of elements implying an aluminosilicate component (clay minerals cementing quartz grains). A depletion of volatile elements (alkalis, Zn, As, Br, Sb, etc.) may reflect their evaporation loss during the impact. Higher Zr contents coupled with elevated contents of heavy rare earth elements may reflect melting of refractory zircon. LDG has recently been associated with the Kebira Crater on the Libya-Egypt border. The impact area was flooded with seawater during Cenomanian/Turonian stage and the assumed origin of LDG parent materials – compact sandstone with accessory minerals – in marine environment has been supported also by previous Li isotope investigation. No contamination of LDG by meteoritic material has been evidenced.

The study was supported by the projects 13-22351S of the Czech Science Foundation.

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ACTIVATION CROSS-SECTION AND ISOMERIC RATIO STUDIES FOR THE ^{nat}Ag(n,x)^{106g,m,105,104g,m}Ag REACTIONS FOR NEUTRONS WITH AVERAGE ENERGIES FROM 15.11 MeV TO 35.3 MeV

M. Nadeem, G. N. Kim, M. Zaman, K. Kim, H. Naik, M. Shahid, T. Hien

Department of Physics, Kyungpook National University, Daegu 702-701, Republic of Korea

The neutron induced cross-sections for the ^{nat}Ag(n,x)^{106g,m,105,104g,m}Ag reactions and isomeric cross-section ratios for ^{nat}Ag(n,x)^{106g,m,104g,m}Ag were determined by an activation and off-line γ-spectrometric technique with average energies from 15.11 MeV to 35.3 MeV. The quasi-mono high energetic neutron beam was produced via the 9Be(p,xn) reaction through proton energies of 25 MeV, 35 MeV and 45 MeV at KIRAMS, Seoul. Average weighted neutron energies <En> were used in the measurements to compensate the effect of broad quasi mono energy neutron beam.

Experimentally, neutron flux was determined by measuring activity of 24Na through 27Al(n,α)24Na reaction. In order to measure all induced activities, gamma spectroscopy was done by P-type high purity germanium (HPGe) detector.

It was also found that for the same neutron spectrum, cross-section for the ^{nat}Ag(n,x)^{106g,m}Ag reaction is higher than the ^{nat}Ag(n,x)^{105}Ag, which in turn higher than the ^{nat}Ag(n,x)^{104g,m}Ag. It is due to increase number of neutron emissions and also increase in reaction threshold energy from the former to the latter.

It was also studied that cross-sections for ground state isotopes have higher cross-section values. All the attained results have been compared with TENDL-2014 library and related literatures as well.

Neutron flux was simulated by MCNPx code and the discussed cross-sections were calculated by TALYS 1.6 code. Both measured and calculated results were found in good agreement, which shows the validity of the codes.

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HIGH-ENERGY CALIBRATION DATA FOR NEUTRON ACTIVATION ANALYSIS

László Szentmiklósi[1]*, *Zsolt Révay*[2], *Boglárka Maróti*[1], *Dénes Párkányi*[1], *Ildikó Harsányi*[1]

[1]Centre for Energy Research, Hungarian Academy of Sciences, Budapest, Hungary, *e-mail: szentmiklosi.laszlo@energia.mta.hu
[2]Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II), Garching, Germany

Keywords: NAA, gamma spectrometry, efficiency calibration

In neutron activation analysis (NAA), there is a need to calibrate the HPGe detectors up to about 3.1 MeV, in order to properly analyse elements like Na, Ca and S. Commercially available radioactive sources cover the energy range only up to about 2.2 MeV, but not beyond. With activation in the reactor, however, several nuclides can be produced at low cost having high-energy gamma lines, such as Ga-72, Mn-56, Na-24. The application of such isotopes for calibration is hindered by imprecise or confronting nuclear data.

At a PGAA station, where the detector calibration is done on a routine basis up to 11 MeV, one can find ideal conditions to derive energies and relative intensities for such high-energy gamma emitters. In the paper we report about the recent experiments made at the Budapest PGAA facility and at the PGAA station of FRM II Garching, to produce a coherent dataset of such nuclides and apply them for efficiency and nonlinearity calibration. After verification this could form a basis of a more advanced detector calibration procedure for NAA.

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k0-NAA FOR DETERMINATION OF REE IN REFERENCE MATERIALS OF ORE SOURCES

Caijin Xiao[1], *Yonggang Yao, Long Hua, Xiangchun Jin, Pingsheng Wang, Bangfa Ni*

[1]Department of Nuclear Physics, China Institute of Atomic Energy, P.O. Box 275-50, Beijing, China, e-mail: cjshaw@ciae.ac.cn

Keywords: rare earth elements, k0-NAA, interference corrections

The rear earth elements (REE) have been analysed by k0-NAA in three kinds of reference materials of ore sources from Australia nuclear science and Technology organization (ANSTO). The sample irradiation was carried in China Mianyang Research Reactor (CMRR). The gap of REE concentration is much difference in three kinds of reference materials and one has the high concentration of uranium. In this work, purity iron wire and Zr foil were used to monitor the neutron spectrum parameters (f, φ_{th}) at irradiation positions. Duo to the high concentration of uranium, fission products interference have been considered carefully and the factors from fission interference (IK0) of Nd, Ce, La and gamma interference of Sm form ^{239}Np were determined. The effective interaction depth (EID) is employed to normalize sample radioactivity at different counting positions due to the big difference of components between three kinds of reference materials. The concentrations of La, Ce, Eu, Tb, Nd, Nb in three samples were determined by k0 neutron activation analysis. Two kinds of certified reference materials was also analysed at same procedure for quality control. The results indicated a good agreement with certified values of REEs.

Nuclear forensics

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LOW LEVEL DETERMINATION OF URANIUM IN CONCRETE BY LASER-INDUCED BREAKDOWN SPECTROSCOPY

Alonso Castro[1], *Helen Boylan*[2], *Ben Griffiths*[3], *Ning Xu*[1]

[1]Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA, e-mail: acx@lanl.gov
[2]Westminster College, New Wilmington, PA 16172, USA
[3]AWE, Aldermaston, Reading RG7 4PR, United Kingdom

Keyword: LIBS

We conducted an evaluation of commercially available Laser-Induced Breakdown Spectroscopy (LIBS) instruments with the purpose of determining their suitability for the analysis of actinides in urban debris. Pellets of uranium dioxide in a concrete matrix were prepared and analyzed by LIBS. The precision and limits of detection of the technique were evaluated using a multivariate algorithm. The possible use of this method for nuclear forensics applications is discussed.

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IDENTIFICATION OF HIGH CONFIDENCE NUCLEAR FORENSICS SIGNATURES BY ANALYSIS OF CONFISCATED NUCLEAR MATERIALS

Bernadett Henn, Katalin Tálos, Kornél Fél, István Almási, András Kocsonya, Péter Völgyesi, Nguyen Cong Tam, László Lakosi, András Kovács, Éva Kovács-Széles, Tamás Bíró

Hungarian Academy of Sciences, Centre for Energy Research, Konkoly-Thege Miklós út 29–33, H-1121 Budapest, Hungary

Illicit trafficking of nuclear and other radioactive material is a subject of serious concern due to the radiological hazard to the public and the environment as well as the security risks associated nuclear and other radioactive material out of regulatory control. The problem of theft or loss of nuclear materials has affected countries on all five continents emphasizing the international scale of this issue.

To increase confidence in determining the origin and history of questioned materials, analysis of numerous comparison samples from the same and also different confiscations and batches with different origin is necessary. This method can serve the relevant signatures of the nuclear materials for real origin assessment.

In this work analysis of nuclear materials obtained during past seizures by the Hungarian authorities was performed and the results were statistically evaluated to find the high confident signatures. Different techniques and methods were used which are available at the Hungarian Academy of Sciences Centre for Energy Research (e.g. Mass Spectrometry, Gamma Spectrometry, Scanning Electron Microscopy, X-ray Fluorescence, X-ray Diffraction, Laser Induced Breakdown Spectroscopy, etc.) to obtain a relatively large and informative database.

The analysis contents both conventional parameters (isotope ratios, enrichment, production date, morphology, surface, structure, physical parameters, impurities, reprocessing, etc.) as well as new parameters obtained during the method developments or adaptations. After the evaluation of the database obtained from measurements conclusion for high confidence nuclear forensic signatures was made an attempt.

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COMPLETE ICP-MS ANALYSIS OF PLUTONIUM SAMPLES CONTAMINATED WITH URANIUM

Doris Ho Mer Lin, Diane Tiong, Boon Kin Pong*

DSO National Laboratories, 20 Science Park Drive, Singapore 118230, *e-mail: hmerlin@dso.org.sg

Keywords: plutonium, uranium, ICP-MS

ICP-MS analysis of plutonium that contains or is contaminated with uranium requires complete separation to overcome isobaric interference of U-238 on Pu-238. Current separation method with separation resins is not able to achieve 100% separation of U from the Pu sample. A second and complementary technique, such as alpha spectrometry, has to be utilized to determine the quantities of Pu-238. To overcome the need for a second technique, we explored the approach of *in-sample* correction on the m/z 238 data (Pu-238 + U-238) by deriving information of U-238 signal contribution from the m/z 235 data (U-235 only).

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APPLICATION OF IBA IN THE FORENSIC PROFILING OF ENVIRONMENTAL POLLUTION OF NATURAL RESOURCES

J. A. Mars[1], J. F. Guambe[2, 3], J. Day[2]

[1]Faculty of Health and Wellness Sciences, Cape Peninsula University of Technology, PO Box 1906, Bellville, 7535, South Africa
[2]Physics Department, Eduardo Mondlane University, PO Box 257, Maputo, Mozambique
[3]Freshwater Research Unit, Department of Zoology, University of Cape Town, Private Bag, Rondebosch, 7701, South Africa

Introduction: Environmental pollution events occur over extended time periods. It is difficult to pinpoint the pollution origin and so holding perpetrators legally responsible. Fish-scales are suitable in monitoring pollution as the contaminants are incorporated into the scale matrix. *Objectives:* 1) To use IBA techniques, to analyse scales of four types of fish, *P. kaakan*; *L. gibbus*; *P. pinjalo* and *L. mormyrus* were; 2) Mathematically model growth characteristics of the scales. *Principle results:* The homogeneity of major components in the fish scale matrices differed significantly. Concentrations of trace elements, toxic to biota and present in the matrices were identified. *Major conclusions:* A basis for forensic profiling of environmental pollution is provided.

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ON THE ACCURACY OF GAMMA SPECTROMETRIC ISOTOPE RATIO MEASUREMENTS OF URANIUM

H. Ramebäck[1, 2], P. Lagerkvist[1], S. Holmgren[1], S. Jonsson[1], B. Sandström[1], A. Tovedal[1], A. Vesterlund[1, 2], T. Vidmar[3], J. Kastlander[4]*

[1]Swedish Defence Research Agency, FOI, CBRN Defence and Security, SE-901 82 Umeå, Sweden, *e-mail: henrik.ramebeck@foi.se
[2]Chalmers University of Technology, Department of Chemistry and Chemical Engineering, SE-412 96 Göteborg, Sweden
[3]SCK-CEN, Belgian Nuclear Research Centre, Boeretang 200, 2400 Mol, Belgium
[4]Swedish Defence Research Agency, FOI, Defence and Security, Systems and Technology, SE-164 90 Stockholm, Sweden

The isotopic composition of uranium was measured using high resolution gamma spectrometry. Two acid solutions and two samples in the form of sintered UO_2 pellets were measured. The measurements were done in close geometries, i.e. directly on the endcap of the high purity germanium detector (HPGe). Applying no corrections for count losses due to true coincidence summing (TCS) resulted in up to about 40% deviation in the abundance of ^{235}U from the results obtained with mass spectrometry. However, after correction for TCS, excellent agreement was achieved between the results obtained using two different measurement methods, or a certified value. Moreover, after corrections, the fitted relative response curves correlated excellently with simulated responses which were based on a semi-empirical calibration, for the different geometries, of the HPGe detector.

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RECERTIFICATION OF A ^{84}Sr ISOTOPE REFERENCE MATERIAL

Mark Tyra[1]**, *Jacqueline Mann*[1]*, *Robert Vocke*[2]

[1]Physical Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Dr. Gaithersburg, MD 20899, USA, *e-mail: mark.tyra@nist.gov
[2]Materials Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Dr. Gaithersburg, MD 20899, USA

Keywords: radiochronometric reference materials, strontium isotopes, isotope dilution tracer

Isotopic Reference Materials (iRMs) ensure that nuclear forensic analyses are accurate, comparable, and traceable when being used to identify the origin of a material and assess the amounts and types of nuclear fuel products. The National Institute of Standards and Technology (NIST), with the U.S. Department of Homeland Security (DHS), is re-certifying a Sr-84 iRM; Sr-84 is a stable nuclide of Sr that can be used as an isotope dilution mass spectrometry (IDMS) tracer to measure the stable-and-radioactive Sr isotope amount content in nuclides such as Sr-90, a nuclear fission product. We possess a stock of SRM 988 (a 99.892% Sr-84 solution created in 1973) and will use it to create the new iRM. A detailed characterization of the tracer will be performed to determine the Sr isotopic composition and the amount content of the tracer. We plan to produce 500 units of this iRM for sale, with enough solution for an additional 1500 units held in reserve. The 500 SRM units will contain a total of 5 mg Sr in 25 mL of 2% (g/g) HNO_3, at a mass fraction of 200 ng Sr/g, and will be stored in 30 mL PFA bottles packaged in Mylar bags.

The Sr-84 characterization will be done at NIST. After the 500 SRM units are bottled, approximately six samples will be selected by stratified random sampling to be used for both assay and isotopic characterization. In the analysis, the relative abundance of ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr will be measured. All samples will be measured in duplicate. Associated blank samples will bracket all sample measurements, and potential molecular interferences, abundance sensitivity issues, and other factors affecting measurement accuracy will be quantified. The ^{86}Sr/^{88}Sr ratio of NIST SRM 987 (a terrestrial strontium-carbonate strontium isotope reference material) will be used in a sample-standard bracketing routine for the MC ICP-MS analyses to correct for mass bias. Mass bias samples will bracket all sample measurements and correction factors will be calculated and applied to other Sr isotopic ratios. SRM 3153a (a Sr standard solution certified for Sr concentration) will be used as a reverse IDMS spike. The IDMS isotopic analyses will be performed intermixed with the Sr isotopic ratio samples and reference materials mentioned above. For IDMS, the ^{84}Sr/^{86}Sr ratio will be measured. Statistical evaluation of the data will follow standard GUM procedures to arrive at an uncertainty budget.

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COMPARISON OF METHODS FOR MEASURING LANTHANIDES IN URANIUM MATRICES

Anna Vesterlund[1, 2]**, *Petra Lagerkvist*[1]*, *Christian Ekberg*[2]*, *Henrik Ramebäck*[1, 2]

[1]Swedish Defence Research Agency, FOI, CBRN Defence and Security, 901 82 Umeå, Sweden, *e-mail: anna.vesterlund@foi.se
[2]Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Nuclear Chemistry, Göteborg, Sweden

Keywords: lanthanides, uranium, ICP-MS, chemical separation

Lanthanide patterns are useful for attribution of uranium ore. Mass spectrometric measurements of lanthanides provide low detection limits but there are a number of isobaric interferences as well as polyatomic interferences such as oxides or hydrides that may distort the results. If the interferences are not corrected for, the measurement results may be invalid. In this work measurements of lanthanides are performed by two methods; either by using a dry plasma to drastically lower the oxide formation, or by using a chemical separation to divide the lanthanides into fractions which prevents the formation of spectral interferences by both isobars and oxides.

Nuclear instrumentation and methodology

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MONTE CARLO METHODS FOR GAMMA SPECTROMETERY EFFICIENCY CALIBRATION FOR ENVIRONMENTAL APPLICATIONS

Tareq Alrefae

Physics Department, Kuwait University, Khaldia, Kuwait, e-mail: tareq@uw.edu

Keywords: Monte Carlo, GEANT4, gamma spectrometry

Gamma spectrometry is an effective tool for detecting and measuring environmental radiation. An important requirement for accurate measurement is proper calibration for the efficiency of the spectrometer. This task is typically performed by counting a standard source of known radioactivity with the same geometry and composition of the samples under investigation. A problem arises, however, when such a source is unavailable, or when a certain targeted radionuclide has decayed or is not present in the source. Nonetheless, an alternative exists with the utility of computational approaches that simulate interactions of photons with matter. Although these computer programs are commercially available, their hefty prices which could reach four-figure numbers make them unavailable to many labs.

A remedy was sought for this work by developing an in-house computer code that simulated interactions of photons with the materials of the sample of interest and the counting system. This program which was written in the C++ syntax of GEANT4, utilized Monte Carlo methods for repeated random sampling of the photon interactions. To provide flexibility and control, the code allowed its users to freely create the desired geometries and compositions of the modelled samples and detectors. Moreover, the code offered its users the selection of the appropriate physics of interactions to simulate the photon-material behaviour. Running on a personal computer, this code gave an output that was in close agreement with experimental results for a set of standard sources that covered various geometries and compositions. With this achievement, a practical, free-of-charge method was made available to environmental radioactivity labs for accurate gamma spectrometry measurements.

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ACTIVITY DETERMINATION OF ALPHA AND BETA EMITTERS IN ORGANIC AND AQUEOUS AGRESSIVE MEDIA BY CROSSLINKED PLASTIC SCINTILLATORS (C-PS)

Héctor Bagán[1], Alex Tarancón[2], Lei Yei[1], José Francisco García[2]

[1]Department of Pure and Applied Biochemistry, Lund University, Getingevägen 60, 22100 SE, Lund, Sweden
[2]Department of Analytical Chemistry, University of Barcelona, Martí I Franqués, 1-11, 08028, Barcelona, Spain,
e-mails: jfgarcia@ub.edu, alex.tarancon@ub.edu

Keywords: Crosslinked Plastic Scintillator, organic media, aqueous media

Plastic Scintillation is an interesting alternative to Liquid Scintillation for activity determination of alpha and beta emitters. However, the physico-chemical characteristics of Plastic Scintillation microspheres (PSm) used for this purpose, linear polymeric chains, allow that this material is dissolved or degraded in aggressive aqueous or in organic media. This drawback can be overcome with the addition of a crosslinker that transforms the polymer structure into a three-dimensional network that confers to the polymer resistance and rigidity. However, this addition may lead to an important reduction on the detection efficiency of Plastic Scintillation materials.

The *objective* of this study is the synthesis and evaluation of a suitable Crosslinked Plastic Scintillator(C-PS) for radioactivity determination in organic and aqueous aggressive media.

The study was organized in different steps: first, it was considered the influence of the crosslinker: polymer proportion. The results showed that an increase in the crosslinker content reduces the detection efficiency. Next, it was studied the use of two different crosslinker molecules. In this case, the inclusion on the structure of a more flexible molecule yields to an improvement on the detection efficiency. The study of the fluorescent molecule and its concentration were also evaluated. The results showed that 2,5- diphenyloxazole (PPO) is the most adequate fluorescent solute and that an increase on its concentration causes little change on the detection efficiency. On the contrary, the addition of a secondary fluorescent solute 1,4-bis-2- (5-phenyloxazolyl) benzene (POPOP) improves the C-PS radiometrical characteristics.

Finally, the detection capabilities of C-PS were studied in different aqueous and organic media. The C-PS shows a good stability and reproducibility in all conditions. The measurements of H-3, C-14, Sr-90/Y90 and Am-241 in the considered aqueous aggressive media (hydrochloric acid, nitric acid and hydrogen peroxide) showed similar detection efficiency values to the commonly achieved on the analysis of non-aggressive aqueous solutions by PSm but with the spectra shifted to lower energies. The detection of the same radionuclides by C-PS in organic media (toluene, hydrotreated vegetable oil (HVO) and methanol) showed higher detection efficiency values than those commonly found in aqueous media by PSm with the spectra located at the same position. This behavior is probably due to the more similar polarity between the polymer (with high surface area) and the media.

These results show the suitability of this new material for the measurement of radioactivity samples in aggressive and especially in organic media.

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COMPARING DOSE CALIBRATION METHODS OF NIPAM GEL DOSIMETER USED FOR RAPIDARC™ TREATMENT

Chin-Hsing Chen[1], Min-Jia Tsai[2], Yuk-Wah Tsang[3], Chung-Yu Chiu[3], His-Ya Chao[3],
Chun-Hsu Yao[2, 4], Yuan-Jen Chang[1]

[1]Department of Management Information Systems, Central Taiwan University of Science and Technology, No.666, Buzih Road, Beitun District, Taichung City, Taiwan 40601, R.O.C., e-mails: chchen@ctust.edu.tw, ronchang@ctust.edu.tw

[2]Department of Biomedical Imaging and Radiological Science / School of Chinese Medicine, China Medical University, No. 91, Hsueh-Shih Road, Taichung City, Taiwan 40402, R.O.C., e-mail: b50703@gmail.com

[3]Department of Radiation Oncology, Ditmanson Medical Foundation Chiayi Christian Hospital, No. 539, Zhongxiao Rd., East Dist., Chiayi City, Taiwan 60002, R.O.C., e-mail: 07130@cych.org.tw

[4]Department of Biomedical Informatics, Asia University, 500, Lioufeng Rd., Wufeng, Taichung City, Taiwan 41354, R.O.C., e-mail: chyao@mail.cmu.edu.tw

Keywords: RapidArc, gel dosimeter, dosimeter, optical-CT

The NIPAM gel dosimeter has been revealed by Senden et al. since 2006. As compared with other polymer gel dosimeter, NIPAM gel dosimeter has many advantages such as low toxicity, high spatial uniformity, and long-term stability. However, Sedaghat et al. (2011) claimed that the exothermic nature of polymerization reaction may cause deviation of dose response. And physicochemical error can be observed between small calibration vials and in-phantom calibration methods. Therefore, the aim of this study was to evaluate quantitatively the error using gamma evaluation technique. A NIPAM gel dosimeter was prepared with 5% gelatin, 5% NIPAM, 3% *N,N'*-methylene bisacrylamide, and 10 mM Tetrakis (hydroxymethyl) phosphonium chloride. Then it was irradiated by RapidArc™ (Varian Medical Systems). The irradiation energies for VMAT were set as 6 MV photons and prescribed dose was 5 Gy. In current study, two calibration methods were used for dose conversion. The first method is the small vial calibration method, and the dose response curve of NIPAM gel dosimeter was proposed by Chang et al. (2011). Five glass vials (Pyrex model no. 9826, 13 mm outer diameter, 100 mm length) filled with NIPAM gel and each vial was irradiated at various doses (i.e. 0, 1, 2, 5, and 8 Gy) by the same accelerator. The second method is the in-phantom calibration method proposed by DeJean et al. (2006). A phantom filled with NIPAM gel were irradiated by four pencil beams irradiation at dose 1Gy, 2 Gy, 5Gy and 8Gy, respectively. Two calibration curves were obtained from the small vial calibration and in-phantom calibration, and can be used for dose conversion of NIPAM gel dosimeter. The gamma evaluation was adopted and the pass rates were calculated point by point by comparing the dose distribution between TPS and measured data from gel dosimeter. The criterion 3% dose difference and 3 mm dose-to-agreement criterion for gamma evaluation was used. The pass rate was calculated from the percentage of points with $\gamma < 1.00$. Although some previous researches claimed that discrepancies between small vials calibration and in-phantom calibration methods, the gamma pass rates obtained from two methods were in the same level. Detailed discussion will present in current study.

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EXAMINATION OF LARGE FUSION DEVICE BY MEANS OF NANOSECOND NEUTRON PULSE GENERATED BY DENSE PLASMA FOCUS PF-6

Vladimir Gribkov[1, 2], *Barbara Bienkowska*[1], *Slawomir Jednorog*[1]*, *Marian Paduch*[1]

[1]Institute of Plasma Physics and Laser Microfusion, Hery 23, 01-494 Warsaw, Poland, *e-mail: slawomir.jednorog@ifpilm.pl
[2]The A.A. Baikov Institute of Metallurgy and Material Science, Russian Academy of Sciences, 119991, Moscow, Leninskii pr., Russia, e-mail: gribkovv@rambler.ru

Keywords: dense plasma focus, PF-6, PF-1000, anisotropy, fusion of light elements

The aim of presented research was to investigate, an angular distribution of neutron emission of plasma focus (PF) device PF-6 and afterward the use of the above device for the examination of large Z-pinch fusion facility. As a result of deuterium-deuterium (D-D) fusion reaction this PF-6 generates a quasi-monoenergetic single neutron pulses that have duration of 10–20 ns. The total neutron yield is in the range of $10^8 \div 10^9$ neutrons per pulse. The device has been chosen for the experiment on modelling of the interaction of neutron pulse with a vacuum vessel of a fusion facility. Large stainless steel Dense Plasma Focus (DPF) vacuum chamber of a PF-1000 facility was used as a subject of investigation.

The anisotropy measured on particular direction is expressed as the neutron flux ratio while the distinguish direction is perpendicular to the main axis of the device.

In order to investigate the response of target device the activation monitors with silver and yttrium were applied. The initial anisotropy of neutron emission of the PF-6 was investigated in a quasi non scattering condition. Than the PF-6 device was mounted inside the vacuum vessel of PF-1000 device. Significant change has been observed in this characteristic after penetration of neutrons through the PF-1000 device. Discussion of the reason of this data modification is connected with the absorption and elastic scattering of neutrons on obstacles belonging to the device.

It was shown that in case of large plasmas facilities like JET and ITER their examination with DPF source alternatively to the other calibration sources could fulfil us with basic information regarding neutron interaction with mainstream plasma devices.

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STUDY ON DETERMINATION OF LOW NEUTRON DOSE IN STRONG X(γ) RADIATION FIELD

Zhang Guiying[1, 2], *Li Jingyun*[2], *Xu Guoliang*[2], *Li Jue*[2], *Wang Jianguo*[2], *Niu Dongsheng*[2], *Cao Lei*[2], *Ni Bangfa*[1], *Xiao Caijin*[1], *Jin Xiangchun*[1], *Yao Yonggang*[1], *Guo Zeqin*[2], *Wang Zhichao*[2], *Qiu Yutong*[2]

[1]China Institute of Atomic Energy, Fangshan District, Beijing, China, e-mail: 18600668652@163.com
[2]Beijing Institute of Occupational Medicine for Chemical Industry, Beijing, China

Keywords: Bubble Neutron detector, γ rays, 6 MV medical accelarators

X-rays produced by medical accelerators have been widely used in radiotherapy. During the process of therapy, a certain level of photonuclear neutrons may be produced by the (γ,n) and (γ,2n) reactions on elements in surrounding materials. These neutrons are potentially harmful for medical personnel and patients. It has been a difficult problem to evaluate the neutron radiation dose levels of medical accelerator and the occupational health effects on related personnel, so as to effectively control the neutron dose received by the staff and patients. Bubble Neutron detector (BND) is one of the most promising neutron dosimeters to solve the above-mentioned problem for its stable energy response over wide range of neutron energy, low detection limit, high detection sensitivity, real-time monitoring of neutron dose and – insensitivity to γ rays. In this work, the experimental results have been shown as followed:

1) BND is responsive to γ rays with the energy and dose higher than 6 MeV and 2Gy.
2) There are no photonuclear neutrons produced in the treatment plane of 6 MV medical accelarators.
3) The bubble signals produced in the BND in the treatment plane of 6 MV medical accelarators are from γ rays.

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ANALYTICAL METHODS FOR USING ALPHA-SPECTROMETRY

Jenny Halleröd, Lovisa Bauhn, Christian Ekberg, Emma Aneheim*

Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Kemivägen 4, Gothenburg, Sweden,
*e-mail: hallerod@chalmers.se

Keywords: alpha-spectrometry, zaphonelack, analytical methods

Alpha-spectrometry is a useful measurement technique within the fields of partitioning and transmutation of used nuclear fuel. The alpha-spectrometry can measure and distinguish between several alpha emitters present in the same sample, something that few other measuring techniques can manage. Due to this is the alpha-spectrometry a very useful measurement technique, but there are however some draw backs. At Chalmers University of Technology a source of error has been found within the sample preparation resulting in unreliable results. In this work have different methods of sample preparation been investigated.

There are several different protocols for preparation of alpha-spectrometry samples. A common method for alpha spectrometry measurements is electroplating, at Chalmers a liquid sample is placed on an alpha planchet and mixed with zaphonelack. The sample mixture is dried under an IR-lamp and the organic residue is burnt of using a gas burner. Problems has however been found concerning the reliability and repeatability of the method. To be able to find a reliable method for the sample preparation, different approaches have been investigated.

Some of the investigated parameters are the possible measurement differences if the sample is premixed with the zaphonelack before placement on the alpha planchet, how the volume and placement of the sample on the planchet affect the measurement and how the burning affect the sample, is there a difference if the sample is burnt from the bottom of the planchet or from above?

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A NEW ALLOY COMPENSATION METHOD FOR THICKNESS MEASUREMENT

Jin-Woo Lee[1, 2], Jongho Jeon[1], Chang-Hyeong Kim[3], Sang-Jin Kim[4], Jong-Il Kim[2]

[1]Radiation Safety & Protection Team, KAERI, Jeongeup-Si, Korea, e-mail: jinwoo@kaeri.re.kr
[2]Department of Radiation & Science Technology, Chonbuk National University, Jeonju-Si, Korea
[3]Department of Nuclear Engineering, Hanyang University, Seoul-Si, Korea
[4]Gwangyang Works, POSCO, Gwangyang-Si, Korea

Keywords: accuracy, alloy, compensation, correction value, density, high-strength steel, radioisotope thickness gauge

The thickness of a steel product is one of the most important quality factors. In addition, an accurate thickness measurement using radiation is essential for a quality assurance. In on-line manufacturing iron-making processes, several kinds of elements are mixed in the iron to meet the required quality for the final products. Moreover, the influence of the alloyed elements on the thickness deviation measurement is due to their own properties.

The conventional method using a sample acquired at the trial production to compensate thickness deviation from the mixture of elements is very limited because there are many new alloy steel products.

In the present study, a high-quality alloy compensation method for a thickness measurement is developed in the form of a correction function of each element's weight percentage based on the analysed data of the MCNP code.

Our results show that the new alloy compensation method satisfies the accuracy requirement for thickness gauges, which is ±0.5% of the target thickness. The new method has been successfully adopted in high-strength steel product lines at POSCO in Korea.

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LUMINESCENCE CHARACTERISTICS OF Al_2O_3:C TL GLOW PEAKS SEPARATED BY COMPUTERIZED GLOW CURVE DECONVOLUTION

Y. J. Lee[1], *M. J. Kim*[1], *D. G. Hong*[2]

[1]Radiation Technology Institute, Neosiskorea Co. Ltd., Daejeon 305-380, South Korea
[2]Department of Physics, Kangwon National University, Chuncheon 200-701, South Korea

Since the introduction in the early 1990s, high sensitive Al_2O_3:C for ionization radiation has attracted considerable attention as a material for TL dosimeter to measure an environmental radiation dose, e.g. a very low radiation dose. This material, however, indicates a limit of TL dosimeter due a serious thermal quenching, that caused reduction of the TL signal at high temperature. The interest in this phosphor was further intensified when it was considered as a sensitive and practical material for OSL dosimetry because of its excellent OSL properties and capability of avoiding the thermal quenching. It shows linearity of light output for radiation doses of seven orders of magnitude, no fading of information due to the deep nature of the traps, and extremely good environmental stability. Although the exploitation of the TL glow curves of Al_2O_3:C for OSL dosimetry has been extensively investigated, most previous works have been based on the TL intensity integrated over a particular temperature range on the glow curve, without any separation of peaks. In this presentation, we discuss the physical characteristics of the overlapping peaks in the TL glow curves of Al_2O_3:C sample.

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PRELIMINARY DESIGN OF CR39 FAST/THERMAL NEUTRON PERSONAL DOSIMETER USED IN OIL & GAS FIELD LOGGING

Cao Lei[1], *Wang Jianguo*[1], *Li Jingyun*[1], *Zhang Guiying*[1], *Deng Jun*[2], *Song Yanchao*[2], *Guo Zeqin*[1], *Wang Zhichao*[1], *Qiu Yutong*[1]

[1]Beijing Institute of Occupational Medicine for Chemical Industry, No.50 Road Xiangshanyikesong, Haidian District, Beijing, China,
e-mail: caolnirp@163.com
[2]Chinese Center for Disease Control and Prevention, Beijing, China

Keywords: fast/thermal neutron personal dosimeter, externally assigned response, BN track pre-adaptor

Objective: To increase externally-assigned response, improve energy response of CR39 and develop positive fast/thermal neutron personal dosimeter applicable for occupational exposure in oil & gas field logging by using pre-recoil layer. *Methods:* The externally-assigned response of CR39 detector was improved through increasing the track density by using the α particle induced by the reaction of $^{10}B(n,\alpha)^7Li$ with the BN as pre-recoil layer, and the increase was vilified by using both Monte-Carlo simulation and experiment exposed by standard neutron source. *Results:* Fast/thermal neutron personal dosimeter's neutron flux sensitivity and neutron dose equivalent sensitivity are 3.46×10^{-4} track per neutron, $7.57\pm0.41\times10^2$ track × cm^2 × mSv^{-1} respectively. The detecting linearity range is between 0.013 and 52.8 mSv. *Conclusions:* According to theoretical derivation and experiment of standard 241Am-Be neutron source, detecting efficiency and energy response of CR39 were effectively improved, and quantitative measurement of dose contributed by thermal neutron was realized. CR39 fast/thermal neutron personal dosimeter of high sensitivity is applicable to oil & gas field logging environment and of potential development.

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DEVELOPMENT OF ANALYSIS TECHNIQUES FOR PRECISE MEASUREMENTS OF ^{233}U IN ENVIRONMENTAL SAFEGUARDS SAMPLES WITH HIGH THORIUM CONTENTS

Sang Ho Lim, Sun-Ho Han, Ranhee Park, Minyoung Lee, Chi-Gyu Lee, Jinkyu Park, Kyuseok Song

Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daedeok-daero 989-111, Yuseong-gu, 34057 Daejeon, Republic of Korea, e-mail: slim@kaeri.re.kr

Keywords: environmental safeguards samples, uranium, thorium, MC-ICP-MS, chemical separation

Environmental safeguards samples often contain various species depending on sampling environments such as locations and facilities, etc., which may interfere with the target isotopes or elements. Among the interfering species, ^{232}Th is one of the major interfering isotopes in analysis of ^{233}U by using ICP-MS due to the formation of [^{232}ThH]. In this study, two major improvements were adopted in order to minimize the influence of [^{232}ThH] on ^{233}U isotopic analysis. The first was the use of desolvator (Aridus II, CETAC), which induces decrease of the formation of [^{232}ThH], in the sample introduction system of MC-ICP-MS (Neptune Plus, Thermo Scientific). The formation ratios of [^{232}ThH]/^{233}U were evaluated using various concentrations of U/Th mixture solutions. The result showed that the formation ratios of [^{232}ThH]/^{233}U decreased along with the use of desolvator. The second was UTEVA-based chemical separation technique in environmental samples with high thorium contents by adjusting separation parameters of uranium and thorium. The appropriate eluents were identified as 5 M HCl and 0.01 M HCl for thorium and uranium, respectively. The chemical separation yields for uranium and thorium were achieved more than 95% based on the elution curves of these elements. In particular, separation factor of thorium from uranium was estimated as ~10^6.

