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E-mail: ak@akademiai.hu
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Contents

Hevesy Awardee

275

Hevesy Medal 2023 Award Lecture

Melissa A. Denecke

International Atomic Energy Agency, Department of Nuclear Sciences and Applications,
Division of Physical and Chemical Sciences, Vienna, Austria
E-mail: m.denecke@iaea.org

Keywords: actinide chemistry, X-ray spectroscopy, radionuclide speciation

Over the past decades, radionuclide speciation research using innovative X-ray spectroscopy techniques in combination with classical physical/inorganic methods and quantum chemical and atomistic modelling has helped improve scientific understanding of radiochemical processes important for numerous application areas and secure basic knowledge of relativistic (many electron) heavy elements. In this Hevesy Medal Award Lecture, examples of these advanced techniques and their evolution in applications to 4f/5f element systems to address scientific challenges across the nuclear fuel cycle will be presented. In addition, recent trends in other radiochemistry applications will be highlighted as well as opportunities for using dynamic sources. In closing, reflections on science diplomacy in such scientific endeavours to find solutions to challenges will be considered.

Plenary Speakers

147

Recent activities in prompt gamma and instrumental neutron activation analysis at NIST

*H. Heather Chen-Mayer**, *Rick Paul, Nicholas Sharp, Maria Vega Martinez, Jamie Weaver*

Chemical Sciences Division, Materials Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA
*E-mail: chen-mayer@nist.gov

Keywords: neutron activation analysis, prompt gamma imaging, portable neutron generator

The NBSR reactor has not been operational since Feb 2020, impacting the standards reference material (SRM) measurement operation and research effort in prompt gamma activation analysis (PGAA) and instrumental neutron activation analysis (INAA). Nevertheless, efforts leading up to the shutdown generated large amount of data warranting subsequent data reduction and reporting. In addition, samples from various projects were prepared and sent to other facilities for irradiation and testing. This presentation highlights activities in five areas: 1) cold neutron PGAA facility update, which includes a linear neutron beam chopper for in-beam NAA for short-lived nuclei, and the addition of a second sample/detector open-air station in tandem with the original sample chamber/detector operation. The goal of the addition is two-fold: to increase the distance between the sample and the beam-dump to lower the gamma background, and to carry out research-oriented projects while preserving the standards measurement environment upstream. 2) Non-standard PGAA activities, include the measurement of chloride diffusion profile by scanning bulk concrete cylinders, development of prompt gamma imaging methods (Compton imaging and Ghost imaging x-ray analog). 3) The INAA of glass and concrete samples, including those irradiated in other facilities. 4) Investigation of material classification using statistical models trained by existing PGAA spectra. 5) Development of portable neutron generator based PGAA for chloride in concrete at the levels relevant to corrosion of steel rebars, assisted by Monte Carlo simulation. Additionally, the backlog of measurements planned for when the reactor restarts are described, notably the H in Ti SRM project to reconcile the difference between PGAA and destructive methods at the lowest level previously certified. Finally, after the NCNR planned cold source upgrade, the cold neutron flux will double at long wavelengths. The anticipated improvement in measurement sensitivity for PGAA will be assessed.

2

The superheavy elements – their production and chemical properties

Christoph E. Düllmann[1,2,3*]

[1]Department of Chemistry – TRIGA Site, Johannes Gutenberg University Mainz, Mainz, Germany
[2]GSI Helmholtzzentrum für Schwerionenforschung GmbH, Darmstadt, Germany
[3]Hemholtz Institute Mainz, Mainz, Germany
[*]E-mail: duellmann@uni-mainz.de

Keywords: superheavy elements, transactinides

The synthesis of elements up to oganesson (Og, element 118) has been reported [1,2], reaching well into the realm of the long-sought "island of stability of superheavy nuclei". Long-predicted [3], this is made up of nuclei wtih long nuclear lifetimes, due to nuclear shell effects associated with the next nuclear shell closures beyond $^{208}_{82}\mathrm{Pb}_{126}$, commonly expected around proton number $Z \approx 114\text{-}126$. Experimental data validate the concept, but the location of the center as well as the extension of the "island" are not yet clear.

Electron shells around superheavy nuclei experience a strong Coulomb attraction, accelerating electrons near the nucleus to relativistic velocities, rending atoms of these elements prime laboratories for studying the influence of relativistic effects on atomic and chemical properties [4].

Correspondingly, the following topics are of prime interest in superheavy element research:

- their production, in heavy-ion induced fusion-evaporation reactions. Main aims include identifying the most promising routes to produce yet unknown nuclei, including those of elements beyond Og [5];
- their nuclear structure, studied by nuclear spectroscopy, by high-precision atomic mass studies, and by laser spectroscopic hyperfine structure studies, employing the interaction of electrons with the nucleus [6];
- their atomic structure, studied by laser spectroscopic methods [6];
- their chemical properties, typically studied by single-atom gas chromatography on hetero-surfaces [7].

A comprehensive study of these aspects has been a pillar of the research programme at my home institution, GSI Darmstadt [8]. After a general introduction to the topic of superheavy element research, I will highlight the experimental progress in the field in the above mentioned areas in the main laboratories for superheavy elements, with a focus on their chemical studies. Here, the elements $_{113}\mathrm{Nh}$, $_{114}\mathrm{Fl}$ [9], and $_{115}\mathrm{Mc}$ are currently in the focus, and technical developments to extend such studies to still heavier – and more short-lived – elements have already started [10]. The outlook will show that a next phase in superheavy element research will profit from accelerator developments, as they are ongoing in many of the main labs [11]. These shall provide substantially higher beam intensities to reach new elements and isotopes accessible with smaller cross sections as well as providing higher rates of known nuclei to allow for in-depth next-generation nuclear, atomic, and chemical studies.

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184

Radioanalysis of long-lived radionuclides, mass spectrometry vs. radiometric techniques

Xiaolin Hou[1, 2, 3*]

[1]Department of Environmental and Resource Engineering, Technical University of Denmark, Risø, Denmark
[2]Xi'an AMS Center, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China
[3]School of Nuclear Science and Technology, Lanzhou University, Lanzhou, China
[*]E-mail: xiho@dtu.dk

Keywords: ICP-MS, AMS, environmental radioactivity, decommissioning, radionuclide

Accurate determination of radionuclides in various environmental and waste samples is critical for investigation of environmental radioactivity, radioecology, evaluation nuclear environmental safety, nuclear forensics, environmental process tracing using radionuclide, decommissioning of nuclear facilities and repository of radioactive waste. Besides relative easy measurable gamma emitters, large number of radionuclides in the environmental and waste samples are pure beta and alpha emitting radionuclides, their concentrations are different by a few orders of magnitude, and therefore hard to measure (HTM). The conventional analytical methods for their measurement are radiochemical separation from matric and all radionuclides followed by radiometric measurement, such as liquid scintillation counting, low beta counting, and alpha spectrometry, and have being used for decades. But, it suffers a few difficulties such as long analytical time up to a few weeks, low sensitivity for long-lived radionuclides (e.g. ^{238}U, ^{235}U, ^{232}Th, ^{126}Sn, ^{99}Tc, ^{237}Np, ^{129}I, unable to measure some low-level and similar decay energy radionuclides, such as ^{135}Cs, ^{239}Pu/^{240}Pu and ^{236}U). Mass spectrometry is a sensitive technique for measurement of long-lived radionuclides. but often suffer from serious interference from high-level stable isotopes and polyatomic ions. The rapid improvement of accelerator mass spectrometry (AMS), especially ICP-MS in the past years make these mass spectrometry techniques significantly improved and accessible, and becoming more attractive and competitive for the determination of radionuclides of long-lived, even middle-lived with half-life of a few tens of years.

A critical review of the present status and perspective of AMS and ICP-MS on the determination of long-lived radionuclides in environmental and waste samples against radiometric techniques is presented, with some examples on the determination of important radionuclides such as ^{90}Sr, ^{99}Tc, ^{126}Sn, ^{129}I, ^{135}Cs, ^{234}U, ^{235}U, ^{236}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Am. The main challenge and strategy on the determination of these radionuclides in different environmental and waste samples are discussed, focusing on the pros and cons of each measurement techniques. The requirement and strategies on radiochemical separation for the determination of these radionuclides with different techniques are also discussed. A special effort on elimination of isobaric and polyatomic ion interference in ICP-MS and high sensitive measurement are presented aiming to obtain a reliable analytical results. Application of these methods on the investigation of environmental radioactivity and evaluation of radiation risk, as well as tracing environmental processes using artificial radionuclides is highlighted.

Acknowledgments

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236

Focused R&D to advance the science of nuclear forensics and ensure a pipeline of future expertise

Stephen LaMont[*], *Mitzi Boswell, Jo Denton, Mark Edwards, Jeremy Inglis, Kara Luitjohan, Zsuzsanna Macsik, Ben Naes, Matt Sanborn, Travis Tenner, Kim Wurth, Robert Steiner*

Los Alamos National Laboratory, Los Alamos, New Mexico, USA
[*]E-mail: lamont@lanl.gov

Keywords: nuclear forensics, mass spectrometry, radiation spectrometry, education and training

Advancing the science of nuclear forensics requires investigating a broad set of topics including investigating how forensic characteristics are created in nuclear materials, improved techniques for measuring those characteristics, and better methods for assessing nuclear forensic data. When considering the scope of potential efforts to understand the forensics of every potential fuel cycle material or radioactive source material, and the need to characterize samples ranging in size from kilograms to individual particles, there are almost endless topics worthy of investigation. We are actively prioritizing and tackling projects in each area. For example, experiments to recast well-characterized uranium metal are revealing how uranium progeny behave during casting, which creates discordance between the ^{230}Th – ^{234}U and ^{231}Pa – ^{235}U radiochronometers. Other efforts are focused on improving radiochemical purification and measurement of trace actinides in a variety of sample types ranging from bulk uranium to environmental samples and further our understanding the isotopic signatures present. This work includes using complimentary mass spectrometry and radiation spectrometry measurements and careful intercalibration to ensure activity and atom counting techniques are fully comparable. In addition to advancing our nuclear forensics capabilities, these projects also present an important opportunity to train the next generation of nuclear forensic scientists. Teaching them not only good laboratory skills, but also how to evaluate data to answer specific investigative questions about the production history or provenance of materials.

217

Trends in scientific journal publishing – The perspective of Springer Nature

Steffen Pauly

Publishing Director Chemistry, Springer Nature
E-mail: steffen.pauly@springernature.com

Current trends in scientific journal publishing will be highlighted, such as the transformation to open research. The presentation will also cover the ways in which the publisher Springer Nature is responding to these trends.

90

New directions in nuclear data research for accelerator-based production of medical radionuclides

Syed M. Qaim

Institute of Neuroscience and Medicine: INM-5 (Nuclear Chemistry), Forschungszentrum Jülich,
52428 Jülich, Germany
E-mail: s.m.qaim@fz-juelich.de

Keywords: nuclear data, medical radionuclide, accelerator, production

Nuclear data play an important role in the production and clinical application of radionuclides. Extensive studies have been carried out over the last 30 years in the context of accelerator-based production of radionuclides and the achieved database is fairly good [1,2]. Yet there are some deficiencies or new needs of data in several areas. Those needs are generally associated with new emerging clinical applications of radionuclides, e.g. theranostic approach, bimodal imaging, radioimmuno-therapy, etc. [3]. This talk gives an overview of on-going nuclear data research utilizing charged particle accelerators in four directions, namely low-energy region, intermediate energy range, use of α-particle and heavy-ion beams, and utilization of secondary radiation generated at accelerators. Wherever possible, a comparison of experimental data with theoretical estimates will be presented.

With the fast increasing number of small medical cyclotrons (E_p<20 MeV; E_α<10 MeV) in the world, besides production of standard positron emitters for patient care via Positron Emission Tomography (PET), interest in production of non-standard positron emitters, using low-energy (p,n) and (d,n) reactions on highly enriched targets, is increasing. To meet the demand of higher accuracy in data, some new measurements are being performed near reaction thresholds, e.g. for ^{44}Sc, ^{64}Cu, ^{75}Br, ^{86}Y, etc. The major emphasis of measurements, however, lies today on nuclear reactions induced by intermediate energy protons, leading to the formation of therapeutic radionuclides, e.g. β^- emitters ^{47}Sc and ^{67}Cu, or the α-particle emitter ^{225}Ac. Besides protons, the α-particle beam is also interesting. It is of paramount importance in the production of the α-particle emitting therapeutic radionuclide ^{211}At. Furthermore, investigation of (α,x) reactions to produce high-spin isomers like ^{117m}Sn and ^{193m}Pt, which emit low-energy conversion and Auger electrons of therapeutic interest, is attracting great attention. Heavy-ion beams are occasionally used to prepare tracer quantities of positron-emitting rare-earth isotopes.

Accelerators are also being considered intensively as strong sources of secondary radiation, namely fast neutrons and hard photons, to produce medical radionuclides, e.g. via the reactions ^{68}Zn(n,np)^{67}Cu, ^{100}Mo(n,2n)^{99}Mo, ^{68}Zn(γ,p)^{67}Cu, ^{100}Mo(γ,n)^{99}Mo, etc. Some of the recent integral data measurements will be discussed.

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188

How accurate are half-lives of long-lived isotopes?

Dorothea Schumann[*]
for the SINCHRON and ERAWAST collaborations

Laboratory of Radiochemistry, Paul Scherrer Institut Villigen, Switzerland
[*]E-mail: dorothea.schumann@psi.ch

Keywords: long-lived radionuclides, radiochemical separations, half-life

Isotopes with comparatively long half-lives (we take an arbitrary cut at 70 years, which is as good as any) are of particular interest to nuclear scientists for a number of reasons:

- Depending on the type and intensity of the emitted radiation, long-lived isotopes can pose a high radiological hazard during the operation of nuclear facilities (reactors, accelerators) as well as after disposal.
- The so-called "branch points" in the nuclear s-process, as well as some other long-lived isotopes, are of great importance for understanding element synthesis in the early solar system and the evolution of our universe.
- A number of these isotopes are used for nuclear dating of environmental samples to reconstruct climate changes, matter cycles, and other processes relevant to earth sciences and climate research.

Precise knowledge of the nuclear properties, in particular the half-lives and branching ratios, as well as the cross sections of a large number of nuclear reactions (mainly by neutrons and charged particles) of these isotopes is a prerequisite for the assessment of all these influencing factors. But how accurate are the currently known data on the decay properties of such isotopes? A recent publication [1] provides an overview of the current situation and points out some of the main shortcomings in the nuclear data landscape. One of the main reasons why reliable data are still not available in a number of cases is the very limited amount of sample material. Targeted irradiation campaigns and subsequent radiochemical separations of element fractions can help to improve this situation.