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CALIBRATION OF GAMMA-RAY DETECTORS USING GAUSSIAN PHOTOPEAK FITTING IN THE MULTICHANNEL SPECTRA WITH LABVIEW-BASED DIGITAL SYSTEM

Leo Schlattauer[1], Jiri Pechousek[1], Levent Parali[2], Israfil Sabikoglu[3], Cuneyt Celiktas[4], Gozde Tektas[4], Petr Novak[1], Ales Jancar[5], Vit Prochazka[1]*

[1]Department of Experimental Physics, Faculty of Science, Palacky University, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic, *e-mail: jiri.pechousek@upol.cz
[2]Celal Bayar University, Departments of Electronics and Automation, 45400 Turgutlu, Manisa, Turkey
[3]Celal Bayar University, Faculty of Arts and Sciences, Department of Physics, 45140 Muradiye, Manisa, Turkey
[4]Department of Physics, Faculty of Science, Ege University, 35040 Bornova, Izmir, Turkey
[5]VF, a.s., Svitavska 588, 679 21 Cerna Hora, Czech Republic

Keywords: detector calibration, Gaussian fit, LabVIEW™

Different methods and processes are used in the field of gamma-ray detector calibration. The aim of the presented work is to validate the newly implemented calibration concept with a well-known Gaussian fit in the developed software application.

Various source's pulse-height spectra have been recorded utilizing the gamma-ray spectrometry system and two similar NaI:Tl detectors. The detector signal acquisition uses digital oscilloscope card, personal computer and dedicated software application which works as a pulse-height spectra recorder (two channels are simultaneously digitized) and main application as multichannel analyser (MCA) for off-line spectra analyses. All steps were controlled by LabVIEW™ (National Instruments) graphical programming.

The energy scale calibration of gamma-ray detectors and other parameters evaluations were performed with various radioactive sources of gamma-rays: ^{22}Na (511.0 keV, 1274.5

keV), ^{60}Co (1173.2 keV, 1332.5 keV), ^{137}Cs (661.66 keV), ^{152}Eu (121.78 keV, 344.28 keV). Several source-detector distances with linear geometry were measured. Then all the parameters such as linearity of the energy scale, FWHMs of selected photopeaks, stability of the peak centre position, detection efficiency, detector dead time, etc. were analysed.

Analysed regions of interest as photopeak positions were selected manually. The photopeak background correction was performed automatically expecting its linear behaviour. Data above the correction background line was further analysed. Presented method uses Gaussian function for peak fitting by least square method built in LabVIEW™. The outputs of this function are centre of the Gaussian, area, amplitude, standard deviation and residua.

After analysis of all relevant photopeaks, the detector energy calibration is done by least square method with linear or polynomial fit (the 2nd order). This calibration resulted in average Gaussian centre positions (x-axis, channels) displayed in the accordance to energies (y-axis, keV). A calibration lines and equations are calculated for both detectors.

Results have been evaluated and compared with the results taken from commercial gamma-ray spectroscopy systems MAESTRO® (ORTEC) and ProSpect® (Canberra) calculated on the same data. Evaluations declared the compliance of developed method, for some parameters a better precision was reached. The developed application can be used for a spectrometer testing, evaluation purposes and for getting detailed description of the nuclear detection system.

Nuclear safeguards

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ON-SITE GAMMA-SPECTROMETRIC ASSAY OF URANIUM AND THORIUM IN SUPPORT OF SAFEGUARDS VERIFICATIONS AT BULK HANDLING FACILITIES

Andrey Berlizov, Fabian Rorif, Volkan Unsal, Kerrin Swan, Albert Bopape, Jean Millon*

Department of Safeguards, International Atomic Energy Agency, PO box 100, Vienna, Austria, *e-mail: a.berlizov@iaea.org

Keywords: non-destructive assay, gamma-spectrometry, international safeguards

Quantitative verification of nuclear material in bulk form involves material net weight, element concentration and isotope abundance determinations. The net weight is normally determined by inspectors during field activities, while element concentration and isotopic abundance are determined either on-site or off-site. The off-site determination aiming the highest analytical accuracy is performed using destructive assay methods, which are normally executed under well-controlled environment in the Nuclear Material Laboratory of IAEA Safeguards Analytical Services. This type of analysis aims at detecting so-called bias defect scenarios, where only a small fraction of the declared amount of nuclear material is missing. Contrary to that, the on-site determinations are performed by inspectors in the field, mostly using non-destructive assay (NDA) methods. These verification measurements address partial defect diversion scenarios where some fraction of the declared amount of nuclear material has been removed. It has been common that NDA in-field measurements mostly addressed isotopic abundance determination, while elemental concentrations were assumed from chemical compound (for pure materials) or taken from declaration (for scrap and impure materials). To address this insufficiency, a portable gamma-spectrometric system for in-field measurements of uranium and thorium concentration in different matrices has been developed. A sample of the verified powder or solution is measured in a fixed geometry, which has been pre-calibrated using well-characterized reference material. A correction, taking into account differences between the verified and calibration samples (e.g. on the density and elemental composition), is calculated analytically or by Monte Carlo. Non-equilibrium due to recent chemical separation of analyzed material is taken into account. The paper presents the system components, including methodology and software supporting evaluation of the measurement data, as well as results of its recent field deployments at conversion and fuel fabrication facilities.

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DEPTH PROFILE OF A HEATED RED BRICK FOR RETROSPECTIVE DOSIMETRY USING THE SAAD-POSL METHOD

M. J. Kim[1], Y. J. Lee[1], I. Chang[2], J. I. Lee[2], J. L. Kim[2], D. G. Hong[3]

[1]Radiation Technology Institute, Neosiskorea Co. Ltd., Daejeon 305-380, Korea
[2]Health Physics Department, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea
[3]Department of Physics, Kangwon National University, Chuncheon 200-701, Korea

The methodology for the application of retrospective dosimetry using TL/OSL measurement of building materials is now well established. Especially, the TL/OSL signal is measured from quartz inclusions extracted from the building materials and the absorbed dose is mainly evaluated using single aliquot regenerative dose (SAR) method. Under the procedures, it has been demonstrated that it is feasible to routinely determine an absorbed dose to ~20 mGy in typical bricks that are less than 50 years [1]. Recently, for establishing a fast assessment method of accidental dose using building materials as like heated red brick, roof tile, ceramic tile, and toilet porcelain, SAAD-POSL method with core-disc sampling was newly introduced [2, 3]. Using this method, the reliability of the SAAD-POSL method was proven for doses up to 7 Gy with a minimum detectable dose as low as 10 mGy. Additionally, the calculation time for the equivalent dose was about 2 h. These results indicated that the SAAD-POSL method is more effective than the conventional SAR-OSL method as a fast assessment method of the accidental dose. In this study, we first analysed the TL/OSL characteristics after beta, X-ray and gamma irradiation. Then we compared the depth profile of a heated red brick between the SAAD-POSL method and the SAR-OSL method with Cs-137 gamma irradiation. Finally the depth profiles of a heated red brick after beta, X-ray and gamma irradiation were evaluated, respectively.

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THE STUDY ON PORTABLE NEUTRON SOURCE PROTECTIVE EQUIPMENT OPTIMIZATION FOR RADIOACTIVE WELL LOGGING FIELD WITH MCNP CODE

Zhang Feng, Wu He, Gu Mingxiang, Han Zhongyue*

College of Geosciences, China University of Petroleum (East China), Qingdao, Shandong Province, China, *e-mail: easywh@163.com

Keywords: radioactive well logging, neutron source, portable protective equipment, MCNP

The radioactive well logging method has the unique advantages in some aspects, and absolutely impossible be replaced by other geophysical logging technology. With the wide application of nuclear logging and the development of new generation compact logging equipment. In addition, the HSE management philosophies have paid sufficient attention in many fields, and the nuclear well logging in petroleum industry is no exception. Furthermore, radioactive sources utilized in the logging tools usually have the characteristic of highly mobility and transported cross the world, and there should be a matching portable protective equipment, which is specially designed.

In the present work, we develop a transferable neutron source protective tank rather than the indoor ponderous shielding facility by Monte Carlo simulation, using MCNP code. Based on the two aspects of moderation and absorption of neutron transport process, the tank is divided into two layers and filling with different shielding materials, respectively. Firstly, moderating properties of various high density metal are compared, the stuffing of inner layer is selected, naturally. After optimizing filling material of the inner layer by MCNP code, and then different hydrogen-rich, boron-containing materials for thermal neutron-absorbent are examined. Finally, according to the IAEA radiation protection standards, dimensional requirement and material availability to determine the size of the protective equipment. The study result shows that the new portable neutron source protective tank is safe, portable and high efficiency.

Production of radionuclides

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DEVELOPMENT OF HIGH-DENSITY LEU DISPERSION TARGET AT KAERI

Yong Jin Jeong, Sung Hwan Kim, Ki Nam Kim, Kyu Hong Lee*

Research Reactor Fuel Development Division, Korea Atomic Energy Research Institute, Daedeokdaero 989-111, Daejeon, Korea,
*e-mail: yjjeong@kaeri.re.kr

Keywords: high-density, LEU, dispersion target, atomized powder

KAERI has been developing dispersion commercial-grade LEUAlx target to provide it to KiJang Research Reactor(KJRR) for Mo99 production in Korea. Because it is also necessary to develop high-density dispersion target with low enriched uranium(LEU) in order to enhance Mo99 production efficiency, KAERI is focusing on developing high-density dispersion target in parallel with developing commercial-grade dispersion target.At last RRFM2015, KAERI proposed atomized metallic uranium powder and UAlx powder to manufacture commercial-grade and high density-density dispersion targets. For high-density dispersion target, KAERI is using two kinds of atomized powders which are metallic U powder and U-10wt.% powder consist of alpha uranium and UAl2 phases. In this paper, the results of developing high-density dispersion target with using two kinds of atomized powders will be presented.

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GAS PHASE CONVERSION OF Sr, Mo, AND U(VI) COMPOUNDS IN NITRATING MEDIA

Sergey A. Kulyukhin, Yurii M. Nevolin, Margarita P. Gorbacheva*

IPCE RAS, Leninskii prospekt, 31-4, Moscow, Russia, *e-mail: kulyukhin@ipc.rssi.ru

Keywords: gas conversion, uranium, fission product, nitrous gases

The current plans calling for the transition to fast-neutron reactors, as well as to reactors with a high fuel burn-up have stimulated an active search of spent nuclear fuel (SNF) reprocessing techniques that would be alternative to the classical Purex process. One of the promising technologies of short-cooled SNF reprocessing is voloxidation (volume oxidation) of both SNF and zircalloy fuel cladding, followed by treatment of voloxidation products in the atmosphere of NOx gases. Although the technology allows obtaining water-soluble actinide salts, the behavior of fission elements occurring in various chemical forms in NO_x gas media remains little-studied.

Our previous studies using U_3O_8, MoO_3, ZrO_2, and SrO as an example showed that during their gas-phase conversion in the atmosphere of (NO_x + vapor H_2O) or HNO_3 (vapor), separation of U and fission products (Mo, Zr) could take place possible. However, after voloxidation, U, Sr, and Mo may occur in SNF as not only oxide phases, but also as other compounds. According to literature data, U, Sr, and Mo can be present in SNF as UO_2MoO_4, $SrUO_4$, and $SrMoO_4$. The aim of this work was to study the gas-phase conversion of the above-mentioned compounds of U, Mo, and Sr in nitrating media.

The compounds were synthesized using the techniques described in literature. The phase composition of the obtained products was studied using powder diffractometry, which showed the following phase composition of the compounds: $(UO_2)_x(OH)_y(MoO_4)_z$, $SrUO_4$, and $SrMoO_4$.

The obtained compounds were kept for 1 to 12 d at room temperature (20–25 °C) or at a temperature of 130 to 150 °C for 3–5 h in the atmosphere of (NO_x + vapor H_2O) or HNO_3 (vapor). The powder diffraction patterns of the resulting compounds were obtained, and the solubility of the compounds in water was measured. The U(VI) content in the aqueous phase was measured using spectrophotometric analysis, content of Sr and Mo – using ICP mass-spectrometric method.

According to the findings, gas-phase treatment of $(UO_2)_x(OH)_y(MoO_4)_z$ leads to formation of new phases. Uranium partially converts to water-soluble compounds, whereas Mo remains in the insoluble phase virtually fully. For $SrUO_4$, a complete conversion of the compound takes place, with both U and Sr taking insoluble forms. Gas treatment of $SrMoO_4$ does not lead to the conversion of the compound, and Sr and Mo remain insoluble. Thus, in contrast to U, Mo, and Sr oxides, the gas-phase conversion of their compounds in nitrating media does not allow carrying out a complete separation of U from Mo.

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PRODUCTION OF ^{99m}Tc BY IRRADIATION OF $^{nat/100}$Mo TARGETS AT TR-19 CYCLOTRON

Radu Leonte[1, 2], Dana Niculae[1], Gheorghe Căta-Danil[2], Lidia Matei[3], R. R. Johnson[4]*

[1]Department of Radioisotopes and Radiation Metrology, “Horia Hulubei” National Institute for R&D in Physics and Nuclear Engineering, str. Reactorului 30, Magurele, IF, Romania, *e-mail: radu.leonte@nipne.ro
[2]Faculty of Applied Sciences, University Politehnica of Bucharest, Splaiul Independenței 313, Bucharest, Romania
[3]Best Theratronics, 413 March Road, Ottawa, ON, Canada
[4]Best Cyclotron Systems, 8765 Ash St., Vancouver, BC, Canada

Keywords: ^{99m}Tc, cyclotron, target processing, dry distillation

The most used radioisotope in nuclear medicine is technetium-99m. The availability of ^{99m}Tc became a worldwide concern after the supply crisis of ^{99}Mo starting in 2008. This paper presents our results for an alternative route, cyclotron based, of direct production of ^{99m}Tc, by irradiation of molybdenum targets. The irradiation experiments were performed at a TR-19 cyclotron. The targets used to produce ^{99m}Tc must withstand the temperatures generated by high-power irradiation and must be maintained below the volatilization temperatures of any molybdenum trioxide or technetium oxides that may be generated. The targets must be resilient during the irradiation process, yet, they must be easily post-processed to separate the ^{99m}Tc. We used copper supports, in which was pressed natural molybdenum ^{nat}Mo and enriched ^{100}Mo respectively [1]. The targets were irradiated for 1 hour with a proton beam of 15 MeV and 50 μA, obtaining up to 6.6 GBq (decay corrected to EOB, ^{100}Mo target). After irradiation, the ^{99m}Tc was ultimately recovered as sodium pertechnetate (Na^{99m}TcO$_4$). This was accomplished by a chemical pre-processing step, followed by separations based on differences in physical and chemical properties of the components. ^{99m}Tc have been separated from neutron-irradiated $^{nat/100}$Mo by their different sublimation temperatures. After dry distillation in oxygen flow, the ^{99m}Tc activity was determined along the length of the tube, the different active regions were recovered in NaOH 1M and the resulted solutions were analysed by gamma spectrometry for radionuclide composition and by thin layer chromatography to asses the radiochemical purity of Na^{99m}TcO$_4$. The overall process yield was about 55% and the presence of ^{100}Mo was not detected in the purified solution. Most of the radioactivity was recovered in the final solution, while the radiochemical purity was higher than 95%.

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ACTIVATION CROSS-SECTIONS OF ^{3}He-PARTICLE INDUCED NUCLEAR REACTIONS ON ^{nat}Ti UP TO 70 MeV: NEW DATA AND COMPILATION

Ferenc Szelecsényi[1], Zoltán Kovács[1], Kotaro Nagatsu[2], Ming-Rong Zhang[2], Kazutosi Suzuki[2]*

[1]Cyclotron Application Department, Institute for Nuclear Research of the Hungarian Academy of Sciences, ATOMKI, 18/c Bem tér, H-4026 Debrecen, Hungary, *e-mail: szele@atomki.hu
[2]Molecular Imaging Center, National Institute of Radiological Sciences, NIRS, 4-9-1 Anagawa, Inage-ku, Chiba, Japan, e-mail: nagatsu@nirs.go.jp

Keywords: ^{3}He-particle induced reactions, natural Ti target, excitation functions, monitor reactions

Well-measured excitation functions of ^{nat}Ti + ^{3}He nuclear processes have broad practical applications including medical radioisotope production (^{48}V ($T_{1/2}$ = 15.976 d)), ^{3}He-beam intensity/energy monitoring, thin layer activation etc. In spite of their importance, there are only a few works in the literature which reports on cross sections for the ^{nat}Ti(^{3}He,x)^{48}Cr, ^{nat}Ti(^{3}He,x)^{48}V, ^{nat}Ti(^{3}He,x)^{48}Sc, ^{nat}Ti(^{3}He,x)^{47}Sc, ^{nat}Ti(^{3}He,x)$^{46m+g}$Sc and ^{nat}Ti(^{3}He,x)^{44m}Sc nuclear reactions.

The aim of the present work was to provide new cross-section values for the above reactions up to 70 MeV. (Only one group reported data above 36 MeV.)

The excitation functions were measured using the standard stacked-foil method. Commercially available thin ^{nat}Ti foils were activated in four different irradiations, performed with ^{3}He-particle beams (70 and 42.6 MeV) of the AVF-930 isochronous cyclotron of NIRS, Chiba. Parts of the target holder formed a Faraday-cup which was connected to a current integrator in order to determine the charge collected during the irradiations. For 'consistency check', we employed the well measured excitation function of the ^{nat}Cu(^{3}He,x)^{66}Ga reaction. The radioactive decay of the residual nuclei in the activated samples was followed without chemical separation using high-resolution off-line gamma-ray spectroscopy. The results obtained from the analysis of several clear gamma-lines originated from the same radioisotope were averaged, if it was possible. Our new cross-section values were also compared with the earlier reported literature data as well as the evaluated theoretical predictions by means of the TALYS code as compiled in the TENDL-2014 library. The datasets showed good agreement in the overlapping energy regions for all reactions. Our results revealed that although the status of the experimental database of the ^{nat}Ti(^{3}He,x)^{48}V nuclear process seems to be useful even to prepare recommended excitation function up to 70 MeV, the presence of the co-formed ^{48}Cr and ^{48}Sc activities in the irradiated sample renders more difficult the immediate use of this process for monitor purpose. (The ^{48}Cr ($T_{1/2}$ = 21.56 h) decays directly to the ground state of ^{48}V via EC (100%) while the ^{48}Sc ($T_{1/2}$ = 1.821 d) has almost the same strong gamma-lines (at 983.526 (Iγ = 100.1%) and 1312.121 (Iγ = 100.1%) keV) as the ^{48}V.) Our calculations suggest at least 300 h waiting time before starting the ^{48}V activity measurement for beam monitoring.

Based on the well measured nuclear properties and the reliable cross-section database of the ^{nat}Ti(^{3}He,x)^{44m}Sc and ^{nat}Ti(^{3}He,x)^{47}Sc nuclear processes, we recommend them for monitoring of ^{3}He-particle beams above 40 MeV.

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ACTIVATION CROSS SECTIONS OF PROTON INDUCED NUCLEAR REACTIONS ON PALLADIUM UP TO 80 MeV

Ferenc Tárkányi[1]*, *Ferenc Ditrói*[1], *Sándor Takács*[1], *Julius Csikai*[1], *Alex Hermanne*[2], *M. Shuza Uddin*[2], *Mamoru Baba*[2]

[1]Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI), Debrecen. Hungary, *e-mail: tarkanyi@atomki.hu
[2]Cyclotron Laboratory, Vrije Universiteit Brussel (VUB), Brussels, Belgium
[3]Cyclotron and Radioisotope Center (CYRIC), Tohoku University, Sendai, Japan

Keywords: proton irradiation, palladium target, Ag, Rh, Pd and Ru radioisotopes

Activation cross sections of proton induced nuclear reactions on palladium were measured up to 80 MeV by using the stacked foil irradiation technique and gamma ray spectrometry. The beam intensity, the incident energy and the energy degradation were controlled by a method based on flux constancy via normalization to the excitation functions of parallel measured monitor reactions. Excitation functions for direct and cumulative cross-sections were measured for the production of ^{104m,104g,105g,106m,110m}Ag, ^{100,101}Pd, ^{99m,99g,100,101m,101g,102m,102g,105}Rh and ^{97,103}Ru. The cross section data were compared with the theoretical predictions of TENDL-2014 library. For practical applications thick target yields were derived from the measured excitation functions. Applications for production of some medically related radioisotopes (^{104}Ag, ^{101}Rh, ^{103}Pd) and thin layer activation (^{105}Ag) are discussed.

Prompt gamma activation analysis

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THE IMPROVEMENT OF ELEMENTS DETECTION IN AQUEOUS SOLUTION USING PGAA TECHNIQUE

*Hei Daqian**, *Jia Wenbao*

Institute of Nuclear Analysis Techniques, Nanjing Universityof Aeronautics and Astronautics, Nanjing, Jiangsu, China, *e-mail: heidq@nuaa.edu.cn

Keywords: PGAA, aqueous solution, scintillate detector, liner approach, spectrum analysis

Because of the homogeneousness of destiny and composition, aqueous solution can be considered the best sample in Prompt Gamma-ray Activation Analysis (PGAA) research. A measurement platform based on PGAA technique, which was built for elements detection research in aqueous solution, has been designed and assembled in the Institute of Nuclear Analysis Techniques of NUAA (Nanjing University of Aeronautics and Astronautics). And a series work have been studied on this platform, including the optimization of setups, MDC (minimum detectable concentration) studies of interest elemental, non-liner fitting between character peaks and concentrations, neutron self-shielding effect and internal standard method research. Furthermore, to avoid the disadvantages of traditional approaches, as non-liner problem and huge libraries requirement of LLS method, a novel approach has been studied for the whole spectrum analysis. This approach can be used to analyse the complex spectrums, which was acquired by the poor resolution scintillate detectors as large BGO or NaI. In this approach, the non-liner issue has been turned into liner issue with some immediately corrections and the full spectrum of single element can be extracted. More effective information can be used to improve the analytic level of PGAA by this novel approach.

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COMPLEMENTARY ANALYTICAL AND IMAGING METHODS IN THE INVESTIGATION OF ARCHAEOLOGICAL METAL FINDINGS

Boglárka Maróti[1], László Szentmiklósi[1], Zoltán Kis[1], Eszter Mitcsenkov-Horváth[2], Éva Liptay[3], Tamás Belgya[1]

[1]Centre for Energy Research, Hungarian Academy of Sciences, Budapest, Hungary
[2]Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary
[3]Museum of Fine Arts, Budapest, Hungary

Keyword: prompt-gamma activation imaging

Prompt-gamma activation analysis (PGAA) is a well applicable tool in the archaeometric metal analysis, because, in contrast to the surface analytical methods, the obtained elemental composition represents well the bulk phase. In the present work, prompt-gamma measurements were made on a valuable Egyptian sculpture, and as a complementary method, neutron imaging was used, both at the NIPS-NORMA station of the Budapest Neutron Centre. Local elemental compositions were determined at different parts of the object as shown in the middle figure. The presumably iron-containing parts were analysed to confirm or disprove its meteoritic origin, as well as the structure of the sculpture was investigated.

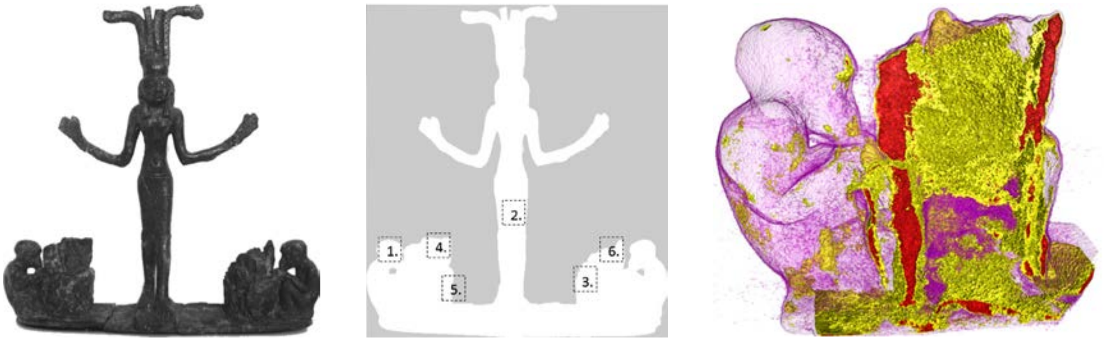

Fig. 1. The photo of the Egyptian Goddess sculpture (left), the spots of the completed element analyses (middle). Neutron imaging also helped to differentiate between different materials (right)

With PGAA, the bronze alloy of the statue was determined to contain 86 wt% Cu and 14 wt% Sn. Based on the elemental composition and visual information, we concluded that the bearing, the goddess, the monkeys and the hollow mounts of the palms are all from the above material. The different statuettes bear no traces of soldering or riveting, thus they were probably made in one single casting process. Considering the missing Ni and Co signatures we can state that the palm stumps were made of non-meteoritic iron. The distribution of the corrosion products was also visualized.

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THE MCNP SIMULATION OF A PGNAA SYSTEM AT TRR-1/M1

Siriyaporn Sangaroon[1], *Wichian Ratanatongchai*[2], *Sasiphan Khaweerat*[2], *Roppon Picha*[2], *Jatechan Channuie*[2]

[1]Department of Physics, Faculty of Science, Mahasarakham University, Mahasarakhum, 44150 Thailand, e-mail: siriyaporn.s@msu.ac.th
[2]Thailand Institute of Nuclear Technology (Public Organization), Bangkok, Thailand

Keywords: MCNP simulation, Thai research reactor (TRR-1/M1), PGNAA

The prompt gamma-ray neutron activation analysis system (PGNAA) has been constructed and installed at a 6 inch diameter neutron beam port of the Thai Research Reactor-1/Modification 1 (TRR-1/M1) since 1989. It was designed for the reactor operating power at 1.2 MW. The purpose of the system is for an elemental and isotopic analytical. In 2016, the PGNAA facility will be developed to reduce the leakage and background of neutrons and gamma radiation at the sample and detector position. In this work, the designed condition of these facilities is carried out based on the Monte Carlo method using MCNP5 computer code. The conditions with different modification materials, thicknesses and structure of the PGNAA facility, including gamma collimator and radiation shields of the detector, are simulated, and then the optimal structure parameters with a significantly improved performance of the facility are obtained.

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HYPEGAM-P SOFTWARE FOR PROMPT GAMMA ACTIVATION ANALYSIS

Gwang Min Sun

Neutron Utilization Technology Division, Korea Atomic Energy Research Institute, 111, Daedeok-Daero, 989Beon-Gil, Yuseong-Gu, Daejeon, Korea, e-mail: gmsun@kaeri.re.kr

Keywords: HYPERGAM, prompt gamma activation analysis

HYPERGAM has been developed as a generalized gamma-ray spectrum analysis software since 2000 and its variant versions were also developed for various applications like typical environmental gamma-ray analysis, neutron activation analysis, fissile nuclear material analysis and so on. HYPERGAM-P is one of the variant versions, which is specialized for the application of prompt gamma activation analysis. It utilizes all the functions of HYPERGAM itself and it also includes useful functions for prompt gamma measurement and analysis. Data acquisition can be carried out using MCBs from ORTEC or CANBERRA companies. The measured spectrum is analysed by choosing the analytic method among absolute, relative and k_0 standardization methods. Efficiency and energy calibration procedures for a broad energy range up to about 11 MeV are more complex and more difficult comparing with those in a typical gamma-ray spectroscopy and instrumental neutron activation analysis, whose calibration energy range is limited to less than 3 MeV. An automatic or manual efficiency calibration routine for the voluminous PGAA samples is possible. Sometimes a recalibration or modification technique of energy and efficiency using internal elements within the sample is very convenient or necessary for users. The user-friendly report with an easy and simple format is also given.

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NUMERICAL SIMULATION ON SCINTILLATOR DETECTOR RESPONSE FOR DETERMINING ELEMENT CONTENT IN PGNAA SYSTEM

Zhang Feng[1, 2]*, *Tian Lili*[1], *Liu Juntao*[1], *Wang Xinguang*[1, 2]

[1]School of Geosciences, China University of Petroleum, Qingdao, Shandong Province, China, 266580
[2]Key Laboratory of Well Logging, China University of Petroleum, Qingdao, Shandong Province, China, 266580, *e-mail: zhfxy_cn@upc.edu.cn

Keywords: element content, gamma ray spectrum, scintillator detector response, PGNAA, Monte Carlo simulation

$LaBr_3$(Ce) and BGO scintillators were often used for spectra detection to determine element and mineral content in the PGNAA system, and it is generally applied in the coal, mineral and oil exploration, etc. The crystal scintillator style, size and energy resolution are critical factors for measuring element content accuracy. The detector response characteristics of $LaBr_3$(Ce) and BGO scintillators were simulated by using Monte Carlo method. In addition, the gamma ray spectra of $LaBr_3$ and BGO scintillator induced by neutron were obtained by establishing numerical models consisting of different multi-element mineral condition, respectively. When the formation rock has the lesser type of element, the calculation results based on different scintillator is similar, and when it has the major type of element, the spectral characteristics of each element in the gamma ray overlap, influence obviously. The higher energy resolution, $LaBr_3$ detector got the more accuracy result than that of BGO detector. The result provides technical support for designing PGNAA system and processing spectrum data to determine element content.

Radiation chemistry

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ABOUT THE MECHANISM FOR PEROXYNITRITE FORMATION UNDER THE RADIOLYSIS OF CRYSTALLINE INORGANIC NITRATES

Anan'ev V., Miklin M., Dyagileva E., Pak V.

Kemerovo State University, Russia, e-mail: eprlab@kemsu.ru

Among the many ways of a point defect formation in ionic crystals with complex ions, with covalent structure of the bonds, are its dissociation and isomerization. The efficiency of the end-product formation via the former process may depend on the free volume of crystal (V) when the initial charge of complex ion localize on the fragment outside the lattice site. In this case Coulomb interaction will lead to a shift some of the charged fragments to lattice sites occupied with uncharged fragments to result the recombination. At the same time other part of the charged fragments will be stable if they are in the interstitial. So, the increase of the free volume results in the decrease of efficiency of end-product formation.

The efficiency of the end-product formation does not depend on the free volume of crystal if the initial charge of complex ion localize on the fragment in the lattice site and the reaction between genetically coupled fragments is forbidden. For example, the values of the initial radiation chemical yield of the nitrite ion – $G(NO_2^-)$ in γ-irradiated alkali and alkaline earth nitrates [1, 2] are not depend on the free volume (see *Table 1*) because the reactions between NO_2^- and O (^{1}P) is forbidden.

Table 1. $G(NO_2^-)$ and $G(ONOO^-)$ for γ-irradiated alkali and alkaline earth nitrates

Nitrate salt	$Sr(NO_3)_2$	$NaNO_3$	$Ba(NO_3)_2$	$RbNO_3$	$CsNO_3$	KNO_3	$Ca(NO_3)_2 \times 4H_2O$	$Mg(NO_3)_2 \times 4H_2O$
V, Å	40	44.5	48	51.1	52.5	55	98	129
$G(NO_2^-)$	0.56	0.21	2.08	0.61	1.61	1.57	1.04	1.83
$G(ONOO^-)$	0.014	0.60	0.040	0.35	0.65	0.14	0.08	0.01

If radiolysis product is formed by isomerization of complex ion then the efficiency of its formation does not depend on the free volume of crystal. As known, the peroxynitrite ion $(ONOO^-)$ is the product of the nitrate ion isomerization under photolysis. The goal of the present paper is to study the radiolysis of alkaline-earth nitrates to develop the mechanism of radiation induced peroxynitrite formation in ionic-covalent crystals.

All nitrates used were analytical reagent grade. The crystals were grown by slowly evaporating from the solutions.

The samples were irradiated with ^{60}Co γ-rays at ~310 K. The dose rate 0.16 Gy/s was measured with a Fricke dosimeter, assuming the radiation chemical yield of Fe^{3+} to be equal to 15.6 $(100\ eV)^{-1}$. The dose absorbed by the sample was calculated using the mass energy absorption coefficients.

The method to determine the peroxynitrite concentration in the sample was described earlier [3].

The values of the initial radiation chemical yield of the peroxynitrite – $G(ONOO^-)$ in γ-irradiated alkaline-earth nitrates are given in Table. Also given in Table is $G(ONOO^-)$ in γ-irradiated alkali nitrates from the literature [4] for comparison. As seen, the dependence of $G(ONOO^-)$ vs. free volume in all nitrates (except $NaNO_3$) can be described by a curve with maximum. We can assume that peroxynitrite is formed as follows.

The irradiation of crystalline nitrates results in the formation of the excited nitrate ions. Decay of such ions results in NO in lattice site and O_2^- outside it. Most of these fragments recombine to result in the nitrate ion, if the free volume is small. If the free volume large enough that rearrangement of fragments occurs first, followed by recombination of the fragments to result in the peroxynitrite ion formation. The fragments are stable, if the free volume is large. In the first and third case, the effectiveness of peroxynitrite formation is small.

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HYDROGEN PRODUCTION FROM THE RADIOLYSIS OF TODGA

Katherine C. Bates, Simon M. Pimblott*

School of Chemistry, University of Manchester, United Kingdom, *e-mail: katherine.bates@postgrad.manchester.ac.uk

Investigation of the hydrogen produced by TODGA under gamma and alpha radiolysis.

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USING N-ISOPROPYLACRYLAMIDE GEL DOSIMETERS TO VERIFY THE DOSE DISTRIBUTION OF INTENSITY MODULATED RADIATION THERAPY

Hsi-Ya Chao[1, 2], Yuk-Wah Tsang[2], Chih-Chia Chang[2], Bor-Tsung Hsieh[1]

[1]Department of Medical Imaging and Radiological Science, Central Taiwan University of Sciences and Technology, Taiwan, R.O.C.
[2]Department of Radiation Oncology, Ditmanson Medical Foundation Chia-Yi Christian Hospital, Taiwan, R.O.C., e-mail: cych06261@gmail.com

Keywords: NIPAM, IMRT, CT, MatriXX

N-isopropylacrylamide (NIPAM) polymer gel dosimeters were employed to verify the dose distribution of clinical intensity modulated radiation therapy (IMRT) treatment planning systems (TPS). Gel preparation was primarily based on the formula proposed by Senden et al.; and 5% NIPAM monomers, 5% gelatin, and 3% BIS were used. Finally, 5 mM of THPC was added to the solution to reduce oxygen content and enhance sensitivity and reproducibility. The gels were irradiated 0, 1, 2, 4, 5, 6, 8, and 10 Gy absorbed doses respectively by a Clinac iX linear accelerator using 6MV X-ray. After polymerization had completed, an X-ray computed tomography HiSpeed scanner was employed to extract the sliced images of the gel. In the present study, five irradiation field IMRT verification plans were created and the irradiation angles were 100°, 135°, 165°, 210°, and 250°, respectively. To create these plans, we first extracted the complete treatment plans of brain tumor patients from the Eclipse^{tm} treatment planning system. Cylindrical acrylic phantoms and MatriXX were then selected to simulate the patients. MATLAB was used to analyze the sliced images and the results of the gamma tests (γ-tests) were performed on the treatment plan and the NIPAM gel dosimeters. The results were then compared to those produced by the MatriXX. To verify the IMRT dose, γ-tests were performed according to the gamma criteria of 3% and 3 mm. Results indicated that the NIPAM gel achieved a 95.02% pass rate in the coronal section image and a 97.57% pass rate in the axial section image. The pass rate produced by MatriXX was 98.90%. The results confirmed the feasibility of using NIPAM polymer gel dosimeters to verify clinical radiotherapy doses.

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THE RADIOLYSIS OF GLYCERALDEHYDE: IMPORTANCE IN CHEMICAL EVOLUTION

J. Cruz-Castañeda[1], E. Aguilar-Ovando[1], Thomas Buhse[2], S. Ramos-Bernal[1], Alicia Negron-Mendoza[1]

[1]Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, México D.F., México
[2]Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Cuernavaca, Morelos, México

Keywords: glyceraldehyde, gamma radiation, chemical evolution

In chemical evolution, the study of the chemical stability of molecules that may have been present under the environmental conditions that may exist on primitive Earth and that exist in extra-terrestrial environments is crucial. This research is focused on analysing the effect of high radiation and mineral surfaces in the survival of racemic glyceraldehyde. Many theories have been proposed to explain the origin of chirality, but accurate physicochemical processes remain controversial. Recently, some these theories have been re-examined experimentally. It is reasonable to consider the participation of heterogeneous catalysts in the prevalence of one enantiomer. In addition, these systems represent a plausible geochemical scenario for possible glyceraldehyde chiral separation.

The experimental part was divided into three groups: (A) Adsorption of racemic glyceraldehyde in different mineral surfaces; (B) the study of the stability of the glyceraldehyde in high-radiation fields in aqueous solution, free or adsorbed on mineral surfaces; (C) Stability under irradiation in the solid state.

The analytical tools used in this study involved UV spectroscopy, high-performance liquid chromatography (HPLC), liquid chromatography-mass spectrometry and electron paramagnetic resonance (EPR).

The results show that this compound is very labile under irradiation and forms a yet-unidentified compound, sugar-like that has a higher absorption in UV, accompanied by a hypochromic shift in peak absorption at 251 nm. This shift increases with irradiation dose. A possible preliminary explanation is that this maximum corresponds to the dihydroxyacetone tautomeric form of glyceraldehyde that polymerizes under these conditions. Experiments conducted with minerals, like Na-Montmorillonite, a type of Smectite clay, produced similar results.

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USUAL AND UNUSUAL PATHWAYS OF OXIDATION AND REDUCTION IN RADIATION CHEMISTRY

Mila D'Angelantonio

Institute of Organic Synthesis and Photoreactivity – National Research Council of Italy – CNR-ISOF, Via Gobetti 101, 40129 Bologna, Italy, e-mail: mila.dangelantonio@isof.cnr.it

Keywords: radiation chemistry, oxidation, reduction, materials, pulse and continuous radiolysis

Radiation chemistry offers a broad range of suitable reaction pathways that include primarily oxidation and reduction of substrates.

Knowledge of (almost) every chance to induce these reactions can be very useful to researchers seeking the right way to address radiation induced processes.

More than thirty years of research in the field allows a collection of tips and tricks to get, in the most effective, the reactivity that best suits the desired reaction. In the poster will be shown some examples of reductions or oxidations exploiting the multiplicity of radicals obtained in a selective manner with pulse radiolysis and / or continuously. From the use of alcohols for obtaining specific reducing conditions, to oxidations induced introducing easily removable ions in organic moieties, to strong oxidation conditions for the characterization of complexes to be used in the energy conversion, to the conversion of less selective radicals into more addressed transient species.

This series of examples will perhaps be useful also to open new horizons in the use of radiolitic techniques.

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RADIOLYSIS OF AIR-WATER SYSTEMS

Ivan Kajan, Christian Ekberg

Department of Chemistry and Chemical Engineering, Nuclear Chemistry, Chalmers University of Technology, Kemivägen 4,
41296 Göteborg, Sweden

The interaction of radiation with oxygen-nitrogen systems leads to the formation of several radiolysis species. The most prominent ones are nitric and nitrous acid that will effect the pH and thus also chemistry of water systems. This will affect the chemistry in nuclear reactor wet wells or burned fuel repository sites. The formation of radiolysis products is represented by a radiolytic yield so called G-value. The G-value represents a number of moles of particular compound formed or destroyed by absorbing one joule of energy delivered by radiation.

A set of experiments with the aim to determine the G-value of nitric and nitrous acids in the air-water systems under the gamma radiation was performed. The effect of the air-water ratio, as well as the obtained dose was examined. For the experiments the gamma source with a dose rate of ≈8.5 kGy/h was utilized delivering the doses ranging from 8.5 kGy up to 180 kGy. As a result the effect of received dose on the pH of water and as well the quantities of formed nitric and nitrous acids were determined.

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ENHANCING THE BIOLOGICAL DEGRADABILITY OF SULFAMETHOXAZOLE BY IONIZING RADIATION TREATMENT IN AQUEOUS SOLUTION

Gyuri Sági[1], Krisztina Kovács[1], Anikó Bezsenyi[2], Erzsébet Takács[1], László Wojnárovits*

[1]Radiation Chemistry Department, Institute for Energy Security and Environmental Safety, Centre for Energy Research, Hungarian Academy of Sciences, Konkoly Thege Miklós út 29–33, Budapest, Hungary, *e-mail: sagi.gyuri@energia.mta.hu
[2]South-Pest Wastewater Treatment Plant, Budapest, Hungary, e-mail: bezsenyia@fcsm.hu

Keywords: sulfonamide antibiotics, ionizing radiation, biodegradation, activated sludge, toxicity

Removal efficiency of persistent organic substances in wastewater is mostly described by the rate of degradation. In numerous studies complete removal of target molecules have been reported, indicating a reasonable alternative for the waste treatment. However, these studies often ignore considerations of the inevitable questions of toxicity and biodegradability of the resulting solutions. Although the high removal rate is very important, but it does not necessarily have to be privileged, since minor alteration of the chemical structure may lead to considerable quality changes that improve the degradation efficiency by conventional technologies. It has been shown that the treatment of persistent organic pollutants by ionizing radiation leads to changes in chemical structure even at very low doses. Nevertheless, very little is known about the biological effects of the treated solutions.

Preparatory to recent study, degradation of sulfonamide antibiotics during ionizing radiation treatment was examined and general degradation mechanism was proposed after applying a large variety of analytical techniques in order to characterize the different stages of decomposition [1, 2]. In the knowledge of the chemical background, this presentation aims to introduce results obtained on sulfamethoxazole irradiation treatment in the 0–10 kGy range, in terms of crucial parameters mentioned in previous paragraph. Biological degradability and inhibitory effects were both investigated using municipal activated sludge. The biodegradability in 0.1 mmol dm^{-3} solutions was increased with only 0.4 kGy and prolonged irradiation induced further conversion to biologically treatable substances. At 2.5 kGy, 16% of the chemically oxidizable organic matter was degraded by biological processes. The total organic carbon content showed a decrease of only 15% at this point, thus high degree of mineralization is not necessary to make the initial molecule available for microorganisms. During the process, formation of H_2O_2 was observed that may decisively influence the biological processes due to its bactericidal effect.

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INNOVATION IN METROLOGY: FAST AUTOMATED RADIOCHEMICAL SEPARATION AND MEASUREMENT FOR STRONTIUM 89 AND 90

Céline Augeray, Magalie Mouton, Lucie Tarlette, Isabelle Baconet, Danièle Dias Varela, Laëtitia Foulon, Fabrice Leprieur, Romain Vidal, Marc Gleizes*

Environmental Sample Processing and Metrology Département, Institut de Radioprotection et de Sûreté Nucléaire, 31 rue de l'Ecluse, 78770 le Vésinet, France, *e-mail: celine.augeray@irsn.fr

Keywords: crisis metrology, strontium 89, strontium 90, ionic chromatography, Cerenkov Effect, mass spectrometry

Measuring radioactivity in food and for radiological monitoring of the environment around nuclear facilities or mining sites requires the quantification of the radionuclides present in the different compartments (liquids or solids), especially of the beta emitters.

Strontium 89 and 90 [1], both pure beta emitters are radioactive isotopes of interest. Because of their toxicity and the similarity of their chemical and physical behavior with calcium, these elements may be found through the food chain. After the Fukushima accident, the necessity of quantifying quickly artificials radionuclides such as strontium 89 and 90 appeared.

The technique developed by IRSN concerns the determination of the activity concentration of strontium 89 and 90 in water, according to the ^{89}Sr/^{90}Sr ratio. It consists of three stages: the chemical separation by ionic chromatography and the measurement of the activity concentration of strontium 89 and 90 by Cerenkov Effect with a liquid scintillation counter (LSC) and/or mass spectrometry (ICP-MS).

The results we want to present at RANC 2016 concern the development of the chemical separation by ionic chromatography and the measurement of strontium by Cerenkov Effect and by mass spectrometry. Studied parameters such as the collection time, the test sample volume, the resin capacity, the quenching parameter, the addition of dioxide introduced into the ICP-MS and the influence of ^{89}Sr/^{90}Sr ratio will be discussed. This technique has been tested with standard solutions and proficiency test samples.

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STRUCTURAL CHARACTERIZATION OF MAGIC POLYMER GEL DOSIMETERS UNDER GAMMA IRRADIATIONS

S. Brahimi-Moussa[1], T. Medjadj[2], Y. Berkani[3], M. El. A. Benamar[1], Z. Lounis-Mokrani[2]

[1]Laboratoire Physique Fondamental Appliquée: Université Saad Dahleb Blida, Algérie
[2]Laboratoire Dosimétrie: Centre de Recherche Nucléaire d'Alger, Algérie
[3]C.A.C: Centre Anti Cancéreux: Centre Hospitalo Universitaire Franz franon de Blida, Algérie, e-mail: b.sounila@hotmail.fr

New, complex radiotherapy techniques require dosimeters that are able to measure complex three-dimensional dose distributions accurately and with good spatial resolution. Polymer gel is an emerging dosimeter being applied to these challenges. The 3D radiation dose distribution using these gel dosimeters may be assessed by magnetic resonance imaging MRI, optical-computerized tomography (optical-CT), X-ray Tomodensitometry (CT-Scan) or ultrasound. As these gel dosimeters are radiologically soft-tissue equivalent with properties that may be modified depending on the environmental and irradiation conditions and the technique of dose assessment, it is important to determine their effects on the dose response.

In this communication, we purpose to characterize the modification induced by photon irradiation on the structure of the MAGIC, normoxic gel polymer under different experimental conditions. The structural modifications induced by irradiation have been investigated using UV-Visible, MEB, FTIR, HPLC techniques. Cobalt gamma rays have first been used for these irradiations under reference conditions at the Secondary Standard Dosimetry laboratory (Algiers) in the dose range 0–12 Gy. The dosimetric characteristics, its sensitivity and stability have also been determined using high energy X ray radiotherapy external beam (6 and 18 MV) in the dose range 0–60 Gy, performed in framework of feasibility study in order to introduce this technique at anti cancer radiotherapy service at Blida hospital.

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DIRECT DETERMINATION OF Pb-210 AND RADIOSTRONTIUM FROM WATER SAMPLES

Carina Dirks[1]**, Aude Bombard*[1]*, Steffen Happel*[1]*, Jackie Pates*[2]

[1]TrisKem International, France, *e-mail: cdirks@triskem.fr
[2]Lancaster Environmental Center, Lancaster University, UK

Extraction chromatographic resins based on crown-ethers such as Sr and Pb Resin are often used for the separation and determination of Pb-210 and radiostrontium in environmental samples, including aqueous samples.

As these resins only show significant Pb and Sr retention at moderate to high acid concentrations they do not allow for the direct loading of the analytes from water samples, accordingly pre-concentration steps such as ion exchange or co-precipitation have to be employed prior to their use.

Two commercially available extraction chromatographic resins (TK100 & TK101 Resin) have been developed with the aim of simplifying the determination of radiostrontium and Pb-210 in aqueous samples by allowing direct loading of the analytes from water samples at pH 2–8. Both resins are based on a crown-ether with high selectivity for Sr and Pb, however including HDEHP (TK100) or a short chained ionic liquid (TK101) into its composition allows for extracting Pb and Sr at a much wider range of pH values. Once loaded onto the respective resin the analytes are purified on and eluted from the same resin prior to their determination by liquid scintillation counting (LSC) or gas proportional counting (GPC).

It has been shown [1] that Sr can be separated from 250 mL (R_{Sr} = 95.2% +/– 2.5%, N = 3) – 500 mL (R_{Sr} = 88.2% +/– 4.3%, N = 3) water samples (pH 7) with high yields using TK100 resin, even when employing sample load flow rates of up to 10 mL/min. The TK101 Resin will at similar flow rates retain Pb near quantitatively ($R_{Pb} \geq 95\%$) even from water samples of up to 5 L; Pb can then be purified and recovered in high chemical yield and purity [1].

In order to further facilitate the Pb-210 analysis in water samples TK101 based discs were prepared, allowing for Pb extraction and purification at even higher flow rates (up to 100 mL.min^{-1}). The intended use of these discs is the determination of Pb-210 after its retention and purification on the TK101 discs, followed by direct liquid scintillation counting of the discs after transfer into a LSC vial and addition of a suitable LSC cocktail; thus significantly facilitating counting sample preparation. First results on the use of these discs will be presented.

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TIME OPTIMIZATION OF ^{90}Sr MEASUREMENTS: SEQUENTIAL MEASUREMENT OF MULTIPLE SAMPLES DURING DECAY OF ^{90}Y

Stina Holmgren[1], Annika Tovedal[1], Oscar Björnham[1], Henrik Ramebäck[1, 2]*

[1]Swedish Defence Research Agency, CRBN-Defence and Security, Umeå, Sweden, *e-mail: stina.holmgren@foi.se
[2]Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Nuclear Chemistry, Göteborg, Sweden

Keywords: ^{89}Sr, ^{90}Sr, MDA, detection limit, interferences, optimization

When measuring ^{89}Sr and ^{90}Sr, with possibly radioactive interferences after e.g. a reactor incident, it becomes important to ensure sufficient removal of interferences from the sample. Previous studies have shown that without adequate decontamination ^{90}Sr measurement on samples containing radioactive nuclides associated with the fission process will often be biased, due to the chemical similarities to strontium. When short lived radionuclides are present in the samples, one common practice is to separate the mother nuclide, ^{90}Sr, from ^{90}Y. As a consequence, the ^{90}Y activity of the sample will decrease from the time of separation. This work presents an improved method for measuring multiple samples sequentially during the decay of ^{90}Y. In a series of *n* samples the first sample will have the highest relative ingrowth of ^{90}Y. This implies that when the minimum detectable activity (MDA) is set as constant, for the entire series, the measuring time needed for each consecutive sample will increase.

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SILVER MEASUREMENT IN PRIMARY WATER

Zsolt Kerner[1], Éva Kovács-Széles[2], Nóra Vajda[3]

[1]Surface Chemistry and Catalysis Department, MTA Centre for Energy, Konkoly-Thege út 29–33, 1121 Budapest, Hungary,
e-mail: kerner.zsolt@energia.mta.hu
[2]Nuclear Security Department, MTA Centre for Energy, Konkoly-Thege út 29–33, 1121 Budapest, Hungary, e-mail: eva.szeles@energia.mta.hu
[3]RadAnal Ltd., Budapest, Hungary, e-mail: vajdanor@gmail.com

Keywords: silver, primary circuit, ion exchange chromatography, gamma spectrometry

^{110m}Ag is a common radioactive contaminant in the primary circuit of nuclear power plants. ^{110m}Ag originates in fission of uranium and activation process of natural silver also. In case of hermetic fuel assemblies the last source can contaminate the primary circuit. Activity concentration of ^{110m}Ag is measured and controlled in the water and on some surfaces regularly. At the same time the inactive silver is invisible for the operators because of the ultralow concentration. For the understanding of silver transport process and calculating balance it is essential to measure the concentration of natural silver also. A new analytical method was developed for the separation and concentration of silver from primary water samples based on the extraction of silver ions using (silver free) TrisKem International CL-Resin. This resin has excellent distribution coefficient and selectivity for silver. On the other hand it is not possible to eluate linked silver quantitatively so acidic digestion, separation from the supporting materials and organic residue is necessary to get the concentrated sample. Yield is typically above 80 percent. The silver content can be measured by high sensitivity ICP-MS equipment. Detection limit of the method is around 1–5 ng/L.

40 primary water samples of Paks NPP was analysed. All samples was filtered to solution, colloid and particle fraction. The fractions was processed separately. Silver concentration in the working reactors is very low (2–10 ng/L), and much higher (100–300 ng/L) during the transients. Silver can be found in solute, colloidal and particle forms also.

Plant applied chemicals also was analysed by a similar method. The silver content is negligible.

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X-RAY SPECTRA CALCULATION FOR INSPECTION OF SEMICONDUTOR WITH DIFFERENT TARGET/FILTER COMBINATION USING MCNPX

JeongHo Kim, HeyMin Park, KoanSik Joo

Department of Physics, University of Myongji, Cheoin-gu Yongin-si, Korea, e-mail: jeongho5248@gmail.com

Keywords: MCNPX, semiconductor inspection, filter

As is well known, X-ray is the most commonly used technique for inspection of semiconductor. However, excessive radiation dose to the semiconductor may increase the probability of trouble of semiconductor. Therefore, unnecessary exposure needs to be reduced. Generally, ray quality in the radiation imaging is an important factor that determines the amount of ray exposure, and they are affected by tube voltage and filter. A filter can reduce the dose received by the semiconductor. In this study, we designed an X-ray tube for inspection of semiconductor with different target/filter combinations and calculated X-ray spectra using the MCNPX (Monte Carlo n-particle extended) code. The target materials used were W. Further, the filter was made from Mo, W and Zr. The results confirmed that in the whole region, W/W combination had the lowest flux value. It seems that if the MCNPX code is used, time and cost can be reduced in the development of target/filter combination for inspection of semiconductor.

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^{197}Au MÖSSBAUER SPECTROSCOPY ON THIOL STABILIZED GOLD NANOPARTICLES

Károly Lázár[1]*, *Sándor Stichleutner*[1], *Ernő Kuzmann*[2], *Edit Csapó*[3], *Imre Dékány*[3]

[1]Centre for Energy Research, Hungarian Academy of Sciences, Department of Nuclear Analysis, Konkoly Thege M. 29–33, 1121 Budapest, Hungary, *e-mail: lazar.karoly@energia.mta.hu
[2]Institute of Chemistry, Eötvös Loránd University, Pázmány Péter sétány 1, 1117 Budapest, Hungary, e-mail: drkuzmann@gmail.com
[3]Department of Medical Chemistry, University of Szeged, Dóm tér 8, 6720 Szeged, Hungary, e-mail: tidecs2000@yahoo.co.uk

Keywords: ^{197}Au Mössbauer spectroscopy, gold nanoparticles

^{197}Au Mössbauer spectroscopy can be used to determine the actual oxidation state of gold. Thus, among others, this technique has successfully been applied to study complex molecules, catalysts, etc. [1]. There is an in-beam Mössbauer facility under construction at the Centre of Energy Research, which provides means for obtaining ^{197}Au spectra [2]. As one of the first applications, spectra were collected on gold nanoparticles (GNPs) as well.

GNPs were prepared by transferring Au^{3+} ions from aqueous solution to organic phase (toluene) and reduced with $NaBH_4$ in simultaneous presence of buthyldithiol. GNPs were washed with ethanol and dried afterwards. The product was studied with various methods (TEM, XRD, thermogravimetry, Raman spectroscopy). Particles were covered with monolayer of dithiol, their diameters fall into the 1.3–3.9 nm range. Sulfur may play an important role in stabilization of GNPs, as reported earlier [3]. In correspondence, presence of various types of gold was revealed in their Mössbauer spectra. Namely, beside presence of metallic gold in a significant fraction, gold atoms located on the surface and Au(I) ions bonded to sulfur can also be distinguished (singlet and two doublets, respectively in the decomposition of spectrum in *Fig. 1*).

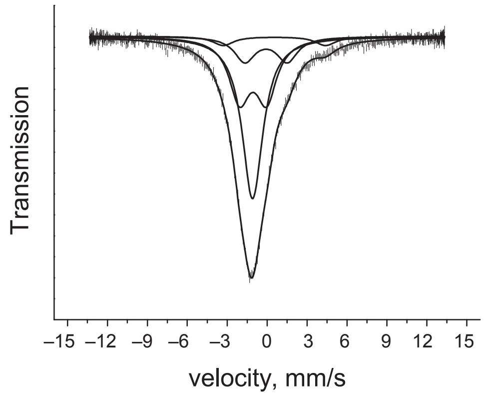

Fig. 1. ^{197}Au Mössbauer spectrum of buthyldithiol stabilized gold nanoparticles (with contributions of various gold species)

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INFLUENCE OF THE DECONTAMINATION OF A HIGH RADIOACTIVE SOLUTION FROM CESIUM ON ANALYSES RELATIVE TO ITS MULTI-ELEMENTARY COMPOSITION

Christophe Maillard, Valerie Boyer-Deslys, Jean-Luc Dautheribes, Eric Esbelin, André Bères, Cédric Rivier*

CEA, Nuclear Energy Division, RadioChemistry & Processes Department, Analysis and Materials Metrology Laboratory, BP 17171,
30207 Bagnols sur Cèze, Cedex, France, *e-mail: Christophe.maillard@cea.fr

Keywords: ^{137}Cs, chromatography, AMP-PAN

The high rate of irradiation of certain samples is essentially due to the presence of the ^{137}Cs. Removing selectively Cs from these samples provides several advantages : 1) a weaker dilution to make possible the samples manipulation and to carry out their analyses by techniques usually implanted in glove boxes (ICP-AES, ICP-QMS, radiometry, etc.), 2) a lower detection limit of analyzed elements, 3) a minimization of the Compton effect on gamma spectra.

The method of cations / Cs+ separation is very important. It must lead to the highest possible cesium decontamination factor, the quantitative recovery of the other elements and the lowest possible dilution factor of the sample. The implemented method is extraction chromatography using the AMP-PAN resin (ammonium molybdophosphate embedded in polyacrylnitrile). It consists in adding the sample, firstly adjusted at a nitric acidity of 2M on a AMP-PAN column, then in adding a washing solution ($[HNO_3] = 2M$). During these two stages, the cesium is expected to be retained by the chromatographic support whereas the other cations cross the column.

The efficiency of this method was tested by comparison of analyses by gamma and alpha spectrometry, by X-ray fluorescence and by ICP-AES realized with a sample, taken in a storage tank of fissions products, before and after its passage on an AMP-PAN column.

The results of analyses were very satisfactory. A strong decontamination of the initial sample from ^{137}Cs (FD > 5.104) and a quasi-quantitative recovery of the other analyzed elements were observed. The gamma spectra showed in particular several radionuclides which were not quantified on the initial sample and led to detection limits twenty times lower.

The description of the chromatographic cycle on AMPAN resin and all the analyses will be presented during this talk.

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APPLICATION OF NUCLEAR TECHNIQUE FOR THE CHARACTERISATION OF IAEA CERTFIED REFERENCE MATERIALS FOR RADIONUCLIDES IN MARINE SAMPLES

Mai Khanh Pham, Arend Victor Harm, Iolanda Osvath*

IAEA-Environment Laboratories, Monte Carlo, 98000, Monaco, *e-mail: m.pham@iaea.org

Keywords: nuclear technique**, r**eference material, marine environment, radionuclides, quality control, quality assurance

Accurate and precise determination of radionuclide activity concentrations in marine samples is important for marine radioactivity assessments and for the use of radionuclides in the study of oceanographic processes. To address the problem of data quality, the IAEA's Environment Laboratories (IAEA-EL) in Monaco have conducted inter-laboratory comparison exercises (and later the characterisation) on radionuclides in marine samples for almost fifty years as part of their contribution to the IAEA's programme of Analytical Quality Control Service (AQCS), currently named as "IAEA's Reference Products for Science and Trade" (Povinec and Pham, 2001; Sanchez-Cabeza et al., 2008).

The IAEA's Reference Products for Science and Trade programme for radionuclides in the marine environment has recently focused on the production of Certified Reference Materials (CRMs) (ISO 35) with the aim to improve the accuracy and precision of analyses carried out by the laboratories and thus the quality of data, and to provide traceability to SI standards. At present the characterisation of CRMs is being upgraded with accreditation following ISO 35, ISO 34 and ISO/IEC 17025. An important part of this activity was the production of CRMs using different nuclear techniques for the determination radionuclides in different matrices of marine samples.

An overview and comparative assessment of the nuclear analytical techniques used (γ-spectrometry, α-spectrometry, β-counting and/or mass spectrometry such as ICP-MS and AMS) for the characterisation of CRMs for radionuclides in support of marine environmental studies is presented. CRMs are in consequence, valuable standards for method development and validation: they can indicate the need to improve or change existing methods and/or the need of further training.

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LIQUID-LIQUID MICROFLOW PATTERNS OF TWO RADIOCHEMICAL SYSTEMS USED IN THE NUCLEAR FIELD: PREDICT THE FORMATION OF SEGMENTED FLOW

Axel Vansteene[1], Marion Losno[1], Jean-Philippe Jasmin[1], Gerardo Vera De La Cruz[2], Siméon Cavadias[2, 3], Clarisse Mariet[1], Gérard Cote[2]

[1]CEA Saclay, DEN/DANS/DPC/SEARS/LANIE, 91191 Gif-sur-Yvette cedex, France, e-mail: axel.vansteene@cea.fr
[2]PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie Paris, 75005, Paris, France
[3]UPMC – Univ Paris 06, 4 Place Jussieu, 75005 Paris, France

Keywords: liquid-liquid microextraction, lab-on-chip, radiochemical analysis, microfluidics, hydrodynamics, mass transfer, Comsol Multiphysics®, modeling

One of the most important separation techniques in radiochemical procedures is solvent extraction. In the last decade, a growing interest in its use in microsystems with multiphase micro-flows has emerged because such systems allow a good control of the interface area between aqueous and organic phases as well as of the contact time of the two phases. In order to design a microfluidic device for an extraction process, it is necessary to have a deep understanding of the fundamental mechanisms involved in fluid flow. In this study, flow patterns of two aqueous-organic binary systems in micro-channels are discussed, either for a liquid anion exchanger (extraction of uranium in HCl by Aliquat 336®) or a neutral extractant (extraction of europium in HNO_3 by the N,N'-dimethyl N,N'-dibutyl tetradecylmalonamide). As parallel flows between two phases always show the same interface, the relative importance of this interface as a mass transfer parameter could not be investigated. Then, after a previous study of parallel flow [1, 2], our objective is to predict and compare the formation of segmented flow for different geometries (T-junction, flow focusing, co-flow). In droplet-based microsystems, internal circulation stimulated within the droplets by their passage along the channel is responsible for a large enhancement in the interfacial mass transfer and reaction rate. Therefore, an improvement in liquid-liquid extraction yield might be expected.

Thanks to Navier-Stokes equations, using Computational Fluid Dynamics (CFD) models, we determined the influence of viscosity, dimensional parameters and operating conditions on flow patterns. The size of droplets and their generation rate were shown to be key parameters for liquid-liquid extraction optimization. Microsystems design was therefore investigated in order to determine the operating conditions to control the size and frequency of the droplets.

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PIXE/PIGE BEAM LINE AT THE CENTA FACILITY OF THE COMENIUS UNIVERSITY IN BRATISLAVA

Jakub Zeman[1], *Miroslav Ješkovský*[1], *Ralf Kaiser*[2], *Andrej Kováčik*[1], *Pavel P. Povinec*[1]*

[1]Centre for Nuclear and Accelerator Technologies (CENTA), Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, 84248 Bratislava, Slovakia, *e-mail: povinec@fmph.uniba.sk
[2] Department of Nuclear Sciences and Applications, International Atomic Energy Agency, Vienna, Austria

Keywords: PIXE, PIGE, X-rays, elemental analysis, silver coins

First results obtained with PIXE/PIGE beam line installed at the Bratislava CENTA tandem accelerator facility are resented. The PIXE/PIGE reaction chamber is equipped with a vertically movable sample holder for positioning of up to 8 samples depending on their dimensions. The holder is capable of rotation around its vertical axis to adjust the angle how the incident beam should hit the sample. The ^{4}He ion beam has been used for the PIXE analysis because of its better detection limits when compared with protons of the same energy and beam intensity. For detection of produced X-rays, the CANBERRA Broad Energy Germanium detector has been used, covering the energy range from 3 keV to 3 MeV. Optimizations of the helium beam from the Alphatross ion source through the injection beam line, the Pelletron tandem accelerator, the high-energy analyzer and the PIXE/PIXE beam line were carried out. First measurements with ^{4}He ions of 3.5 MeV energy included calibration runs with standards, as well as analyses of old coins from the previous Slovak State and from the Austro-Hungarian Empire. Further measurements included analyses of exposed nitrocellulose filters for atmospheric aerosols, previously used for analyses of radionuclides in the Bratislava air, as well as analyses of iron and stony meteorites.

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LIQUID SCINTILLATION COUNTING METHODLOGY FOR ^{99}Tc ANALSYIS IN VARIOUS AQUEOUS MATRICES

Mumtaz Khan[1], *Wooyong Um*[1, 2]

[1]Nuclear Environment Laboratory, Division of Advance Nuclear Engineering, Pohang University of Science and Technology, Pohang, South Korea, e-mail: mumtazkhan03@postech.ac.kr
[2]Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, Washington 99354, USA, e-mail: wooyong.um@pnnl.gov

Keywords: liquid scintillation counting, Ultima Gold, Ultima Gold LLT, ^{99g}Tc

Current work presents a unique and new approach for liquid scintillation counting (LSC) analysis of single-radionuclide samples containing appreciable organic or inorganic quench for deionized water, tap water, groundwater, seawater, and urine samples. Analytical parameters were measured in the presence of various quench impurities including 1.9 to 11,900 ppm dissolved solids and nitromethane using liquid scintillation counter. Counting efficiency was found to be 91.66% for Ultima Gold LLT (ULG-LLT) and Ultima Gold (ULG). Relative error in spiked ^{99g}Tc samples was ±3.98% in ULG and ULG-LLT cocktails. Minimum detectable activity was determined to be 25.3 mBq and 22.7 mBq for ULG-LLT and ULG cocktails, respectively. A pre-concentration factor of 1000 was achieved at 100 °C for 100% chemical recovery. Current method facilitates to select cocktail according to matrices chemistry of the ^{99g}Tc sample. The method has more sensitivity than previous reports and a range of matrices can be analysed.

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ACTIVITY DETERMINATION OF URANIUM AND PLUTONIUM ISOTOPES IN SOIL AND CONCRETE SAMPLES USING ALKALI FUSION AND EXTRACTION CHROMATOGRAPHY PROCESS

Jong-Myoung Lim, Hyuncheol Kim, Yoon-Hee Jung, Ji-Young Park, Kun-Ho Chung, Mun-Ja Kang, Geun-Sik Choi*

Environmental Radioactivity Assessment Team, Korea Atomic Energy Research Institute, 111, Daedeok-daero 989, Yuseong, Daejeon, 305-353, Korea, *e-mail: jmlim@kaeri.re.kr

Keywords: actinide, plutonium, uranium, fusion, ICP-MS

Actinide (e.g., plutonium and uranium) in the environment are known to have a relatively high toxicity. Thus these nuclides have been a focus of interest not only in environmental studies for the origin of the nuclear materials, but also in waste management field from nuclear power plants. Moreover, the isotopic composition of actinides (Pu and U) provides the source information of nuclear and radiological materials used during illegal activities. For emergency preparedness for nuclear accidents, as an attempt to reduce the social costs and apprehension arising from radioactivity in the environment, an accurate and rapid assessment of actinide radionuclide deposition levels or contamination is highly desirable. Thus a rapid and accurate analytical method that can be used to evaluate the radioactivity of actinides (e.g., ^{238}U, ^{235}U, ^{239}Pu, and ^{240}Pu) should be developed and validated.

While α-spectrometry has a prominent measurement capability at a very low activity level of ^{238}U, ^{235}U, ^{239}Pu, and ^{240}Pu, it has a major disadvantage of a long counting time for the determination of α-nuclide activity, and cannot separate Pu nuclides. Contrary to the α-spectrometry method, a measurement technique using ICP-MS with an advanced sample introduction and mass counting system allows radioactivity in many samples to be measured with a short time period with a high degree of accuracy and precision. Both methods also encounter the most significant difficulties during pretreatment (e.g., purification, speciation, and dilution/enrichment). Since the pretreatment process consequently plays an important role in the measurement uncertainty, a method of development and validation should be performed.

In this study, a rapid digestion and separation method for U and Pu radionuclides was developed in soil and concrete matrix samples. The soil samples were digested using $LiBO_2$ fusion and the target nuclides were extracted sequentially through $Fe(OH)_3$ and LaF_3 co-precipitation. In addition, U and Pu nuclides were separated and concentrated using TEVA and UTEVA resin. Finally, the mass concentrations of U and Pu isotopes were determined using sector-field ICP-MS system with an APEX nebulizer. For an evaluation of the accuracy and precision of evaluated method, various reference materials (RMs) from IAEA and NIST were analyzed. Based on the analytical results, one may draw conclusions that the evaluated method for actinides using alkali-fusion, LaF_3 co-precipitation, the extraction chromatography process, and ICP-MS measurements is fast and fairly reliable owing to its recovering efficiencies.