With this paper, we will present the current state of the art with some prominent examples, focusing in particular on some of the recent new measurements and the reassessments made as a result. We will discuss the implications of inaccurate or erroneous data, highlight obvious data deficiencies, explain the reasons for them, and offer some suggestions for future improvements.

Acknowledgments

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136

Using $^{135}Cs/^{137}Cs$ as a signature in environmental nuclear forensics

Georg Steinhauser[1*], *Felix Stäger*[2], *Dorian Zok*[2], *Bin Feng*[1,3]

[1]TU Wien, Institute of Applied Synthetic Chemistry & TRIGA Center Atominstitut, 1060 Vienna, Austria
[2]Leibniz Universität Hannover, Institute of Radioecology and Radiation Protection, 30419 Hannover, Germany
[3]Leibniz Universität Hannover, Institute of Inorganic Chemistry, 30167 Hannover, Germany
[*]E-mail: georg.steinhauser@tuwien.ac.at

Keywords: radiocesium, environmental monitoring, environmental radioactivity, nuclear release

Radioactive ^{137}Cs is one of the most prominent fission products. Due to its high volatility, it has been released in significant amounts into the environment (nuclear weapons fallout as well as in the course of nuclear accidents such as Chornobyl, Fukushima, Kyshtym, etc.), and due to its fairly long half-life (30 y), it has become a ubiquitous contaminant in almost any environmental compartment on Earth.

In nuclear accident preparedness as well as in environmental sciences, it is quite unfortunate that the various source of ^{137}Cs cannot be distinguished from one another. However, when long-lived ^{135}Cs ($T_{1/2}$= 2 My) is taken into consideration, a distinct ratio $^{135}Cs/^{137}Cs$ can be calculated that serves as a fingerprint in many environmental questions.

In this keynote lecture, we will show recent advances in this field and discuss possible applications that lead us deep into the field of environmental nuclear forensics.

253

Photonuclear reactions: The future of large scale theranostic radionuclide production

Prof. Dr. Andreas Türler

Department of Chemistry, Biochemistry and Pharmacy, Laboratory of Radio- and Environmental Chemistry, University of Bern, Switzerland
E-mail: andreas.tuerler@unibe.ch

Photonuclear reactions have been known since nearly 100 years, but only recently, discussions about using this type of reaction for the production of radionuclides for medical applications (i.e. diagnosis and therapy) have surfaced. In a photonuclear reaction a high-energy gamma-ray is interacting with a target nucleus, whereby a particle (or several particles) such as protons or neutrons are ejected. Such (γ,n) or (γ,p)-reactions give access to several, medically interesting radionuclides.

With the commercial availability of high-energy and high-power electron accelerators, intense Bremsstrahlung can be generated, which is able to induce photonuclear reactions. Although the reaction cross sections are lower compared to particle-induced reactions, the penetrating nature of heigh-energy gamma-rays allows the use of much thicker targets, largely overcompensating the lower reaction cross section.

There remain a number of challenges to be solved before a large scale production of radionuclides can be envisaged. First, the intense electron beam of typically about 40 MeV energy and about 125 kW of beam power has to be converted to Bremsstrahlung. This is done by means of a converter target that must be able to withstand the enormous beam power. Second, the chemical separation of radionuclides in no-carrier added form from several tens of grams of target material remains a chemical challenge.

In the presentation calculations of the yield of photonuclear reactions with high-power accelerators are given and some ideas how to convert the enormous beam power are discussed. Furthermore, first examples of experiments conducted at the 22 MeV microtron for the production of ^{47}Sc and ^{67}Cu in Bern are presented.

Invited Speakers

Actinide analytical chemistry

220

Determination of americium-241 from environmental samples for plutonium age dating purposes at the Safeguards Analytical Laboratory, IAEA

Renata Bujak[1*], *Yoshiyuki Sato*[2], *Robert Katona*[1], *Stefanie Konegger-Kappel*[1], *Andreas Koepf*[1], *Sergei Boulyga*[1], *Matthew Kilburn*[1]

[1]Safeguards Analytical Laboratory, Office of Safeguards Analytical Services,
Department of Safeguards, International Atomic Energy Agency, 1400 Vienna, Austria
[2]Current address: Japanese Atomic Energy Agency, 2-4 Shirakata, Tokai-Mura, Naka-gun, Ibaraki, Japan
[*]E-mail: R.Bujak@iaea.org

Keywords: americium, plutonium, age dating, isotope dilution MC-ICP-MS, extraction chromatography

Environmental sampling using cotton swipes is an important tool utilized by the International Atomic Energy Agency (IAEA) to assess the completeness of States' declarations. Nuclear signatures collected on cotton swipes provide valuable information that, along with other sources of information, are used by the IAEA to draw safeguards conclusions. Determination of the age of plutonium collected on a cotton swipe is a relatively new undertaking by the IAEA Safeguards Analytical Laboratory (SAL). Plutonium age determinations are made by measuring Pu-241 and its daughter isotope Am-241. Here we present the results of tests to determine Am-241 on cotton swipes down to the femtogram (fg) level. A bulk analysis method is applied to obtain information on the average isotopic compositions and amount contents of U, Pu, and Am contained within the whole cotton swipe after digestion. Uranium, Pu, and Am are separated and further purified to remove interfering impurities ahead of the determination of amount content by isotope dilution analysis using mass spectrometry. In SAL the routine method for Am determination using TRU resin did not satisfy the requirements for Pu age determination because the separated product contained several hundred ng g^{-1} of rare earth elements (REE). Two other extraction chromatographic (EC) resins – TEVA and DGA-N – were investigated for separation and purification of the Am fraction. The applicability of the different combinations of these resins was experimentally verified by doping cotton swipes with known amounts of CRM 137, which is a Pu isotopic reference material that is certified for Pu isotopic composition. The model purification age of the material is also well known. Since the goal of the work was to apply the new procedure to very small quantities of Pu and Am, and also to explore the limitations associated with chemical sample preparation and mass spectrometric analysis, test materials were prepared with 6 - 12 fg Am-241 and 0.6 - 1.2 fg Pu-241. All tested methods satisfactorily removed the REE to below one ng g^{-1}. The Am and Pu isotope ratio measurements were performed on a Neptune Plus^{TM} multi-collector ICP-MS in which the collector block was configured to optimize measurement of low ion intensities using ion counters. The average bias to the expected value was within 4% for Am-241, while the relative expanded uncertainty (k=2) was in the 3-5% range. The calculated age of the CRM 137 agreed with the consensus value within uncertainties, whereas the expanded uncertainty (k=2) of the age varied between 4 and 4.5 years due to the very low amounts of Am and Pu analyzed.

64

Destructive analysis tools to support production and certification of a new plutonium metal standard, CRM126B

Angela Olson[1*], *Lav Tandon*[2], *Cecilia Eiroa-Lledo*[1], *Victor Aldana*[2], *Richard Clore*[2], *Jason Cooley*[3], *John Davis*[4], *Tabitha Kalin*[2], *Peter Mason*[5], *William Peach*[2]

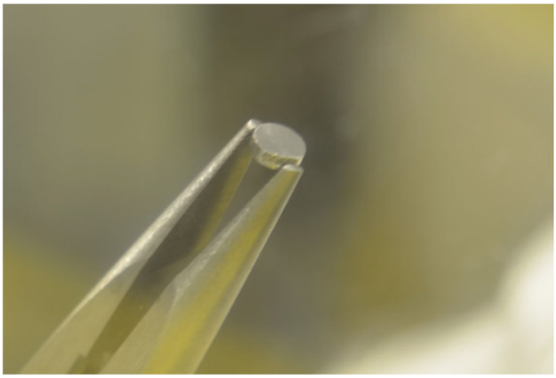
[1]Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, NM, USA
[2]Pit Technologies, Los Alamos National Laboratory, Los Alamos, NM, USA
[3]Fabrication Manufacturing Science, Los Alamos National Laboratory, Los Alamos, NM, USA
[4]Operational Safety & Compliance Programs, Los Alamos National Laboratory, Los Alamos, NM, USA
[5]NBL Program Office, NNSA, Oak Ridge, TN, USA
[*]E-mail: aolson@lanl.gov

Keywords: actinide analytical chemistry, plutonium metal standard, certified reference material, standard production

A series of nine plutonium (Pu) metal certified reference materials (CRMs) have been produced in the Unites States since the 1960s, beginning with the National Bureau of Standards (NBS) Standard Reference Material SRM 949 and most recently concluding with CRM126A (C126A) in 2004. Plutonium metal standard C126A resulted from a joint effort between Los Alamos National Laboratory (LANL) and the New Brunswick Laboratory (NBL). The collaboration ensures that material production – and measurements leading to the certification of a material – are performed to the highest standards. The production of a new Pu metal standard, CRM126B (C126B), is being undertaken in a continued partnership between LANL and the NBL Program Office. The newly produced C126B material will be used for the calibration and quality control of measurement systems performing Pu mass fraction (assay) and Pu isotopic composition determinations.

With Pu standard characteristics and fabrication parameters defined, the challenge lies in producing a standard that meets the requirements for a Certified Reference Material of the highest metrological quality. Attaining high purity, well-characterized, homogeneous, and stable material is of critical importance. This presentation will describe the C126B material production approach, as well as the analytical tools that are being used to address key technical questions throughout the production sequence. Leading up to C126B production, several experiments have been executed to test key steps in the process. Results from those experiments will be described, including: 1) testing to ensure material integrity will be maintained, and 2) mold design testing and modelling for foundry processing. Finally, perspective on LANL's work with the certifying agency (NBL) to devise an analytical plan for material certification will be provided.

Figure



Polished Pu metal Certified Reference Material

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62

Challenges associated with analysis of common and unique nuclear materials

Lav Tandon[*], *Angela C. Olson, Kevin J. Kuhn, Lisa M. Colletti, Elmer J. W. Lujan, Cecilia Eiroa-Lledo, Laurie F. Walker, Khalil J. Spencer, Kattathu J. Mathew, Michael S. Rearick, Michael F. Schappert, Lisa E. Townsend, Dylan J. Klundt, Jung H. Rim, Christopher G. Worley, Ning Xu*

P.O. Box 1663, Los Alamos National Laboratory, Los Alamos, NM, 87545 USA
[*]E-mail: tandon@lanl.gov

Keywords: actinide analysis, plutonium metal, plutonium beryllium, clad uranium fuel

Complete destructive characterization of special nuclear materials for actinide content, isotopics, and impurities can offer challenges even for common materials such as metals or oxides. Moreover, interesting challenges can arise for unique materials such as clad reactor fuels, plutonium-beryllium alloys, or plutonium fluoride – especially in cases where literature precedence is sparse. Chemical analysis of an actinide metal, for example, begins with initial processing that includes sub-sampling using various cutting tools and polishing which could be either mechanical or chemical. These methodologies can have a potential impact on the results that are obtained in downstream analytical processing especially for high accuracy and precision analysis such as coulometric or titrimetric methods for actinide content determination. Examples of studies that have been conducted by our team will be discussed in this presentation. The recovery of fuel materials for analytical processing may in certain cases be complicated by encapsulation that requires preliminary characterization merely to plan and execute test material extraction. Non-destructive assay techniques such as gamma spectrometry, x-ray fluorescence, and x-ray diffraction can be vital tools in directing material recovery and subsequent destructive characterization efforts. For example, upon material extraction in clad fuels, problems may arise with the suitability of existing dissolution protocols to completely solubilize samples for destructive analysis without losing or introducing matrix constituents. For dissolved materials, existing chemical separation (ion-exchange or solvent extraction) schemes may require modification or further development work to provide high quality results. Chemical analyses discussed in this presentation will include measurements for radionuclides, assay, isotopic abundances, trace actinides, trace metals, and non-metals. The studies also examine material science details that offer critical clues to supplement chemical processing information. The outcomes of this work have provided fundamental information that is critical for nuclear applications and have a tremendous impact on safeguards verification and nuclear security. LA-UR-23-20355

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Advances in radiochemistry supporting the nuclear fuel cycle

249

Applications of liquid scintillation counting on Savannah River Site high activity matrices

David DiPrete[*], *Tad Whiteside*

Savannah River National Laboratory, Aiken, South Carolina, USA
[*]E-mail: david.diprete@srnl.doe.gov

Keywords: liquid scintillation counting, high activity waste, Savannah River Site, HLW

The Savannah River Site (SRS) is a US Department of Energy nuclear reservation established in the early 1950's as part of the US government's nuclear weapons programs. Currently, SRS is undergoing a process of environmental remediation, emptying waste tanks containing the residues from various neutron activated target processing as well as from the reprocessing of spent nuclear fuel to run the Site reactors. SRS continues to dissolve and dispose of spent nuclear fuel from its past processes as well as that retrieved from various research reactors in the SRS H-Canyon Separation Facility. H-Canyon process solutions, when injected into the waste processing system, is rendered caustic. The waste, when rendered caustic, separates into two phases. The two phases compose of a 6M sodium liquid phase with radiological constituents predominantly made up of Cs-137, and a sludge phase predominantly made up of Sr-90. The bulk of the actinide and lanthanide inventory are also contained in the sludge phase. The caustic phase is decontaminated of Cs-137 using a calixarene-based solvent-solvent extraction facility (Salt Waste Processing Facility). The extracted Cs-137 and the high-level sludge from the waste tanks are vitrified in SRS glass vitrification plant (Defense Waste Processing Facility). The decontaminated solutions are grouted and stored On-Site at the SRS Saltstone Facility.

The Nuclear Measurements Group (NMG) of SRNL is responsible for providing radiological characterizations for these highly radioactive processes, providing analyses for over 100 radioisotopes. Ironically, due to the wide swings in beta versus alpha activities in the various processes, one of the more challenging analyses are simple gross alpha and gross beta analyses. The NMG measures gross alpha and gross beta using a variety of methodologies, including analyses using gas flow proportional counters (GFPC), silicon charged particle spectrometers, and liquid scintillation counters. Liquid scintillation counters offer some advantages over the other methodologies for these higher activity matrices in that the sample aliquots are contained in liquid scintillation vials. LSC vials provide more contamination control, especially when measurement of low levels of alpha activity in the presence of orders of magnitude more beta activity or vice versa is desired. LSC is also less affected by high levels of dissolved solids often found in these waste matrices than are the GFPC or charged particle spectrometers.

The NMG makes heavy use of pulse shape discrimination with liquid scintillation counting to differentiate between alpha and beta activity when making these gross alpha/beta measurements. The laboratory uses both Perkin Elmer Tri-Carb and Hidex scintillation counters equipped with pulse shape discrimination. Performance of the two types of liquid scintillation counters, plus the challenges of using these pulse shape discrimination technologies in a production mode on the wide variety of sample matrices analysed in this laboratory will be discussed.

102

Tensioned metastable fluid detector sensing technology for multifarious-multiscale applications in the nuclear fuel cycle

Rusi Taleyarkhan

School of Nuclear Engineering, Purdue University, West Lafayette, Indiana, USA
E-mail: rusi@purdue.edu

Keywords: TMFD, negative pressure, neutron, alpha, fission, gamma-beta blind, dosimetry, medical

The nuclear fuel cycle presents multiscale and multitude detection-energetics-security-safeguards-dosimetry challenges which involve high-efficiency spectroscopic sensing of alpha-neutron-fission radiation signatures, for example, to identify U/Pu/Am/..Rn/Po isotopes – which may be terrestrial-air-fluid borne, moving/stationary, shielded-unshielded, etc., and which may need to be identified at ultra-trace (~10 nSv/h) levels, even under intense (>10^4 R/h) gamma-beta radiation fields which saturate most detectors. The novel tensioned metastable detector (TMFD) sensor technology[1] offers unique, cost-effective complement/alternative solutions for gaps in 80-y old state-of-art systems. Not well known is the ordinary fluids (like solids), can indeed be tensioned and placed under negative (sub-vacuum) pressure (*Pneg*) states at desired ambient temperature. The greater is the *Pneg*, the weaker become the intermolecular fluid bonds such that external stimuli) can provide the required excess energy to snap the bonds, leading to nano-to-macro space-time scale cavitation - manifesting as audible-visible-recordable detection events. In this regard TMFD sensors are unique and offer significant enabling attributes and unique enabling features (summarized in Table 1). The lecture will introduce TMFD developments, and present results of studies comparing TMFDs vs state-of-art systems for: (1) H*10-neutron (spectroscopy weighted) radiation health dosimetry for continuous and pulsed source spectra; (2) Air and/or liquid-borne trace (10^{-3} Bq/mL) quantity, high (keV) resolution hybrid mass-alpha Rn/Po/U/Pu/Am isotope assay; (3) Directionality enabled active-passive special nuclear material interrogation; (4) ~100% (10,000 R/h) gamma-beta rejected alpha-neutron-fission signals -low cosmic intensity (nSv/h) to high (multi Sv/h) environments, covering ranges of interest in the nuclear fuel cycle related fields.

Table 1 Why TMFDs for Nuclear Fuel Cycle?

✓ Thermal (eV) and Fast (1-100 MeV) Neutron Detection in single TMFD
  ☐ Without need for moderators, nor pulse-shape discrimination
✓ Tunable on demand (10-3-80%) intrinsic neutron detection efficiency
✓ ~95-100 %+ intrinsic (alpha/fission) efficiency –incl. trace mBq/mL levels.
✓ ~1.4 keV energy resolution
✓ 100% gamma-beta-muon blind (to 15,000+ R/h fields)
✓ Real-time neutron-alpha spectroscopy (without need for peak shape fitting)
✓ On-Off within seconds to microseconds –pulse mode enabling
✓ 10-9s event timing and multiplicity potential
✓ Directionality/source positioning with 1/2 TMFD units
✓ Air/fluid borne U/Am/Pu monitoring (100% Rn+progenyrejected)
✓ Rn+Poprogeny (pCi/L) in air spectroscopy monitoring (<2 min. air sampling)
✓ Active and Passive SNM Standoff Interrogation of stationary-moving SNMs
✓ Operation Space: Temperatures (0-50oC); >95% RH; Shock Tolerant
✓ Low-cost sensing material (<<0.1$/g)
✓ Open to Synergistic Collaborations

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Collaborative material excercise

251

Outcomes from the Seventh Collaborative Materials Exercise of the Nuclear Forensics International Technical Working Group

Olivia Marsden[1*], *Chloe Edgar*[1], *Andrew Heydon, Jon Schwantes*[2]

[1]Radiochemistry Group, AWE, UK
[2]Pacific Northwest National Laboratory, Richland, WA & Pennsylvania State University, University Park, PA, USA
[*]E-mail: Olivia.Marsden@awe.co.uk

Keywords: nuclear forensics, ITWG, CMX-7

The Nuclear Forensics International Technical Working Group (ITWG) is an informal association of official nuclear forensic practitioners (including law enforcement representatives, regulators, policy makers and scientists) dedicated to combatting the illicit trafficking of nuclear and radioactive materials. The ITWG is dedicated to improving nuclear forensic science primarily through the facilitation of table top and materials exercises. There is a total of 6 task groups that manage various aspects of the activities of the ITWG: ITWG's Nuclear Forensic Laboratories Task Group is responsible for promoting R&D activities and assisting in Nuclear Forensics investigations, the Outreach and Training Task Group shares technical developments and scientific findings, the Libraries Task group demonstrates the utility of a National Nuclear Forensics Library (NNFL), the Guidelines Task Group develops consensus guidelines for the Nuclear Forensics community, the Evidence and Testimony Task Group looks at crime scene management and the use of conventional forensic science, while the Exercise Task Group is primarily responsible for organizing and facilitating materials exercises, known as Collaborative Materials Exercises (CMXs), for the community. These materials exercises have been a prominent feature of ITWG activities since 1998. Since that time, a total of seven CMXs have been designed and executed, with participation by laboratories representing 29 countries and the European Commission. The purpose of the exercises is to advance nuclear forensics capabilities of the ITWG Nuclear Forensic Laboratories (INFLs) by tracking the state of practice and art of nuclear forensic science, identifying analytical techniques ready for operational use and new laboratory methods worthy of additional development.

Here an overview of the 7th, and most recently completed, CMX is provided. The CMX-7 included a new optional radiological crime scene module in collaboration with the Evidence and Testimony Task Group to encourage participation by law enforcement counterparts. A total of 19 laboratories have completed the exercise with 12 of those labs participating in the crime scene in a box. Each laboratory was asked to analyse three depleted uranium samples with varying matrices and compare it to an exemplar. The labs submitted preliminary reports to the exercise facilitator at 24 hours and 1 week, with final reports due after 2 months. A summary of those results will be given in the context of the exercise scenario and objectives of the mock nuclear forensic investigation.

174

Correlative morphological, elemental and chemical analyses of actinide-bearing particles - case of the CMX-7 exercise

Fabien Pointurier[*], *Olivier Marie*

CEA, DAM, DIF, F-91297 Arpajon, France
[*]E-mail: fabien.pointurier@cea.fr

Keywords: Raman spectrometry, scanning electron microscopy, nuclear forensics, uranium, chemical phases, correlative analysis

The objective of a nuclear forensic examination is to obtain information on the origin (place of production), the intended use and the processing history (including identification of the industrial process and date of production) of seized nuclear materials. Measurements of the isotopic composition of the main elemental constituent (by means of various mass spectrometry techniques) and of the radioactive emissions of the seized objects (by gamma-spectrometry) are generally carried out as a priority to address the threats of nuclear terrorism and proliferation. However, the laboratories involved in nuclear forensics investigations must measure many other characteristics of the nuclear materials to identify the origin and history of the seized objects. During the last decades, many signatures have been evaluated for these purposes, among which: concentrations of elemental impurities at trace level, the date of the last chemical purification of the materials, the isotopic compositions of stable isotopes (oxygen, lead, sulphur, etc.), surface morphology, crystalline structure and molecular composition, radioactive impurities at ultra-trace level (for instance plutonium and fission products in uranium), etc.

Besides, answers may be required even when “bulk” quantities of the materials are not available and when a small aliquot of dust or particles are the only available sample. Moreover, analyses at the micrometric level provides information on homogeneity of the materials and allow identifying possible mixtures of several materials. Therefore, to complement analyses performed on macroscopic amounts of nuclear materials, several laboratories implement micro-analytical techniques on tiny fragments, or even on µm-sized particles, extracted from the “bulk” objects, primarily mass spectrometry techniques to determine uranium isotopic composition [1]. At CEA/DAM, we also carry out morphological and elemental analyses of micrometric particles by means of scanning electron microscopy (SEM) combined with energy dispersive X-ray spectrometry (EDS). In addition, we regularly implement micro-Raman spectrometry (MRS) to identify the chemical phases in micrometric actinide particles [2] and when relevant a coupling device between a SEM (FEI “Quanta 200”) and a MRS (Renishaw “In Via”) which allows performing Raman analysis within the SEM [3,4] and, thus, correlating surface morphology, elemental composition and chemical phases for the same micrometric area.

In this presentation, we will discuss the pro and cons of the combined MRS, SEM and EDS analyses, and show several examples of correlative analyses in the field nuclear forensics (collaborative material exercises, or CMX). We will focus on the implementation of these techniques in the framework of CMX-7.

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Education in radiochemistry

166

A-CINCH project: Summary of the latest developments

Mojmír Němec[1*]*, Vivien Pottgießer*[2]*, Marko Štrok*[3]*, Elena Macerata*[4]*, Jan John*[1]*,*
Paul Scully[5]*, Roberta Cirillo*[6]*, Clemens Walther*[2]

[1]Czech Technical University in Prague, Department of Nuclear Chemistry, Prague, Czech Republic
[2]Institute of Radioecology and Radiation Protection, Leibniz Universität Hannover, Hannover, D-30419, Germany
[3]Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, Ljubljana, 1000, Slovenia
[4]Department of Energy, Politecnico di Milano, Piazza L. da Vinci 32, Milano, I-20133, Italy
[5]National Nuclear Laboratory, Warrington, England, UK
[6]European Nuclear Education Network (ENEN), Rue d'Egmont 11, 1000 Brussels, Belgium
[*]E-mail: mojmir.nemec@fjfi.cvut.cz

Keywords: CINCH, A-CINCH, nuclear, radiochemistry, education, training

The A-CINCH ("Augmented Cooperation in education and training In Nuclear and radio-CHemistry") is a Horizon 2020 project No. 954301 that has started in October 2020 with 17 partners from 13 countries with a duration of 36 months. It is built on and augments CINCH teaching tools developed in the three previous CINCH projects – CINCH, CINCH II and MEET-CINCH – in the CINCH project series (www.cinch-project.eu), and adds new tools and approaches based on actual technological and pedagogical development. CINCH project series in general focuses on coordination activities in both education and training field at all levels of academic and professional career in nuclear and radiochemistry (NRC). Regarding educational curricula and mutual interconnection between educational levels, it addresses also secondary, high school students and teachers with the aim to bring young generation to NRC thus making carrier in this field more understandable and attractive. Actual A-CINCH progress will be presented in more detail including overview of e-learning tools designed to attract younger students to the field of radiochemistry and chemistry in general.

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Mass spectrometry

219

Testing of ^{14}C excursions in tree rings from high- and mid-latitudes to explore other cosmic-ray events beyond intense solar flares

A. J. Timothy Jull[1,2*], *Irina Panyushkina*[3], *Mihály Molnár*[2], *Tamas Varga*[2], *Valerie Livina*[4], *Chris Baisan*[3], *Gregory C. Wiles*[5], *Nicholas Wiesenberg*[5], *Fusa Miyake*[6]

[1]Department of Geosciences, University of Arizona, Tucson, Arizona, USA
[2]Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Debrecen, Hungary
[3]Laboratory for Tree-Ring Research, University of Arizona, Tucson, Arizona, USA
[4]National Physical Laboratory, Teddington, Middlesex, UK
[5]School of Natural Resources, College of Wooster, Ohio USA
[6]Institute for Space-Earth Environmental Research, Nagoya University, Nagoya, Japan
[*]E-mail: jull@arizona.edu

Excursions in the annual ^{14}C production rate in the atmosphere can result in an excess of up to 20‰ in tree rings, caused by transient increases in the ^{14}C production rate. These signals or "spikes" rise rapidly over a period of 1–2 yr and have decay times of about 15-20 yr. These events are generally explained as a rapid increase of incoming cosmic rays or gamma rays. Only a few have been reproduced in multiple tree-ring records from many locations around the globe, particularly at 7176BCE, 5259BCE, ~660BCE, 774-775CE and 993-994CE reported by different laboratories. These excursions are positively connected to the impact of strong Solar Energetic Particles (SEP) events and are also confirmed from ^{10}Be and ^{36}Cl excursions in polar ice cores. Other events show different structures and either coincide with Grand Solar Minima or other effects of a lesser magnitude, including possible effects from supernovae. These include reported events at 815BCE, 5480BCE, 5410BCE, 1052/1054CE and 1279CE. We focus on a new detailed record of the 664-660BCE events from diverse locations and possible new records in the 11–13th century CE. It appears that the intensity and structure of the ^{14}C signal can be multifaced in space and time, which complicates understanding of the forcing and attribution to the underlying astrophysical events. Timing of these events is important to register the recurrence intervals of these events for past and future ^{14}C excursions and to understand the spatial dispersal of the ^{14}C signal. In addition, the presence of one of these "spikes" is in a tree-ring record also useful to tie down precise dating of archaeological samples.

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205

Fast and effective sample preparation and AMS C-14 analyses of iron material at HEKAL AMS Lab, Debrecen, HU

Mihály Molnár[1,2*], *Balázs Áron Baráth*[2], *László Szolnoki*[3], *János Dani*[1,3], *Anthony John Timothy Jull*[2,4]

[1]Isotoptech Zrt. H-4026 Debrecen, Hungary
[2]INTERACT Centre, ATOMKI, H-4026, Debrecen, Hungary
[3]Déri Museum, H-4026 Debrecen, Hungary
[4]Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA
[*]E-mail: molnarmihaly@isotoptech.hu

Keywords: iron, radiocarbon, AMS, sample preparation

In this study, we present a novel approach for C-14 analyses of iron material. C-14 contamination of iron material could happen in nuclear reactors, where the neutron flux could produce significant amount of C-14 atoms inside the iron based construction elements (vessel wall, tubes, etc). If those elements are going to be disposed in waste, then the C-14 concentration should be measured, reported. On the other hand, artefacts made from wrought iron, could also incorporate some C content from the applied heating material (charcoal, wood), which also deliver a measurable C-14 content into the iron. This C and C-14 might allow the C-14 based dating of the production of the iron tool. Iron meteorites also contain C-14 atoms due to the cosmic irradiation induced nuclear reactions, which could be used as estimation of the size of the object and their residence time on Earth.

For all the above listed applications, we need a good sample preparation method, to extract the C from the iron, without any external contamination. As the typical concentration is maximum a few percent C in the iron (m/m%), a complete combustion/oxidation of 0.1–1 g iron for this purpose is necessary. We present an elegant way of this preparation, using a LECO C744 type iron – C analyser. The exhaust gas of this automatized oxidizer is applied for trapping the produced CO2, for further isotope analyses. About 1g of iron is completely oxidized within 1 minute by the C744 unit, and the exhaust gas is collected. C yield, and reproducibility of this preparation method is investigated by AMS C-14 analyses of known age iron artefacts, and several C-14 reference materials.

This method could play an important role, when nuclear power plants are decommissioned and significant amount of iron waste has to be classified according their C-14 isotope content.