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LOW-LEVEL GAMMA RAY SPECTROMETRY FOR THE DETERMINATION OF ^{210}Pb

Nikola Marković, Per Roos, Sven Poul Nielsen*

Center for Nuclear Technologies, Radioecology Department, Technical University of Denmark, Roskilde, Denmark, *e-mail: nikmar@dtu.dk

Keywords: gamma spectrometry, environmental, lead-210, beta counting, ICP-MS

A recently installed well HPGe gamma spectrometer at DTU Nutech specially designed for the low-level measurements was used for the ^{210}Pb determination in environmental samples. We describe installation and calibration of the well HPGe spectrometer along with the optimization of the NaI crystal used as Compton anticoincidence shield. The system is compared to planar HPGe spectrometer. The choice between high efficiency well and planar detectors as well as optimum sample size depending on the available sample quantity are discussed. Besides gamma spectrometry, beta counting (GM and LSC) and mass spectrometry (ICP-MS) were also used for the determination of ^{210}Pb.

Beta counting in general gives better detection limits at the cost of more complicated and time consuming sample preparation and the expanded uncertainty due to lack of suitable radioisotope yield determinants, while ICP-MS enables rapid determination but with substantial interference problems in mass spectra.

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COMPARISON OF DIFFERENT METHODS USED FOR DETERMINATION OF AMERICIUM IN URINE

Péter Rell, Szabolcs Osváth, Júlia Kövendiné Kónyi

National Public Health Center, National Research Directorate for Radiobiology and Radiohygiene, Anna utca 5, 1221 Budapest, Hungary,
e-mails: peter.rell@osski.hu, szabolcs.osvath@osski.hu, konyi@osski.hu

Keywords: americium, urine, gamma-spectrometry, alpha-spectrometry

After an incident lot of human urine samples were taken and analysed in our laboratory in 2014 and 2015. The samples can be categorized in two main groups: usual urine samples and urine samples taken after DTPA treatment of persons. In this poster the methods and procedures used for determination of activity concentration of ^{241}Am in these urine samples are discussed in details.

The simplest method is gamma-spectrometry. ^{241}Am has a low energy gamma photon at 59.5 keV, which (among other, even lower energy gamma photons) can be easily detected using n-type high purity germanium detectors. Special sample preparation is not needed. The minimum detectable activity concentration (MDA) is around 1 Bq/L (using a 900 mL Marinelli beaker and 80,000 s measuring time). In spite of the simplicity of this technique, some processes occurred that could make the detection difficult. For example black precipitate could be formed and settled during measurement (especially in DTPA treated person's urine). Am could be adsorbed on this precipitate (although samples were acidified according to literature), so detection geometry was changed leading to false results.

The other technique to determine ^{241}Am in urine samples is alpha-spectrometry with a lower MDA (approximately 1 mBq/L, if 1 L sample was processed and 300,000 s measuring time was used). Complex sample preparation procedure (consuming 6–8 days/sample) is needed for alpha-spectrometry. A well-known validated separation procedure was used, containing addition of tracer, destruction of sample, adjustment of oxidation states, separation on 3 chromatographic columns and LaF_3 micro co-precipitation. (Two columns were filled with anion exchange resin and the last one was filled with TRU Resin.)

Time is the most important factor in accidental situations, so another procedure with lower time consumption was tested. Lengthy destruction and the anion exchange chromatography steps were substituted by co-precipitation with $Ca_3(PO_4)_2$. Using this method, ca. 4 days can be saved. Comparing the two methods it can be concluded that there are no significant differences in the obtained results and in the method characteristics (for example their chemical yields are approximately 70–80%).

Some samples were processed using other techniques as well, for example a newly developed radioanalytical method of RadAnal Ltd. was also tested to separate Am before alpha-spectrometry. Results taken by different methods were in acceptable agreement.

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RAPID METHOD FOR THE DETERMINATION OF Am, Pu AND U IN URINE SAMPLES

M. Zagyvai[1], N. Vajda[2], J. Groska[2], P. Szeredy[2]

[1]Energy Research Institute of Hungarian Academy of Sciences, Hungary
[2]RADANAL Ltd., Hungary

Rapid determination of actinides in urine is of major concern in controlling internal doses of radiation workers. Our purpose was to develop a simple and fast procedure for the separation of actinides from urine samples followed by α-spectrometryic determination.

DGA resin was selected as a selective extraction chromatographic material for the separation of U, Th, Pu and Am due to the extremely high distribution coefficients. DGA resin® is the registered trade name of the resin that contains N,N,N',N'-tetra-n-octyldiglycolamine on an inert support [1].

(It is commercially available from Triskem International.) A method developed for the analysis of actinides in radioactive wastes [2] was adopted for urine analysis. The tedious digestion and preconcentration steps before DGA resin separation were omitted, and urine samples acidified with HCl to 4M were loaded directly on to a DGA column. α-sources of different actinides were prepared by coprecipitation with NdF_3. Measurements were performed by alpha spectrometry using Si α-detector. In order to optimize the elution sequence model experiments with single actinide tracers were performed by LSC measurements.

Am, Pu and U were separated with acceptable high recoveries (>50%) and decontamination factors. The Am, Pu and U content of 100-200 mL urine samples were determined within 24 hours with detection limits as low as 0.1 Bq/L. It was realised that high carbamide content can affect actinide separation deleterously. The effect of carbamide was investigated with ^{14}C-spiked carbamide.

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ANNUAL VARIATION OF RADIOCAESIUM IN MARINE ENVIRONMENT OFF FUKUSHIMA AFTER THE FUKUSHIMA NUCLEAR POWER STATION ACCIDENT

Tatsuo Aono[1], Miho Fukuda[1], Sinnosuke Yamazaki[1], Takashi Ishimaru[2], Jota Kanda[2], Yukari Ito[2],
Tadahiro Sohtome[3], Takuji Mizuno[3], Manabu Yamada[3], Akibumi Yamanobe[3]

[1]Project for Environmental Dynamics and Radiation Effects, Fukushima Project Headquarters, National Institute of Radiological Science (NIRS), 4-9-1 Anagawa, Inage-ku, Chiba 263-8555, Japan, e-mails: t_aono@nirs.go.jp, mhfukuda@nirs.go.jp, s_yamaza@nirs.go.jp
[2]Department of Ocean Sciences, Tokyo University of Marine Science and Technology (TUMSAT), 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan, e-mails: ishimaru@kaiyodai.ac.jp, jkanda @kaiyodai.ac.jp, yukari-i@kaiyodai.ac.jp
[3]Fukushima Prefectural Fisheries Experiment Station, Onahama, Iwaki, Fukushima 970-8477, Japan,
e-mails: yamada_manabu_01@pref.fukushima.lg.jp, yamanobe_akibumi_01@pref.fukushima.lg.jp

Keywords: radiocaesium, seawater, plankton net sample, Fukushima

About five years since an accident of the TEPCO's Fukushima Daiichi Nuclear Power Station have passed. Radiocaesium activities in seawater and plankton net samples collected off Fukushima have been monitored from 2012 to 2015. The radiocaesium activities in seawater in the coastal area (less than the depth of 100m) were gradually decreased from over 100 mBq/L to less than 10 mBq/L near the coastal area, although these in the offshore area have observed the same levels as before the accident. The radiocaesium activities were ranged from 1 Bq/kg-wet to over 100 Bq/kg-wet in the plankton net samples collected in the coastal area in autumn 2012, and these were higher than these in 2013–2015. Marked decrease of radiocaesium activities was not observed in the plankton net samples in this period, and no significant influence from the accident was observed in the coastal area samples collected off Fukushima in 2015. The apparent concentration ratios (CR)-Cs were estimated using the obtained activities of radiocaesium in seawater and the plankton net samples and they ranged from 34 to 9,400, and their geomean was 420 (n = 52). Sediment-seawater distribution coefficients Kd (L/kg) were observed to be from 1,900 to 25,000 in the same area in 2013. The estimated CR-Cs of plankton in 2012–2015 was 10–70 times higher than in 2005–2006. For CR-Cs values, it is necessary to consider the influence by the sediment and suspended particles in seawater than the plankton, as plankton net samples contain not only plankton but also caesium-rich particulate matter and sediment in the coastal area.

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POLONIUM ^{210}Po IN SWEAT SAMPLES OF NORTHERN POLAND

Alicja Boryło, Grzegorz Romańczyk, Bogdan Skwarzec, Dagmara Strumińska-Parulska

Department of Analytical and Environment Radiochemistry, Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland

This paper presents the results of the determination of polonium ^{210}Po in samples of sweat. Analyzed samples were taken from Gdańsk agglomeration volunteers (northern Poland). The volunteers were subdivided in classes of males and females, cigarette smokers and non-smokers and lifestyle differences were taken into account. The results show that the all obtained results of ^{210}Po concentration in sweat samples were between 0.65±0.02 mBq×g^{-1} and 6.29±0.20 mBq×g^{-1} (with the average value 3.05±0.13 mBq×g^{-1}). The differences between women and man were not observed (the average value is 2.97±0.14 mBq×g^{-1} and 3.13±0.13 mBq×g^{-1}, respectively). The slightly higher ^{210}Po concentration was observed in smoker class (5.35±0.20 mBq×g^{-1}) than non-smoker class (1.98±0.10 mBq×g^{-1}). There were no significant difference between the average values of ^{210}Po in classes of people eating one or more fish per week than people non eating fish per week. The average ^{210}Po concentration was 2.66±0.13 mBq·g^{-1} and 1.35±0.07 mBq·g^{-1} respectively for both analyzed groups. Levels of ^{210}Po activity in normal human body may differ from one person to another depending upon the mode life as diet habits, origin of drinking water, residence place which effects radon exposure rate and also smoking habits. The method used in this study presents a high accuracy, reproducibility and sensitivity. The data obtained were statistically processed by using the *t*-test or ANOVA for determining whether observed differences invariables among analyzed groups are statistical significant. The presented data show that statistical significant differences was observed for smoker class.

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NATURAL RADIONUCLIDES IN RIVER WATERS IN THE CENTRE OF PORTUGAL

Fernando P. Carvalho, J. Maria Oliveira, Margarida Malta

Laboratório de Protecção e Segurança Radiológica, Instituto Superior Técnico/Campus Tecnológico Nuclear, Universidade de Lisboa, Estrada Nacional 10, km 139,7; 2695-066 Bobadela LRS, Portugal, e-mail: carvalho@itn.pt

Keywords: uranium mines, radium, environmental contamination, agriculture, radionuclide transfer

Analyses of the main alpha emitters of uranium series were performed in the surface waters of river Mondego and tributaries, the main river system of the centre north of Portugal, in July 2014. This region is an old uranium producing province with legacy uranium mines and milling tailings, many not yet properly decommissioned. Results of analyses indicated very high radionuclide concentrations in acid mine waters and in water and sediments of some streams contaminated by mine discharges. For example, untreated mine water from Quinta do Bispo mine contained 25770±1190 mBq/L of dissolved 238U and 1460±70 mBq/L of dissolved 226Ra. Water and sediments of Mondego River displayed enhanced levels of radionuclides near the discharges of tributary streams. However, due to strong dilution in the Mondego River the water in the artificial lake of Aguieira displayed 35±1 mBq/L of 238U and 45±8 mBq/L of 226Ra, and this water was potable from the radiation point of view. Nevertheless, uncovered waste heaps and mine drainage from uranium legacy areas in the catchment are a threat to water quality. Environmental protection measures are discussed. On one hand enhanced environmental remediation of abandoned mine areas is needed and, on the other hand, water supplying companies shall implement periodic radioactivity monitoring of water quality as prescribed in the EU water directive.

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RADIONUCLIDES AND AMBIENT RADIATION AT AN OLD RADIUM MINE SITE IN THE VILLAGE OF REBOLEIRO, PORTUGAL

Fernando P. Carvalho, J. Maria Oliveira, Margarida Malta

Laboratório de Protecção e Segurança Radiológica, Instituto Superior Técnico/Campus Tecnológico Nuclear, Universidade de Lisboa, Estrada Nacional 10, km 139,7; 2695-066 Bobadela LRS, Portugal, e-mail: carvalho@itn.pt

Keywords: uranium mines, radium, environmental contamination, agriculture, radionuclide transfer

Radium production in Portugal started in 1908 and mining of radioactive ores for radium and uranium production continued until 2001. One of early radium producing mines was located at the rural village of Reboleiro (Trancoso), Centre-North of Portugal, and ceased activity by 1926. No clean-up of the site was made and, over the years the village expanded around the mine site. Recently, the measurement of ambient radiation doses and analysis of materials in waste heaps, soils and horticultural products were carried out to assess radiological risks for the population. Ambient radiation dose rates in the area rise from regional background values around 0.30 µSv/h to 0.5–2.5 in the old mine area with a maximum of 4.1 µSv/h on top of waste heaps. Analyses of radionuclides in materials from waste heaps were much higher for 238U (29470±1420 Bq/kg) and 230Th (23520±1590 Bq/kg) than for 226Ra (13180±620 Bq/kg), confirming that this mine produced radium but was not exploited for uranium. Radionuclide analyses in soils from horticultural plots in the neighbourhood showed an increase of radioactivity compared with other soils from the area Radionuclide activity concentration ratios 226Ra/238U in waste heap materials was 0.45 and in soils nearby was 75, indicating that contamination of adjacent soils occurred especially with radium dissolved in rainwater and transported by surface runoff. Horticultural products from the mine area showed enhancement of radionuclide concentrations in comparison with other products from surroundings of the village area. Measurements of radon outdoors in houses near the mine site averaged 70 Bq/m3, but indoors was higher, in some houses above 1000 Bq/m3 and in one house averaged 12000 Bq/m3. Materials from mining waste might have been reused in house construction in the early 20th century. Full survey of this legacy site is recommended and cleanup and remediation seems needed to ensure radiation protection of the population.

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URANIUM IN THE KOREAN GROUNDWATER

Sungwook Choung[1], Woosik Shin[2], Jungsun Oh[3], Byungwook Cho[4], Kwang-Sik Lee[5], Uk Yun[6], Nam-Chil Woo[7], Munsoo Kim[8]

[1]Department of Environmental Monitoring & Research, Korea Basic Science Institute, 162 Yeongudanji-ro, Ochang-eup, Cheongju, Republic of Korea, e-mail: schoung@kbsi.re.kr
[2]Korea Basic Science Institute, Cheongju, Republic of Korea, e-mail: sws3286@kbsi.re.kr
[3]Yonsei University, Seoul, Republic of Korea, e-mail: jungsunoh@yonsei.ac.kr
[4]Korea Institute of Geoscience and Mineral Resources, Daejeon, Republic of Korea, e-mail: cbw@kigam.re.kr
[5]Korea Basic Science Institute, Cheongju, Republic of Korea, e-mail: kslee@kbsi.re.kr
[6]Korea Institute of Geoscience and Mineral Resources, Daejeon, Republic of Korea, e-mail: yunuk@kigam.re.kr
[7]Yonsei University, Seoul, Republic of Korea, e-mail: ncwoo@yonsei.ac.kr
[8]National Institute Environmental Research, e-mail: hyd009@korea.kr

Keywords: uranium, groundwater, spatial distribution, geological relationship, uranyl species

Uranium is the most ubiquitous element among naturally occurring radioactive materials (NORMs) in environmental system because of its abundance in the Earth crust and long half-life ($t_{1/2} \approx 4.5\times10^9$ years). Although the specific radioactivity of natural uranium in groundwater is extremely low, chronic exposure results in kidney problems and potential toxicity in bones. This study was conducted on a nationwide scale for 9 years through 2006–2014 to determine the spatial distribution of uranium in groundwater, and to evaluate geological relationship with uranium occurrence. The higher uranium concentrations than the WHO guideline value of 30 mg L^{-1} for drinking water were found in the midland of South Korea (i.e., Chungcheong, Gyonggi, and Gangwon Province). The bedrock geology of the central regions mainly comprises plutonic and metamorphic rocks. Granite, granitic gneiss and black shales could act as source rocks for the uranium component in the groundwater system. The Spearman's correlation coefficients showed moderate relationship between the uranium and other ions of F, Na, Ca, HCO_3, and SO_4 in the plutonic and metamorphic regions. Also, the groundwater chemistry indicated that Ca-HCO_3 and (Na,K)-HCO_3 were predominant types for the investigated groundwater samples. These results suggested that the uranium component may be associated with dissolution of secondary minerals such as feldspar, gypsum, and micas into groundwater. Estimated aqueous species of uranium are uranyl carbonate complexes under neutral and oxidizing conditions as a typical groundwater circumstance in Korea. In particular, the calcium contents facilitates the formation of calcium-uranyl carbonate complexes that increase the uranium mobility in the groundwater environments. Therefore, the uranium contents in groundwater must be continuously monitored and properly reduced for the drinking purpose, especially, at the midland of Korea.

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LEVELS OF CESIUM ISOTOPES CONTAMINATION AND THEIR POSSIBLY ORIGINS IN LICHENS AND MOSSES FROM WESTERN ARCTIC

Anna Cwanek[1], Jerzy W. Mietelski[1], Maria A. Olech[2], E. Łokas[1]*

[1]The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, E. Radzikowskiego 152, 31-342 Cracow, Poland, *e-mail: anna.cwanek@ifj.edu.pl
[2]Institute of Botany, Jagiellonian University, Zdzisław Czeppe Department of Polar Research and Documentation, Kopernika 27, 31-501 Cracow, Poland

Keywords: Arctic, cesium, contamination, lichens, mosses

The presence of radioactive elements is related to both the natural processes and human activity. The result of human activity is raising the level of natural radioactivity and the introduction of new, artificially produced radioisotopes, such as: Sr-90, Cs-134, Cs-137, Pu isotopes, Am-241, etc. Investigations of organisms such as lichens or mosses can provide a lot of valuable information about these contaminants. They are widely used as biological indicators of environmental pollution.

Samples of lichens and mosses were collected during two scientific expedition in 2012 and 2013. Study area include the vast Arctic region: West Greenland, islands and peninsulas along the sea route connecting the Atlantic Ocean with the Pacific Ocean, known as the Northwest Passage, coastal zone of Labrador and Newfounland, Canada.

The main aim of this study is estimation the level of activity concentration of Cs-134, and Cs-137 and identification of potential sources of these contaminants. Samples were measured using high resolution low-background gamma spectroscopes with HPGe detectors. In order to determine activity concentration of Cs-134 and Cs-137 there were made necessary calibration measurements too. The obtained activity concentrations of Cs-137 range from 11.0± 2.2 to 145.1±12.3 Bq/kg. In the case of Cs-134 results are much lower, reaching only a few Bq/kg.

There have been shown the presence of anthropogenic radionuclides pollution deriving from global fallout in terrestrial environment in considered area of the Arctic. Additional sources of investigated contamination could be: Satellite Kosmos 954 crash over the Great Slave Lake in Northern Canada (1978), the Chernobyl fallout (1986) and nuclear power plant disaster in Fukushima (2011). In particular, contribution of Fukushima fallout can be evidenced by traces of Cs-134.

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EXPERIMENTAL STUDY FOR THE RELEASE OF RADIUM ISOTOPES INTO SALINE WATER

N. Dietrich, D. Degering*

VKTA – Radiation Protection, Analytics & Disposal Rossendorf e. V., P.O. Box 510119, 01314 Dresden, Germany, *e-mail: norman.dietrich@vkta.de

Keywords: radionuclides, radium, saline water, α-recoil

Highly saline fluids as e.g. produced by geothermal plants show very low solubility for all Uranium and Thorium isotopes, but enhanced levels of some 10 $Bq \cdot l^{-1}$ for the unsupported Radium isotopes ^{226}Ra (half life 1600 y), ^{228}Ra (5.75 y) and ^{224}Ra (3.63 d) [1]. Especially the occurrence of ^{224}Ra indicates that – in contrast to ^{226}Ra and ^{228}Ra – only a short time period elapsed since the radionuclide release. Therefore, the Radium concentration must be the result of a presently ongoing process.

Processes leading to a radionuclide release are physicochemical (sorption, dissolution, …) and nuclear processes (alpha-recoil). The interaction processes take place between three phases: mineral grains, active surface layer and fluid. While sorption and solution processes are related only to the liquid–solid boundary layer, the alpha-recoil also takes place in mineral grains [2] and was suggested as ongoing process that permanently supplies Radium isotopes [1]. Physicochemical processes are specific for the element Radium, but alpha-recoil is specific for each isotope and the release depends on the half-life of the Radium isotope currently viewed.

The investigation of Radium release from solid surfaces into water is aim of this work. An experimental approach was developed using the isotope ratios ^{224}Ra/^{228}Ra, ^{224}Ra/^{226}Ra and ^{228}Ra/^{226}Ra to quantify the ratio of physicochemical processes and alpha-recoil. The effect of varying contact time between solid and fluid was investigated in experimental series. A kaolin sample is used as model solid, because of its high specific surface area (17 $m^2 \cdot g^{-1}$) and sufficient specific activities for ^{228}Ra (107 $Bq \cdot kg^{-1}$) and ^{226}Ra (131 $Bq \cdot kg^{-1}$), and a Na-Ca-Cl solution (110 $g \cdot l^{-1}$) as fluid (solid/fluid-ratio 1:4).

In kaolin the ^{238}U- and ^{232}Th-decay chains are in radioactive equilibrium, i.e. particularly the isotopes ^{228}Ra and ^{224}Ra have the same specific activity. Thus the release of ^{224}Ra due to physicochemical processes should reach the same activity concentration as ^{228}Ra, while the ^{224}Ra/^{228}Ra-ratio should remain constant. The observed increase of ^{224}Ra activity in solution as well as ^{224}Ra/^{228}Ra- and ^{224}Ra/^{226}Ra-ratio with contact time is in contrast to constant ^{226,228}Ra concentrations and ^{228}Ra/^{226}Ra-ratio, but in agreement with the model of predominating alpha recoil in Radium isotope release. The release of ^{228}Ra and ^{226}Ra is only due to physicochemical processes, because of short contact times compared to the half-life of these isotopes. The extended release of ^{224}Ra is due to alpha recoil. In our experiments the ratio of physicochemical processes and alpha-recoil after reaching equilibrium is 2/3.

The effect of varying salinity and specific surface area on Radium release is part of further experimental series.

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PREPARATION OF OPTIMAL THORON SOURCE FOR THORON CALIBRATION CHAMBER

Ferenc Fábián, Anita Csordás, Tibor Kovács, Zoltán Sas*

Institute of Radiochemistry and Radioecology, University of Pannonia, Veszprém, Hungary, *e-mail: fabianf@almos.uni-pannon.hu

Keywords: thoron source, calibration, Ac-228 separation

Recently the accurate determination of thoron concentration came to the fore. During long-term surveys solid-state nuclear track detectors (SSNTDs) are commonly used. For the application of these integral devices it is important to solve that calibration. A thoron calibration chamber has been developed at the Institute of Radiochemistry and Radioecology at University of Pannonia (RRI) recently; however, examinations performed until now showed that its development is necessary for the more accurate operation. Development of a method for the preparation of a “radon-free” (with low Ra-226 content) thoron source with high emanation capability is an important task of the improvement. During this work techniques capable for thoron source preparation found in the literature were tested, such as preparation of ceramic sources contain thorium nitrate in natural composition, preparation of thorium containing gas mantle based thoron sources and preparation of thoron sources after chemical separation of Ac-228. Based on the results a proposal is given for the optimal method for thoron source preparation and its parameters.

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RADON EXPOSURE IN UNDERGROUND LABORATORY OF SPACE RESEARCH CENTRE IN KSIĄŻ (POLAND)

Lidia Fijałkowska-Lichwa

Wrocław University of Technology, Faculty of Civil Engineering, Wybrzeże S. Wyspiańskiego 27, 50-370 Wrocław, Poland,
e-mail: lidia.fijalkowska@pwr.edu.pl

Keywords: radon, radon activity concentration measurements, exposure to ionizing radiation, effective radiation dose, underground laboratory

Radon exposure assessment was based on estimated levels of the effective radiation dose that could be received by anyone staying inside underground geodynamic laboratory of Space Research Centre in Książ for a particular period of time (hour, day, year). Effective radioactive doses were defined in compliance with UNSCEAR guidelines based on values of ^{222}Rn activity concentration measured during one year between half of May 2014 and half of May 2015 in the air of the studied space, the ratio of the number of conversion emitted per unit time (adopted the value of 0.00000017 mSv/Bq·h/m^3), exposure time (8 hour a day during 52 weeks) and coefficient of radioactive equilibrium between ^{222}Rn and its short–lived progeny (adopted the value of 0.4). The radon measurements had been performed for the first time and with the use of three semiconductor SRDN-3 probes located in selected facility.

In order to assess the radiation exposure of people staying inside, all the estimated effective radiation doses were used. However, only the maximum doses, making it possible to present the conditions which in light of Polish radiological protection regulations were the least advantageous, were considered representative for the studied underground laboratory.

In underground geodynamic laboratory of Space Research Centre in Książ, the maximum value of effective radiation dose received during a 1-hour, ranging average 0.007 mSv/h–0.02 mSv/h. Effective radiation doses are on the same level regardless of the time of day and time of measurements. The highest values of radon activity concentration and effective radiation dose are noticed in warmer periods of the year. The value of annual effective radiation dose was average 15–20 mSv/year, the maximum reached more than 35 mSv/year.

The values of effective radiation dose are dependent on the seasonal changes of radon activity concentration but are not dependent on the hour of measurement during a day (short-term, diurnal cycles). From autumn (between late October and late January) to spring (between February and April), when the air inside the laboratory has a higher temperature than the atmospheric air, radon is carried out to the atmosphere with the warmer air flowing out of the object. In the warmer season between late April to September, the air inside is cooler than the atmospheric air outside and it is accumulated with radon inside laboratory. This fact is linked to the natural ventilation (convection) of the laboratory.

In underground geodynamic laboratory of Space Research Centre in Książ exists the risk of receiving doses that exceed the allowable annual effective radiation dose limits specified by the polish Atomic Law, but the probability of its occurrence is very low.

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DISSOLVED RADIOCAESIUM IN SEAWATER OFF FUKUSHIMA PREFECTURE IN 2013–2015

Miho Fukuda[1], Sinnosuke Yamazaki[2], Tatsuo Aono[3], Takashi Ishimaru[4], Jota Kanda[5]

[1]Project for Environmental Dynamics and Radiation Effects, Fukushima Project Headquarters, National Institute of Radiological Science (NIRS), 4-9-1 Anagawa, Inage-ku, Chiba 263-8555, Japan, e-mail: mhfukuda@nirs.go.jp
[2]Project for Environmental Dynamics and Radiation Effects, Fukushima Project Headquarters, National Institute of Radiological Science (NIRS), 4-9-1 Anagawa, Inage-ku, Chiba 263-8555, Japan, e-mail: s_yamaza@nirs.go.jp
[3]Project for Environmental Dynamics and Radiation Effects, Fukushima Project Headquarters, National Institute of Radiological Science (NIRS), 4-9-1 Anagawa, Inage-ku, Chiba 263-8555, Japan, e-mail: t_aono@nirs.go.jp
[4]Department of Ocean Sciences, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan,
e-mail: jkanda@kaiyodai.ac.jp
[5]Department of Ocean Sciences, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan,
e-mail:ishimaru@kaiyodai.ac.jp

Keywords: Fukushima coastal area, seawater, radiocaesium

The 2011 off the Pacific coast of Tohoku Earthquake and subsequent tsunami on 11 March 2011 caused damages that led to the accident at TEPCO's Fukushima Dai-ichi Nuclear Power Station (FDNPS). Large amounts of radionuclides were dispersed by hydrogen explosions, and radionuclides also leaked from the FDNPS into the terrestrial and marine environments. In the approximately 5 years that have passed since the accident, radiocaesium activities in seawater in the Fukushima coastal area have decreased, but are about 10 times higher than before the accident [1]. There are some controversies about the factors affecting radiocaesium activities in the seawater which seem to be sensitive to river input and land erosion. This study aimed at elucidating the factors affecting the distribution and behaviour of dissolved radiocaesium in seawater by analysing samples collected off the coast of Fukushima Prefecture during six-month periods (May and October) in each year from 2013 to 2015. In that three-year period, the dissolved ^{137}Cs activities were 1.8–220 mBq L^{-1} and the activities in October were totally higher than those in May. In surface-layer seawater (water depth, 0–20 m), the activities at the sampling stations located within 10 km of the coast of Japan were higher than those at other stations and the trends were particularly observed in October. On the other hand, the relationships between the activities and distance from the continent or salinity in bottom water (water depth, >20 m) were not clear. In mid-October 2013, Typhoon Wipha passed through the eastern part of the main Japanese island, and at the Haranomachi weather station (37°38′ N, 140°59 E) in Fukushima Prefecture, the total rainfall exceeded 100 mm on 16 October 2013, which was a sampling date for this study [2]. It seems that the increased fresh water input, including input of radiocaesium from rivers or land erosion caused by the heavy rain of the typhoon affected the sampling results. In the presentation, we will also discuss the factors for radiocaesium distribution and temporal variation in 2013–2015.

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RADIATION SITUATION AT THE PLACES OF PEACEFUL NUCLEAR EXPLOSIONS IN KAZAKHSTAN

Viktor Gluchshenko, Anatoliy Poleshko, Galina Gluchshenko, Mikhail Levashov*

Institute of Nuclear Physics, Ibragimov St. 1, Almaty, 050032, Republic of Kazakhstan, *e-mail: vik.inp.kz@gmail.com

Keywords: peaceful nuclear explosions, spectroscopic and radiochemical methods of analysis, radiation situation

The Republic of Kazakhstan is a unique state combining its modern nuclear-free status with a serious nuclear past. There is a large number of radiation-hazardous objects of various types throughout the territory of Kazakhstan: the sites of nuclear testing, research and energy nuclear plants, organizations and plants of uranium mining and processing industry, oil fields.

The particular public attention is directed to the places of nuclear explosions. For several decades, a significant amount of underground nuclear explosions (UNE) have been made on the territory of Kazakhstan. Most of them are associated with the tests of nuclear weapons performed at the Semipalatinsk test site. In addition, the series of peaceful nuclear explosions was performed for solving the number of national economic problems – Azgir test site, the "Lira", "Mangyshlak", "Meridian", "Batholith", "Region" facilities. After some years the negative effects caused by the UNE consequences have been observed in some regions. The negative consequences of UNE imply the inflow of radionuclides and other contaminants into the groundwater and productive strata. The outflow of these contaminants to the day surface is also possible as a result of their migration through the weakened zones and extrusion of the radiation contaminated solutions from the UNE cavities due to their collapsing.

The paper presents the main results of the investigations performed at the locations of peaceful nuclear explosions with application of modern spectroscopic and radiochemical methods of analysis. The areas of anthropogenic radioactive contamination of equipment and soil were identified during the survey at some sites. As the result of the performed remediation measures all detected radiation anomalies have been liquidated.

Currently, the radiation situation in the territories and settlements adjacent to the places of peaceful nuclear explosions is normal. All objects of peaceful nuclear explosions are radiation dangerous and require constant monitoring at the state level. The most probable mechanism of threat is the spreading of radionuclides from groundwater.

To ensure the continuous monitoring of the radiation situation and the required operative actions to ensure the radiation safety of the population it is necessary to develop and implement the unified system of radiation monitoring at the places of peaceful nuclear explosions on the territory of the Republic of Kazakhstan.

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MEASURING NATURAL RADIATION (NORM) INSIDE SOME OIL FIELDS IN LIBYA

Ezeddine Hamida

Theoretical Studies Department, Petroleum Training & Qualification Institute, Tripoli, Libya, e-mail: Ezzdinelgali@yahoo.com

In this work, we measured the natural radiation, known in the scientific community NORM (Naturally Occurring Radioactive Materials), where we collected 6 different specification samples of different fields. Sample 1, 2 and 3 were crude oil mixed with soil (Sludge) taken from the oil lakes (pits); Sample 4 is a crude oil taken from one of the storage depots; samples 5 and 6 are a squamous crust (Scales) accumulated in the production & pipelines.

NORM was measured by High pure Germanium Spectroscopy-HPGe in the prevention building of Nuclear Research Center/ Tajura,Tripoli-Libya and the results were as follows:

Sample	1	2	3	4	5	6
Radioactive Activity (Bq/kg)	54.6±7.38	19.69±4.43	12.27±3.5	3.97±1.99	4017.2±63.38	5522.6±74.31

From these results, it is clear that the squamous crust (scales) samples contain the largest radiation.

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DETERMINATION FOR ^{106}Ru IN SEAWATER USING γ-RAY SPECTROMETRY

Dekun Huang

Laboratory of Marine Isotopic Technology and Environmental Risk Assessment, Third Institute of Oceanography, SOA, Xiamen 361005, China, e-mail: dkhuang@tio.org.cn

Keywords: ^{106}Ru, seawater, cobaltous sulphide, γ-ray

The radio ruthenium (^{106}Ru) is the non-negligible nuclide in the nuclear facilities' monitoring of fission products. ^{106}Ru is toxic, when it enters the seawater, it can path through the food chain via shellfish (such as clams and oyster). Different methods (CCl_4 extraction-β counting, distillation and sulfide-ion-exchange resin) are used for the measuring of ^{106}Ru, however, those methods are complex and time consuming. With the improvement of instrument, HPGe γ-ray spectrometry is now widely used for the measuring of radionuclides due to its simple preparation, and hence more efficient. The cobaltous sulphide (CoS) precipitation method is commonly used to concentrate the ^{106}Ru from the seawater when using HPGe γ-ray spectrometry to determine ^{106}Ru. However, the factor reported for the concentrating ^{106}Ru varies in different studies. The objective of present study is to explore the effect of different factors (Co^{2+} concentration, Thioacetamide (TAA) concentration, heating temperature and heating time for the precipitation) on the measurement of Ru, and try to find out the optimal method. Preliminary results show that the method is sensitive to the TAA concentration, when the TAA concentration is 30 times of Co^{2+} concentration, the recovery efficiency of ^{106}Ru is the highest; while Co^{2+} concentration didn't show significant effect. We also compare the CoS method with other methods (MnO_2, $Fe(OH)_3$ and CuS precipitation). The optimal method was then applied to several seawater samples from the coast of China and the west Pacific.

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SURVEY OF THE DISSOLVED 14C OF THE GROUNDWATER AT THE PAKS NUCLEAR POWER PLANT, HUNGARY

Róbert Janovics, Anita Molnár, Mihály Veres, Mihály Molnár*

Hertelendi Laboratory of Environmental Studies, MTA Atomki-Isotoptech Zrt, Debrecen, Hungary, *e-mail: janovics@atomki.hu

Keywords: organic radiocarbon, groundwater, environmental monitoring

In practice the monitoring of the underground radiocarbon emission by the nuclear facilities (also at the Paks NPP) is based on the survey limited to the dissolved inorganic carbon forms of groundwater. However the emitted radiocarbon can be present in organic forms as we know from our previous study at the Püspökszilágy Radioactive Waste Treatment and Disposal Facility [1]. For the exact and correct dose estimation it would be necessary to know rather the total radiocarbon content of the groundwater samples.