Acknowledgments

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214

Recent and future possibilities of ^{14}C analyses using AMS in the Czech Republic

Ivo Svetlik[*], *Kateřina Pachnerová Brabcová*

CRL, Nuclear Physics Institute, AS CR, Prague, Czech Republic
[*]E-mail: svetlik@ujf.cas.cz

Keywords: ^{14}C analysis, AMS, radiocarbon dating, non-dating applications of ^{14}C analysis

The Czech Radiocarbon Laboratory (CRL) has been running since 2004. The initial method, which was applied in our workplace, was based on benzene synthesise and liquid scintillation counting. The need of AMS based analytical methods was evident since the beginning. Throughout these years the demand for AMS analysis of small-mass samples began to increase radically. Therefore, approximately since 2009 our laboratory started with the first experiments for AMS based analysis of ^{14}C. Since the year of 2012 were our graphites prepared and sent for AMS measurement abroad. In 2018, our laboratory succeeded with a project proposal, which then allowed us to purchase and install the AMS facility MILEA (Multi-Isotope Low-Energy AMS) from Switzerland company Ionplus (Macková et al. 2021). This specific project RAMSES (Ultra-trace isotope research in social and environmental studies using accelerator mass spectrometry) also allowed us to intensively refine our methods of ^{14}C samples processing and thus our possibilities have been widened for both; dating and non-dating applications of ^{14}C analysis.

At present, besides the development of ^{14}C analysis methods (direct measurement of $^{14}CO_2$, scaling of sample matrix, reduction of the mass of analysed carbon), we are also involved in checking the reliability of radiocarbon dating, developing methods of dating historical mortar, using statistical methods and improving the ways of indicating disturbing effects, esp. Fresh Water Reservoir Effect, old wood effect, presence of difficult to remove residues (Pachnerová Brabcová et al. 2022). In combination of bomb radiocarbon peak dating with Wiggle Matching method and improved knowledge in the chronology of gradually regrowing tissues, our analyses find application in the protection of endangered species following the international CITES convention. Last but not least, we are trying to expand the use of ^{14}C analyses for non-dating applications such as monitoring ^{14}C activity around Nuclear Power Plants, estimation of local or regional Suess effect, determination of "biocarbon" content in raw materials or final products in chemical, pharmaceutical and food industries and in motor fuels or exhaust gases. The forthcoming presentation will provide a brief history of our laboratory and its current capabilities. We will also discuss future directions for the development of analytical methods and their applications, so that the current needs arising from the development of society at the domestic and international level can be taken into consideration.

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Neutron activation analysis

238

NAA for metrological applications at CENA/USP, Brazil

*Elisabete A. De Nadai Fernandes**, *Márcio Arruda Bacchi*

Nuclear Energy Center for Agriculture, University of São Paulo, Piracicaba, Brazil
*E-mail: lis@cena.usp.br

Keywords: agriculture, environment, food, interlaboratory comparison, reference material

Instrumental analytical methods were developed following the increasing demand for chemical measurements. In highly automated methods, some analysts use the instruments as "black boxes" that always produce correct results. However, interferences and calibration, amongst other issues, can cause poor results. In fact, the analysis starts by taking a representative sample of the bulk material, which is then prepared, often including separation and/or preconcentration of the analyte of interest. In these stages, critical errors may occur, such as loss by adsorption or volatilization, and contamination from air, glassware, reagents, etc. The implementation of good metrological practices is essential for quality assurance, comprising the use of certified reference materials and the frequent participation in proficiency tests or interlaboratory comparisons. Even when an analytical method is fully validated and proven to provide correct results within given uncertainties, there is the possibility for failure due to inadequate matrix-matching or different analyte level in a new sample. In this context, neutron activation analysis (NAA) is recognized for its special characteristics, presenting excellent linearity, little matrix effects, well-identified interferences, and no need for sample preparation. NAA has been applied in metrology studies at the Nuclear Energy Center for Agriculture (CENA) for about thirty years, with emphasis on agriculture and environment. The first relevant activity was the development of a reference material of soybean flour for major and trace elements, in a project coordinated by the International Atomic Energy Agency (IAEA) in the early 1990s. The systematic concern with the application of quality management and metrology began in 1995, through involvement in two projects coordinated by the IAEA (ARCAL XXVI and ARCAL LXXVI). The successful participation in the Inorganic Analysis Working Group (IAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM), initiated in 2001, contributed to provide practical evidence for the recognition of NAA as a primary method of measurement. Following the development of a green coffee reference material, which was a pioneer initiative in the country, several other actions were taken for developing reference materials, with the financial support of Brazilian agencies and association with other research groups. Now organized as a technological innovation center on metrology and quality for agriculture, the actions aim at providing reference materials and interlaboratory comparisons for public and private laboratories, considering the difficult access to such metrological tools available at international level. Seven interlaboratory comparisons were run from 2015 to

2022 with the reference materials produced, composed of different matrices as rice, tomato leaves, sugarcane leaves, tomato pulp, pet food, and organic coffee. A record subscription of 84 laboratories was achieved in the ongoing comparison on the biodynamic brown rice reference material. Here, data will be presented to illustrate the relevance of the NAA for these metrological applications.

58

Neutron activation analysis of matrices and elements difficult to assay by other methods

Jan Kučera[*], *Jan Kameník*

Nuclear Physics Institute of the Czech Academy of Sciences, Husinec-Řež 130, Czech Republic
[*]E-mail: kucera@ujf.cas.cz

Keywords: neutron activation analysis, trace elements, nanocarbons, biochar, plastics, uranium materials, nuclear forensics

There are several specimen types and elements that are difficult to assay by conventional analytical techniques, especially if the complete sample decomposition is required, and that can conveniently be assayed by neutron activation analysis (NAA). We provide several examples of such cases, namely nanocarbon materials, biochar, plastics, and uranium materials.

Nanocarbons are currently on the cutting edge of material science research due to their exceptional properties and interesting applications. However, their properties are frequently depending on the content of elemental impurities. Their determination by classical analytical techniques is a challenging task due to difficulties in dissolution of these materials without analyte losses and/or contamination. We determined by instrumental NAA (INAA) that graphene prepared from graphite by several synthesis procedures contains highly variable amounts of metallic contaminations that originate from the reagents themselves and significantly influence graphene electrocatalytic properties. On the other hand, using INAA we found that graphene purified of in a stream of CF_2Cl_2 at 2500°C contains 3 to 4 orders of magnitude lower levels of elemental impurities and exhibits poor electrocatalytic activity. The use of INAA for elemental characterization of a certified reference material (CRM) SWCNT-1 (Single Walled Carbon Nanotubes) allowed to extend certified values for 5 elements determined by ICP-MS with mass fractions of 13 additional elements, assigned as reference values. INAA of commercial SWCNTs revealed low recoveries of several elements by ICP-OES when alkaline oxidation was used as a digestion method.

Biochar is obtained by pyrolysis of sewage sludge (SS) and can be used as a soil amendment and fertilizer. However, biochar can contain, in addition to numerous nutrients, also potentially toxic elements and compounds and therefore its composition needs to be investigated to assure its safe use in agriculture. A comparison of biochar analysis by ICP-OES after various digestion procedures and by INAA is presented. We found significant differences in contents of several elements, as well as differences in certified values of one SS CRM.

Polymers to be used in the containment of nuclear power plants, e.g., as insulation of electrical cables of safety systems must nowadays be qualified as concerns their maximum allowable content of halogens and metals with low melting point. Similar restrictions also apply for polymers to be used in cables of high energy physics facilities, such as the Large Hadron Collider at CERN. These cables should be "halogen and sulfur free" to prevent a serious damage of such facilities in the case of fire. Here we present the use of INAA for the determination of halogens and sulfur, which can be accomplished in a shorter time and with a smaller sample mass compared with alternative analytical methods.

Finally, we present a novel NAA procedure with pre-irradiation removal of uranium for panoramic determination of trace elements in uranium materials for nuclear forensics purposes. The determination of more than 10 trace elements allowed us to obtain information about a linkage among 4 samples analyzed. Such analysis is difficult to be carried out by other techniques, including ICP-MS.

Using the above cases, which are certainly not exhaustive, we have again demonstrated that NAA is the favourable and sometimes indispensable technique for assay of certain matrices and elements.

244

Self shielding effect in a strong absorber of Gd in neutron activation analysis

Gwang-Min Sun[1*], *Kishore B. Dasari*[1,2], *Jaegi Lee*[1], *B.G. Park*[1], *M.S. Kim*[1]

[1]Neutron Utilization Research Division, Korea Atomic Energy Research Institute, Daejeon, Republic of Korea
[2]Research Institute of Natural Science, Gyeongsang National University, Jinju, Republic of Korea
[*]E-mail: gmsun@kaeri.re.kr

Keywords: self-shielding effect, strong absorber, Gd, effective absorption radius

^{155,157}Gd are non-1/v absorbers and 2200 m/s absorption cross-sections of ^{155}Gd and ^{157}Gd$_{⍰}$is 60,900(1,100) b and 254,300(4,900) b, respectively, which are the highest among the stable natural isotopes. Their effective absorption radii are 1.38 Å and 2.84 Å, respectively. Macro cross-section for ^{157}Gd($\Sigma_{\gamma,157}$) is about 970 cm^{-1}, and absorption mean free path(λ_γ) is about 10 μm. The neutrons with energy around a resonance at 0.0314 eV, and the lower-energy neutrons undergo the self-shielding effect due to the strong absorption within the target. And the thick target also shows heavy self-shielding effect. To check the change of the neutron spectral density inside the target, we investigated the absorption rate of neutrons at the condition of the parallel neutron beam incident on a purely absorbing planar Gd target of various thicknesses and the diluted Gd samples with thin target approximation. The effect of strong absorption within the target was investigated on the concept of effective absorption radius. Considering the actual experimental environment, it was difficult to make a thin target ($⍰_{⍰}(v_r)$ t<<1) because the cross-section of Gd is very large even when t ~ 1 μm. In order to satisfy the condition of $⍰_{⍰}(v_r)t \sim 0.1\% \ll 1$, the thickness of t ~ 10^{-8} cm must be implemented. Therefore, in the case of an element with a high cross-section such as Gd like this study, target was made as a diluted target by dissolving Gd_2O_3, $^{155}Gd_2O_3$, and $^{157}Gd_2O_3$ in nitric acid and diluting them respectively. We investigated the non-linearity in the analytical sensitivity of Gd according to the Gd mass and some theoretical evaluation was done and the simulation was compared with the experimental results.

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Nuclear forensics

246

Results from the fourth version of the Galaxy Serpent exercises demonstrating the utility of nuclear forensics libraries

James Borgardt[1]*, Naomi Marks*[2]*, Stephen LaMont*[3*]

[1]Department of Physics, Juniata College, Huntingdon, PA, USA
[2]Lawrence Livermore National Laboratory, Livermore, CA, USA
[3]Los Alamos National Laboratory, Los Alamos, NM, USA
[*]E-mail: lamont@lanl.gov

Keywords: national nuclear forensics library, nuclear forensics, Galaxy Serpent, uranium fuel pellets

Galaxy Serpent is an ongoing series of virtual, web-based exercises designed to develop and strengthen nuclear forensics capabilities of participating teams. Each offering of the exercise is based upon a different nuclear or other radiative (RN) material, and features a hypothetical storyline involving recovery of material out of regulatory control. Teams are provided a robust but manageable dataset for surrogate RN material from which the organize a model nuclear forensics (NF) library, and answer mock investigative questions asking them to assess consistency with the material in their model library and ascribe confidence levels. The exercises are designed to provide demonstrate the value of national nuclear forensics libraries in support of an investigation involving RN material found out of regulatory control, and allow teams to simulate dialogue between a NF lab and an investigative team. The fourth iteration of the exercise, using model data from intact and crushed uranium fuel pellets as the material of interest, was recently concluded, and summative findings from will be presented including technical methodologies employed, and benefits and challenges teams have reported. These exercises have been conducted over the past decade, with a fifth iteration underway, and the online nature of the exercises allowed them to continue during recent challenges associated with the pandemic. A fifth version of the exercise is currently underway.

163

Direct measurement of Pb isotopic composition by laser ablation multi-collector ICP-MS in uranium ore concentrates

Zsolt Varga[*], *Adrian Nicholl, Maria Wallenius, Klaus Mayer*

European Commission, Joint Research Centre (JRC), Karlsruhe, Germany
[*]E-mail: zsolt.varga@ec.europa.eu

Keywords: Pb isotopic composition, LA-MC-ICP-MS, uranium ore concentrate

Nuclear forensics is a key tool in nuclear security and serves to address the threats of nuclear smuggling, nuclear proliferation and nuclear terrorism. The aim of a nuclear forensic examination is to provide clues on the history of the material and on its intentional use. This is accomplished by measuring material properties, which are indicative of the material's origin and production method [1, 2]. In nuclear safeguards and nuclear forensics, several characteristics (material properties) of the material in question can be applied either to verify the declared origin (*safeguards*) or to identify the source of an unknown, often illicit nuclear material (*nuclear forensics*). These characteristics involve, for instance, concentrations of major, minor and trace-level constituents, isotopic composition of the major and (selected) minor components, material morphology or molecular structure [2, 3]. However, accurate measurement of the isotopic composition of trace-level impurities (e.g. S, Sr, Pb or Th) often turns out to be tedious, time consuming and labour-intensive.

Pb isotopic composition plays a significant role in the origin assessment of U-based materials (e.g. U ores, U ore concentrates). As the isotopes of radiogenic lead (^{206}Pb, ^{207}Pb, and ^{208}Pb) derive from the decay of the parent uranium and thorium radionuclides, their relative amounts depend on the age and the composition of the ore deposit. Another advantage of using Pb isotope ratios is that since U is present at elevated levels in uranium ores compared to the average values of the Earth's crust, the Pb isotopic composition is significantly different from the natural lead and its documented variability. Thus, Pb isotope ratios are widely used in nuclear forensics in spite of the often encountered difficulties related to the measurements problems (e.g. time-consuming chemical separations required, cross-contamination).

In this work, we used a laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) technique to measure directly the Pb isotopic composition in uranium ore concentrates (yellow cakes). We analysed several yellow cake samples of world-wide origin. As for this technique virtually no manipulation or chemical separation is needed, we can avoid the problems deriving from tedious sample preparation, laboratory blanks and cross-contamination. The analysis could be performed in a few hours. Moreover, the Pb isotopic-inhomogeneity at micron-scale was measured to assess the different constituents, another advantage that cannot be accomplished by the traditional, bulk method. The achieved precision of the Pb isotope ratios was ~0.1%, so it enabled us to easily differentiate the samples with different origin. The developed technique proved to provide useful additional information and is considered a promising method in addition to the existing nuclear forensic tools. Also, other stable isotope ratios using laser ablation ICP-MS are foreseen to be measured in the future.

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Nuclear instrumentation and methodology

239

CHNet-MAXI: Muonic atoms X-ray spectrometry for isotopic analysis of cultural heritage samples

Massimiliano Clemenza[1*]*, Adrian Hillier*[2]*, Matteo Cataldo*[1,2]*, Katsu Ishida*[2]*,*
Oliviero Cremonesi[1] *and CHNET_MAXI Collaboration*

[1]INFN Division of Milano-Bicocca, Milan, Italy
[2]ISIS Neutron and Muon Source, Science and Technology Facilities Council (STFC), Didcot, UK
[*]E-mail: massimiliano.clemenza@mib.infn.it

Keywords: muonic atoms, isotopic analysis, cultural heritage samples

The measurement of isotope ratios, especially for samples containing lead, is a powerful tool for provenance studies of ancient artefacts [1], but the techniques used in the archaeometry field are all invasive and destructive (TIMS, ICPMS) [2]. This kind of approach makes them hardly usable on valuable objects since the authorities and museum for cultural heritage are hesitant to grant authorization for the use of analytical techniques that are invasive. The technique that CHNET_MAXI experiment aims to develops, and optimize, is based on the detection of characteristic Gamma and X radiation emitted by the atoms/isotopes following negative muons irradiation performed at the Rutherford Appleton Laboratory ISIS Neutron and Muon source in United Kingdom. In the next few years, ISIS has planned to install an array of detectors to achieve a solid angle coverage of at least 2π, thus significantly increasing the detection efficiency and consequently the sensitivity, for the measurement of both elements and single isotopes. The goal is to study and select among all the possible reactions, the most "sensitive" figures of merit that are created following the irradiation of samples containing different isotopes. A fundamental phase of the experiment would be the study, by irradiating plates of material enriched in the isotopes 204-206-207-208 of Lead, of all the possible figures of merit: the isotopic shift of the lead muonic X-rays; the gamma prompt emission following muon capture; the activated nuclides with their half-life and the emission of characteristic gamma rays.

In this work, a fundamental contribution will come from Monte Carlo simulations. Starting from the results obtained with the current measurement setup present at PORT4 of the ISIS Muon source facility, simulations will be performed to evaluate the capabilities of a high-efficiency germanium array and of a more compact system based on innovative scintillator crystals. The latter combine good energy resolution with a response speed that allows an increase in the solid angle, bringing the detection system closer to the sample without excessively increasing the detection dead time. A simulation software that precisely implements the entire experimental setup will be of fundamental importance. With mu-ARBY, an application based on GEANT4 it will be possible not only to model different experimental set-ups and reproduce calibration and measurement experiments on samples of interest, but it will be possible to simulate the entire measurement setup including the incident muon beam and the emission of X-rays and gamma prompts from muon atoms. In particular, the first phase of the experiment will involve the irradiation of plates of isotopically enriched material for the isotopes 204-206-207-208 of Lead for the characterization of all the possible "figures of merit": the isomeric "shift" of muon X-rays, the prompt gamma emissions following simple muon capture or with neutron emission and finally the activated radionuclides with characteristic half-life and gamma emissions. The second phase, on the other hand, will involve, through Monte Carlo simulations, a sensitivity study by "extrapolating" from the results obtained with the current measurement setup, those obtainable with the high-efficiency Germanium array.

The development/optimization of the hardware will be a prerequisite for the sensitivity study; it will be necessary to: implement an acquisition system with bi-parametric analysis using the latest generation digitizer, to be tested with the current set-up and then implemented in the 7 HpGe "mini-array"; set up a compact detection system based on innovative scintillators read by SiPM; implement an ad hoc beam monitor for small tags with a compact acquisition system; purchase and test a portable laser scanner system for the implementation of samples with complex geometries within the mu-ARBY software

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120

The experience with five years exploitation of digital germanium gamma spectrometers with muon sensitive veto shields

Jerzy W. Mietelski[*], *Krzysztof Gorzkiewicz*

Institute of Nuclear Physica, Polish Academy of Sciences, Kraków, Poland
[*]E-mail: jerzy.mietelski@ifj.edu.pl

Keywords: digital gamma spectrometer, anticoincidence shield, low background gamma spectrometry, comic muon flux

In September 2018 we started operation of our first digital gamma spectrometer equipped with veto shield. It consist of Canberra (USA) BEGe 5030 detector situated in passive shield of 15 cm lead shield (inner 5 cm made of 2500 years old lead) with acrylic, Cu, and Cd linings with LN_2 flush through shield [1]. The external active shield consist of five large plastic scintillators (by Scionix, The Netherlands) with the biggest from top having 70x70x5 cm dimensions. Acquisition is based on CAEN (Italy) digitizer DT5725. Data is registered event by event with time stamp resolution of up to 4 ns. The analyses if performed off –line using home written software VETO. The analyses of coincidences allows to find the relative delays between each pair of detectors. In January 2021 we started operation of the second similar system, this time with the coaxial type 35% efficiency HPGe detector (by Baltic Scientific Instruments, Latvia), 10 cm lead shield (~60 years old lead),five large scintillators (by Scionix) and again CEAN digitizer and VETO software used off line. The main feature of veto shield is approximately 63% further reduction of background in case of detector with 15 cm lead shield and 42% for the second system (with 10 cm lead). Inside this second shield we installed 12 containers with distilled water (5 L each) and we started to observe presence of 2223 keV n-capture gamma line. Applied digital acquisition system and off-line data analyses along with manifold ways of data exploration methodes allowed to study muon flux time variation on a long time basis [2] and now the 60 L of water inner shield allows us to do similar for neutrons. Despite the appearance of additional gamma line within background the presence of water reduces the continuum background in range 250-1250 keV and diminished the other neutron induced gamma lines. The off-line analyses allows also to find the events with simultaneous passing of more than one muon at time. Moreover, it allows also to analyse the structure of gamma spectrum in certain time period after passing of muon [3]. For example, the neutron effects start to appear about 1900 ns after a passage of the muon what is a result of production of neutrons in shield by impacting muon. Plotting a map where on the energy of registered gamma ray is presented versus the delay from a passage of muon the X-ray fluorescence peaks are clearly delayed regarding the moment of an appearance of the annihilation line.More details will be given during a conference.

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Nuclear methods in material structure studies

8

Development of non-destructive and depth-selective carbon quantification method in steel by negative muon lifetime analysis

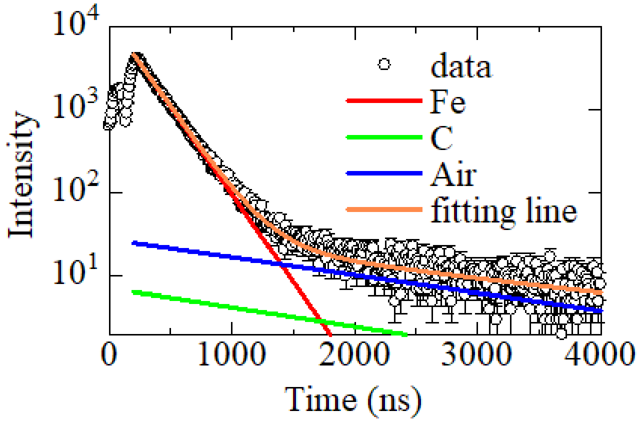
Kazuhiko Ninomiya[1,2*], *Michael Kenya Kubo*[3], *Makoto Inagaki*[4], *Go Yoshida*[5], *I-Huan Chiu*[1], *Takuto Kudo*[2], *Shunsuke Asari*[2], *Sawako Sentoku*[3], *Soshi Takeshita*[6], *Koichiro Shimomura*[6], *Naritoshi Kawamura*[6], *Patrick Strasser*[6], *Yasuhiro Miyake*[6], *Takashi U. Ito*[7], *Wataru Higemoto*[7], *Tsutomu Saito*[8]

[1]Institute for Radiation Sciences, Osaka University, Toyonaka, Osaka, Japan
[2]Graduate School of Science, Osaka University, Toyonaka, Osaka, Japan
[3]Division of Natural Sciences, International Christian University, Mitaka, Tokyo, Japan
[4]Institute for Integrated Radiation and Nuclear Science, Kyoto University, Kumatori, Osaka, Japan
[5]Radiation Science Center, High Energy Accelerator Research Organization, Tsukuba, Ibaraki, Japan
[6]Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki, Japan
[7]Advanced Science Research Center, Japan Atomic Energy Agency, Tokai-mura, Ibaraki, Japan
[8]National Museum of Japanese History, Sakura, Chiba, Japan
[*]E-mail: ninomiya@rirc.osaka-u.ac.jp

Keywords: muon, non-destructive analysis, muonic atom, lifetime analysis

Steel is one of the most fundamental and important materials for human kinds. It is known that the properties of steel are influenced by the amount of impurity elements, such as carbon. Although there are great needs to quantification of carbon contents in steel, general non-destructive analytical methods such as X-ray fluorescence (XRF), cannot be applied. Here, we propose a completely new non-destructive quantification method of sub-percent carbon contents using negatively charged muons based on their lifetime in a material.

Muons are obtained as a beam with an intensity of about 10^6 /s by accelerator facilities. When a muon stops in a substance, the muon is trapped in the Coulomb field of a nucleus and forms a bound state with the nucleus. Such an atomic system having one muon instead of an electron is called a muon atom. The captured muon is finally absorbed by the nucleus or decays into an electron (β^- decay). Since the absorption rate of muon into the nucleus differs depending on the atomic number (more precisely, isotope) of muon capturing atom, it is possible to identify the element by measuring the lifetime of decay electrons.



We have been developing this method at the muon facility in J-PARC (J-PARC MUSE); the world's highest intense pulsed muon beam source. Muon irradiation experiments for steel samples placed in air were conducted and emitted decay electrons were measured by a large solid-angle electron detector system. Figure 1 shows the muon lifetime spectrum obtained from muon irradiation for the steel sample containing 0.42% carbon. The spectra were analyzed by 3 components; iron, carbon and air, and intensity of each component was determined.

Using standard steel samples, the relation between the muon capture probabilities of C/Fe and elemental composition of C/Fe was obtained. The detection limit of this method was estimated to be 140 ppm. Furthermore, by controlling the incident kinetic energies of muons, non-destructive and depth-selective analysis have been demonstrated for analysis of a stacked sample consisting of three kinds of steel plates with the carbon contents of 0.2, 0.5 and 1.1%.

In this study, we clarified that high-sensitive, non-destructive and regioselective analysis of the carbon contents in steel can be achieved by measuring lifetime of muon. Since this method is non-destructive, this method can be applied for various research fields; it becomes a powerful tool not only for quality control analysis of steel production, but also for analysis of precious iron archaeological artifacts.

Production of radionuclides

173

Networking activities of European Research Reactors to sustain scientific use, industrial services, and radioisotope supply

László Szentmiklósi[1]*, on behalf of the TOURR*[2]*, SECURE*[3] *and LENS*[4] *collaborations*

[1]Nuclear Analysis and Radiography Department, Centre for Energy Research, Budapest, Hungary
[2]Towards Optimized Use of Research Reactors in Europe (TOURR)
[3]Strengthening the European Chain of sUpply for next generation medical RadionuclidEs (SECURE)
[4]League of Advanced European Neutron Sources (LENS)
[*]E-mail: szentmiklosi.laszlo@ek-cer.hu

Keywords: research reactors, neutron sources, networking, irradiation, transnational access, medical isotopes

For many years Europe has had a powerful ecosystem of neutron facilities, supporting an expert community of researchers, and delivering science, innovation, and competitive advantage through economic impact for the European society. However, the European neutron ecosystem is experiencing a period of significant change and has been destabilized following the closure, prolonged maintenance downtime periods, COVID-19 pandemic-related issues, or underutilization of a number of facilities.

The TOURR (Towards Optimized Use of Research Reactors in Europe, https://www.tourr.eu/) project, funded by the Euratom research and training programme 2019–2020 under grant agreement No. 945 269, aims to evaluate the current and future needs for Research Reactors and neutron sources in Europe. The main targets of the project are to assess the impact of the decreasing number of RRs, identify future needs (including potentially new neutron sources), draw a roadmap for the upgrade of the existing RR fleet, and develop a model for harmonized resource utilization. The natural starting point for this analysis was to get a picture of the current situation. A questionnaire has been distributed among RR operators and based on the results of the initial analysis, ENEN produced a data base of European research reactors and their respective utilization. Based on these inputs, a detailed SWOT and gap analysis has been made. A common toolkit and a collaboration platform are being developed to facilitate smooth collaboration and to take advantage of the complementarities.

Another aim of the TOURR project has been to evaluate the current and future need for neutron sources to produce medical radioisotopes in Europe. This effort culminated in the idea of the SECURE project (Strengthening the European Chain of sUpply for next-generation medical RadionuclidEs, https://enen.eu/index.php/portfolio/secure-project/), financed in the HORIZON-EURATOM-2021 call. SECURE project aims to make a major contribution to the sustainability of medical isotope production and its safe application in Europe. It is focusing on promising developments in the design of irradiation targets and production routes for existing and new isotopes in nuclear therapy and diagnostics. Isotopes critical in the success of nuclear medicine are selected and research activities are identified to address some of the major challenges in securing its future availability, with the objective to remove critical barriers along the production of selected alpha- and beta-emitting isotopes that restrict their sustainable production by reactors and accelerators.

The League of advanced European Neutron Sources (LENS, https://lens-initiative.org/), a collaboration comprising nine European-level neutron research facilities, supports the international scientific community by providing access to beamline instruments and/or offering related expertise. Within this collaboration, BNC called for "BNC LENS beam time" proposals in February 2022 to ease the unprecedented shortage of neutrons in several neutron sources all over the world. The action targeted neutron users whose experiment(s) have allocated beam time at any LENS facility's user program but not yet scheduled for any reason, provided that - at least an essential part of - the experiment is technically feasible to accomplish on BNC instruments.