Knowing the above we measured the specific radiocarbon concentration separately of the inorganic, the total (inorganic and organic together), and the non-volatile organic compounds of the groundwater from the monitoring wells at Paks NPP. By the separate measurement of these three compounds the radiocarbon contamination getting into the groundwater of the power plant is mostly present in the inorganic forms (typical specific C-14 in the activity: 270±190 pM) and the organic fraction does not have significant radiocarbon contribution as the specific C-14 activity is close to the natural background (110±20 pM) level.

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SELF-ATTENUATION CORRECTION IN 210Pb GAMMA-SPECTROMETRY MEASUREMENTS BASED ON SAMPLE CHEMICAL COMPOSITION; REQUIREMENTS FOR SCOPE OF CHEMICAL ANALYSES

Paweł Jodłowski, Przemysław Wachniew, Chau Nguyen Dinh, Jakub Nowak*

AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. Mickiewicza 30, 30-059 Kraków, Poland, *e-mail: jodlowski@fis.agh.edu.pl

Keywords: gamma-ray spectrometry, self-attenuation, Pb-210, chemical composition, Monte Carlo simulation

Naturally occurring radionuclide Pb-210 is commonly used in research of processes connected with sediment accumulation in aquatic environment and river basins. The most common application of Pb-210 is connected with determination of sediment age and tracing of eroded soils and sediments. Gamma-ray spectrometry method enables accurate Pb-210 determination but the key issue for measurement accuracy, especially for low-energy radiation, is self-attenuation correction (C_s) determination.

The presented paper is a part of a larger project that elaborate methodology to determine correction C_s in sample on the basis of chemical composition and density of the analysed material. In the presented paper analysis of sensitivity of C_s to the accuracy of chemical composition analysis was presented. In order to determine C_s correction, it is necessary to know chemical composition of the analysed sample, however, it is needless to determine all elements in a sample. The aim of the work is to find minimal requirements for the scope of chemical analyses, and the list of elements in particular, which determination is necessary.

The analyses were done by means of Monte Carlo simulation method for a cylindrical sample with 3 cm height and for 7 typical materials that can be found in the environment such as: peat, water, sediment, chernozem, ash, quartz sand and soil. For each of these materials the elements were selected, which determination in the analysed material is necessary, assuming accuracy of a sample C_s correction determination (e.g. 3%). For the remaining elements that often appear in environmental samples, “limit levels” of their concentration were determined – if the expected element concentration in a sample exceeds this value, its determination is necessary.

Thus, for example, for the soil of 1.4 g/cm^3 density, with typical concentrations of essential elements, with the expected uncertainty correction of C_s below 3%, it is necessary to determine the concentration of Si and O, whereas limit levels for C, Al, K, Ca, Fe, Pb amount to 20%, 40%, 4%, 4%, 5% and 0.2% accordingly.

The results presented in the paper enable to limit the range of chemical analyses essential to determine C_s correction and, thereby, lead to cost reduction of Pb-210 determination in environmental samples.

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RAPID METHOD FOR THE DETERMINATION OF STRONTIUM ISOTOPES IN FOOD AND BEVERAGE SAMPLES

Eva Kabai, Angela Poppitz-Spuhler, Birgit Savkin*

Department Radiation Protection and the Environment, Federal Office for Radiation Protection, Ingolstädter Landstr. 1, 85764 Oberschleißheim, Germany, *e-mail: ekabai@bfs.de

Keywords: strontium, Sr-89, Sr-90, Sr resin, LSC, food, beverage

Rapid methods are essential for a fast response in the case of a radiological emergency. In order to provide information on the activity levels in food and beverages to decision makers and the public, it is important to develop fast laboratory methods for these types of samples. For pure beta emitting fission products like Sr-89/Sr-90 fast radioanalytical methods are needed.

The method developed for the rapid determination of Sr-89/Sr-90 is based on the chemical microwave digestion of the food and beverage samples. After obtaining a transparent liquid solution, an aliquot can be premeasured directly in a liquid scintillation counter (LSC) for Cherenkov counting and liquid scintillation. The rest of the sample can be further purified using the Sr resin for the selective separation of strontium isotopes and then measured by LSC. The whole procedure allows the selective determination of Sr-89/Sr-90 in one working day. The typical detection limits of the direct measurement are around 200 Bq/l for beverage and 1000 Bq/kg for food samples, respectively. The achieved detection limits after purification are close to 1 Bq/l and 1 Bq/kg, respectively.

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MEASUREMENT OF RADON AND THORON EXHALATION RATE IN SOIL SAMPLES OF JAMMU DISTRICT, JAMMU AND KASHMIR, INDIA

Manpreet Kaur, Ajay Kumar, Sumit Sharma

Post Graduate Department of Physics, DAV College, Amritsar-143001, India

Keywords: soil, exhalation rate, Smart Rn Duo technique

The soil, bedrock beneath a building and building materials are three main source of the radon gas, which is present in the indoor environment of the dwellings. The radon originating from the underneath soil comes out by emanation and exhalation. Exhalation of radon and thoron from building material also causes health problems. The radon exhalation rate from the ground is one of the most important factors that is useful to classify areas that could be building ground, if it has a high radon risk (indoor radon will be high), or not. The aim of present survey was focused on determining the radon mass and thoron surface exhalation rate by extrapolating the data in soil samples collected from Jammu district, Jammu and Kashmir, India. There are many techniques used to measure radon exhalation rate directly from ground, soils and rocks or from building materials. “Smart Rn Duo technique” which is an active device has been employed for the measurement of radon mass and thoron surface exhalation rate in soil samples collected from under study areas. The radon exhalation rate in these samples has been found to vary from 14.9 to 35.5 m Bq kg^{-1} h^{-1} and thoron exhalation rate has been found to vary from 0.024 to 1.35 $Bqm^{-2} s^{-1}$. The concentrations for exhalation rate are compared with the reported data from other countries. The porosity of soil samples has been measured. Thoron mass exhalation rate was also measured and varied from 2.58 to 184.83 $Bqkg^{-1} h^{-1}$.

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CONCENTRATION AND CHARACTERIZATION OF AIRBORNE RADIOACTIVE CESIUM IN TOKYO MAJOR METROPOLITAN AREA AFTER FUKUSHIMA NUCLEAR ACCIDENT

Yoshikazu Kikawada[1], Ko Nakamachi[2], Masaaki Hirose[1], Takahiro Ono[2], Takao Oi[1], Yukiko Okada[2], Haruaki Matsuura[2], Katsumi Hirose[1]*

[1]Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyoda, Tokyo 102-8554, Japan, *e-mail: y-kikawa@sophia.ac.jp
[2]Graduate School of Engineering, Tokyo City University, 1-28-1, Tamadutsumi, Setagaya, Tokyo 158-8557, Japan

Keywords: radioactive cesium, particulate matters, Fukushima accident, anthropogenic radionuclides

We have been measuring radionuclides in airborne particulate matters (APMs) by gamma-ray spectrometry, which continuously collected at Kawasaki City, Kanagawa Prefecture, located near Tokyo since 2001. The APMs sampling has been conducted weekly with a high volume air sampler equipped with a quartz fiber filter at the monitoring station in the campus of the Atomic Energy Research Laboratory, Tokyo City University. Concentrations of radioactive cesium in the APMs had increased drastically just after the occurrence of the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in March 2011, reaching the highest value of 0.60 Bq/m^3 for ^{137}Cs. Shortly after that, however, it started to show a decreasing trend, and the concentrations of ^{137}Cs in the AMPs decreased to one 10-thousandth of the highest value by the end of 2011. The decreasing rate of the airborne ^{137}Cs was high in the first few months after the FDNPP accident, slowed down by September 2011, a half year after the accident, and since the end of 2012, no appreciable decrease of the ^{137}Cs concentration in the AMPs has been observed. The major source of radioactive cesium in the APM samples has been considered to be suspension of soil particles in and after 2012. The mean concentration of ^{137}Cs in the APMs throughout 2014 was 9×10^{-5} Bq/m^3, which is about two orders of magnitude greater than the pre-Fukushima level.

On the other hand, it has been suggested that temporal variations of the deposition of radioactive cesium in the APMs in the Kanto area could not be explained only by the soil resuspension process [1]. We, thus, conducted extraction experiments on the APMs to have information on chemical characteristics of airborne radioactive cesium, which is important to identify the source of airborne radioactive cesium. The experimental results reveal that the extraction behavior of radioactive cesium in the APMs is obviously different from that in soil contaminated by the FDNPP accident. The radioactive cesium in the APMs has been easily extracted by water, whereas that in the soil has hardly been extracted by water and partially extracted only by aqueous solutions containing some kind of salts like ammonium salts [2]. That is to say, the airborne radioactive cesium in recent days may not always be supplied by soil resuspension process. The possible candidates for the source of radioactive cesium in the recent APMs may be dust from cleanup operations in the disaster area and/or soot with an open-air burning of combustible wastes including leaves, grass, and wood.

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INDOOR RADON, THORON AND THEIR PROGENY MEASUREMENT IN DWELLINGS OF JAMMU DISTRICT, JAMMU & KASHMIR, INDIA

Ajay Kumar, Manpreet Kaur, Sumit Sharma

Post Graduate Department of Physics, DAV College, Amritsar-143001, India

Keywords: radon, thoron, annual effective dose, gamma dose rate

Indoor radon/thoron has been recognised as one of the health hazards for mankind. In present investigations, pinholes based single entrance Rn^{222} / Rn^{220} discriminating dosimeter, with LR-115 type- II track detector were used for estimating annually radon (Rn^{222}), thoron (Rn^{220}) gas concentration levels. The measurements have been carried out in 120 dwellings of 40 different villages situated in Jammu district of Jammu & Kashmir, India. Indoor and outdoor ambient gamma dose rates were also calculated and varied from 0.08 to 0.17µSv/h and 0.02 to 0.25 µSv/h. Villages were divided into three different zones according to gamma dose rate. Dwellings were selected in villages mainly targeting different types of building material used in construction of houses like concrete-brick, mud-brick and marble-cemented along with an idea of different ventilation conditions. Radon concentrations varied from 12.69Bqm^{-3} to 48.74 Bqm^{-3} with average 25.88 Bqm^{-3} in 8 villages in first zone, from 10.08 Bqm^{-3} to 83.96 Bqm^{-3} with average 47.02 Bqm^{-3} in 25 villages in second zone and from 13.97 Bqm^{-3} to 85.29 Bqm^{-3} with average 49.63 Bqm^{-3} in 7 villages in third zone. Similarly thoron concentrations varied from 48.00 Bqm^{-3} to 149.00 Bqm^{-3} with average 97.88 Bqm^{-3} in 8 villages in first zone, from 14.44 Bqm^{-3} to 150.92 Bqm^{-3} with average 95.27 Bqm^{-3} in 25 villages in second zone and from 64.39 Bqm^{-3} to 237.1 Bqm^{-3} with average 127.95 Bqm^{-3} in 7 villages in third zone. Total radon concentration levels in the studied dwellings were found to vary from 10.08±4.60 Bqm^{-3} to 85.29±23.89 Bqm^{-3} with average 47.69±14.25 Bqm^{-3} and total thoron concentrations were found to vary from 14.44±2.80 Bqm^{-3} to 237.1±90.88 Bqm^{-3} with average 125.77±46.84 Bqm^{-3}. Indoor radon concentrations from various dwellings in the studied area were lower than the limit 100 Bqm^{-3} recommended by WHO (2009). Annual effective dose was also calculated. Average annual effective dose for radon was found 1.38±0.081 and for thoron was found 3.17±1.18.

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A COMPARATIVE STUDY ON SORPTION AND DIFFUSION OF CESIUM IN CRUSHED ARGILLITE AND GRANITE

Chuan-Pin Lee[1], Ming-Chee Wu[1], Yu-Lin Tu[1], Lin-Chen Kang[1], Shih-Chin Tsai[2], Tsuey-Lin Tsai[2], Hwa-Jou Wei[2]*

[1]Department of Earth Sciences, National Cheng Kung University, University Road, Tainan City, 70101, Taiwan, *e-mail: cplee@mail.ncku.edu.tw
[2]Nuclear Science and Technology Development Center, National Tsing Hua University, Hsinchu, 30013, Taiwan
[3]Chemistry Divisions, Institute of Nuclear Energy Research, Taoyuan, 32546, Taiwan

Keywords: sorption, diffusion, cesium, argillite, granite

This study was conducted using batch and column methods in order to investigate the sorption and diffusion of cesium (Cs) for two potential host rocks in Taiwan: argillite from Taitung and granite from Kinmen Island, with the purpose of establishing a reliable safety-performance assessment methodology for the final disposal of spent nuclear fuel. The methods were applied on crushed rock samples to simulate the *in-situ* geological environment. The mineral component and basic characteristics of the host rock samples were obtained using solid-phase analyses, i.e., X-ray diffraction (XRD), elemental analysis, N_2-BET surface area analysis, and cation exchange capacity (CEC). Furthermore, the distribution coefficients (K_d) of Cs were obtained using batch tests with various sample grain size. The results showed that higher sorption capacities were found for argillite than granite; due to the higher clay mineral content in the argillite. Experiments for diffusion of Cs both in crushed argillite and granite were also conducted. The apparent diffusion coefficients (D_a) were analysed and plotted as accumulating curves, respectively. However, the values estimated for the diffusive results (D_a) of Cs in argillite were revealed to be lower than those of granite. In addition, the diffusive results showed that the major retardation factor (R_f) of Cs was dependent upon the micro-porous structure of the tested media, e.g., a decrease in constrictivity (δ) and an increase in tortuosity (τ). The solid/liquid (S/L) ratio, in fact, decreased, as it was in the case when switching from the batch method to a through-diffusion experiment, of which the analysis results indicated that the sorption effect on the minerals was even more negligible in regard to the retardation of radionuclide migration.

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MONITORING OF CAESIUM-137 IN SURFACE SEAWATER AND SEAFOOD IN BOTH THE IRISH AND NORTH SEAS: RECENT TRENDS AND OBSERVATIONS

Kinson Leonard[1], Andras Donaszi-Ivano[2], Alastair Dewar[1], Victoria Ly[1], Trevor Bailey[1]*

[1]Cefas, Lowestoft Laboratory, Pakefield Road, Lowestoft, Suffolk NR33 0HT, UK, *e-mail: kins.leonard@cefas.co.uk
[2]Food Standards Agency, Aviation House, 125 Kingsway, London, WC2B 6NH, UK, e-mail: andras.donaszi-ivanov@foodstandards.gsi.gov.uk

Keywords: monitoring, OSPAR, Irish Sea, North Sea, caesium-137

The objective of the OSPAR Commission's Radioactive Substances Strategy is to prevent pollution of the OSPAR maritime area (North East Atlantic) from ionising radiation through progressive and substantial reductions of discharges, emissions and losses of radioactive substances. The UK Governments are committed to preventing pollution of the marine environment. The continuation of UK annual surveillance programmes to determine the distribution of radionuclides in the food and the environment is maintained year on year. Selected results of monitoring at UK nuclear licensed sites and in adjacent coastal seas contribute to the data collected by the OSPAR Commission. The information provided in this paper is taken from data submitted by the UK (since 1998) to the OSPAR Commission for the purpose of evaluating the extent to which the Radioactive Substances Strategy is being met (by the year 2020). Data are also published annually in the Radioactivity in Food and the Environment Report (RIFE) report series by the UK.

The objective of this paper is to provide selected concentrations of caesium-137 in the Irish and North Sea coastal waters and seafood, and to assess the impact upon the surrounding environment. These data give a clearer and broader picture of caesium-137 trends in the environment which are not obvious from the annually submitted or published technical reports. The data have been summarised, at a variety of sampling locations, to produce a review of trends and observations over time, from 1998 until the present time. (OSPAR evaluation period, to-date).

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ACCUMULATION OF ANTHROPOGENIC AND NATURAL RADIONUCLIDES IN CRYOCONITES FROM SOUTHERN CAUCASUS (GEORGIA)

Edyta Łokas[1], Anna Cwanek[1], Katarzyna Szufa[1], Paweł Gaca[2], Krzysztof Zawierucha[3]*

[1]Department of Nuclear Physical Chemistry, Institute of Nuclear Physics PAS, Radzikowskiego 152, 31-342 Krakow, Poland,
*e-mail: Edyta.Lokas@ifj.edu.pl
[2]GAU-Radioanalytical Laboratories, Ocean and Earth Science, University of Southampton, National Oceanography Centre, European Way, Southampton, United Kingdom, e-mail: p.gaca@noc.soton.ac.uk
[3]Department of Animal Taxonomy and Ecology, Adam Mickiewicz University in Poznań, Poland, e-mail: k.p.zawierucha@gmail.com

Keywords: cryoconites, radionuclides, isotopic ratios

Cryoconites are the airborne dust which accumulate on the surface of glaciers, from the atmosphere by dry or/and wet precipitation. Material aggregates in cryoconites consist of a mixture of mineral particles, organic substances and living microorganisms, common among them being the filamentous cyanobacteria. The quasi-spherical aggregates increase their size due to the growth of cyanobacteria and physical entrapment of mineral material or by fusion of smaller granules. Cryoconite holes, are small water filled depressions, common in the ablation zones of glaciers, located in polar, as well as mountain regions. The contaminants are effectively trapped in cryocnite holes and may be stored inside them for many years leading to very high concentrations of contaminants. The objectives of this study were to: (1) evaluate the contamination level of artificial (^{137}Cs, $^{238,239+240}$Pu, ^{241}Am, ^{90}Sr) and natural (^{230,232}Th, ^{234,238}U, ^{210}Pb) radionuclides of cryoconites sampled from Adashi glacier (Svaneti region, Georgia); (2) distinguish the sources of contamination based on artificial radionuclides ratios (^{238}Pu/$^{239+240}$Pu, ^{241}Am/$^{239+240}$Pu, $^{239+240}$Pu/^{137}Cs and ^{240}Pu/^{239}Pu, ^{90}Sr /^{137}Cs, ^{90}Sr/ $^{239+240}$Pu); (3) determine the external dose from both natural and anthropogenic radionuclides. Analyses of fine-grained deposits from cryoconite holes located on Adashi Glacier revealed unexpectedly high activity concentrations of fallout radionuclides reaching 4900 Bq/kg, 2.5 Bq/kg, 107 Bq/kg and 68 Bq/kg for ^{137}Cs, ^{238}Pu, $^{239+240}$Pu and ^{241}Am, respectively. The average activity ratios for ^{238}Pu/$^{239+240}$Pu (0.031) and ^{240}Pu/^{239}Pu (0.16) suggest the global fallout as the dominant source of Pu. $^{239+240}$Pu/^{137}Cs (0.013) and ^{241}Am/$^{239+240}$Pu (0.86) activity ratios point to possible other sources of ^{137}Cs and ^{241}Am. The average isotopic ratios of ^{90}Sr/ ^{137}Cs (0.023) suggests the Chernobyl fallout as a dominant source of Cs. On the other hand the mean value of ^{90}Sr/ $^{239+240}$Pu isotopic ratio (0.81) suggests that the global fallout is the dominant source of Pu. This result points to a very high depletion of Sr possibly due to its high mobility in the environment, especially when compared to Cs and Pu. The natural radionuclides (isotopes of U and Th) originating from the surrounding rocks weathering are transferred to the glacier surface with larger grains and do not concentrate in cryoconite holes. ^{210}Pb in cryoconites is derived mainly from the atmospheric deposition and its activity concentrations reach high values up to 12000 Bq/kg. Because of small dimensions of the cyanobacteria cells, smaller than the range of gamma rays and beta particles of caesium, potassium and strontium in water, the external dose to cyanobacteria comes mainly from the alpha emitters decay, reaching only up to 0.5 μGy/h.

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SOURCES OF URANIUM IN LICHEN NEAR THE MOUND SITE

Kelly C. McHugh, Elisabeth Widom, David C. Kuentz*

Department of Geology & Environmental Earth Science, Miami University, Oxford, Ohio, USA, *e-mail: widome@MiamiOH.edu

Keywords: uranium isotopes, TIMS, lichen, Mound Site, SW Ohio

The Mound Site, in SW Ohio USA, is a former U.S. Atomic Energy Commission and Department of Energy site that was established for atomic weapons related research and development [1]. The site was in operation from 1948 to 2003, during which time a variety of radionuclides were released to the local environment, including Pu, U, and Th; depleted U (DU) metal was "suspected" to be present in some locations on site [2]. The Mound was designated a Superfund site in 1989, and was remediated for use as an industrial park, now under the long-term surveillance of the DOE Office of Legacy Management [2].

In this study, we collected lichens from the vicinity of the Mound Site in order to evaluate the utility of lichens as monitors of past airborne releases of radionuclides. Seven lichen samples collected within a 3.5 km radius of the Mound Site (mostly in the downwind direction) were ashed, and analyzed for U concentration by ICP-MS and isotopic composition by thermal ionization mass spectrometry (TIMS) [3]. Uranium concentrations in the lichen ash range from 0.23–1.17 ppm, significantly higher than background concentrations of 66 ppb determined previously in SW Ohio tree bark [4] and in some cases higher than local background soil concentrations (0.8 ppm; [5]). Measured 235U/238U ratios in all samples are within error of the natural value (0.00725 ± 0.00001), thus the major isotopes of U do not indicate any presence of DU in the lichen samples. However, five of the seven samples have measureable 236U with 236U/238U ratios ranging from 4.4E-8 to 6.2E-6, clearly indicating the presence of non-natural U in these samples. Furthermore, a positive correlation of 236U/238U with U concentration indicates that the elevated U concentrations in these lichen samples are due to contaminant U from nuclear materials, and thus is most likely attributable to releases to the environment from the Mound Site. Analyses of Th and Pu in the lichen samples should provide further evaluation of the nature and extent of environmental contamination in the vicinity of the Mound Site.

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FIRST REPORT ON PRIMORDIAL AND ANTHROPOGENIC RADIONUCLIDES IN INDIAN SUNDARBAN MANGROVE ECOSYSTEM

Nabanita Naskar[1], Susanta Lahiri[2], Punarbasu Chaudhuri[1]

[1]Department of Environmental Science, University of Calcutta, 35 Ballygunge Circular Road, Kolkata, India,
e-mails: g.nabanitanaskar94@gmail.com, punarbasu_c@yahoo.com
[2]Chemical Sciences Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata, India, e-mail: susanta.lahiri@saha.ac.in

Keywords: naturally occurring radionuclides, Sundarban, mangrove ecosystem, surface soil, γ-ray spectrometry

Primordial long-lived radionuclides ^{232}Th,^{238}U along with ^{40}K contribute vividly to the natural radiation present around us. While anthropogenic radionuclides ^{90}Sr, ^{137}Cs are the aftermath products of human activities like mining, radiotracer studies, nuclear tests or accidents, etc. The objective of the present study is to assess the radionuclide characterisation of soil samples collected from the world's largest deltaic mangrove ecosystem, 'Sundarban' using gamma-ray spectrometry. Sundarban wetland spreads across two neighbouring countries India and Bangladesh. This first time radioactivity measurement attempts to sketch the base-line data of Indian Sundarban mangrove area for future radiological assessment. Sampling was done from 30 different estuarine locations of Sundarban mangrove delta, one of the most productive ecosystems with enriched biodiversity. Pre-treatment of samples included air-drying, pulverization to ensure homogeneity, weighing and keeping in hermetically sealed petri-plates for 45 days. Activity of naturally occurring radionuclide(NOR), ^{238}U ($T_{1/2}$ = 4.468×10^{9}a), ^{232}Th ($T_{1/2}$ = 1.40×10^{10}a) and anthropogenic radionuclide/ Technologically enhanced NOR(TeNOR), ^{137}Cs ($T_{1/2}$ = 30.08a) was measured using highly shielded high purity Germanium (HPGe) detector having 50% relative efficiency. Radioactivity level of ^{238}U laid in the range of 31.7±10.5 Bq/kg to 55.2±14.5 Bq/kg, with mean and median activity at 45.5 Bq/kg and 44.8 Bq/kg, respectively. Similarly, ^{232}Th radioactivity ranged between 51.4±4.8 Bq/kg to 85.0±4.3 Bq/kg with mean and median activity at 72.2 Bq/kg and 72.1 Bq/kg, respectively. The same value of mean and median indicates normal distribution of ^{238}U and ^{232}Th activity. ^{137}Cs activity varied from BDL to 7.3 Bq/kg. The NOR values are slightly above the global averages of 35 Bq/kg and 45 Bq/kg for ^{238}U and ^{232}Th respectively [1], which may be attributed to the cumulative accumulation of the same from upstream Gangetic trail, flowing via several inter-connected rivers of Ganga-Brahmaputra-Meghna basin [2]. The activity of ^{137}Cs is well below the radar, but in some places minute activity was observed, which may be due to localized concentration of ^{137}Cs due to radiotracer studies on river sediments by ^{137}Cs tracer.

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THE RADIOACTIVE CAESIUM DISTRIBUTION BROUGHT BY THE FLOOD

Naoto Nihei[1]*, *Yoshikatsu Ueda*[2], *Keitaro Tanoi*[1], *Tomoko M. Nakanishi*[1]

[1]Graduate School of Agricultural and Life Science, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo, Japan,
*e-mail: anaoto@mail.ecc.u-tokyo.ac.jp
[2]Research Institute for Sustainable Humanosphre, Kyoto University, Gokasho, Uji, Kyoto, Japan

Keywords: radiocesium, soil, river sediment, rainfall, nuclear accident, Fukushima

Iitate village (Fukushima prefecture) was contaminated by radiocesium because of the fallout from the Fukushima Daiichi-Nuclear Power Plant accident on March 11th, 2011. To decontaminate the place, the contaminated surface soil was collected and packed in containers. On September 12th 2015, there was a heavy rainfall of 200 mm/day, which increased the volume of water in many rivers flowing into Iitate village. Some rivers were flooded causing the sediment flow over the fields. It was considered that the newly brought sediment by the flood caused the contamination of the place where decontamination was performed. The investigated place was chosen where two rivers merged and the sediment from both rivers was estimated to be delivered. The sampling points were 3, 6, 9 and 12 m from the river and the soil was collected 0, 2, 4, 6, 8, 10 and 12 cm down from the surface at each point. The radioactivity was counted by a NaI scintillation counter and some interesting results were suggested. At the point, 3 m from the river, the highest concentration of the radiocesium was found at the deepest layer from the surface (12~14 cm), whereas at 12 m from the river, the concentration of the radiocesium was the highest at the surface layer (0~2 cm). From these measurements, it was indicated that there were two floods caused by the heavy rain. The first flood brought the high radioactive sediment in the wide range of the place, more than 12 m from the river. Then the second one brought the lower concentrated sediment till 9 m from the river. It was also suggested that there was a difference in the contamination level of the sediments in two rivers.

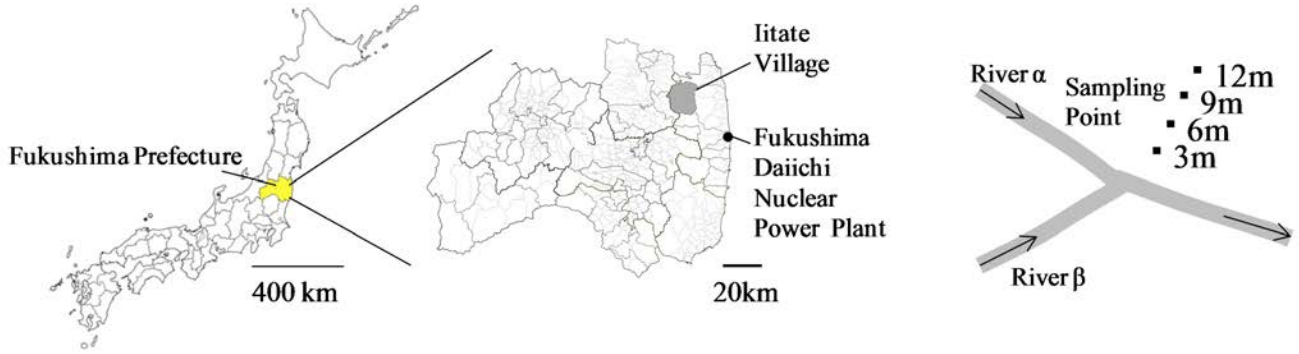

Fig. 1. Iitate village and the sampling points

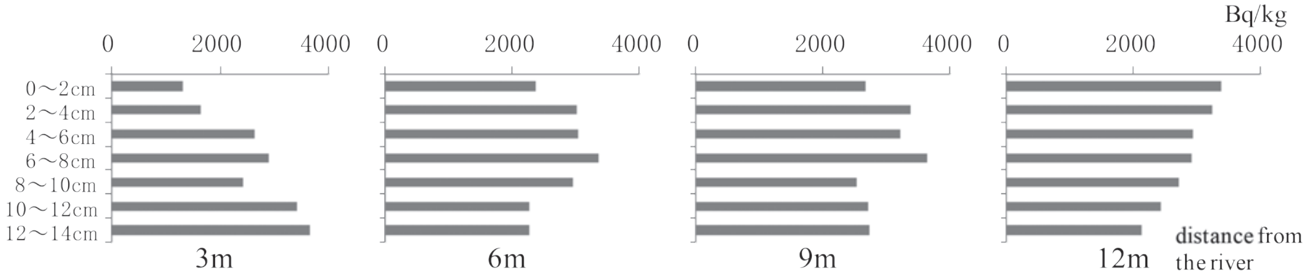

Fig. 2. The radiocesium concentration of the field near the flooded river

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NATURAL RADIONUCLIDES IN ROCHA'S SANDS AND SOILS

A. Noguera, H. Bentos Pereira, L. Fornaro*

Grupo de Desarrollo de Materiales y Estudios Ambientales, Centro Universitario de la Región Este, Universidad de la República, Ruta 9 y Ruta 15, Rocha, Uruguay, *e-mail: anoguera@cure.edu.uy

Keywords: natural radiactivity, external hazard index, radium equivalent activity

The Uruguayan east coast has several mineral resources, which include black sand ores, with 7 million tons of heavy minerals evaluated in the Aguas Dulces-Valizas area. These ores have a mean composition of 50% of ilmenite, 20% of magnetite, 5% of zircon, 1% of rutile and 0.6 % of monazite. As a result of this, all radionuclides belonging to the ^{238}U and ^{232}Th series are present in the Uruguayan east coast. The activity concentration of ^{238}U, ^{232}Th and ^{40}K in sand and soil in Rocha's coast was determinated to evaluate the external hazard index, the outdoor annual effective dose equivalent and the radium equivalent activity in order to determine if those represent a risk for the inhabitants. For the quantification of those radionuclides in sand and soil, three samples of ten different beaches with different composition were collected at a typical depth of 5 cm from the top surface layer to produce aproximately 2 kg wet weight sample. Each sample was dried at a temperature of 60 °C until a constant weight was reached, the samples were filled into 500 mL Marinelli flasks. After approximately four weeks in order to reach secular equilibrium of the ^{238}U and ^{232}Th series, samples were measured by gamma-spectrometry with a High Pure Germanium Detector GMX35P4-76-RB, 35% efficiency and 1.75% resolution for photopeak of ^{60}Co. IAEA reference materials RGU-1, RGK-1 and RGTh-1 were used for efficiency calibration. ^{238}U series was studied by the weighted mean of the photopeaks of ^{234}Th (63.3 and 92.8 keV), by the weighted mean of the photopeak of ^{214}Bi (609.3 keV) and of the two photopeaks of ^{214}Pb (295.2 and 352.0 keV). ^{232}Th series was evaluated by the photopeak of ^{228}Ac (911.1 keV) and the photopeaks of ^{212}Pb (583.1 keV) and ^{208}Tl (238.6 keV), ^{40}K was evaluated by its own photo peak 1460 keV.

The range of activities concentration of ^{226}Ra, ^{232}Th and ^{40}K were found to be 12.4–30.3, 10.2–70.7, and 150.2–482.3 Bq.kg^{-1}, respectively. The outdoor annual effective dose equivalent, the radium equivalent activity and the external hazard index associated with the samples were evaluated. The results indicates that the radiation hazard from natural radionuclides in all samples studies in the current work is not significant.

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ENVIRONMENTAL IMPACT ASSESSMENTS OF NATURALLY OCCURRING RADIONUCLIDES ON INHABITANTS OF ABUJA, NORTHCENTRAL NIGERIA

M. Omeje[1, 2], *H. Wagiran*[2], *E. S. Joel*[1], *O. O. Adewoyin*[1], *O. T. Kayode*[1]

[1]Department of Physics, Covenant University Ota, Ogun State, Nigeria
[2]Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310, Skudai, Johor Baru, Malaysia

The study of activity concentration of ^{232}Th, ^{238}U and ^{40}K from selected soil samples 10–20 cm below ground level in strategic positions within Abuja has been presented for environmental risk assessments to the inhabitants. Activity concentrations were analysed using a high resolution co-axial HPGe gamma ray spectrometer system. The activity concentration from the soil samples ranges from 46±4 to 84±7 Bq kg^{-1} for ^{232}Th with a mean value of 53 Bq kg^{-1}, 23±2 to 52±5 Bq kg^{-1} for ^{238}U with a mean value of 34 Bq kg^{-1} and 119±15 Bq kg^{-1} to 1011±128 Bqkg^{-1} for ^{40}K with a mean value of 236 Bq kg^{-1}. The gamma dose rate (D_c) exposure to the inhabitant ranges from 58 to 81 nGy h^{-1} and the radium equivalent (Ra_{eq}) from the samples ranges from 124 to 180 Bq kg^{-1}. The external hazard index (H_{ex}) varies between 0.34 to 0.49 and the Annual Effective Dose (AED) ranges from 71 to 99 µSv y^{-1}. In contrast, some values distinctly exceed the international standard reference level twice according to UNSCEAR. The high radioactivity and radiological risks posed to the inhabitants may attribute to basaltic intrusions within near surface from the deep seated source.

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DETERMINATION OF RADIOCESIUM IN LARGE ENVIRONMENTAL WATER SAMPLES USING COPPER HEXACYANOFERRATE AND SODIUM TETRAPHENYLBORATE

Lyubomir Popov

Radioecological Monitoring, Safety Division, Kozloduy Nuclear Power Plant, 3321 Kozloduy, Bulgaria, e-mail: POPOV_LA@yahoo.com

Keywords: method, radiocesium, water, river, Danube, hexacyanoferrate

Cost efficient method for the radiochemical separation and radiochemical purification of radiocesium (^{134}Cs and ^{137}Cs) in bulk environmental water samples with large volume (up to 200 L) is proposed. Radiocesium was quantitatively removed from the water by cation-exchange with copper hexacyanoferrate(II) and finally it was purified additionally by precipitation with sodium tetraphenylborate. The influence of the concentration of potassium in the water sample on the chemical yield was investigated. The cost of analysis by this method is much lower than the traditional method with ammonium phosphomolybdate (AMP) and hexachloroplatinic acid. The validation of the proposed method was carried out by analyzing various reference materials. The application of the method was demonstrated with the determination of the concentration of radiocesium in water samples from rivers around Kozloduy NPP (Bulgaria) Danube and Ogosta.

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HUMIC ACID-CHITOSAN-SILICA GEL – AN EFFICIENT AND ECONOMICAL ADSORBENT FOR Th AND U REMOVAL

Erik Prasetyo[1, 2], *Kazuhiro Toyoda*[1, 3]

[1]Graduate School of Environmental Science, Hokkaido University, 060-0810 N10W5, Sapporo, Japan
[2]Indonesian Institute of Sciences, Jl. Ir. Sutami km 15, Bandar Lampung 35361, Indonesia
[3]Faculty of Environmental Earth Science, Hokkaido University, 060-0810 N10W5, Sapporo, Japan

Keywords: silica gel, humic acid, chitosan, adsorbent, thorium, uranium

A novel and low-cost adsorbent was prepared by immobilization of humic acid on silica gel surface coated with cross linked chitosan (SiChiHA), which was developed for Th and U removal from aqueous solution. The method is very simple and eco-friendly compared to previous reports on humic acid based adsorbents. The adsorbent was characterized by SEM-EDS method to describe the chitosan coating and humic acid immobilization on silica gel surface. The performance of adsorbent in Th and U removal was investigated in terms of pH, solid-liquid ratio, contact time, ionic strength and isotherm capacity. The optimum pHs for Th and U removal were 3.5 and 5, and Langmuir adsorption model showed the maximum sorption capacities were 30.67 and 81.97 mg/g for Th and U, respectively. The adsorption process was best described by pseudo-second order equation and correspondingly the times required for a quantity to fall to half its initial concentration (50 mg/L) were 10 and 0.2 minutes for Th and U, respectively. In solution, sodium concentration up to 2 mol/L did not significantly affect the removal efficiency. High recovery rates (>99%) were found in the system of solid-liquid ratio higher than 1.5 g/L and 1 g/L for Th and U, respectively. These results show that SiChiHA can be employed as an effective low-cost adsorbent for Th and U removal.

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LEVELS OF ^{210}Po AND ^{210}Pb IN URINE OF GDAŃSK AGGLOMERATION INHABITANTS IN POLAND

Grzegorz Romańczyk, Alicja Boryło, Bogdan Skwarzec, Dagmara Strumińska-Parulska*

Department of Analytical and Environment Radiochemistry, Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80—308 Gdańsk, Poland, *e-mail: alicja.borylo@ug.edu.pl

The urine samples were collected from volunteers from Gdańsk, Gdynia and Sopot agglomeration. The ^{210}Pb and ^{210}Po activity levels in the urine samples were next examined to determine whether and how they are related to cigarette smoking, age, diet and sex. The obtained results indicated that ^{210}Po and ^{210}Pb concentrations were variable within each group of volunteers. The study shows that the amount of ^{210}Po and ^{210}Pb are incorporated into the human body and slightly dependent upon the life mode including diet habits, smoking habits, sex, and age. The activities of ^{210}Po and ^{210}Pb in urine are widely disparate, slightly higher activity values are listed among females than males and were 4.13±0.44 $mBq\cdot d^{-1}$ and 6.17±0.86 $mBq\cdot d^{-1}$ for ^{210}Po and 3.35±0.42 $mBq\cdot d^{-1}$ and 4.93±0.57 $mBq\cdot d^{-1}$ for ^{210}Pb. The higher values of ^{210}Po and ^{210}Pb activities were observed in the age group of 24 to 45 years (4.37±0.49 $mBq\cdot d^{-1}$ and 6.70±0.95 $mBq\cdot d^{-1}$, respectively) than in the other analyzed classes. Relatively small differences were observed among people with different dietary habits: the smaller activity was observed for people, who eat less than once fish per week, the higher among people who eat once or more fish per week (3.72±0.33 $mBq\cdot d^{-1}$ and 3.95±0.75 $mBq\cdot d^{-1}$ for ^{210}Po; 5.56±0.44 $mBq\cdot d^{-1}$ and 5.87±1.59 $mBq\cdot d^{-1}$ for ^{210}Pb). Higher values of the ^{210}Po and ^{210}Pb activity were found in the group of vegetarians (the class of people who include eggs, dairy, beeswax and honey, but exclude meat - red meat, poultry, seafood and the flesh of any other animal) (4.52±0.72 $mBq\cdot d^{-1}$ and 7.43±1.70 $mBq\cdot d^{-1}$ respectively) than for meat consumers group (3.47±0.31 $mBq\cdot d^{-1}$ and 5.00±0.39 $mBq\cdot d^{-1}$, respectively). All mentioned above differences are however not statistically significant.

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LUNG DISSOLUTION RATES FOR AIRBORNE URANIUM PARTICLES GENERATED DURING CRITICAL ASSEMBLY EXPERIMENTS

Emily Schmidt[1], William Kinman[1], Donald Dry[1], Robert Steiner[1], Stephen LaMont[1], Luiz Bertelli[2], Tom Waters[2], John Klumpp[2], Jeffrey Hoffman[2]*

[1]Nuclear and Radiochemistry, Los Alamos National Laboratory, PO Box 1663 / MS J514, Los Alamos, NM 87545 USA,
*e-mail: stephen.lamont@lanl.gov
[2]Radiation Protection Services, Los Alamos National Laboratory, PO Box 1663 / MS G761, Los Alamos, NM 87545 USA,
e-mail: hoffman@lanl.gov

Keywords: uranium oxide, lung dissolution rate, internal dosimetry

An *in vitro* study of airborne uranium oxide collected during a critical assembly experiment was carried out to determine the dissolution rate in synthetic lung fluid (SLF). Subsamples of a filter used to collect airborne uranium were placed in a 20 ml 9 kDa molecular weight cut off ultracentrifugation buffer exchange device constructed of regenerated cellulose membrane. While typically utilized for molecular biological techniques, this apparatus was ideal for isolating a sample of uranium particulate from the bulk SLF. The regenerated cellulose membrane is designed to fit in standard 50ml conical tubes, allowing for easy exchange of SLF samples containing dissolved uranium during the course of the 100 day study. The buffer exchange device was filled with 10 ml of SLF, while the lower 50 ml conical tube was filled with 20 ml SLF. A CO_2 environmental control incubator with a built in orbital shaker was utilized to regulate pH, control the temperature at 37 °C, and provide gentle agitation. The study was run in triplicate, and the uranium in each fraction collected during the study, and the amount of uranium that did not dissolve during the 100 days was determined using HR-ICP-MS. Plots of the fraction of uranium undissolved as a function of time were constructed, and fit with a three component exponential decay mode to determine the dissolution rates. The uranium showed three distinct dissolution rates, including a very fast fraction, and two distinct moderate dissolution rate fractions.

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RADON LEVEL IN GROUNDWATER OF KOREA

Woosik Shin[1], Sungwook Choung[1], Jungsun Oh[2], Byungwook Cho[3], Kwang-Sik Lee[1], Uk Yun[3], Tae Seung Kim[4], Hyun Koo Kim[4], Munsoo Kim[4], Soo Young Cho[3]

[1]Department of Environmental Monitoring & Research, Korea Basic Science Institute, Cheongju, Republic of Korea, e-mail: sws3286@kbsi.re.kr
[2]Yonsei University, Seoul, Republic of Korea, e-mail: jungsunoh@yonsei.ac.kr
[3]Korea Institute of Geoscience and Mineral Resources, Daejeon, Republic of Korea, e-mail: cbw@kigam.re.kr
[4]National Institute Environmental Research, e-mail: hyd009@korea.kr

Keywords: radon, groundwater, spatial distribution, geological relationship, guideline

Radon (^{222}Rn) is an alpha-emitting noble gas that is colorless, odourless, and water soluble. It is naturally derived from successive decay of uranium-238. The radon has been known to induce lung or stomach cancer due to internal radiation via inhalation or ingestion. It was reported that 52% of annual exposed radiation is derived from inhalation of radon gas, and annually deaths of about 21,000 persons were associated with lung cancer due to the inhalation of radon gas in U.S., particularly. Therefore, the International Agency for Research on Cancer (IARC) designated radon-222 as a carcinogen of Group 1 and many authorities of foreign countries such as US EPA, Denmark, Sweden, Norway and Finland regulate radon level between 2,700–27,000 pCi L^{-1} in drinking water for the decrease of radon exposure. In the case of Korea, there are no established standards for radon in drinking water. This study was carried to determine the spatial and geological distribution of radon in groundwater, to compare radon level in Korea with the standards of other foreign countries, and to provide the scientific background information for the establishment of radon standard in drinking water. The radon level in groundwater were investigated nationwide for 9 years (2006–2014). Samples were collected from 4,123 public and private wells, and analysed by Liquid Scintillation Counter (LSC). The radon level in groundwater is up to 195,000 pCi L^{-1} with an arithmetic mean of 2,700 pCi L^{-1}. Compared to AMCL standard (4,000 pCi L^{-1}) of U.S., 18% of samples were exceeding the AMCL standard for radon in drinking water, and the boreholes were distributed mainly into the central region of Korea (i.e., Chungcheong, Gyeonggi, and Jeolla Province). Most of samples exceeding the AMCL value were distributed into plutonic and metamorphic regions. The geological distribution of radon is comparatively consistent with naturally occurring uranium occurrence in Korea. Given that most of samples were collected from wells for drinking water, proper management is required by the authority to reduce radon level in drinking water.

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A METHOD OF ^{14}C FORMS DETERMINATION IN LIQUID RELEASES FROM NUCLEAR POWER PLANTS

Ivo Svetlik[1], Michal Fejgl[2], Pavel P. Povinec[3], Tereza Kořínková[1], Pavel Simek[1], Lenka Tomášková[1]*

[1]Department of Radiation Dosimetry, Nuclear Physics Institute CAS, Na Truhlarce 39/64, CZ-180 86 Prague, Czech Republic,
*e-mail: svetlik@ujf.cas.cz
[2]National Radiation Protection Institute, Bartoskova 1450/28, CZ-140 00 Prague, Czech Republic, e-mail: michal.fejgl@suro.cz
[3]Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, SK-842 48, Slovak Republic, e-mail: povinec@fmph.uniba.sk

Keywords: ^{14}C, liquid releases, nuclear power plants, liquid scintillation spectrometry

There is a lack of data in scientific literature on the quantity of ^{14}C released to surface waters from nuclear power plants. Therefore, it is difficult to estimate the contribution of this radionuclide in the liquid releases to the dose load of population from the vicinity of nuclear power plants. Following requests of the regulatory (The State Office for Nuclear Safety), we developed a method of ^{14}C determination in samples of surface water (liquid releases from Nuclear Power Plants). This analytical method makes it possible to distinguish the inorganic forms (dissolved $^{14}CO_2$ and carbonates) and ^{14}C in organic compounds. The method was tested with real water samples with addition of both carbonate and organic forms of ^{14}C. The method enables processing of water samples up to the volume of 1.8 litres. To convert the organic compounds to CO_2, a wet oxidation is carried out in acidic solution, using the $KMnO_4$. To achieve high yields, the $^{14}CO_2$ liberated from the sample is transferred and trapped into a sorbent by the means of long-term circulation, the yields obtained in this way exceed 98%. The measurement of activity by the means of liquid scintillation spectrometry (LSS/LSC) can be carried out directly in aliquots of the sorbent (quick measurement, but high limit of detection) or by measurement of ^{14}C in precipitated $BaCO_3$ (time consuming, but low detection limit). In our contribution, we will report and discuss the particular phases of the procedures, the parameters of analytical routine and also the methods used for indicating the presence of interfering radionuclides in the samples measured by liquid scintillation spectrometry.

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POLONIUM ^{210}Po AND RADIOLEAD ^{210}Pb IN EDIBLE MUSHROOMS COLLECTED IN NORTHERN POLAND

Karolina Szymańska, Dagmara Ida Strumińska-Parulska, Grażyna Krasińska,
Bogdan Skwarzec, Jerzy Falandysz

University of Gdańsk, Faculty of Chemistry, Environmental Chemistry and Radiochemistry Chair, Wita Stwosza 63, 80-952 Gdańsk, Poland

The aim of the study was activities determination of naturally occurring ^{210}Po and ^{210}Pb in caps and stems of mushrooms collected in Pomerania (northern Poland): Hazel bolete *(Leccinum pseudoscabrum)*, Red-capped scaber *(Leccinum aurantiacum)*, Foxy bolete *(Leccinum vulpinum)*, Slate bolete *(Leccinum duriusculum)* and Orange Oak bolete *(Leccinum quercinum)*.

The fruiting bodies of mushrooms are generally considered as absorbing mineral constituents, including heavy metals and radionuclides. They could be used as environmental biomonitoring indicators to evaluate the level of the environment contamination as well as the chemical quality of the ecosystem. Mushrooms also influence natural radionuclides migration in soil and food chains transfer.

Many species of wild edible mushrooms adsorb and bioaccumulate mercury, chrome, silver, cadmium as well as radionuclides, i.e. cesium, strontium, polonium, radiolead, uranium, plutonium. Special attention should be given to the fruiting bodies while growing up and the contaminated soil substrate.

Our study showed the average ^{210}Po concentration in mushrooms caps and stems ranged from 0.85±0.09 Bq·kg^{-1} in orange oak bolete *(L. quercinum)* stem to 10.77±0.47 Bq·kg^{-1} in hazel bolete *(L. pseudoscarbum)* cap, while the highest ^{210}Pb activity concentration was observed in hazel bolete (4.92±0.17 Bq·kg^{-1}) and the lowest in red-capped scaber *(L. aurantiacum)* stem (0.31±0.03 Bq·kg^{-1}).

Edible wild mushrooms accumulate different amounts of ^{210}Po and ^{210}Pb and this process depends on soil type and dry atmospheric fallout. Sand and gravel does not stop minerals and radionuclides, they have high permeability while podsol, colloidal loam and clay are characterized by long-lasting retention of radionuclide in topsoil. Overcapacity of ^{210}Po content in soil was simply the subtraction of the activity of ^{210}Pb, while in mushrooms it could be an effect of two processes: selective or increased ^{210}Po transfer and bioaccumulation of more reactive ^{210}Po or its surface adsorption.

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VERTICAL VARIATIONS OF PARTITION COEFFICIENTS OF ^{125}I, ^{137}Cs AND ^{85}Sr IN PASUTURE AND FOREST SOILS IN ROKKASHO, JAPAN

Yusuke Unno[1], *Hirofumi Tsukada*[2], *Akira Takeda*[3], *Yuichi Takaku*[4], *Shun'ichi Hisamatsu*[5]

[1]Department of Radioecology, Institute for Environmental Sciences, 1-7 Ienomae, Obuchi, Rokkasho, Kamikita, Aomori, Japan, e-mail: unno@ies.or.jp
[2]Institute for Environmental Sciences; Present address, Fukushima University, Fukushima, Japan, e-mail: hirot@ipc.fukushima-u.ac.jp
[3]Institute for Environmental Sciences, Aomori, Japan, e-mail: takeda@ies.or.jp
[4]Institute for Environmental Sciences, Aomori, Japan, e-mail: ytakaku@ies.or.jp
[5]Institute for Environmental Sciences, Aomori, Japan, e-mail: hisamatu@ies.or.jp

Keywords: radioactive substance, soil core, K_d

A part of long-lived radionuclides released to the atmosphere from nuclear facilities is deposited on the ground followed by penetrating subsurface soil and reaching to the groundwater in mid-to-long term. Therefore the behavior of radionuclides in surface to deep soil is important for assessing human health risk. The Japanese first commercial large-scale spent nuclear fuel reprocessing plant in Rokkasho is under review for operation commencement by Nuclear Regulation Authority. Since long half-lived ^{129}I, of which behavior in the environment is not yet sufficiently clear, is emitted from the plant, it is important for public acceptance of the plant to obtain the basic information of its migration in the local soil environment. We measured soil water distribution coefficients (K_d), which was used for important parameter to estimate migration in soil, of ^{125}I for soil core samples, which were collected from a pasture land and a forest near the reprocessing plant. Since radiocesium and radiostrontium are important fission radionuclides, the K_d values of ^{137}Cs and ^{85}Sr were also measured and discussed together with those of ^{125}I.

A core sample up to 3 m and 0.5 m depth collected at a pasture land and a forest, respectively, was cut into each layer, and an aliquot of the layer sample was used for K_d measurement without drying. After the sample was mixed with pure water with solid/liquid ratio of 1/10, it was gently shaken for 2 weeks in room temperature followed by measurement of the K_d value. Soil characteristics, such as pH and organic material content, were also measured for each layer sample. The K_d values in soil samples up to 0.5 m depth collected at both locations were found to increase in the order of ^{85}Sr<^{125}I<^{137}Cs. The K_d values of all radionuclides also significantly increased with depth up to ~0.2 m depth. In the top surface soil, the K_d values of all radionuclides at the forest were lower than those at the pasture. The K_d values of all radionuclides at forest increased with depth up to ~0.2 m, but decreased from ~0.3 m. For the subsurface soil at the pasture, the K_d values of ^{137}Cs were almost constant up to 3 m depth, while those of ^{85}Sr increased to with depth but with plateaus in mid and deep soils. The variation pattern of ^{125}I from 0.5 m to 3 m was different from the other radionuclides with gradually decreasing in the depth range of 0.5 m to 2 m and steep decreasing from 2 m. The depth distribution patterns of K_d values will be discussed in the relation with soil characteristics at the conference. This study was performed under a contract with the government of Aomori Prefecture, Japan.

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PROMPT DETERMINATION OF ^{137}Cs IN LARGE VLOUME SEAWATER USING Cu-HEXACYANOFERRATES CARTRIDGES

Suputtra Visetpotjanakit, Yutthana Tumnoi

[1]Bureau of Technical Support for Safety and Regulation, Office of Atoms for Peace, 16 Vibhavadi rangsit road Ladyao Chatuchak, Bangkok, Thailand, e-mails: panlant_ja@hotmail.com, yutthana@oaep.go.th

Keywords: large volume seawater, ^{137}Cs and Cu-hexacyanoferrates cartridges

A rapid method to determine ^{137}Cs in seawater has been developed based on Cu-hexacyanoferrates scavenger. The Cu-hexacyanoferrates supported on cotton cartridges were used to absorb ^{137}Cs from seawater by passing a variety of large volumes over the cartridges with a slow flowrate. The Cu-hexacyanoferrates cartridge samples were converted to ash through a heating step and directly measured with gamma ray analysis using HPGe detector. The results of the developed method were compared with the traditional AMP pre-concentration technique. Both results when using 200 L of seawater samples gave similar values i.e. 0.760 mBq/L for the AMP pre-concentration technique and 0.768 mBq/L for the Cu-hexacyanoferrates cartridge method. This developed method is more cost-efficient and less time consuming. In addition it can be easily performed in a sampling field.

Radiolabeled compounds and radiopharmaceuticals

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[^{68}Ga]RADIOLABELLING OF SHORT PEPTIDE THAT HAS A PET IMAGING POTENTIAL

Mohammed Al-Qahtani, Yousif Al-Malki

Cyclotron and Radiopharmaceuticals Department, King Faisal Specialist Hospital and Research Center, Riyadh, Saudi Arabia

Keywords: ^{68}Ga, peptide, PET

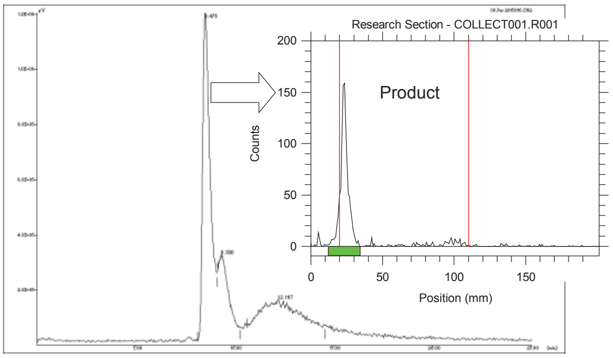
Targeting short peptides are gaining interests in the molecular imaging field. Choosing the radioisotope to label those peptides is a challenging stage in the process of identifying the right imaging modality.

All needed reagents and solvents were used with no further purifications unless it's necessary. Peptide used was purchased from GenScript and used without further purifications. Reaction progress was monitored using both radio-analytical thin-layer chromatography (Radio-TLC) and high pressure liquid chromatographic (Radio-HPLC). Radio-HPLC analyses were carried out on semi-preparative Phenomenex C-18 (250 mm × 10 mm). Radiolabeled peptide was detected with the eluting of 0.065% TFA in water and 0.05% TFA in MeCN at 2 ml/min applying gradient elution mode. Radiochemical yields were calculated based on the Radio-HPLC collections. Sodium Citrate Buffer (PH = 7.5) wa the Radio-TLC mobile phase.

Synthesis of DOTA-peptide conjugate. 9.97 E-7 mol of the intended peptide dissolved in DMSO reacts with 1.18 E-6 mol of (DOTA-NHS-ester) that was prepared in MeCN. The reaction was done in a phosphate buffer with PH = 8 and heating at 90 °C for 30 min.

^{68}G -labeling of DOTA-peptide. ^{68}G solution was added to 60 µg of conjugated DOTA-Peptide in 100 µl of HEPES buffer (PH = 4) and the mixture allowed to react for 30 min at 80 °C.

[^{68}G-DOTA-Peptide] was analysed on Radio-HPLC; the ration time of the product was 8.4 min and Radio-TLC checks for the collected product confirm the high radiochemical purity.



The labelled peptide is produce in good radiochemical yields and high radiochemical purity. Initial biological works are ongoing to evaluate its imaging potential mainly on a melanoma cell line. The findings will be presented.

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FASTER HIGH RESOLUTION QUALITY CONTROL OF RADIOPHARMACEUTICALS: RADIO-UPLC VS RADIO-HPLC

HoSze Chan, Rory de Zanger, Erik de Blois, Wouter Breeman*

Department of Nuclear Medicine, Erasmus MC, Wytemaweg 12, Rotterdam, the Netherlands, *e-mail: h.s.chan1982@gmail.com

Keywords: quality control, radiopharmaceuticals, conversion, parameter, resolution, gradient, sampling frequency

Introduction: For clinical applications high resolution quality control (QC) of short lived radiopharmaceuticals (PET) is performed on a radio-HPLC. Radio-UPLC should provide similar or better resolution quality controls than radio-HPLC with the advantage of faster measurements. However, while being identical in measurement method the conversion from one system (HPLC) to another (UPLC) is not as straight forward as expected. Thus, optimization for radio-UPLC is required.

Objective: A basic measurement method conversion from HPLC to UPLC is easily obtained. However, achieving a resolution and overall quality on UPLC that is as good or better than on HPLC requires a proper understanding of parameters that are involved. Therefore, the aim is to determine and optimize the parameter(s) contributing to the resolution and overall quality on UPLC.

Methods & Materials: Our QC systems consist of an Alliance HPLC and an Aqcuity H-class UPLC (Waters), a NaI(Tl) crystal and Osprey multichannel analyser (MCA) connected to an amplifier box (Canberra). Both system are controlled using Empower software. The connection between radio detection and chromatograph was made using a Waters PCM module (BUS SAT-IN) for HPLC and a Waters E/SAT-IN module for UPLC. ^{68}Ga-DOTA^0,Tyr^3-Octreotate was used as model and analysed multiple times while parameters such as slope of the gradient, flow of the eluents and the sampling rate of the Empower software were varied.

Results: The most important parameter for optimization of the resolution was the interaction time between radioactivity and detector. In case of HPLC this was ~60 s versus ~5 s for UPLC. After decreasing the slope of the gradient by a factor of 3, the interaction time increased to about 11 s. Other important parameters are the sampling rate of the Empower software and the sampling frequency the radio detector. These were optimized equalizing both to 2 Hz. This also resulted in a smoother radio peptide peak.

Conclusions: Fast measurements on UPLC at high resolution requires sufficient interaction time between radioactivity and detector. Optimizing this and equalizing sampling frequency and sampling rate of detector and software respectively resulted in a smoother radio peptide peak and a better overall quality of the chromatogram.

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THE NEW SEMI-PREPARATIVE HPLC DEVELOPED ON FLUORO-18-FLUMAZENIL LABELING

Kang-Wei Chang, Kai-Hung Cheng, Yuan-Ruei Huang, Jenn-Tzong Chen, Wuu-Jyh Lin*

Institute of Nuclear Energy Research, Taoyuan, Taiwan, *e-mail: kwchang@iner.gov.tw

Keywords: flumazenil, GABA$_A$/BZR receptor, anxiety

Radioactive antagonist, F-18-Flumazenil (F-18-FMZ), is a potential positron emission tomography agent. The radiopharmaceutical can be used to assess the changes in GABA$_A$/BZR receptors, evaluated the brain damage in stroke, alcoholism and Alzheimer disease investigation. In this study we represent carrier-free nucleophilic radiofluorination method on automatic synthesizer with direct labeling on nitro-flumazenil precursor. The semi-preparative HPLC purification method has been applied to get high purity of F-18-FMZ. Replace of solid extraction purification or tradition method of HPLC purification for radio-synthesis of F-18-FMZ.

Then, F-18-FMZ NanoPET/CT brain images were acquired from both anxiety animal model disease and bretazenil-treated control group. In the image analysis software showed that the binding ratios of F-18-FMZ significantly results in prefrontal cortex, hippocampus, cortex and amygdala in different groups. The result can be a reference for new drug studies of GABA$_A$/BZR receptor in the future.

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IN VITRO BINDING KINETICS STUDY OF GOLD NANOPARTICLES FUNCTIONALIZED WITH ^{68}Ga-DOTA CONJUGATED PEPTIDES

Livia E. Chilug[1, 2]**, Radu A. Leonte*[1, 3]*, Alina Raicu*[1]*, Marcela E. Barbinta Patrascu*[4]*, Alexandru C. Ion*[5]*, Catalin S. Tuta*[1]*, Dana Niculae*[1]

[1]Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), 30 Reactorului Street, P.O.BOX MG-6, Bucharest – Magurele, Romania, *e-mail: livia.chilug@nipne.ro
[2]Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, 1-7 Gheorghe Polizu Street, 011061, Romania
[3]The Faculty of Applied Sciences, University Politehnica of Bucharest, 313 Splaiul Independentei Street, 060042, Bucharest, Romania
[4]Faculty of Physics, University of Bucharest, 405 Atomistilor Street, P.O. Box MG-11, Bucharest-Magurele, 077125, Romania
[5]Research and Development Center for Nanotechnology Aquanano, 48 C Muntii Carpati Street, Bucharest, Romania

Keywords: gold nanoparticles, cancer, radiolabeled peptides

In the recent years, gold nanoparticles (AuNPs) proved a promising tool for cancer diagnostic and therapy, based on their photothermal properties and ease to surface modification. In this study we used functionalized AuNPs as an improved drug delivery tool in pancreatic and colon cancer cell lines AR42J and HT-29.

Transmission electron microscopy (TEM), dynamic light scattering (DLS) and phase analysis light scattering (PALS) techniques have been employed to characterize the synthesized NPs features such as hydrodynamic diameter or zeta potential.

Further functionalization with ^{68}Ga-DOTA radiolabeled neurotensin and somatostatin analogs through N-terminal primary amine group, has been assessed using wavelength shift in the UV-Vis optical absorption spectra.

In vitro tumor binding kinetics evaluation of the radiolabeled compound has showed over 70% increased retention of the positron emitter radionuclide ^{68}Ga in the presence of the gold nanoparticles. This result is attributed to receptors mediated uptake of the nanoparticles inside the tumor, and their possibility to bind several peptides on their surface, increasing the available radioisotope inside the tumor cells.

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RADIOANALYTICAL METHODS FOR QUALITY CONTROL OF ^{68}Ga RADIOLABELLED PEPTIDES

Mirela Mihon[1, 2]**, Dana Niculae*[1]*, Radu Leonte*[1, 2]*, Alina C. Ion*[2]*, Catalin S. Tuta*[1]*, Vasile Lavric*[2]

[1]National Institute for Physics and Nuclear Engineering "Horia Hulubei", 30 Reactorului St., Magurele, Ilfov, Romania,
*e-mail: mirela.mihon@nipne.ro
[2]University Politehnica of Bucharest, 313 Splaiul Independentei St., Bucharest, Romania

Keywords: gallium-68, quality control, chromatography, peptides

Positron Emission Tomography (PET) is a medical imaging technique that consists in introducing into the body of a small amount of a biologically active chemical compound labelled with positron-emitting radioisotopes (^{18}F, ^{11}C, ^{68}Ga). Recently, a variety of ^{68}Ga-labelled peptides have been introduced as PET tracers for imaging of somatostatin expressing tumors.

The increasing clinical demand of ^{68}Ga radiopharmaceuticals determined the need for optimization of the radioanalytical methods in the quality control laboratory. The aim of this study was to select the best method in determination of radiochemical purity of ^{68}Ga labelled peptides using high performance liquid chromatography and thin layer chromatography and, also, to optimize the quality control process. Radiochemical impurities may originate from incomplete purification and radiolysis after synthesis. Chromatographic settings such as composition and flow rate of the mobile phase and column temperature were the independent variables used in the optimization process.

Several peptides (neurotensin, cRGD, octreotide) conjugated with macrocyclic chelators (DOTA, NOTA, NODAGA) were labeled with ^{68}Ga. Parameters of quality control were investigated to determine the purity and stability of the products.

The HPLC and TLC methods for comparative measurement of radiochemical purity were optimized and validated. The HPLC method was found to be precise, accurate and specific assets recommending its use for determination of radiochemical purity ^{68}Ga radiolabelled peptides. The method was reproducible as the relative standard deviation of the peak area was less than 5%.

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SYNTHESIS AND PRECLINICAL EVALUATION OF ^{68}Ga-NODAGA-NOC FOR EARLY DETECTION OF GLIOBLASTOMA

Elena A. Min[1, 2]*, *Livia E. Chilug*[1, 3], *Alina Raicu*[1], *Radu M. Serban*[1], *Radu A. Leonte*[1, 4], *Dana Niculae*[1]

[1]Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), 30 Reactorului Street, P.O.BOX MG-6, Bucharest – Magurele, Romania, *e-mail: elena.min@nipne.ro
[2]Faculty of Pharmacy, University of Medicine and Pharmacy “Carol Davila, 6 Traian Vuia Street, Bucharest, 20956, Romania
[3]Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, 1-7 Gheorghe Polizu Street, 011061, Romania
[4]The Faculty of Applied Sciences, University Politehnica of Bucharest, 313 Splaiul Independentei Street, 060042, Bucharest, Romania

Keywords: glioblastoma, octreotide, ^{68}Ga, chelators

Glioblastoma, a high incidence brain malignancy is one of the most aggressive cancers with a very low survival rate. Therefore, in the field of this malignancy, there is a growing interest in developing new therapeutics and improved early detection approaches. This work presents the automated radiolabelling of DOTA-NOC peptide (NODAGA-dPhe-Cys-1Nal-dTrp-Lys-Thr-Cys-Thr(ol)), a somatostatin analogue, with ^{68}Ga. Binding characteristics of the radiolabelled peptide on U87 MG glioblastoma cells were determined using Ligand Tracer method, based on the overexpression of somatostatin receptors [1]. A short radiolabelling and purification time (25 min), a very good radiochemical yield (83%) and radiochemical purity of the final product in the range of 95-100% were obtained after the process optimization and automation. The process parameters are superior comparing with other ^{68}Ga-radiolabelled peptides obtained by our research group, such as ^{68}Ga-DOTA-TOC, ^{68}Ga-DOTA-(cRGD)$_2$ and ^{68}Ga-NOTA-(cRGD)$_2$. The biological *in vitro* study show a rapid uptake of ^{68}Ga-NODAGA-NOC on U87 MG glioblastoma cells and a retention of 70% of the radioactivity up to 85 min, suggesting a promising receptor specific candidate for detection of glioblastoma.

Acknowledgement
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THE CONSTRUCTION OF ^{99m}Zn- AND ^{67}Zn-CONTAINING PHARMACEUTICALS

Marina Orlova[1, 2]*, *Tatiana Trofimova*[1, 2], *Ramiz Aliev*[1], *Alexey Orlov*[1]

[1]Department of Chemistry, M.V. Lomonosov Moscow State University, 1/3, Leninskie Gory, Moscow, 119992, Russia,
*e-mail: orlova.radiochem@mail.ru
[2]Rogachev Federal Scientific Clinical Centre of Pediatric Hematology, Oncology and Immunology, 1, st. Samory Mashela, 119997, Moscow, Russia

Keywords: zinc-69m, zinc-67, derivatives of 2-amino-dihydrothiazine, 2-aminothiazole and of substituted thiourea

Zinc, as an essential trace element, ensures the functioning of biological systems and multiple signaling pathways of the body. To perform these functions, there are specific and nonspecific zinc transporters. Hence the pharmaceuticals for radiodiagnostic, radiotherapy, antileukemic, anti-shock and others actions can be produced by introduction of radioactive (^{99m}Zn) and stable magnetic (^{67}Zn) zinc isotopes in the biologically active molecule. As active molecules, we are using both simple zinc salts, and inhibitors of inducible NO-synthase (NOS), which is hyper-expressed in the case of acute leukemia. Some of NO-synthase effectors are demonstrating cytotoxicity against both different leukemic cell lines (HL-60, K-562 and MOLT-4) and bone marrow cells of patients diagnosed with acute leukemia: acute B-lymphoblasic (B-ALL), acute T-lymphoblastic (T-ALL), acute myeloid (AML).

Derivatives of 2-amino-dihydrothiazine, 2-aminothiazole and of substituted thiourea with various substituents are used as the base of preparations. Compounds of these classes are radioprotectors or radiosensitizers and easily form chelates with zinc.

Using ^{67}Zn was aimed to consider the possibility of the magnetic isotope effect (MIE) to impact on leukemic cells and on the mechanisms leading to acute leukemia and/or appearing due to leukemia. The MIE is the result of weak interactions, and its effect was detected only in the case of patients with B-lymphoblastic leukemia.

^{99m}Zn ($T_{1/2}$ = 13.78 h) was produced by reaction of ^{71}Ga (γ, np) ^{99m}Zn followed by separation in two steps: by extraction and chromatography. Thereafter, the isotopes have been incorporated into chelator and tested for cell cytotoxicity by MTT test and for apoptosis by flow cytometry and fluorescence microscopy.

The most promising compounds for further research were selected. It was found the relationship between radiomodifying features, NOS-inhibitory activity and cytotoxicity respect to different leukemic cells.