44

Extension of IAEA recommended cross section data base for production of therapeutic isotopes

Ferenc Tárkányi[1*], *Alex Hermanne*[2], *Anatolij Ignatyuk*[3], *Sándor Takács*[1], *Roberto Capote*[4]

[1]Institute for Nuclear Research, Debrecen, Hungary
[2]Cyclotron Department - TONA, Vrije Universiteit Brussel, Brussels, Belgium
[3]Institute of Physics and Power Engineering (IPPE), Obninsk, Russia
[4]NAPC, Nuclear Data Section, International Atomic Energy Agency, Vienna, Austria
[*]E-mail: tarkanyi@atomki.hu

Keywords: therapeutic radio-isotopes, charged particle induced reactions, recommended cross section and yield data

Radionuclide-based diagnostics and therapies require a proper selection of the nuclear production route based on knowledge of the reaction excitation functions and the derived achievable yields. Data on the possible radionuclide impurities are also important. Optimization of reliable cross section values for those isotopes of interest in medical applications are of considerable interest to IAEA-NDS. Several actions to set up a database for recommended cross-sections and associated nuclear decay data for the charged-particle reactions used for medical radionuclides production have been started over the last 25 years. In the last period new candidate therapeutic isotopes appear. An extended study of the reaction list makes the selection of the optimal reaction easier and depends on many factors (available beam particles and their achievable energy range, targetry and possible recovery problems with enriched target materials, production yield, radio-nuclidic impurities and necessary chemical separation processes). In the present work the existing IAEA data base for production of therapeutic isotopes was extended, with recommended cross section for 60 nuclear reactions leading to formation of ^{47}Sc, ^{47}Ca(^{47}Sc), ^{58m}Co, ^{71}As(^{71}Ge), ^{71}Ge, ^{77}Br, ^{80m}Br, ^{103}Pd(^{103m}Rh), ^{103}Ru(^{103m}Rh), ^{105}Rh, ^{117m}Sn, ^{119}Sb, ^{134}Ce, ^{135}La, ^{161}Tb, ^{165}Er, ^{165}Tm(^{165}Er), ^{167}Tm, ^{197m}Hg, ^{197g}Hg and ^{230}Pa. Systematics and difficulties encountered during compilation, evaluation and Padé fitting on selected published experimental cross sections values are discussed.

The data base includes figures of all available data in comparison with the theoretical predictions available in the TENDL 2021 library. Also the selected experimental data and the recommended data with uncertainties obtained by Padé fit and the calculated physical yields, based on recommended data are shown. Numerical values for recommended data and for the deduced integral yields are shown in tables and all information will be available on the Web page of the IAEA Nuclear Data Section at https://nds.iaea.org/radionuclides and also at the IAEA medical portal https://nds.iaea.org/medportal.

Prompt gamma activation analysis

63

Improvement of the analytical workflow for prompt-gamma activation analysis

László Szentmiklósi[1*], *Zsolt Révay*[2], *József Östör*[3], *Boglárka Maróti*[1]

[1]Nuclear Analysis and Radiography Department, Centre for Energy Research, Budapest, Hungary
[2]Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II), Technische Universität München, Garching, Germany
[3]HyperLabs Software, Budapest, Hungary
[*]E-mail: szentmiklosi.laszlo@ek-cer.hu

Keywords: prompt gamma activation analysis, digital signal processing, data acquisition, peak fitting, concentration calculation

The analysis workflow of Prompt gamma activation analysis at the Budapest Neutron Centre's PGAA and NIPS-NORMA facilities, at the MLZ FRM II PGAA station, and many other centers worldwide relied on the use of the well-known Hypermet-PC gamma spectrometry software and the ProSpeRo concentration calculation Excel macro. This evaluation procedure was established in the late nineties and was compatible with the computing environment and data acquisition hardware of that era. The procedure has been validated for several matrices and provided excellent results, as well as uncertainty budgets for about twenty-five thousand PGAA spectra over the years. However, the peak fitting procedure was cumbersome and required up to an hour of an experienced analyst for a complicated spectrum, such as metals. Moreover, the event count rate of the detector had to be limited to avoid the distortion of the peak shapes. The sustained interest of our user community called for a higher sample throughput of the existing PGAA facilities, which needed improvement in both hardware and software aspects. To achieve this goal, and establish a common basis for the analytical practice, a Budapest-Garching collaboration was formed.

From the hardware side, computer-controlled sample changers and neutron collimators were installed, the unattended mode of data taking was worked out, and new, state-of-the-art gamma spectrometers were put in place. After careful testing, the ORTEC DSPEC 502A model was found to meet the challenges of neutron-capture gamma spectroscopy. It demonstrated superior energy resolution, a more symmetric peak shape, even in the noisy environment of a reactor's experimental hall, can handle the non-ideal RC-feedback preamplifier signal shape of our HPGe detectors, and can collect energy spectra in 64k histogram bins. With the dual-input model, one can implement digital Compton suppression, which is an alternative to analog Compton suppression circuits made of many NIM modules. Most importantly, the spectrometer has about a threefold increased count rate tolerance, directly reducing the needed beam time per sample, while still maintaining a fittable peak shape.

The much-improved data acquisition had to be matched with a capable and more automated evaluation procedure. The increase of the histogram channels from 16k to 64k makes the bin width comparable to those used in NAA; this improves the attainable Chi-squares during peak fitting, especially for the intense, low-energy multiplets. To properly analyze the 64k SPC spectra and the dual unsuppressed/suppressed output saved in the N42 format, the 2022.2 version of the Hyperlab software package was developed. Its nuclear database, efficiency-, nonlinearity-, and peak width calibrations, as well as its evaluation algorithms, were fine-tuned towards the needs of PGAA so that after an automated fit, the spectrum regions require much fewer user adjustments than previously with the Hypermet-PC. This makes the spectrum evaluation overall more efficient. The PeakFit utility, intended to evaluate the Doppler-broadened boron peak and the annihilation region, was also revised to handle the new spectrum properties.

Finally, the ProSpeRo concentration calculation Excel macro was made compatible with Hyperlab's efficiency and peak list format. The other new features of ProSpeRo will be highlighted in a separate presentation.

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196

Determination of chlorine in the corrosion layer of archaeological iron artefacts by PGAA

Friedrich E. Wagner[1*], *Rupert Gebhard*[2], *Christian Stieghorst*[3], *Peter Albert*[2],
Herbert Hess[2], *Ursula Wagner*[1], *Werner Häusler*[1], *Zsolt Revay*[3], *Petra Kudejova*[3],
Krzysztof Kleszcz[3]

[1]Physics Department, Technical University of Munich, 80747 Garching, Germany
[2]Archaeological Collection of the Bavarian State, 80538 Munich, Germany
[3]Heinz Maier-Leibnitz Zentrum (MLZ), Technical University of Munich, 85747 Garching, Germany
[*]E-mail: fwagner@tum.de

Keywords: chlorine, archaeological iron artefacts, PGAA, X-ray diffraction, Mössbauer spectroscopy, leaching, heat treatment

Archaeological iron finds often undergo a secondary destructive corrosion process after excavation, in which chlorine present in the corrosion layer of such artefacts is supposed to play a major role [1]. It is therefore desirable to be able to determine the chlorine content of such objects in a non-destructive manner. While chemical methods require the dissolution of the objects, and X-ray fluorescence is of little use since it probes only a very thin surface layer, neutron activation analysis using prompt gamma rays (PGAA) is well suited to measure chlorine contents in the ppm range in iron. Since PGAA uses an external neutron beam, rather large pieces can be studied. The neutron irradiation produces practically no long-lived radioactivity in the studied objects. These can therefore be returned to museum collections within days or weeks after the analysis.

PGAA studies of archaeological iron objects were performed at the Heinz Maier-Leibnitz Zentrum in a neutron beam of about 2x2 cm^2 cross section or smaller at an attenuated neutron flux between 1 and 5×10^8 $cm^{-2}s^{-1}$. A Compton-suppressed spectrometer consisting of a 60%-HPGe detector surrounded by a BGO scintillator in anti-coincidence mode was used to detect the prompt gamma radiation of Fe and Cl. The data were acquired by a digital DSPEC-50 spectrometer. The mass of iron in the beam was between 1 and 10 grams. It can be determined from the intensity of the prompt gamma rays of iron. The Cl content was determined from the intensity ratio of typical Fe and Cl gamma lines. Within a measuring time of one hour a relative statistical accuracy of about 5 % can be obtained for this ratio. The detection limit for Cl in iron is about 10 ppm. In order to decide on appropriate methods of conservation of iron artefacts, it is important to know the amount of Cl in an object. In a study of about 50 iron artefacts from Celtic sites in Bavaria, many from the oppidum of Manching, which were excavated between about 1890 and 2013 it turned out that these objects show a considerable scatter of the Cl content (about 20 to 3000 ppm), not only between different objects, but also within the same piece. Objects excavated at the end of the 19th century contain as much Cl as objects excavated only recently, in contrast with the idea that the widespread use of fertilizers in the last decades causes increased Cl contents of buried iron artefacts.

It is common practice in the conservation of iron artefacts to subject them to Cl extraction procedures. The most widespread method is leaching in alkaline solutions, a process that usually takes months. Using standard methods, the effectivity of the leaching process can be estimated only by measuring the amount of Cl in the leaching solution. PGAA allows one to study the residual Cl content of leached objects. We have tested standard leaching methods in this way. The effectivity of heating specimens to temperatures up to 800 °C in reducing atmospheres was also tested, both with archaeological specimens and with test samples prepared in the laboratory. These studies were accompanied by X-ray diffraction and Mössbauer measurements of the transformations of the iron oxyhydroxides in the corrosion layers.

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Radioanalytical methods of long-lived radionuclides

189

Half-life determination of ^{53}Mn

R. Dressler[1*], *J. Ulrich*[1], *D. Schumann*[1], *P. Sprung*[1], *K. Kossert*[2], *N. Kneip*[3], *D. Studer*[3], *T. Kieck*[3], *K. Wendt*[3], *X. Mougeot*[4], *P. Cassette*[5], *Y. Amelin*[6]

[1]Paul Scherrer Institut Villigen, Switzerland
[2]Physikalisch-Technische Bundesanstalt Braunschweig, Germany
[3]Johannes Gutenberg-Universität Mainz, Germany
[4]Laboratoire National Henri Becquerel at the Commissariat à l'Energie Atomique, Palaiseau, France
[5]St. Kliment Ohridski University Sofia, Bulgaria
[6]Australian National University Canberra, Australia
[*]E-mail: rugard.dressler@psi.ch

Keywords: radiochemical separation, inductively-coupled plasma mass spectrometry (ICP-MS), thermal ionization mass spectrometry (TIMS), liquid scintillation counting (LSC), half-life determination

The isotope ^{53}Mn is a radionuclide produced primarily during explosive stellar burning phases in both thermonuclear and core-collapse supernovae explosions. Although the primordial ^{53}Mn in the Early Solar System is now extinct, its former presence can be observed by enhancements of its daughter ^{53}Cr in meteorites and asteroidal samples. The ^{53}Cr/^{52}Cr isotope ratio derived from a "fossil isochron", in conjunction with precisely determined Mn/Cr abundance, provides a proxy of the ^{53}Mn/^{55}Mn isotope ratio at the formation-time of our Solar system and can thus be used as a chronometer for the dating of alteration events in that time period. In addition, the ^{53}Mn/^{55}Mn isotope ratio can be used directly as a chronometer for dating surface exposure and burial time of sediments on Earth up to 20 Ma back [1], given the half-life is known with sufficiently low uncertainty.

The present work reports on the determination of the half-life of ^{53}Mn using a combination of isotope dilution mass spectrometry for the measurement of the numbers of atoms, and liquid scintillation counting for the measurement of activity. A combination of high mass resolution Multi-Collector Inductively-Coupled Plasma Mass Spectrometry (MC-ICP-MS) and Thermal Ionization Mass Spectrometry (TIMS) were used for the determination of the number of ^{53}Mn atoms, whereas the activity was determined using several Triple-to-Double Coincidence Ratio setups (TDCR).

The ^{53}Mn sample, chemically separated from irradiated steel samples, underwent an isotope mass separation using the off-line radioactive ion beam facility of the RISIKO laser mass separator facility to get rid of ^{53}Cr and ^{54}Mn. These isotopes would interfere with the mass spectrometric and activity measurements.

We will present the deduced half-life as well as the details on the sample preparation and the corresponding mass spectrometric and activity measurements [2].

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151

Recent advances in radiochemical methods: How did we get here?

Sherrod L. Maxwell[1*], *Dan McAlister*[2]

[1]Radiochemical Solutions, LLC, Boulder, Colorado, USA
[2]Eichrom Technologies, LLC, Lisle, Illinois, USA
[*]E-mail: smax1500@gmail.com

Keywords: rapid, radiochemical, actinides, separations, radionuclides

Over the last twenty years, we have made tremendous strides in the radiochemistry community to improve analytical techniques to measure actinides such as plutonium, uranium, americium, curium, and thorium in a wide range of challenging sample matrices, including water (seawater to drinking water), soil, air filters, rocks (granite, limestone and marble), bioassay samples (urine and fecal), food samples (animal tissue, up to 1 kg of rice), and building materials (steel and concrete). In addition to long-lived radionuclides, there have been significant analytical advances in rapid analytical techniques to measure shorter-lived radionuclides such as strontium-89/90, radium and polonium isotopes. More recently the radiochemical advances we have developed together are being applied to high level plutonium and uranium materials (metals/oxides), as well as to the fast-changing world of nuclear medicine. How did this happen? What were some of the drivers for these improved capabilities? What gamechangers were in play? The benefits that have been realized include faster turnaround times, reduced costs, improved quality such has higher chemical yields and more effective removal of chemical interferences. These advances have also improved emergency response and response to radiological events, including occupational events such as a puncture wound or inhalation requiring rapid measurements and timely medical treatment to minimize dose. The novel approaches that got us here will be examined, while recent developments will be noted and future needs discussed.

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Radioecology and environmental radioactivity

123

Integrated passive sampling and liquid scintillation counting analysis for high-resolution atmospheric tritium water vapor monitoring

Bin Feng[1,2*], *Martin Ibesich*[2], *Franz Renz*[1], *Georg Steinhauser*[2]

[1]Institut für Anorganische Chemie, Leibniz Universität Hannover, Hannover, Germany
[2] TU Wien, Institute of Applied Synthetic Chemistry & TRIGA Center Atominstitut, Vienna, Austria
[*]E-mail: binfjf@outlook.com

Keywords: tritium, atmosphere, passive sampling, LSC analysis

Rapid development of civilian nuclear power in the global and upcoming discharge of tritium-contaminated wastewater from Fukushima may significantly increase regional tritium levels in the near future[1]. For better assessing the operational status of nuclear faculties and the potential radioecological impacts on environments, there is a need to obtain high-resolution and reliable environmental tritium monitoring data. Although the time-integrated monitoring method, which integrates passive sampling and liquid scintillation counting (LSC) analysis, provides a low-cost and convenient way to achieve the above goal, it is difficult to use a simple sampler design and a single LSC analysis protocol to monitor atmospheric tritiated water vapor (HTO) in varied environments[2]. In this presentation, we would introduce our recent efforts to address these problems. Briefly, we systematically studied the factors controlling sampling performance and developed different sampler designs for indoor and outdoor HTO monitoring[2-3]. Using active sampling devices, we quantitively evaluated the sampling performance (i.e., sampling rate, sampling stability, and environmental flexibility) of new-designed passive samplers. In addition, we optimized the LSC preparation protocols for different monitoring proposes[4]. Combining above efforts, we proposed a framework for atmospheric HTO monitoring in different environments, which has been successfully applied in investigating large-scale HTO baseline in mainland China[5] and constructing 3D HTO distribution matrix in a reactor hall. As a result, our work would provide practical experience in acquiring high-resolution tritium data, which is hoped to better address future challenges posed by increased anthropogenic tritium emissions to the field related to nuclear safety and ecological health.

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243

Intermediate depth underground research laboratory – searching for an optimal location

Renata Kierepko[1*]*, Dominik Grządziel*[1]*, Agata Walencik-Łata*[2]*, Miłosz Ogórek*[3]*,*
Aleksandra Puławska[4]

[1]Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland
[2]University of Silesia in Katowice, August Chełkowski Institute of Physics, Chorzów, Poland
[3]Faculty of Energy and Fuels, AGH University of Science and Technology, Cracow, Poland
[4]Bochnia Salt Mine, Bochnia, Poland
[*]E-mail: Renata.Kierepko@ifj.edu.pl

Keywords: intermediate depth underground laboratory, salt deposit, low radioactive background, in situ gamma-ray measurements, natural radioactivity

The underground laboratory (UL) is an element of the scientific infrastructure system, which enables research to be carried out in low radioactive background conditions. These exceptional (unique) circumstances can be used to conduct experiments in physics, astrophysics, geophysics, biology, electronics, etc. The choice of the optimal location for such UL must be a compromise between economy, access to the site, local structural stability, and the safety of humans, etc. However, one of the most critical parameters is a low radioactive background mainly related to the type of deposit, site depth and ventilation efficiency.

In 2022, the Institute of Nuclear Physics Polish Academy of Sciences (IFJ PAN) signed a letter of intent together with the “Bochnia” Salt Mine (BSM) and the “Wieliczka” Salt Mine (WSM) to conduct joint research. Both mines are well-connected with academic centres in Poland, including Krakow (45 km and 15 km from Bochnia and Wieliczka), capable of providing scientific staff and specialised technical services for future research. BSM and WSM are now official Polish Historical Monuments and UNESCO world heritage sites. However, the lower technical levels (about 200 - 300 m deep) can be used as excellent scientific sites.

Based on the intent document, preliminary studies of the activity concentration of natural radioisotopes (^{234,238}U and ^{232}Th, which required radiochemical preparation and ^{40}K) in rocks and water (brine) using alpha and gamma spectrometry, ^{222}Rn in the air as well as in situ gamma-ray measurements, were carried out. The obtained data set that will be presented at the conference indicates that both locations (BSM and WSM) may be considered as potential UL locations at a depth of about 700 m w.e. (water equivalent) where measured in-situ gamma radiation count rate in the energy range 40 – 2700 keV per mass of Ge is between 40 – 150 $s^{-1}kg_{Ge}^{-1}$, effective radiation dose rate varied from < 10 to 40 nSv/h. Based on the literature data [1], muon flux equals about 0.06 $m^{-2}s^{-1}$. These results showed a low level of natural radioactivity and indicated both locations as appropriate for planned scientific activities.

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192

Experimental and computational study on the inhibitory effect of phytic acid on U(VI) biomineralization by *Shewanella putrefaciens*

Xiaoqin Nie[1*], *Xiaojing Lu*[1], *Yangyang Zhang*[2], *Wencai Cheng*[1], *Xiaoan Li*[4], *Faqin Dong*[1,3], *Jun Li*[2]

[1]Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory, Southwest University of Science and Technology, Mianyang 621000, China
[2]Department of Chemistry and Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China
[3]Key Laboratory of Solid Waste Treatment and Resource Recycle of Ministry of Education, Southwest University of Science and Technology, Mianyang 621010, China
[4]Mianyang Central Hospital, NHC Key Laboratory of Nuclear Technology Medical Transformation, Mianyang 621000, China
[*]E-mail: xiaoqin_nie@163.com

Keywords: *Shewanella putrefaciens*, U(VI), phytic acid, quantum-theoretical modeling, biomineralization

Uranyl (UO_2^{2+}) species with hexavalent U(VI) oxidation state is the most ubiquitous form of uranium in natural minerals, underground water, contaminated soils, and ocean. Interplay between bioorganic molecules and U(VI) is rather complicated due to its various complex configurations and reaction network. In this study, the widely present phytic acid (IP_6) is selected as a model organic molecule together with the bacteria *Shewanella putrefaciens* (*S. putrefaciens*, existing mainly in marine environments) to explore its role on U(VI) biomineralization. We find that phytic acid has a clear inhibition effect on the U(VI) removal of *S. putrefaciens*, with the absorption capacity drop from 382.77 mg/g to 102.45 mg/g. Further Dialysis experiment suggests that phytic acid tends to chelate with U(VI) to form colloid polymer due to the coordination of the oxo-ligand of phytic acid to uranyl dication. Quantum-theoretical modeling has confirmed that phytic acid binds strongly with uranyl ions, while calcium and magnesium ions can bind with phytic acid as well via ionic bonding, thus relieving the inhibition effect of phytic acid in the solution through breaking the hydrogen bonding network. XRD and SEM-EDS results show that phytic acid can hinder the formation of mineralized body (Metanatroautunite [$Na(UO_2)(PO_4)\cdot 3H_2O$]) and prefers to form amorphous material. Further FTIR and XPS data illustrate that the bacteria mainly interact with U(VI) through phosphorous functional groups. This study presents detailed information for colloid formation between phytic acid and U(VI) as well as the critical role of Ca^{2+} and Mg^{2+} ions on the matrix of *S. putrefaciens* bacteria, thus providing molecular-level microscopic understanding on the chemical behavior of U(VI) in the presence of inorganic and organic ions in the soil.

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207

Tracing airborne micro-particles released by Al-industry using actinides

Laurent Pourcelot[1*], *Olivier Masson*[1], *Béatrice Boulet*[2]

[1]Institut de Radioprotection et de Sûreté Nucléaire IRSN, Saint-Paul-lez-Durance, France
[2]Institut de Radioprotection et de Sûreté Nucléaire IRSN, Orsay, France
[*]E-mail: laurent.pourcelot@irsn.fr

Keywords: actinides, aerosols, tree leaves, red muds

Industry remains an important source of environmental contamination by heavy metals and metalloids which may pose a serious threat to the ecosystems and the population. Especially the alumina production from bauxite ore gives rise to large amount of liquid and solid wastes since the production of 1 kg of alumina involves same weight of solid residue, the well-known red muds enriched in iron and heavy metals. Up to now, without any valorization of by-products, the red muds are stored in artificial ponds which are a potential source of pollutants for the surroundings due to the uplift of red dust under strong wind conditions. The study of plants allows filling the gap of knowledge concerning air quality over a wide potentially contaminated area. Thus, the current work aims to compare the activity concentration of natural radionuclides (^{238}U, decay products and ^{232}Th) in plants leaves (*quercus robur* and lettuces), in grains (wheat) and leaf vegetables with those of aerosols and the potential sources of atmospheric particles from soils and above all the red dust emitted from the dried ponds and from the piles of bauxite.

The activity concentration of natural radionuclides such as ^{238}U, some decay products and ^{232}Th was determined in plants samples taken according to the two dominant wind directions, at plots located 100 to 1,500 m from the basins. Furthermore, the atmospheric particles were taken in the same areas, using a high-volume aerosol sampler. The increase of ^{232}Th and ^{238}U activity concentration in a few trees leaves (a factor 9 and 4, respectively) and in some aerosols samples is accompanied by a decrease of ^{238}U/^{232}Th activity ratio of these matrices. Such low ratio suggests that the airborne particles emitted by bauxite piles and red mud basins - those latter's are also characterized by low ^{238}U/^{232}Th - first contaminate the atmosphere and then the leaves surface, after deposition. Available at distance greater than 1,000 m from the ponds, locally produced foodstuffs do not show any excess of radionuclides, suggesting low influence of airborne micro particles from the alumina production. Thus, the actinides measured in leaf vegetables rather derived from the soil micro-particles deposited onto leaves than from an anthropogenic sources.

Radiolabeled compounds and radiopharmaceuticals

23

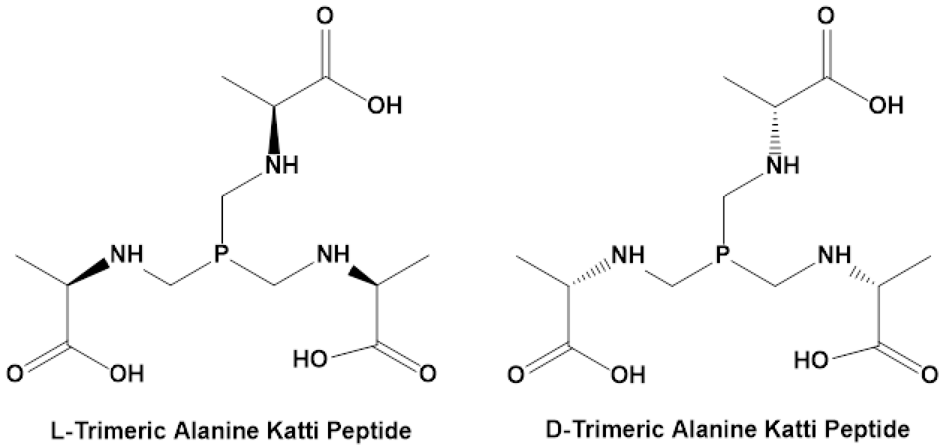
'Katti Peptides' toward green approaches in the creation of breast tumor specific ^{99m}Tc-carbonyl conjugates of trimeric (D- and L-) alanine-conjugates—Radiolabeling and preclinical investigations

Penelope Bouziotis[1], Kavita K. Katti[2], Danai Efraimia Bajwa[1],*
Evangelia-Alexandra Salvanou[1], Alice Raphael Karikachery[2], and Kattesh V. Katti[2]

[1]Radiochemical Studies Laboratory, INRASTES, NCSR "Demokritos", 15341 Ag. Paraskevi, Athens, Greece
[2]Institute of Green Nanotechnology, Department of Radiology, University of Missouri Medical School, One Hospital Drive, Columbia, Missouri 65212, USA
[*]E-mail: kattik@health.missouri.edu

Keywords: Katti Peptides, Tc-carbonyl, breast tumors, SPECT imaging, sustainable and green

In order to meet the increased demand for biomass accumulation and to sustain redox homeostasis, tumor cells manifest diversion of glucose metabolism through upregulation of amino acid metabolism. Mitochondrial dysfunction of cancer cells results in loss of the ability to synthesize essential, as well as specific non-essential, amino acids adequately to support their rapid growth, metastases and proliferation. This results in increased demand from cancer cells for amino acids through upregulation of amino acid transporters which are over expressed on the surface of tumor cells. For example, two amino acid transporters, SLC7A5 and SLC7A11, have been shown to be essential for the growth and proliferation of breast tumor cells. The exogenous amino supply-dependent tumor biological characteristics of tumor cells, therefore, presents unprecedented opportunities to develop amino acid-radiolabeled probes for both diagnostic imaging and therapy of various cancers. Our radiolabeling strategy of amnio acids is based on a trimeric amino acid structural motif because trimeric amino acid/peptide structures efficiently promote receptor-mediated intracellular delivery of radiolabeled drugs into tumor cells. We herein present the utility of both the trimeric D- and L-alanine called as 'Katti Peptides' (See Figure 1), discovered in our laboratories for radiolabeling with a SPECT imaging Tc-99m-tricarbonyl probe. Radiolabeling protocols and preclinical tumor targeting of ^{99m} Tc(CO)3-labled with both trimeric D- and L-alanine 'Katti Peptides' are discussed. We discuss in this presentation on how the efficient metabolism of both D- and L-trimeric alanine (Katti Peptides) by tumor cells can be used as an effective targeting strategy to image breast tumors through SPECT imaging using [^{99m}Tc]Tc-D- (or L-) trimeric alanine peptide radiopharmaceuticals. Green and sustainable approaches for radiopharmaceuticals design using D- and L-alanine Katti Peptides, their radiolabeling protocols with ^{99m}Tc and details of preclinical investigations using tumor-bearing SCID mice bearing 4T1 breast cancer xenografts, and comparisons of the in vivo kinetics of the radiolabeled amino acids will be discussed.



L-Trimeric Alanine Katti Peptide

D-Trimeric Alanine Katti Peptide

Figure 1: Structures of multidentate trimeric D- and L-alanine (Katti Peptides)

270

Ga-68-Trivehexin for imaging of carcinomas: The way to clinics

Johannes Notni

TRIMT GmbH, 01454 Radeberg, Germany
E-mail: tum@notni.de

In the context of nuclear medicine and theranostics, integrin-related research and development was, for most of the time, focused predominantly on 'RGD peptides' and the subtype αvβ3-integrin. However, there are no less than 24 known integrins. The subtype αvβ6-integrin is found on epithelial cells, and is up-regulated in various carcinomas, in fibrotic diseases such as IPF, and furthermore in the lung tissue of patients suffering from Long Covid syndrome. Hence, αvβ6-integrin is a highly interesting target for nuclear imaging and therapy. Ga-68-Trivehexin is a Ga-68-labelled trimeric conjugate of an cyclic nonapeptide as a highly specific PET tracer targeting αvβ6-integrin. A high target specificity of this radiopharmaceutical was confirmed in preclinical studies. First clinical application proved its suitability for sensitive PET-imaging of pancreatic carcinoma and HNSCC [1]. The results of Ga-68-Trivehexin imaging in approx. 50 PDAC patients will be discussed. The results of an on-going immunohistochemistry drived study of αvβ6-integrin expression in human cancer specimen furthermore confirmed its up-regulation in various other carcinomas, e.g., ovarian and lung adenocarcinoma. Since recent literature even reported the expression of αvβ6-integrin in lung lesions associated with the long covid syndrome, Ga-68-Trivehexin seems to be a versatile tracer with a high clinical potential.

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Radionuclide separation

29

Development of radiochemical techniques for the measurement of (n,2n) cross sections at the National Ignition Facility

John D. Despotopulos[*], *Dawn A. Shaughnessy, Narek Gharibyan, Kenneth E. Gregorich, Kenton J. Moody*

Lawrence Livermore National Laboratory, Nuclear and Chemical Sciences Division, Livermore, CA, USA
[*]E-mail: despotopulos1@llnl.gov

Keywords: isotope production, radiochemical separations, target preparation, cross sections

The National Ignition Facility (NIF) is an Inertial Confinement Fusion (ICF) research facility at Lawrence Livermore National Laboratory. During an ICF shot, a high-density carbon (HDC) capsule filled with deuterium and tritium (DT) is compressed to extreme densities and temperatures with 192 high energy laser beams. The resulting DT fusion produces alpha particles and a significant yield (currently up to 10^{18}) of 14.1 MeV neutrons in a short pulse (~100 ps). Material on the inside of the target capsule sees extremely large neutron fluxes ($10^{27\text{-}33}$ n/s/cm^2), allowing cross section measurements to be made with low amounts of target material (~10^{13} atoms). The non-thermal, 14.1 MeV neutron spectrum and exceedingly small amount of target material required for measurements allows for the study of reactions that cannot be measured at conventional nuclear reactor or particle accelerator facilities.