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SYNTHESIS AND BIOAFFINITY PROFILE TO NEUROTENSIN RECEPTORS OF ^{68}Ga-DOTA-NEUROTENSIN

Alina Raicu[1]*, *Elena A. Min*[1, 2], *Livia E. Chilug*[1, 3], *Radu A. Leonte*[1, 4], *Radu M. Serban*[1], *Dana Niculae*[1]

[1]Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), 30 Reactorului Street, P.O.BOX MG-6, Bucharest – Magurele, Romania, *e-mail: alina.raicu@nipne.ro
[2]Faculty of Pharmacy, University of Medicine and Pharmacy "Carol Davila", 6 Traian Vuia Street, Bucharest, 20956, Romania
[3]Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, 1-7 Gheorghe Polizu Street, 011061, Romania
[4]The Faculty of Applied Sciences, University Politehnica of Bucharest, 313 Splaiul Independentei Street, 060042, Bucharest, Romania

Keywords: ^{68}Ga, neurotensin, neurotensin receptors, cancer

Targeting neurotensin receptors may be used with great success in the early detection of many cancers. An increased expression of neurotensin receptors is an early event that occurs in 75% cases of exocrine ductal pancreatic adenocarcinomas, a very aggressive cancer due to the extremely fast growth and the inability of the complete surgical resection treatment [1] and also during colonic tumorigenesis, the third most common cancer and the third leading cause of cancer death [2, 3]. This work presents an automated radiolabeling synthesis procedure of neurotensin (DOTA-pGlu-Leu-Tyr-Glu-Asn-Lys-Pro-Arg-Arg-Pro-Tyr-Ile-Leu) with ^{68}Ga radiotracer and the affinity and retention study of the radiolabeled peptide to AR 42J cell line, widely used as an *in vitro* model to study the exocrine pancreas, HT29 and CaCo2 colonic cell lines. The optimisation of parameters for the radiolabeling and purification processes and automation leads to a short time for preparation (25 min), a high radiochemical yield of 73%, while the radiochemical purity of the final product was 99–100%. The bioaffinity profile shows a rapid and high uptake of the radiolabelled peptide in all tested cell lines, while the retention of the radioactivity in the cells was found to be 30% on the pancreatic cell line AR42J, 40% on HT29 and 25% on CaCo2 colonic cell lines, these values recommend further *in vivo* investigations of the ^{68}Ga-radiolabelled neurotensin, as a promising candidate for the early detection of these types of cancers.

Acknowledgement

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HYDROXYAPATITE PARTICLES AS CARRIERS FOR ^{223}Ra

Aleksandr N. Vasiliev[1, 2], *Valentina S. Ostapenko*[1, 2], *Elena V. Lapshina*[1], *Alexander V. Severin*[2], *Stanislav V. Ermolaev*[1], *Stepan N. Kalmykov*[2, 3]

[1]Institute for Nuclear Research of Russian Academy of Sciences, 60th October Anniversary Prospect, 7a, Moscow 117312, Russia, e-mail: AleksandrNVasiliev@gmail.com
[2]Chemistry Department, Lomonosov Moscow State University, Leninskie Gory 1, 119991, Russia
[3]National Research Center “Kurchatov Institute”, Moscow, 123182, Academician Kurchatov sq., 1, Russia

Keywords: targeted therapy, alpha-emitters, radium-223, hydroxyapatite

Alpha-emitters are of the great interest for nuclear medicine due to the high linear energy transfer of α-particles and recoil nuclei. A pathlength of α-particles in biological tissue is much less than that of β-particles and comparable to a cell size (10–100 µm). Being delivered to the tumor cells, α-particles provide its targeted destruction and minimal damage to surrounding organs.

Among various α-emitters, ^{223}Ra is one of the promising candidates for targeted α-therapy. A radiopharmaceutical Xofigo® on the basis of $^{223}RaCl_2$ is registered and produced by Bayer Company for the therapy of bone metastases. Another approach is a targeted delivery of ^{223}Ra using various transporters to the cancer cells such as peptides, liposomes or various inorganic carriers. Hydroxyapatite (HAP) particles could be considered as possible carriers of Ra.

Two different approaches to HAP labeling were tested: sorption of Ra on pre-synthesized HAP-particles and insertion of Ra into the structure of HAP during its synthesis. Two textural forms of HAP particles were used – nanoparticles and particles with the diameter of 300±20 µm. Kinetics of sorption of Ra on HAP of different particle size and desorption of Ra in 0.9 % NaCl solution was studied. The influence of solution acidity and solid to liquid phase ratio on sorption of Ra was evaluated and the sorption yield of up to 98% was achieved. It was found that the optimal conditions for the sorption includes synthesis of HAP nanoparticles in the presence of ^{223}Ra at pH 4–7 and following annealing at 900 °C. In this case subsequent cumulative desorption of Ra is less than 5% of initial activity.

Cross-sectional distribution of Ra inside a HAP particle with diameter 450–550 µm was studied by autoradiography on the plates of polyallildiglycol carbonate. Kinetics of Ra diffusion into a large HAP particle was estimated.

Using of HAP as carriers is regarded to be prospective for ^{223}Ra α-therapeutic applications due to the similarity of properties of radium and calcium, as well as bioavailability and biocompatibility of hydroxyapatite.

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ONE POT AUTOMATED SYNTHESIS OF [^{18}F]FHBG AS PET HSV-TK GENE REPORTER PROBES

Pei Zou, Hongyong Wang, Yaling Liu*

Key Laboratory of Nuclear Medicine, Ministry of Health, Jiangsu Key Laboratory of Molecular Nuclear Medicine, Jiangsu Institute of Nuclear Medicine, Wuxi 214063, China, *e-mail: zoupei@jsinm.org

Keywords: [^{18}F]FHBG, one-pot, PET-MF-2V-IT-I Synthera

Objective: 9-(4-[^{18}F]fluoro-3-hydroxymethylbutyl)guanine ([^{18}F]FHBG) is a sensitive and specific PET reporter probe for imaging the PET reporter genes, herpes simplex 1 thymidine kinase (HSV1-tk) and its mutant HSV1-sr39tk, An automated and optimized synthesis of [^{18}F]FHBG has been developed on the PET-MF-2V-IT-I synthera (PET CO., LTD., China), utilizing purification with solid phase extraction (SPE) cartridges.

Method: A two-step procedure was used to prepare the precursor, N^2- monomethoxytrityl-9-[4-(tosyl)-3-monomethoxytrityl-methylbutyl] guanine. [^{18}F]FHBG was prepared by nucleophilic substitution of the appropriate tosylated precursors (2 mg) with ^{18}F-fluoride, and subsequent hydrolysis of the intermediate with protecting group with 1 mol/L HCl at the same reaction vessel, and purification with a simplified Silica Sep-Pak instead of HPLC.

Results: Using Penciclovir as the starting material, the precursor was synthesized with a yield of 37%.The radiochemical yield (decay corrected) was 13–16% (n > 10), the synthesis time was 25–30 min, and the radiochemical purity was > 98%.

Conclusions: One pot automated synthesis method of [^{18}F]FHBG is easy to operate and can be used with high radiochemical yield and a low amount of the precursor. The use of PET-MF-2V-IT-I synthera and a Silica Sep-Pak purification simplifies the handling and shortens the total synthesis time.

Radionuclide separation

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SOLVENT EXTRACTION OF EUROPIUM (III+) INTO IMIDAZOLIUM IONIC LIQUID

Barbara Basarabová, Kateřina Čubová, Mojmír Němec*

Department of Nuclear Chemistry, Czech Technical University in Prague, Břehová 7, 115 19 Prague, Czech Republic, *e-mail: basarbar@fjfi.cvut.cz

Keywords: liquid-liquid extraction, europium, 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, citrate acid, oxalic acid

Room temperature ionic liquids (RTILs) are organic salts that tend to melt below 100 °C. RTILs are composed exclusively from ions without a presence of coordinate bonds between cations and anions. Their unique properties, mostly negligible vapour pressure, ability to solvate organic, inorganic and polymeric materials, high ionic conductivity, high thermal and radiation stability, tuneable hydrophobicity make them suitable for separations of radionuclides. RTILs are currently considered to be a promising replacement for volatile organic compounds (VOCs) widely used for radionuclide separation. The solvent extraction systems containing imidazolium RTILs (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide – [EMIM][NTf2] or 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide – [BMIM][NTf2) has been studied. In the first set of experiments, the main aim was focused on europium as a representative of lanthanides. Extractions at various conditions – pH, ionic strength – and with aqueous phase containing various common chelate agents have been carried out.

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NEW CHEMICAL DECONTAMINATION PROCESS FOR THE PRIMARY COOLANT SYSTEM OF A NUCLEAR POWER PLANT

Wangkyu Choi, Huijun Won, Sangyoon Park, Seonbyeong Kim, Jeikwon Moon*

Decontamination and Decommissioning Research Division, Korea Atomic Energy Research Institute, 111, Daedeok-daero 989 Beon-gil, Yuseong-gu, Daejeon, 34057, Korea, *e-mail: nwkchoi@kaeri.re.kr

Keywords: chemical decontamination, primary coolant system, oxidative decontamination, reductive decontamination, hydrazine, catalyst, waste treatment

The metal oxides formed on the surface of the primary coolant system contain radioactive components, and thus the oxides are generally need to be removed by means of chemical decontamination to reduce the exposure of workers during the decommissioning of a nuclear power plant. As a preliminary test for the decontamination of a radioactive oxide surface, the kinetics of the reductive dissolution of Fe(III) oxides, such as magnetite and nickel ferrite in an acidic solution, has been studied at 95 °C and under various concentrations of the reducing agent and catalyst. Transition metal ions as a catalyst, particularly cupric ions, are fairly oxidized into cuprous ions in a reductive solution, and its oxidation on the surface of the metal oxides was found to strongly influence the dissolution rate of magnetite. In addition, the kinetics of protonation was studied with a various concentration of mineral acids for different initial pH values. As a feasibility test to reconcile the observations of the separate unit experiments, we integrated the processes of the solution preparation, oxidative decontamination, and reductive decontamination followed by liquid waste treatment, into a sequential semi-loop test, which is called a one-through process. As an oxidative process, we have chosen the well-known NP (Nitric acid Permanganate) process, which is for the dissolution of chromium oxides by oxidizing Cr(III) to Cr(VI). The reductive chemical decontamination agent is composed of hydrazine as a reducing agent, metal ions of $Cu^{2+/+}$ as a catalyst and inorganic acids such as HNO_3 or H_2SO_4 as a H^+ donor. We have devised this chemical decontamination solution named HYBRID (Hydrazine Base Reductive metal Ion Decontamination) to generate less amount of secondary waste owing to the total decomposition of hydrazine into nitrogen and water followed by the precipitation of ionic species from the waste solution. The HYBRID process unlike other commercial processes using oxalic acid and/or EDTA is also advantageous in the management of secondary wastes since the organic components in a repository may increase the mobility of radionuclides by a complexation reaction. In a cycle of the one-through process, each 4 hour oxidation and reduction process was performed using the described NP and HYBRID processes

respectively. After three cycles of a one-through process, most of the metal components have been dissolved. At the end of the one-through process, we had a post-decontamination solution containing dissolved metal ions, cupric ions, and sulphate ions as well as hydrazine. In the treatment of this solution, the decomposition of hydrazine was first carried out using hydrogen peroxide at a temperature above 60 °C and it was confirmed that the total decomposition reached 100%. The mixed precipitation and ion exchange process to remove metal ions and anions in the solution was then applied and accordingly resulted in a significant reduction of the final waste volume.

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TREATMENT METHOD FOR VOLUME REDUCTION OF SPENT URANIUM CATALYST

Dong-Yong Chung, Keun-Young Lee, Kwang-Wook Kim, Eil-Hee Lee, Jei-Kwon Moon, Jong-Won Choi*

Decontamination & Decommissioning Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 34057, Republic of Korea, *e-mail: ndychung@kaeri.re.kr

Keyword: uranium catalyst

Since the 1970s, a uranium catalyst that is supported by USb_3O_{10}, a complex compounds of uranium (U) and antimony (Sb), on porous silica (support: SiO_2) has been developed in order to produce acrylonitrile ($CH_2 = CHCN$), a building block of synthetic fiber. A private company in South Korea had produced an acrylic synthetic fiber using a uranium catalyst until 2004, and since then has used the nonradioactive catalyst. Thus, approximately 7,100 drums of spent uranium catalyst waste, generated before using nonradioactive catalysts, are stored at their site. Such uranium catalyst waste includes only depleted uranium. Because these are categorized as radioactive waste containing naturally occurring radioactive materials, an appropriate disposal procedure should be performed in the future.

Currently, the radioactivity of the spent uranium catalyst using the depleted uranium generated within South Korea conforms with the standards for transferring radioactive waste to a radioactive waste disposal site operating in the Gyeongju area. The current disposal cost is approximately KRW 14 million per 200 L drum. Moreover, the volume increases due to the additives added in the process of preparing the solid form for the disposal of the spent uranium catalyst. Therefore, the final waste to be disposed of totals nearly 10,000 drums. As a means of effectively using the domestic radioactive waste disposal facilities and minimize the secondary waste for decreasing the disposal cost, an advanced technology is required for reducing the volume of the spent uranium catalyst by separating U exclusively as much as possible while decreasing the disposal cost.

The objective of this study is to develop a treatment method of a spent uranium catalyst. More specifically, this treatment method considerably reduces the volume of the spent uranium catalyst and simultaneously minimizes secondary wastes that can be generated during the treatment process. The method may be effective in maximizing the volume reduction efficiency for the spent uranium catalyst through the processes of dissolving silica supported USb_3O_{10}, further precipitating silica exclusively and selectively from the mixture of dissolved uranium and silica.

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DEVELOPMENT OF A METHOD OF TRITIUM ACTIVITY DETERMINATION IN WATER SAMPLES BY ELECTROLYTIC ENRICHMENT

Małgorzata Dymecka, Katarzyna Rzemek, Tomasz Pliszczyński, Jakub Ośko*

Radiation Protection Measurements Laboratory, National Centre for Nuclear Research, 7 A. Sołtana Str, 05-400 Otwock, Poland, *e-mail: m.dymecka@ncbj.gov.pl

Keywords: tritium measurement, water, isotopic enrichment, liquid scintillation counting

Radiation Protection Measurements Laboratory of the National Centre for Nuclear Research performs environmental radiation monitoring in the vicinity of Nuclear Centre at Otwock and National Radioactive Waste Repository located at Różan. Tritium activity determinations in water samples such as: surface waters, ground waters are, among others, carried out for the purpose of this monitoring. These analyses are realized by the use of direct tritium measurement method (without electrolytic enrichment) whose MDC is 4 Bq×dm^{-3}. However, for the purpose of low-level tritium measurements, for example in drinking waters, a method allowing to achieve a lower MDC value was needed. Therefore, studies aimed at introducing an indirect method of tritium determination in water samples by electrolytic enrichment have been undertaken.

In this paper both methods direct and indirect have been described and compared. For the introduced method of tritium determination by electrolytic enrichment optimal conditions of the electrolysis process were selected. Tritium enrichment procedure which was applied during this study is described below. Apparatus containing cylindrical glass cells with iron cathodes and nickel anodes was exploited to run enrichment process. Initially each cell was filled with an aliquot of 200 ml of distilled sample with addition of NaOH solution. After 48 h of running the process additional 100 ml of the sample were added. The current was stabilized at 5 A and was reduced to 3.5 A when the volume of the sample was reduced to about 30 ml. Electrolysis was continued until reaching the final volume of 15 ml. Samples were distilled after electrolysis in order to separate the electrolyte. A mixture of 10 ml of the distilled sample and 10 ml of Ultima Gold LLT scintillation cocktail (Perkin Elmer) was prepared. Samples were measured in liquid scintillation counter Perkin Elmer Tri-Carb 3180 TR/SL.

Preliminary tests of the selected method were carried out by the use of tritium standard solution. On their basis parameters describing electrolysis process such as: enrichment factor Z, retention factor K and separation factor β were determined. Accuracy of the developed method of tritium determination in water samples was verified by the participation in interlaboratory comparisons.

The conducted studies have shown that the developed method of electrolytic enrichment is applicable to low-level tritium determinations in water samples. Determined parameters describing electrolysis process are satisfactory and allow to achieve MDC of 0.2 Bq×dm^{-3} which is over an order of magnitude lower than MDC for direct tritium determination method.

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DETERMINATION OF THE CAPACITIES OF CERTAIN ANION EXCHANGE RESINS

Noha S. Farahat[1], *N. H. Kamel*[2], *Bahgat E. ElAnadouly*[3]

[1]Egyptian Second Research Reactor, Radioactive Isotope Production Facility, Egyptian Atomic Energy Authority, Egypt, e-mail: nohasammy@yahoo.com
[2]Department of Radiation Protecton, Nuclear Research Center, Egyptian Atomic Energy Authority, Egypt, e-mail: nariman.kamel@yahoo.com
[3]Faculty of Science, Cairo University, Egypt, e-mail: bahgat_elanadouly@yahoo.com

Radioiodine or iodine 131 is probably one of the most highly used radioisotopes in the medical field. Being produced either by uranium fission or neutron bombardment of a tellurium target, the short lived (8.06 days) well known beta emitter as well as gamma emitter formed as sodium iodide targeting the thyroid gland, is used for diagnosing and treatment of thyroid cancer.

Other than its medicinal benefits and from the radiation protection point of view, radioiodine being volatile with high energy, the major health concern is the projections of the risk of thyroid cancer through the lifetime of the exposed individuals.

Radioiodine is purified by successive steps of ion exchange, a highly selective anion exchanger is used baring tertiary amino and quaternary ammonium groups to separate radioiodine from other fission products to yield highest radionuclidic and radiochemical purity. A comparative study was performed on 5 commercial anion exchangers differing in the number and distribution of their active groups and radiation induced polymerization poly glycidylmethacrylate resin modified with tertiary ethyl amine groups was also involved in the study. Factors affecting polymerization were studied namely monomer concentration, radiation dose, solvent and time of exposure.

All resins were studied in batch experiments, different factors were studied as resin weight, ion concentration, time of contact and temperature. Results were applied in monolayer isotherms like Langmuir and Fruendlich, to test the selectivity and total capacity of the resins in interest. The highest selective resins were employed in column experiments to measure their breakthrough capacity.

The successive stages of anion exchange on the selected resins were verified by several analytical techniques namely Infra red spectroscopy and Scanning electron microscope and EDX. Poly glycidylmethacrylate showed promising results and more studies to increase its capacity to iodide ions are yet to be performed.

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METHODS FOR RAPID SEPARATION OF CERIUM ISOTOPES FROM A MIXED FISSION PRODUCT SAMPLE

Zach Finch, Leah Arrigo, Brienne Seiner, Angela Edwards, Stephanie Gregory, Shannon Morley, Erin Finn, James Bowen, Lawrence Greenwood*

Pacific Northwest National Laboratory, 901 Battelle Blvd., Richland, WA, USA, *e-mail: zach.finch@pnnl.gov

Keywords: gamma spectroscopy, radiochemical separations, fission product analysis

A novel separation technique has been developed to separate cerium radioisotopes from trivalent lanthanides and actinides in fresh fission product samples. Lanthanides are traditionally difficult to chemically separate due to their similar properties, such as their tendency to be predominantly found in their trivalent state. Previous work at the Pacific Northwest National Laboratory resulted in a new sequential separation method that utilizes Eichrom's LN resin with a nitric acid gradient. This work has removed several problematic interferences encountered during gamma spectroscopy by separating the lanthanides into discrete fractions. However, the cerium isotopes consistently co-elute with other lanthanides and americium, which hinders certain radiometric detection techniques. The chemistry discussed in this paper is intended to remove radioactive cerium prior to the gradient separation of the lanthanides and relies on the oxidation of cerium(III) to cerium(IV). Two methods were tested. The first utilizes sodium bromate as an oxidant and cerium(IV) is retained on a column of Eichrom's LN resin, while the other analytes are eluted. The second method utilizes lead dioxide mixed with anion exchange resin on a column causing the oxidized cerium(IV) to be retained and later eluted with the intent to purify the sample of cerium. These chemistries were tested on two irradiated samples: a plutonium oxide target bombarded with a deuteron beam and a highly enriched uranium (HEU) foil irradiated by a thermal neutron spectrum. Results from the plutonium oxide sample, which was only tested with the sodium bromate method, produced quantitative separation of cerium isotopes and >90% recovery of americium and lanthanide elements. Both methods were applied to the HEU foil. The sodium bromate chemistry resulted in near complete removal of cerium, with only 3% of the initial cerium activity remaining in the americium fraction. The lead dioxide method resulted in the removal of cerium isotopes to ≤ MDA levels. These findings indicate the methods will result in higher decontamination factors of cerium from lanthanides and americium for improving radiometric counting methods.

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REMOVAL OF CAESIUM AND STRONTIUM USING MODIFIED ATAPULGITE: EVALUATION OF THERMODYNAMIC AND KINETIC DATA

Aysun Kilincarslan Kaygun[1], Sema Akyil Erenturk[2], Meral Eral[3]

[1]Cekmece Nuclear Research and Training Center, Yarimburgaz Mah. Nukleer Arastirma Merkezi Yolu, 34303 Kucukcekmece-Istanbul/Turkey, e-mail: aykilincar@yahoo.com
[2]Energy Institute, Istanbul Technical University, 34469 Maslak, Turkey, e-mail: erenturk@itu.edu.tr
[3]Institute of Nuclear Sciences, Ege University, 35100 Bornova, Turkey, e-mail: meral.eral@itu.edu.tr

Keywords: attapulgite, adsorption, organo-clay, caesium, strontium, heavy metals, rare earth elements

Adsorption of radioactive elements onto various solids is important in purification process, environmental contamination and separation and preconcentration of elements. Many organic and inorganic adsorbents are used treatment of radioactive and industrial wastes. Attapulgite clay was used as an adsorbent to remove of caesium and strontium from solutions. Organo-clay was synthesized from raw attapulgite by treated an organic molecule. Structural features of synthesized organo-clays were characterized by XRF, XRD, SEM, BET surface area and TGA analysis.

Adsorption experiments have been carried out in batch method. Caesium and strontium adsorption on attapulgite clays and organo-attapulgite were investigated in terms of caesium and strontium concentrations, solution pH, contact time and temperature effects. The maximum adsorption efficiency of raw and organo attapulgite in optimum conditions were determined as 80.0±2% and 64.0±2% for caesium; 69.0±1% and 51.0±1% for strontium. Sorption data have been fitted to the isotherm models of Freundlich, Langmuir and Dubinin Radushkevic (D-R). It was determined that for raw clay, caesium adsorption fits Freundlich and for organo-clay, Cs adsorption fits Freundlich whereas strontium adsorption fits Langmuir isotherms. Since E value which is calculated from D-R isotherm is smaller than 8 KJ mol^{-1}, it is concluded that caesium and strontium adsorptions on to raw and organo-attapulgite have physical character. Thermodynamic parameters such as ΔS, ΔH and ΔG were calculated from K_d values which were obtained in various temperatures. ΔS values are calculated as 41.42 J mol^{-1} K^{-1} for caesium adsorption on raw clay, as 58.31 J mol^{-1} K^{-1} for strontium adsorptions on raw clay, as 44.55 J mol^{-1} K^{-1} for caesium adsorption on organo-atapulgitte and as 47.67 J mol^{-1} K^{-1} for strontium adsorption on organo-atapulgitte. ΔH values are calculated as –4.57 kJ mol^{-1} for caesium adsorption on row clay, as 1.91 kJ mol^{-1} for strontium adsorption on raw clay, as –1.78 kJ mol^{-1} for caesium adsorption on organo attapulgite and as 0.50 kJ mol^{-1} for strontium adsorption on organo attapulgite. The effect of heavy metals and rare earth elements in caesium and strontium adsorption on attapulgite and organo-attapulgite were examined. It is observed that existence of these elements effect in tremendously caesium and strontium adsorption efficiency.

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DECONTAMINATION OF URANIUM-CONTAINING AQUEOUS SOLUTIONS USING LAYERED DOUBLE HYDROXIDES AND SPIRAL FILTERING ELEMENTS

Vladimir V. Kulemin, Sergey A. Kulyukhin, Elena P. Krasavina, Vladimir B. Krapukhin, Igor A. Rumer, Viktor A. Lavrikov, Andry V. Gordeev, Margarita P. Gorbacheva*

IPCE RAS, Leninskii prospekt, 31-4, Moscow, Russia, *e-mail: kulemin@ipc.rsi.ru

Keywords: decontamination, layered double hydroxide

One of radionuclides that are quite difficult to remove from aqueous solutions is U(VI). A great number of various inorganic and organic sorbents have been developed to remove U(VI) from aqueous solutions. However, only few of those sorbents retain their U(VI) sorption capacity in aqueous solutions of complex chemical compositions. The majority of authors note that the presence of foreign ions in solution decreases not only the U(VI) sorption rate, but also the sorption capacity of many sorbents. In addition, most of the sorbents effectively take up U(VI) in only a narrow solution pH range. On the other hand, organic compounds and U(VI) ions could be included together in the composition of layered double hydroxides (LDH) during their formation process. The aim of the work was to study the process of decontamination of uranium-containing aqueous solutions, followed by the removal of the LDH solid phase using spiral filtering elements (SFE).

The decontamination of 10^{-3}–10^{-2} mol/l UO_2^{2+} aqueous solutions containing humic acids and β-cyclodexstrine or EDTA during the formation of LDH-Mg-Al-OH was studied. The formation of LDH-Mg-Al-OH in в 10^{-3}–10^{-2} mol/l UO_2^{2+} aqueous solutions containing humic acids and β-cyclodexstrine or EDTA resulted in a virtually complete removal of both U(VI) and organic compounds. The degrees of the decontamination of the aqueous solutions of both U(VI) and organic compounds were higher than 99.9%.

Using SFE allows removing the LDH-Mg-Al-[*U(VI)-organics*]-OH solid phase (with a particle size of more than 5 μm) from the mother liquor virtually completely. In the mother liquor, only solid-phase particles of nanometric size are identified.

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EXTRACTION CHROMATOGRAPHIC SEPARATION AND CONCENTRATION OF ALPHA-EMITTING RADIONUCLIDES AND LANTHANIDES

Elena Lapshina[1], Stanislav Ermolaev[1], Boris Zhuikov[1], Aleksandr Vasiliev[1, 2], Valentina Ostapenko[1, 2], Stepan Kalmykov[2]*

[1]Institute for Nuclear Research of Russian Academy of Sciences, 60th October Anniversary Prospect, 7a, Moscow 117312, Russia,
*e-mail: lapshina@inr.ru
[2]Chemistry Department, Lomonosov Moscow State University, Leninskie Gory 1, 119991, Russia

Keywords: extraction chromatography, separation of actinides and lanthanides, thorium, proton irradiation

Extraction chromatographic resins are of increasing interest for separation and concentration of radioelements displaying similar chemical properties, particularly actinides and lanthanides. The resins may be used in various practical tasks, for instance, the isolation of α-emitting radionuclides for nuclear medicine. One of prospective approaches for production of medical α-emitters is irradiation of natural thorium with medium-energy protons [1, 2]. Besides the desired ^{225}Ac, ^{223}Ra and ^{230}Pa/^{230}U, it also results in generation of a number of spallation and fission products including lanthanides needed to be eliminated.

The extraction chromatographic resins produced by TrisKem Int. Company were systematically investigated for this task, namely, DGA Resin (N,N,N`,N`tetroctyldiglicolamide), TRU Resin (octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide dissolved in tri-n-butyl phosphate), Ln Resin (di(2-ethylhexyl)orthophosphoric acid), Sr Resin (4,4’(5’)-di-t-butylcyclohexano-18-crown-6).

First, the capacity factor *k*` values of the radioelements were determined in static experiments for a wide concentration range of HNO_3, HCl and $HClO_4$. The obtained data were used as starting conditions for column separation.

DGA Resin and Ln Resin were shown to be effective for pre-concentration of actinides and lanthanides and their separation from mono- and bivalent products of thorium irradiation in nitric medium. DGA Resin was also proposed for separation Pa(V) and U(VI). Fractions of radioisotopes Ac(III), La(III), Ce(III) were isolated on Ln Resin under certain conditions.

TRU Resin demonstrated a significant increase in sorption factor for Ac(III) and rare earth elements in a series HCl – HNO_3 – $HClO_4$ (0.01–10M). 2–4 M nitric solutions were optimal for Ac(III) separation from lanthanides and thorium. The combination of TRU Resin and DGA Resin resulted in recovery of Ac(III) with radionuclidic purity >99.5%.

Sr Resin was studied for separation of Ra(II) from radioisotopes of Ba(II) and Sr(II) as well as from other products of thorium irradiation. Ra(II), Ba(II), Sr(II) were adsorbed from 2–4 M $HClO_4$ solution, then Ra(II) was stripped off with small amount of 2–3 M HNO_3 solution. When an anion exchange resin AG 1×8 was used for pre-purification, it was possible to obtain Ra(II) fraction with radionuclidic purity >99.5%.

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ADSORPTION BEHAVIOR OF THORIUM AND URANIUM ON GRAPHENE OXIDE-MANGANESE DIOXIDE

*Ning Pan[1], Long Li[1], Jie Ding[1], Shengke Li[2], Ruibing Wang[2], Yongdong Jin[1], Xiangke Wang[3], Chuanqin Xia[1, 4]**

[1]College of Chemistry, Sichuan University, Chengdu, 610064, P. R. China, *e-mail: xiachqin@163.com
[2]State Key Laboratory of Quality Research in Chinese Medicine, Institute of Chinese Medical Sciences, University of Macau, Taipa, Macau SAR, P. R. China, e-mails: walter_li@live.cn, rwang@umac.mo
[3]School of Environment and Chemical Engineering, North China Electric Power University, Beijing, 102206, P. R. China,
e-mail: xkwang@ipp.ac.cn
[4]Key Laboratory of Radiation Physics and Technology, Ministry of Education, Institute of Nuclear Science and Technology, Sichuan University, Chengdu, 610064, P. R. China, *e-mail: xiachqin@163.com

Keywords: graphene oxide, manganese dioxide, uranium, thorium, selective desorption

Manganese dioxide decorated graphene oxide (GOM) was prepared via crystallographic forms (α, γ) of MnO_2 fixing on the surface of graphene oxide (GO). It was explored as an adsorbent material for simultaneous removal of thorium/uranium ions from aqueous solutions. In single component system, the α-GOM_2 (the weight ratio of GO/α-MnO_2 was 2) exhibited higher maximum adsorption capacity toward Th(IV) (497.5 mg/g)/U(VI) (185.2 mg/g) than that of GO. In binary component system, the adsorption properties towards Th(IV)/U(VI) by α-GOM_2 have been studied under various conditions, for instance, pH, crystallographic forms and amount of MnO_2, adsorption time, ionic strength, and co-existing ions. The saturated adsorption capacity of Th(IV) (408.8 mg/g)/U(VI) (66.8 mg/g) on α-GOM_2 was higher than those on GO. Based on analysis data, the adsorption mechanism of Th(IV)/U(VI) on α-GOM_2 were proposed: (1) the competition adsorption process was presented in the binary component system, the affinities of α-GOM_2 with radionuclides followed the order Th(IV)>U(VI); (2) four molecular interaction (including complexation, electrostatic interaction, cation-pi interaction and Lewis acid-base interaction) were suggested as primary mechanism contributing to α-GOM_2 with Th(IV)/U(VI); and (3) the Th(IV)/U(VI) favored adsorption onto both sides of the surface of α-GOM_2 sheets and likely entered the pores of α-MnO_2. Finally, the Th(IV)/U(VI) on α-GOM_2 can be separated by a two-stage desorption process (Na_2CO_3/EDTA). Those results displayed that the α-GOM_2 may be utilized as an effective adsorbent for removing and potentially separating Th(IV) and U(VI) ions from aqueous solutions.

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SELECTIVE SEPARATION OF RADIUM ISOTOPES FROM PROTON IRRADIATED THORIUM TARGETS

Valery Radchenko[1], Roy Copping[2], Jonathan W. Engle[1], Karen Murphy[2], David Denton[2], Justin R. Griswold[2], Eva R. Birnbaum[1], Saed Mirzadeh[2], F. Meiring Nortier[1], Kevin D. John[1], Michael E. Fassbender[1]*

[1]Los Alamos National Laboratory, Los Alamos, NM, 87545, USA, *e-mail: varad@lanl.gov
[2]Oak Ridge National Laboratory, Oak Ridge, TN, USA

Keywords: DGA resin, 225Ac, lanthanides, proton irradiation, thorium

Targeted alpha therapy (TAT) is an effective treatment method for neoplasms [1]. The main limitation for broader utilization of TAT is the availability of alpha particle emitting radionuclides. High energy proton irradiation of thorium targets results in the formation of several alpha particle emitting radionuclides (e.g. ^{225}Ac/^{213}Bi, ^{230}Pa/^{230}U/^{226}Th, ^{227}Th/^{223}Ra, etc.). The main radiochemical challenge is the recovery of single radionuclides from the bulk thorium mass and the purification from several hundreds of co-produced fission products. In our previous work [2], we proposed a two-step procedure for the isolation of ^{225}Ac. In this study, we propose the co-extraction of $^{225/224/223}$Ra from the same target.

Methods: The two-step liquid-solid sorption method that was previously developed for the isolation of ^{225}Ac was adapted for the separation of Ra isotopes. The thorium metal target was first dissolved in hydrochloric acid in the presence of a small amount of ammonium hexafluorosilicate. The solution was then converted to a citrate matrix (1 M, pH 2) and loaded on a cation exchanger resin column. Under these conditions, the bulk of the thorium mass passes through the column without significant sorption on the resin while Ac and Ra isotopes are retained. The column was stripped with 6 M HNO_3 and the eluent directly loaded on a column of BDGA resin. After loading BDGA resin, was additionally washed with 4 M HNO_3. The thorium fraction, originally eluted from the first cation column, continues to accumulate ^{223}Ra from ^{227}Th decay. This fraction can be reprocessed via the same strategy in order to recover additional ^{223}Ra.

Results: Ac and Ra isotopes were quantitatively retained on the cation exchanger, while no detectable thorium was measured on the solid phase after washing with 10 bed volumes of 1 M citrate. Furthermore, >99% of the Ra was eluted from the cation exchanger with 6 M HNO_3. This fraction was directly loaded on BDGA resin, whereupon most of the Ra passed through without sorption while Ac and other fission products (mainly lanthanides) were retained. Residual Ra was eluted with 4 M HNO_3. The single radionuclidic impurity detected in the Ra fraction was ^{140}Ba, the removal of which still needs to be addressed.

Conclusions: An effective two-step method for the separation of Ra isotopes from irradiated thorium targets was developed, which can easily be integrated into our previously developed Ac separation method.

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DETERMINATION OF ^{238}Pu, $^{239+240}$Pu AND ^{241}Am IN AIR FILTERS

Katarzyna Rzemek[1], Andrzej Czerwiński[2], Jakub Ośko[1], Tomasz Pliszczyński[1]*

[1]Radiation Protection Measurements Laboratory, National Centre for Nuclear Research (NCBJ), 7 Andrzeja Sołtana Str., 05-400 Otwock, Poland, *e-mail: katarzyna.rzemek@ncbj.gov.pl
[2]Faculty of Chemistry, University of Warsaw, Warsaw, Poland, e-mail: aczerw@chem.uw.edu.pl

Keywords: plutonium, americium, air filters, monitoring

Workers at nuclear facilities are exposed to internal contamination with radioisotopes. Thus, routine monitoring programme based on direct measurements (*in vivo* measurements) and analysis of excreta samples (*in vitro* measurements) or samples taken from work environment (e.g. water, air) is carried out. From the point of view of radiological protection, analyses which can determine if internal contamination with alpha emitters occurs are very important due the fact that these isotopes are more radiotoxic and hazardous than others.

For this reason, routine monitoring (individual and of work area) of the group of people who work with alpha sources of ^{238}Pu, $^{239+240}$Pu or ^{241}Am is established. Despite the fact that work with alpha sources takes place in glove boxes, alpha emitters can occur in the air and pose a risk to workers. Air monitoring is very important because inhalation is highly probable route of workers exposure. The monitoring of air is realized by passing the aerosols from the air through the Petrianov filter during the working hours. The filter is replaced once a week, and then the activity of aerosols collected on the filter is measured. Measurement of filter activity was previously performed in gas proportional counter. In this type of measurement it is not possible to determine the activity of individual isotopes, only the determination of the global alpha activity in the sample is possible. Therefore, laboratory developed the method for plutonium and americium activity determination in air filters. Radiochemical preparation and alpha spectrometry, as a method of measurement, which allow to perform qualitative analysis of isotopes occurring in the air and determine their activity have been used.

In the applied analytical method for plutonium and americium determination the following steps can be distinguished: dry ashing in muffle furnace at 600 °C, wet ashing with 65% HNO_3 and 40% HF, selective separation and purification by anion exchange resin (Dowex 1X8) and extraction chromatography (TRU resin), source preparation by electrodeposition. Radiochemical yield of conducted analyses is possible to be determined using ^{242}Pu and ^{243}Am as tracers. Application of described method allows to achieve high chemical recovery, low minimum detectable activity and sources containing purified isotopes. Therefore, analytical and measurement method for plutonium and americium determination are considered appropriate for radiological monitoring of air aerosols. In this work, the results of conducted analyses of air filters will be discussed.

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EVALUATION OF SORPTION AND DIFFUSION BEHAVIOR OF TECHNETIUM-99 (Tc-99) IN THE CRUSHED GRANITE BY THROUGH-DIFFUSION COLUMN

Yu-Hung Shih[1], Tsuey-Lin Tsai[1], Liang-Cheng Chen[1], Tsai Hung-I[1], Te-Yen Su[1], Chuan-Pin Lee[2], Shih-Chin Tsai[3]

[1]Chemical Division, Institute of Nuclear Energy Research, No. 1000, Wenhua Rd., Jiaan Village, Longtan Township, Taoyuan County, Taiwan
[2]Department of Earth Sciences, National Cheng Kung University,No.1, University Road, Tainan City 701, Taiwan
[3]Nuclear Science and Technology Development Center, National Tsing Hua University, Hsinchu 30013, Taiwan

Keywords: sorption, diffusion, granite, distribution coefficient (Kd)

The diffusion and sorption are important processes controlling radionuclide migration in crystalline rocks. Such processes are typically studied in the laboratory using borehole core samples Distribution coefficients (Kd), apparent diffusion coefficients (Da) and retardation factor (Rf) obtained by batch and through-diffusion experiments have been carried out in this work, respectively. The accumulative concentration method developed by Crank (1975) was applied to realize apparent and effective diffusion coefficient (Da and De) of Tc. Besides, a non-reactive radionuclide, HTO, was initially conducted in through-diffusion experiment for assessing the ability of radionuclide retardation. The distribution coefficients (Kd) obtained by batch tests in 7 days under aerobic condition was 0.64 mL/g. $Rf^{H/Tc}$ and $Kd^{H/Tc}$ obtained from accumulative concentration's method in through-diffusion test are lower than those derived from the batch experiments. Therefore, it demonstrates that reliable Rf and Kd of Tc-99 by through-diffusion experiments could be achieved at a non-reactive radiotracer (HTO) prior to tests and will be more confident in long-term performance assessment of disposal repository.

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ADSORPTION OF Sr-90 ON PHOSPHOGYPSUM AND FLY ASH/SLAG BASED SORBENTS

Piotr Szajerski, Andrzej Gasiorowski, Henryk Bem*

Institute of Applied Radiation Chemistry, Lodz University of Technology, Wroblewskiego 15, 90924 Lodz, Poland, *e-mail: szajer@mitr.p.lodz.pl

Keywords: Sr-90/Y-90 separation, Sr-90/Y-90 sorption, Sr-90 liquid waste treatment

The natural consequence of utilization of nuclear technologies, next to their straightforward benefits, is generation of radioactive waste. To ensure safety of the people and environment, radioactive isotopes from all technologically generated wastes be separated and stabilized in order to prevent their release and spreading in environment. Nuclear energy production is the most important sector generating all types of nuclear waste concerning their activity level. The most dominating radionuclides in liquid processing waste are activated corrosion products (Co-57, Co-60, Cr-51, Mn-54, Zn-65, etc.) and fission products which can be released to the cooling circuits due to the nuclear fuel cladding failure and depend on the kind and size of fuel element leak. Among these, ones of the highest importance are strontium isotopes Sr-89 and Sr-90 produced during U-235 and Pu-239 fission, generated with relatively high fission yields. Sr-90 isotope, characterized by its long half-life of 28.8 years, must be considered as especially hazardous, due to the fact of biochemical similarity of strontium to calcium and possibility of accumulation in bones.

For strontium isotopes removal from reactor cooling water, mainly two different techniques are used: application of ion exchange resins or solvent extraction methods. First method is relatively expensive and requires utilization of large quantities of resins, whereas solvent extraction is technologically much more complicated and generates additional amounts of organic liquid wastes. Elaboration of effective adsorption agents for radioactive contaminants separation from contaminated waters would lead to more efficient and more cost effective separation of radioactive isotopes from media used in nuclear industry.

In our work mineral waste based materials were prepared and investigated as a potential agents for strontium removal from Sr-90 contaminated water. As a materials used for sorbents preparation phosphogypsum, fly ash and slags from coal-fired energy sector were used. Both native as well as thermally modified waste materials were used in adsorption experiments in order to estimate their effectiveness towards Sr-90 and Y-90 separation from Sr-90 contaminated water. Sr-90 and Y-90 isotopes in contaminated water were determined using liquid scintillation counting technique. Next to radiochemical separation experiments, prepared materials were characterized by XRD and SEM techniques.

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PREPARATION OF Ho-166 WITH HIGH SPECIFIC ACTIVITY BY SZILARD-CHALMERS EFFECT

Zoltán Szűcs[1], *Sándor Takács*[1], *Jan Rijn Zeevaart*[2]

[1]Radiochemical Laboratory, Institute for Nuclear Research, Bem ter 18/C, Debrecen, Hungary, e -mails: zszucs@atomki.hu, stakacs@atomki.hu
[2]ARST, NWU (North West University), Mmabatho, South Africa, Necsa, e-mail: zeevaart@necsa.co.za

Keywords: Szilard-Chalmers effect, high specific activity, ^{166}Ho, targeted radionuclide therapy, Auger electrons

Objective: ^{166}Ho is a potential radionuclides for targeted therapy modalities due to the optimal energy of its emitted beta particle ($E_{\beta\text{–max}}$ = 1.84 MeV) and Auger electrons (5.5 keV , 39.7 keV) as well as its half-life ($T_{1/2}$ = 26.8 hr). The targeted radionuclide therapy requires highest grade of specific activity, as much as possible. The commonly used method for the production of ^{166}Ho is neutron activation [1] of ^{165}Ho. Unfortunately the same chemical element of the bulk target material makes impossible to reach the above mentioned required high specific activity. Production of ^{166}Ho by double neutron activation from ^{164}Dy is possible avoiding presence of other isotopes from the same element in the target and product material. Additionally the separation method provides stable ^{166}Ho already bonded in a chelate molecule [2]. Our proposed method is based on the Szilard-Chalmers effect [3] and provides free ^{166}Ho cations in water solution suitable for further labelling chemistry.

Experiment and method: 300 mg of Dy_2O_3 was irradiated by thermal neutrons with flux of 3×10^{14}n/(cm^{2}s) for 7 days in the SAFAR-1 nuclear reactor, South Africa. After 3 days of cooling time only the ^{166}Dy and ^{166}Ho radioisotopes remained in the target. The irradiated target was dissolved in 1mol/dm^3 HCl acid and the metal ions were labelled to DOTA-TATE (a functionalised octreotide). This chelate complex was loaded and trapped on the Strata-X column and washed by water to clean it from all unbounded metal ions. After 3 half-life's of ^{166}Ho, close to the secular equilibrium of the two radionuclides the free ^{166}Ho was washed out with a chemical yield of 72±3%, which is in good agreement with the theoretical value deduced from nuclear decay and Auger electron production of ^{166}Dy.

Results: Studying the dosimetric aspects of the ^{140}Nd/^{140}Pr *in vivo* generator the release of daughter ^{140}Pr was discovered even from an extremely stable and inert chelator such as DOTA [4]. However, it was found in our work that the amount of Auger electrons are in good agreement with the chemical yield of the released ^{166}Ho ions [5]. Since the Szilard-Chalmers effect is more general [3] than only the nuclear recoil effect but can also include other processes that results in release of daughter nuclides, therefore we can interpret our separation method as part of the Szilard-Chalmers effect.

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A SEQUENTIAL METHOD FOR THE DETERMINATION OF ^{210}Pb, ^{210}Po, ^{226}Ra, ^{228}Ra AND ^{228}Th IN HUMAN EXCRETIONS

Diana Walther

VKTA – Radiation Protection, Analytics & Disposal, PF 510019, D-01314 Dresden, Germany, e-mail: diana.walther@vkta.de

Keywords: (TE)NORM, incorporation control, excretion analysis, sequential method

Due to technical processes natural radionuclides could be enriched in the handled media above the geogenically present activity resulting in TENORM and, thus, could provide an additional contribution to the radiation exposure of employees and general public.

In deep geothermal facilities (in Germany) hoisting highly saline waters the scales will be formed because of changes in pressure and temperature. Thereby, the concentration of naturally occurring nuclides ^{210}Pb, ^{226}Ra and ^{228}Ra can increase from several 10 Bq l^{-1} in the fluids to specific activities of 100–1000 Bq g^{-1} in the scales. During facility runtime ^{210}Po and ^{228}Th, daughter nuclides of ^{210}Pb and ^{228}Ra, respectively, are growing in to not negligible amounts.

The determination of radionuclides in excretions is an important tool in radiation protection assessing the committed effective dose for employees which in case of naturally occurring nuclides is complicated due to their additional intake with foods and drinking water.

Within a federally sponsored research project, we have developed and optimized an analytical technique for the determination of ^{210}Pb, ^{210}Po, ^{226}Ra, ^{228}Ra and ^{228}Th in urine and feces suitable for the routine application in incorporation control of employees on (TE)NORM working places. With the analysis of these five chemically and radiologically diverse radionuclides in separate aliquots of 24-h excretions (usually collected for incorporation control) the sample amount is often not sufficient for achieving appropriate decision thresholds. Thus, considerations of these facts resulted in the design of a sequential procedure in which course the successive separation of ^{210}Pb, ^{210}Po, ^{226}Ra, ^{228}Ra and ^{228}Th is enabled from one single aliquot using as much as possible from the sample. This procedure combines different radiochemical enrichment, separation and purification steps as mineralization, wet digestion, autodeposition, ion exchange chromatography, liquid-liquid extraction and extraction chromatography [1–4]. After the preparation of suitable sources the measurements were accomplished by γ-spectrometry for ^{226}Ra and ^{228}Ra in feces, by α-spectrometry for ^{226}Ra in urine, by α-spectrometry for ^{210}Po and ^{228}Th in urine and feces, and by proportional counter for ^{210}Pb in urine and feces. Chemical recovery tracers for the α-spectrometrically measured nuclides are ^{209}Po and ^{229}Th in equilibrium with ^{225}Ra. The mathematics for calculation the chemical yield for ^{226}Ra is challenging by the decay characteristics of the short-living and only β-emitting ^{225}Ra forming the α-emitting daughters ^{225}Ac, ^{221}Fr and ^{217}At suitable for this purpose.

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SELECTIVE EXTRACTION OF Am(III) OVER Eu(III) IN NITRIC ACID SOLUTION BY NTAamide(C8) USING A NOVEL WATER-SOLUBLE BISDIGLYCOLAMIDE AS MASKING AGENT

*Zhipeng Wang, Dongping Su, Xiaoyang Hu, Shimeng Li, Songdong Ding**

College of Chemistry, Sichuan University, Chengdu 610064, P.R. China, *e-mail: dsd68@163.com

Keywords: water-soluble bisdiglycolamide, NTAamide, lanthanides, actinides, solvent extraction

NTAamide(C8), a kind of new N-donor ligand, could selectively extract Am(III) over Eu(III). A further investigation on the separation of Am(III) over Cm(III) showed that $SF_{\mathrm{Am/Cm}}$ value can be increased significantly from 1.66 to 6.5 with the presence of 10 mmol/L TEDGA in aqueous phase. In view of this point, it can be inferred that the introduction of water-soluble ligand can improve the selectivity of NTAamide(C8) toward Am(III) over Eu(III). Recently, it was found that $SF_{\mathrm{Eu/Am}}$ value could reach 6-10 for the extraction of Am(III) and Eu(III) by TBE-BisDGA in n-octyl alcohol, which is obviously higher than TEDGA under the same conditions. Thus, there is reason to believe that $SF_{\mathrm{Am/Eu}}$ value for NTAamide(C8) could be also improved in the presence of water-soluble BisDGA.

In this work, a novel water-soluble ligand of TEE-BisDGA was synthesized and used as a masking agent for selective extraction of Am(III) over Eu(III) from HNO_3 solution by NTAamide(C8) in kerosene. In the range of examined acidity from 0.001 to 0.2 mol/L, D_{Am} and D_{Eu} values decreased with the increase of HNO_3 concentration. The maximum $SF_{\mathrm{Am/Eu}}$ of ~26 can be obtained in the presence of 0.01 mol/L TEE-BisDGA at pH 3.0, which was significantly higher than that case with no TEE-BisDGA. Mole ratio method and job's method were employed for mechanism research. It has been shown that 1:1 complexes of TEE-BisDGA and NTAamide(C8) with Am(III) and Eu(III) are formed, respectively. TEE-BisDGA had a stronger complex ability than TEDGA.

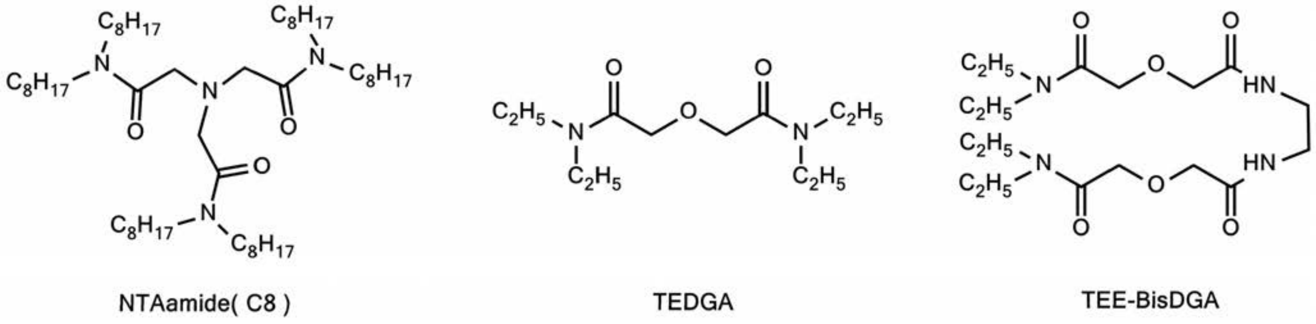

Fig. 1. Chemical structures of NTAamide(C8), TEDGA and TEE-BisDGA

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DEVELOPMENT AND OPTIMISATION OF ON-SITE SEQUENTIAL EXTRACTION SYSTEM FOR RADIOBIOASSAY IN RADIATION EMERGENCY

Seokwon Yoon, Wi-Ho Ha, Jaeryong Yoo, Seung-Sook Lee, Young-Woo Jin*

National Radiation Emergency Medical Center, Korea Institute of Radiological and Medical Sciences, Seoul, Korea, *e-mail: ysw@kirams.re.kr

Keywords: sequential extraction system, radiobioassay, radiation emergency

Internal dosimetry of victims is important information for medical treatment in radiation emergency. Many international organizations have recommended radiobioassay for the efficient medical treatment. In addition, the internal contamination and dosimetry are important information in the beginning step of radiation emergency. However, it is difficult to rapidly conduct *in-vitro* bioassay for verification of internal contamination in radiation emergency. Especially, alpha- and beta-emitting radionuclides should be identified and quantified with *in-vitro* bioassay method. Those radionuclides must be treated using chemical extraction method from the raw biological samples. The rapid sequential extraction method can be effectively used as time-saving technique. In this study, sequential extraction system for rapid response at the scene was developed and the results showed good performance.

The system was designed to perform the alpha- and beta-emitting radionuclides analysis of urine samples collected from victims for internal dosimetry. It consists of sample and reagent introduction, distribution, and extraction column parts. Each sample and reagents are supplied using 8-channel peristaltic pump gear, and each supply is distributed by the solenoid valves following the sequential scenario. To perform the extraction of target radionuclides in a sample, three borosilicate glass columns with adjustable endpiece (Φ10 mm × 100 mm) are applied. In addition, solenoid control modules are applied inside the system to prevent the system fails due to heating. The system is controlled by private program developed using Labview software.

^{238,239}Pu, ^{241}Am and ^{90}Sr in urine samples were analysed for validating the system using TEVA Resin, TRU Resin and Sr Resin, respectively. Flow rate and flux are important factor to perform the efficiency of extraction chromatography. A liquid flow meter was applied and the calibration of the peristaltic pump following the acidity and flux was conducted. The chemical yield and flow rate (1, 3, 5 mL/min) were compared and the most efficient values were discussed compared with the conventional method. To validate the system, synthetic and real urine samples spiked with certified reference source were analysed and the results were well agreed with the radiobioassay criteria.

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COMPARISON OF U(VI) ADSORPTION ONTO NANOSCALE ZERO-VALENT IRON AND RED SOIL IN THE PRESENCE OF U(VI)–CO_3/Ca–U(VI)–CO_3 COMPLEXES

Liu Yunhai[1, 2, 3], Cao Xiaohong[1, 2, 3], Zhang Zhibin[1, 2, 3]

[1]Key Laboratory of Radioactive Geology and Exploration Technology Fundamental Science for National Defense, East China Institute of Technology, Nanchang 330013, PR China
[2]State Key Laboratory Breeding Base of Nuclear Resources and Environment (East China Institute of Technology), Ministry of Education, Nanchang 330013, PR China
[3]Chemistry, Biological and Materials Sciences Department, East China Institute of Technology, Nanchang 330013, PR China

Keywords: U(VI)–CO_3/Ca–U(VI)–CO_3 complexes, red soil, nanoscale zero-valent iron, permeable-reactive barriers, mechanism

The influence of U(VI)–CO_3 and Ca–U(VI)–CO_3 complexes on U(VI) adsorption onto red soil and nanoscale zero-valent iron (NZVI) was investigated using batch adsorption and fixed-bed column experiments to simulate the feasibility of NZVI as the reactive medium in permeable-reactive barriers (PRB) for *in situ* remediation of uranium-contaminated red soils. The adsorption capacity (q_e) and distribution constant (K_d) of NZVI and red soil decreased with increasing pH, dissolved carbonate and calcium concentrations, but the q_e and K_d values of NZVI were 5–10 times higher than those of red soil. The breakthrough pore volume (PV) values increased with the decrease of pH, dissolved carbonate and calcium concentration; however, the breakthrough PV values of the PRB column filled with 5% NZVI were 2.0–3.5 times higher than the 100% red soil column. The U(VI)–CO_3 complexes adsorbed onto the surface of red soil/NZVI(SOH) to form SO–$UO_2CO_3^-$ or SO–$UO_2(CO_3)_2^{3-}$. XPS and XRD analysis further confirmed the reduction of U(VI) to U(IV) and the formation of FeOOH on NZVI surfaces. The findings of this study are significant to the remediation of uranium-contaminated red soils and the consideration of practical U(VI) species in the natural environment.

Special applications on radioanalytical and nuclear chemistry

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NEUTRON ACTIVATION ANALYSIS:
A VALUABLE ANALYTICAL TOOL FOR THE BRAZILIAN SUCROENERGETIC SECTOR

Elisabete De Nadai Fernandes[1], Marcio Arruda Bacchi[1], Gabriel Adrian Sarries[2], Maria Isabel Vega Martinez[1]*

[1]Nuclear Energy Center for Agriculture, University of Sao Paulo, Avenida Centenario 303, 13416-000 Piracicaba SP, Brazil,
*e-mail: lis@cena.usp.br
[2]Luiz de Queiroz College of Agriculture, University of Sao Paulo, Avenida Padua Dias 11, 13418-900 Piracicaba SP, Brazil,
e-mail: gasarrie@usp.br

Keywords: ethanol, sugarcane, bioenergy

Brazil is the world's leading producer of sugar, ethanol and bioelectricity from the sugarcane. The production of sugarcane has been around 600 million tons per year mainly harvested mechanically. Besides being primarily produced from the fermentation of extracted juice and molasses from the sugar industry, the bioethanol can be derived from the transformation of lignocellulosic biomass (bagasse and leaves), which account for two thirds of the sugarcane plant. The industrial productivity is highly dependent on the sugarcane quality delivered to the mill. The presence of mineral impurities provokes losses in the entire process due to equipment wear, impairment of milling tandem and reduced calorific power of bagasse. This paper attempts to outline some of the significant advances of the holistic research approach in the sugarcane agroindustry using neutron activation analysis, as follows: soil tracers to evaluating the amount of soil adhered to the stalks under different climatic conditions and soil types; efficiency of the sugarcane washing system; influence of the mineral impurities on wearing of crushing equipment; dynamics of impurities in the sugar production; dynamics of chemical elements in the fermentation process for ethanol production; influence of mineral impurities on the calorific power of bagasse; mineral impurities in manual and mechanical harvesting systems; representativeness of the sugarcane core sampling systems; development of a certified reference material of sugarcane leaves for nutritional and trace elements contents, and assessment of tracers of vegetal impurities in the green cane harvesting.

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SYNTHESIS AND BIOLOGICAL EVALUATION OF ^{99m}Tc-HYNIC-EDA-FOLATE AS A POTENTIAL FOLATE RECEPTOR-TARGETED TUMOR IMAGING AGENT

Liqin Liu, Xuan Zhang, Fangfang Yuan*

Department of Biological Science and Engineering, University of Science and Technology Beijing, the 30th Xueyuan Road, Haidian District, Beijing 100083, People's Republic of China, *e-mail: liuliqin@ustb.edu.cn

Keywords: folate receptor, ^{99m}Tc, HYNIC, tumor imaging

Objectives: The folate receptor (FR), which is absent in most normal tissues and elevated in over 90% of ovarian carcinomas and at a high frequency in other human malignancies, is an attractive tumor-selective target [1]. We had reported that ^{99m}Tc-Hydrazinonicotinamide-Folte (^{99m}Tc-HYNIC-Folate) had high tumor tissues uptake in KB tumor bearing mice [2]. In this study, a novel compound ^{99m}Tc-HYNIC-EDA-Folate was prepared using hydrazinonicotinamide (HYNIC) as bi-functional chelating agent according to different length of alkyl spacer, and evaluated as a potential folate receptor-targeted tumor imaging agent. *Methods:* HYNIC-EDA-Folate was prepared successfully according to multi-step reaction *(Fig. 1)*. HYNIC-EDA-Folate was labeled with ^{99m}Tc at 100 °C and pH 5 using N-(2-hydroxy-1,1-bis(hydroxymethyl)ethyl)glycine (tricine, 50 mg) and TPPTS (1 mg) as coligands, stannous chloride as a reducing agent. Biodistribution studies were carried out in normal mice and Kunming mice bearing KB tumor. Whole-body gamma imaging was performed using a Kunming mice bearing KB tumor.

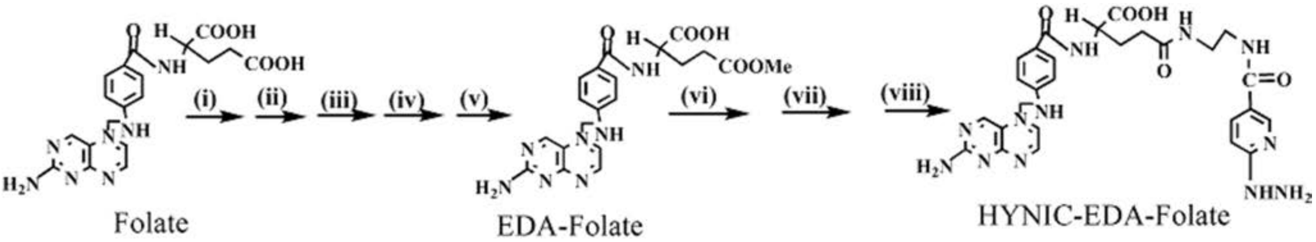

Fig. 1. Synthesis of HYNIC-EDA-Folate.
(i) TFAA/THF; (ii) THF/ice; (iii) NH_2NH_2/DMSO; (iv) t-BuoNo/KSCN/THF;
(v) $HOOCCH(NH_2)COOMe$; (vi) $NH_2(CH_2)_2NH_2$; (vii) 6-chloronicotinic acid/NHS, DCC; (viii) NH_2NH_2 , rt

Results: New complexes of HYNIC-EDA-Folate was synthesized and the structure was determined by ^{1}HNMR and MS. HYNIC-EDA-Folate could be labeled easily and efficiently with ^{99m}Tc using tricine/TPPTS as coligands to form the ^{99m}Tc-HYNIC-EDA-Folate complex in high yield (>95%). The γ scintigraphy and the biodistribution of ^{99m}Tc-HYNIC-EDA-Folate in Kunming mice bearing KB tumor showed relatively high tumor uptake, and low accumulation in non-target organs except in the kidneys, suggesting ^{99m}Tc-HYNIC-EDA-Folate would be a novel potential tumor imaging agent.

Conclusions: ^{99m}Tc-HYNIC-EDA-Folate was prepared in high yields using tricine/TPPTS as coligands and showed high tumor uptake and high target to non-target activity ratios in tumor-bearing mice, suggesting that it could be potentially useful for folate receptor-targeted tumor imaging agent.

Acknowledgements

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ISOMERIC YIELD RATIOS FOR THE ^{110}Pd(γ,n)^{109m,g}Pd REACTION MEASURED AT 50- , 55-, 60-, 65-, AND 70-MeV BREMSSTRAHLUNG ENERGIES

Nguyen Thi Hien[1], *Guinyun Kim*[1]*, *Kwangsoo Kim*[1], *Muhammad Nadeem*[1], *Nguyen Van Do*[2], *Pham Duc Khue*[2], *Kim Tien Thanh*[2], *Sung-Gyun Shin*[3], *Moo-Hyun Cho*[3]

[1]Department of Physics, Kyungpook National University, Daegu 702-701, Korea, *e-mail: gnkim@knu.ac.kr
[2]Institute of Physics, VAST, 10 Dao Tan, Ba Dinh, Hanoi, Vietnam
[3]Department of Advanced Nuclear Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea

Keywords: isomeric yield ratio, photonuclear reaction, ^{110}Pd(γ,n)^{109m,g}Pd, activation method, 50-, 55-, 60-, 65-, and 70-MeV bremsstrahlung, HPGe detector

We measured the isomeric yield ratios for the ^{110}Pd(γ,n)^{109m,g}Pd reaction by the activation method with bremsstrahlung beams of 50-, 55-, 60-, 65-, and 70-MeV generated from an electron linear accelerator at Pohang Accelerator Laboratory. The induced γ-activities of the irradiated samples were measured by a coaxial high purity Gemanium detector coupled to a PC-based multi-channel analyzer. The necessary corrections were made to improve the accuracy of the experimental results. The experimental results at bremsstrahlung energies of 50,55,60,65, and 70 MeV were 0.108±0.007, 0.118±0.008, 0.126±0.009, 0.129±0.009, 0.1297±0.009, respectively. The obtained isomeric-yield ratios in the formation of ^{109m,g}Pd are compared with the corresponding values found in the other experiments, and they also confirm the dependence of the isomeric yield ratios on the incident energy. The present results at 55 MeV and 65 MeV bremsstrahlung energies are the first measurements.

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QUALIFICATION OF ^{68}Ge/^{68}Ga GENERATORS FOR RADIOPHARMACEUTICAL PREPARATIONS

Dana Niculae[1]*, *Filip D. Puicea*[1, 2], *Doina Draganescu*[1, 3], *Catalin Tuta*[1]

[1]Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), 30 Reactorului Street, 077125, Bucharest – Magurele, Romania, *e-mail: dana.niculae@nipne.ro
[2]University Politehnica of Bucharest, Faculty of Applied Sciences, 313 Splaiul Independentei Street, 060042, Bucharest, Romania
[3]Carol Davila University of Medicine and Pharmacy, Faculty of Pharmacy, 6 Traian Vuia Street, Bucharest

Keywords: Ga-68, generators, purification, radiolabelling, peptides

The ^{68}Ge/^{68}Ga generators of a chromatographic type is a glass or polypropylene column with a sorbent based on Al/Zr/Ti/Sn/Sb-oxides or organic matrix. Qualification of generators requires different post processing approaches, to use the eluate for peptides labeling and radiopharmaceutical formulation.

We have tested the generators (n = 5) over 12 months, following the yield, elution profile, and also the labelling parameters and radiopharmaceutical preparation time. ^{68}Ge content, as radionuclidic impurity, was determined using direct measurement on an ionization chamber and also by gamma spectrometry. The eluates from tin oxide based generators are usually containing small amounts of other cations (Ge, Fe, Sn, Zn), competing with Ga in the chelation reaction to the bifunctional chelating agents (DOTA/NOTA/NODAGA) and should be purified prior the radiolabelling of the peptides. The eluate was converted to $GaCl_4^-$ and purified on an anion exchanger, resulting in 0.4 mL of $^{68}GaCl_3$, 500–750 MBq, ready for radiolabelling. The ^{68}Ga solutions eluted in fractions from organic matrix generator type, were used without any chemical changes, but a fractionated elution approach was employed, based on elution profile and ^{68}Ge content in elution fractions, reducing the total process time and thus, increasing the yield. Radiolabelling processes of micrograms of peptides were optimized and transferred on automated synthesis module.

The average elution yield of organic matrix generators was over 90%, with 75% of the activity in 2 mL eluate; ^{68}Ge content in the eluate was stable over 1 year in the range 0.003–0.004%. The elution yield of the tin oxide based generators is highly dependent on HCl concentration, from 80% with 0.6 M HCl up to 92% with 1 M HCl. Ge-68 in the eluate rise from 0.002% up to 0.026% at 1 year after the first elution. Total synthesis time on automated modules was 20 min and 35 min respectively. The resulting radiopharmaceutical has high specific activity as required by receptors density on the cellular surface, in the order of 10–30 MBq/mg (25–50 MBq/nmol).

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DOSE VERIFICATION OF VOLUMETRIC MODULATED ARC THERAPY USING NIPAM GEL DOSIMETER COMBINED WITH PARALLEL-BEAM OPTICAL-CT SCANNER

Chun-Hsu Yao[1, 2]*, *Min-Jia Tsai*[1], *Tung-Hao Chang*[3], *Yuan-Chun Lai*[3, 4], *Yuan-Jen Chang*[5], *Chin-Hsing Chen*[5]

[1]Department of Biomedical Imaging and Radiological Science / School of Chinese Medicine, China Medical University, No.91, Hsueh-Shih Road, Taichung City, Taiwan 40402, R.O.C., e-mail: b50703@gmail.com
[2]Department of Biomedical Informatics, Asia University, 500, Lioufeng Rd., Wufeng, Taichung City, Taiwan 41354, R.O.C.,
*e-mail: chyao@mail.cmu.edu.tw
[3]Department of Radiation Oncology, Changhua Christian Hospital, 135 Nanxiao St., Changhua City, Taiwan 50006, R.O.C.,
e-mail: 81006@cch.org.tw
[4]Department of Physics, National Chung Hsing University, 145 Xingda Rd., Taichung City 402, Taiwan 40227, R.O.C.,
e-mail: 103424@cch.org.tw
[5]Department of Management Information Systems, Central Taiwan University of Science and Technology, No.666, Buzih Road, Beitun District, Taichung City, Taiwan 40601, R.O.C., e-mails: ronchang@ctust.edu.tw, chchen@ctust.edu.tw

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Volumetric modulated arc therapy (VMAT) has been developed to shorten treatment times and to increase target conformance. However, the 3D dose verification is needed. In current study, N-isopropylacrylamide (NIPAM) polymer gel dosimeter was used for recording 3D dose distribution. We developed a CCD-based parallel-beam optical-CT scanner to perform dose measurement. A cylindrical acrylic phantom that measured 10 cm × 10 cm was filled with NIPAM gel. Two treatment plans of lung cancer SBRT were obtained for the same PTV by using VMAT and IMRT calculation software. Irradiation was performed using latest Elekta accelerator (Elekta Axesse™, Sweden), which harnesses the ultra-fast leaf speeds of Agility™ MLC to provide highly conformal beam shaping. The irradiation energies for IMRT and VMAT were set as 6 MV photons and prescribed dose was 5 Gy, but their irradiation angles and dose rates differed during irradiation. The irradiation angles of IMRT were 160°, 130°, 30°, 0°, 330°, 240° and 205°, and the dose rate was fixed at 500 cGy/min. VMAT rotated continuously during irradiation, and the dose rate varied from 133 cGy/min to 562 cGy/min. After irradiation, the gamma evaluation was used for quantitative evaluation. The pass rates of IMRT were 93.5%, 93.6%, 100%, and 100% at depths of 40, 45, 50, and 55 mm, respectively. The pass rates of VMAT were 99.6%, 100%, 95.6%, and 100% at depths of 40, 45, 50, and 55 mm, respectively. The isodose lines of IMRT and VMAT were consistent with those of TPS in most regions. In current study, a simple shape of lung cancer was selected. The result showed that the pass rate of VMAT is higher than that of IMRT even the dose rate variation of VMAT is greater than IMRT. The result of this study indicated that the potential usage of polymer gel dosimeter for radiotherapy. Radiation with higher dose rate up to 1400 cGy/min will be applied to NIPAM gel dosimeter using the same Elekta Axesse™ for further investigation in the future.

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