To take advantage of these unique capabilities for cross section measurements at NIF, target material must be added to the inner surface of HDC NIF capsules. These capsules are 2-mm (outer diameter) with a 10 µm fill hole, which is used to add the DT fuel. Any dopant added to the capsule must be extremely pure and contained in a very small volume of solution as the total volume of the capsules only ~3 µL and contaminants, such as salt (Na, K, Ca, etc.), can easily plug the microscopic fill hole after solution is added and dried. Two systems have been successfully developed with capabilities for doping NIF capsules. The first, Apparatus for NIF-Doping Automated Robotic Injection System for Targets (ANDARIST), is based on microinjection of material through the fill hole with a micro-capillary. The other system, Vacuum Optimized Radionuclide-to-Capsule Administer for NIF (VORCAN), uses a vacuum to pull liquid into the capsule.

To measure a cross section at NIF, the capsule must not only be doped with the nuclide of interest, but also a flux monitor with a well-characterized cross section to enable accurate calculation of the unknown cross section. However, this requires the isotopes with known and unknown cross sections are intimately mixed and chemically similar to minimize fractionation in the NIF shot. Both isotopes must have an additional tracer isotope to quantify for both the insertion into the capsule and the post-shot collection efficiency. Based on these stringent parameters, a specific radionuclide cocktail must be determined for each experiment and new radiochemical techniques that have been developed to meet these needs will be discussed. Reaction products are collected via Solid Radiochemistry Collectors (SRC) in the NIF target chamber. These can be removed post-shot for gamma-ray spectroscopy and radiochemical separations, as needed, to analyse the reaction products. Radiochemical separations for analysis of post shot debris will be discussed.

Initial efforts for cross section measurement at NIF are focused on the measurement of the ^{89}Y(n,2n)^{88}Y and ^{88}Y(n,2n)^{87}Y reaction cross sections, which can be used as a benchmark for future cross section measurements. Initial results from NIF shots with doped capsules will be discussed as well as efforts to quantify rare earth element fractionation during the NIF shot.

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194

Towards aqueous chemistry of superheavy elements @ FAIR

Jan John[1], Pavel Bartl[1], Mojmír Němec[1], Jan Štursa[2], Jon Petter Omtvedt[3],*
Ch.E. Düllmann[4,5,6], A. Yakushev[5]

[1]Department of Nuclear Chemistry, Czech Technical University in Prague, Prague, Czech Republic
[2]Nuclear Physics Institute, Czech Academy of Sciences, Řež, Czech Republic
[3]Department of Chemistry, University of Oslo, Oslo, Norway
[4]Department of Chemistry – TRIGA Site, Johannes Gutenberg University Mainz, Germany
[5]GSI Helmholtzzentrum für Schwerionenforschung GmbH, Darmstadt, Germany
[6]Helmholtz Institute Mainz, Mainz, Germany
[*]E-mail: jan.john@fjfi.cvut.cz

Keywords: FAIR, superheavy elements, transactinides, aqueous chemistry

Currently the international accelerator facility FAIR, one of the largest research infrastructure projects worldwide, is under construction in Darmstadt, Germany. The scientific user community of FAIR is organised in a set of experimental collaborations, one of which is NUSTAR – Nuclear Structure, Astrophysics and Reactions. The NUSTAR collaboration is focused, among others, on Superheavy Element Research (SHE). The SHE-subcollaboration within NUSTAR@FAIR perfors cutting-edge SHE research maintaining also a leading position for the search for new superheavy elements. Among the world-class equipment, the gas-filled physical preseparator TASCA is already operational and studies of the chemistry of SHEs in gas phase, as they are already ongoing, are foreseen to be extended within FAIR.

Czech Republic is an associated member of FAIR since March 2019. Czech research infrastructure FAIR-CZ (Facility for Antiproton and Ion Research - participation of the Czech Republic), included in the Roadmap of Large Infrastructures for Research, Experimental Development and Innovation of the Czech Republic, addresses the approach of the Czech Republic to FAIR. The in-kind contributions to FAIR construction will consist of contribution to some of the experiments and supply of some key equipment. Since 2023, a new research topic and group – Aqueous chemistry of SuperHeavy ElementS (ASHES) – became a part of the FAIR-CZ team.

The ASHES collaboration was formed around a new SHE homologues laboratory commissioned at the Nuclear Physics Institute (NPI) Řež at the U-120M accelerator beamline as a joint effort of Czech Technical University in Prague (CTU), University in Oslo (SISAK group) and the Nuclear Physics Institute Řež. The focus of ASHES is on miniaturization of liquid-phase chemistry by introducing elements of microfluidic chemistry, such as the chemistry-on-the-chip, aiming at orders-of-magnitude decrease of the consumption of chemicals and making full use of its potential for acceleration. The in-kind contribution of ASHES to FAIR will be a microfluidic device for liquid-phase chemistry of SHE comprising a) aerosol-to-liquid low-flow system, b) microfluidic liquid-liquid extraction and phase separation chips set-up, c) electrochemistry chips set-up, and flow-through on-line detectors and verified experimental techniques. The modules are and will continue to be successively tested in the

SHE homologues laboratory in Řež focusing on Sg (Mo and W homologues) and prospectively also Nh (Tl homologue) chemistry and building on the previous and on-going research such as Modular robotic gas-jet target system (MARGE) design and commissioning, new concept for Gas-jet conversion into liquid stream using the Particle into Liquid Sampler (PILS), Microfluidic liquid-liquid extraction set-up commissioning and use for the Sg and Nh homologues studies, microfluidic electrochemistry or on-line gamma- or alpha-spectrometry in solution. Examples of these studies will be given in the presentation.

Acknowledgments

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266

Nature resourced radiochemistry: Proposed in RANC 2019, Status in RANC 2023

Susanta Lahiri[1,2]

[1]Diamond Harbour Women's University, Diamond Harbour Road, Sarisha, South 24 Parganas 743368, India
[2]Sidho-Kanho-Birsha University, Ranchi Road, Purulia 723104, India
E-mail: susanta.lahiri@skbu.ac.in

In the second International conference on radioanalytical and nuclear chemistry (RANC 2019), we proposed nature resourced radiochemistry. In nature resourced radiochemistry, the chemical is identified from nature and would be used in radiochemical separation studies. In 2019, it was a mere proposal and stray literature review, In the conference we received suggestions on this new field of research which helped a lot to develop this new field as scientifically vibrant. In last three years, we have developed successfully radioanalytical separation schemes with nature resourced chemicals mainly with two components of tea, caffeine and catechin. As the radioisotopes are produced in no-carrier-added state, therefore it is not possible to experimentally determine the structure of metal-ligand complex. Therefore, we have taken the help of DFT calculations to determine the structure of radioisotope-caffine or radioisotope-catechin complex. In the conference, I shall discuss in details the development of nature resourced radiochemistry that took place in last four years.

3

Production, separation and detection techniques for chemical studies of superheavy elements

Alexander Yakushev[1,2*]

[1]GSI Helmholtzzentrum für Schwerionenforschung GmbH, Darmstadt, Germany
[2]Hemholtz Institute Mainz, Mainz, Germany
[*]E-mail: a.yakushev@gsi.de

Keywords: superheavy elements, recoil separators, gas chromatography

The 7th period of the periodic table of elements is completed with the discovery of superheavy elements (SHE) up to element 118, oganesson (Og) [1]. With increasing atomic number, the SHE production cross sections and their lifetimes significantly decrease to picobarn and subseconds, respectively. This makes the study of chemical properties of SHE extremely challenging. The high nuclear charge in SHE influences the electron shell structure strongly and thus also their chemical properties. This causes deviations of the chemical behaviour relative to that of their lighter chemical homologs [2]. Chemical studies of SHE comprise several individual tasks: i) SHE production, ii) physical and chemical separation, and iii) detection. Most advanced techniques, ensuring the most efficient production and separation, as well as the unambiguous detection and interpretation, are needed for successful chemical studies [3].

Production requires highly intense beams of rare stable isotopes, provided from continuously improved heavy ion accelerators. These beams impinge on radioactive actinide targets, which have to withstand highest beam intensities. Prior to the chemical separation, atoms or ions of the superheavy elements should be selectively transported from their production site to a chemical setup. The combination with a kinematic recoil separator used as a pre-separator has proven to be the most advanced method in SHE chemistry studies. The chemical separation techniques in the gaseous phase (gas-phase chromatography) are less time consuming and thus more efficient than the separation techniques in (aqueous) solutions, e.g., liquid-liquid extraction and ion exchange chromatography. Thus, to date, only the former technique was applied in chemical studies with elements beyond seaborgium (Sg, element 106) [3].

Comprehensive studies of these aspects resulted in many achievements at GSI Helmholtzzentrum für Schwerionenforschung, similarly to other heavy-ion accelerator laboratories [4]. Continuous developments of the gas chromatography and detection techniques allowed performing series of successful experiments with element 113, nihonium (Nh), element 114, flerovium (Fl) and element 115, moscovium (Mc) at GSI behind the gas-filled recoil separator TASCA [5, 6]. For the chemical identification of more short-lived elements beyond Mc, a new faster technique for the extraction of SHE ions into a chemical separation and detection setup is required. A new compact gas-stopping cell UniCell is being under development now and it will allow shortening the extraction time by a factor of 100 [7].

The breadth of technical aspects of the SHE chemistry will be discussed with the focus on the efficiency and the unambiguous chemical identification of the heaviest elements.

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Oral Presentations

Actinide analytical chemistry

72

Rapid actinide isotopic analysis by wavelength modulation spectroscopy in an atomic beam

Alonso Castro[*], *Wei Wei*

Actinide Analytical Chemistry Group, Los Alamos National Laboratory, Los Alamos, NM, USA
[*]E-mail: acx@lanl.gov

Keywords: isotopic analysis, wavelength modulation spectroscopy

We present our results on the development of methods and instrumentation for the isotopic analysis of the actinides. The method consists of generating an atomic beam by heating a small amount of sample to temperatures up to 2000 °C. The atomic beam is interrogated by a tunable diode laser with a 300 kHz bandwidth, which is much narrower than the typical atomic absorption widths of the actinide isotopes. Thus, measuring the absorption spectrum of the actinide sample reveals its isotopic composition. In addition, in order to greatly increase the sensitivity of the technique, we have incorporated wavelength modulation spectroscopy techniques to our instrument. To this end, the laser wavelength is rapidly modulated at 8 kHz by a sinusoidal current. As the interaction between the rapidly modulated laser wavelength and the frequency dependent cross-sections introduces new frequency content centered at the harmonics of the modulation frequency f_m, absorption can be detected at the modulation harmonics $n \cdot f_m$. By doing so, detection is shifted into the high-frequency domain and low-frequency additive noise can be rejected. We have demonstrated the technique to determine isotope ratios of uranium samples at various levels of enrichment in under 10 minutes.

68

Investigation into plutonium content of pyrochemical processing byproducts

Cecilia Eiroa-Lledo[1], Angela Olson[1], Lav Tandon[2], Jung Rim[1], Nick Hubley[1], Michael Schappert[1], Elmer Lujan[1], Mary Knaak[1], Tabitha Kalin[2], Bonnie Klamm[2], Nick Anderson[2], Fran Rein-Rocha[2], Jared Mason[2], Tracy Wenz[3], Steve Betts[3], Eric Ewing[2], David Rodriguez[2]*

[1]Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, NM, USA
[2]Metal Production, Los Alamos National Laboratory, Los Alamos, NM, USA
[3]Non-destructive Assay and Vault Operations, Los Alamos National Laboratory, Los Alamos, NM, USA
*E-mail: Cecilia.eiroa@lanl.gov

Keywords: analytical chemistry, pyrochemistry, plutonium

Plutonium pyrochemical processes are utilized for various purposes including Pu metal formation and Pu metal purification. This presentation will outline the current investigation of metal pyrochemical processing byproducts for plutonium and other trace metal content. Many large-scale metal separation processes will yield considerable amounts of salt and crucible byproducts that can contain high amounts of Pu and other metal impurities. Understanding the concentrations and total amounts of plutonium and other elements in the byproduct residue is critical for waste management purposes, as material sent for waste disposal needs to contain as little plutonium as possible. The goal of this study is to determine the total Pu content in certain waste materials and identify other trace impurities that might be present alongside Pu, especially those that might impact waste disposal and potential Pu recovery.

Various non-destructive techniques were used to determine concentrations of plutonium, americium-241, and neptunium-237, including gamma spectrometry and neutron counting. For other trace metals, destructive techniques including inductively coupled plasma spectrometry were used. Results from this study can aid in determining if the Pu and other trace element content in byproduct salts and crucibles would make these materials suitable for safe disposal and potential Pu recovery. LA-UR-23-20442.

Acknowledgments

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24

Development of automated microfluidic system for actinide analysis

<u>Shuang Yu Han</u>[1], Bernard Treves Brown[1], Matthew Higginson[2], Philip Kaye[2],*
Clint Sharrad[1], Scott Heath[3]

[1]Department of Chemical Engineering, University of Manchester, Oxford Road, Manchester, M13 9PL, UK
[2]AWE, Aldermaston RG7 4PR, UK
[3]Department of Mechanical, Aerospace & Civil Engineering, University of Manchester, Oxford Road, Manchester, M13 9PL, UK
[*]E-mail: Shuangyu.han@manchester.ac.uk

Keywords: microfluidic device, automation, uranium, solid phase extraction, inductively coupled plasma, mass spectrometry

Advancement in analytical device miniaturisation through microfluidic technology offers an alternative approach towards radiochemical analysis. When compared to traditional macroscale analytical process, microfluidics devices manipulate and process fluid samples typically in the microlitre range, which provides benefits in terms of more efficient mixing and precise conditions control that are not feasible in macroscopic systems while reducing waste generation.

Microfluidic extraction devices are fabricated using poly (methyl methacrylate). Recovery and separation of uranium from trace elements relevant to the nuclear fuel cycle are demonstrated using UTEVA® chromatographic resins packed within the microdevice in concentrated nitric acid media. enabling analysis of nuclear materials with a drastic volume reduction to ≤2 ml per analysis.

A novel online analytical system was also developed in parallel. Where flows from the microfluidic separation system are redirected towards a coupled ICP-MS system, enabling online analysis of trace elements and actinide as it is separated within the microdevice with minimal operator – sample interaction. Such an online microdevice – ICP-MS/OES system enables automated separation-detection of radioactive samples within 2 hours of sample uptake while generates less radioactive waste, satisfying the As Low As Reasonably Achievable (ALARA) principle.

Figures

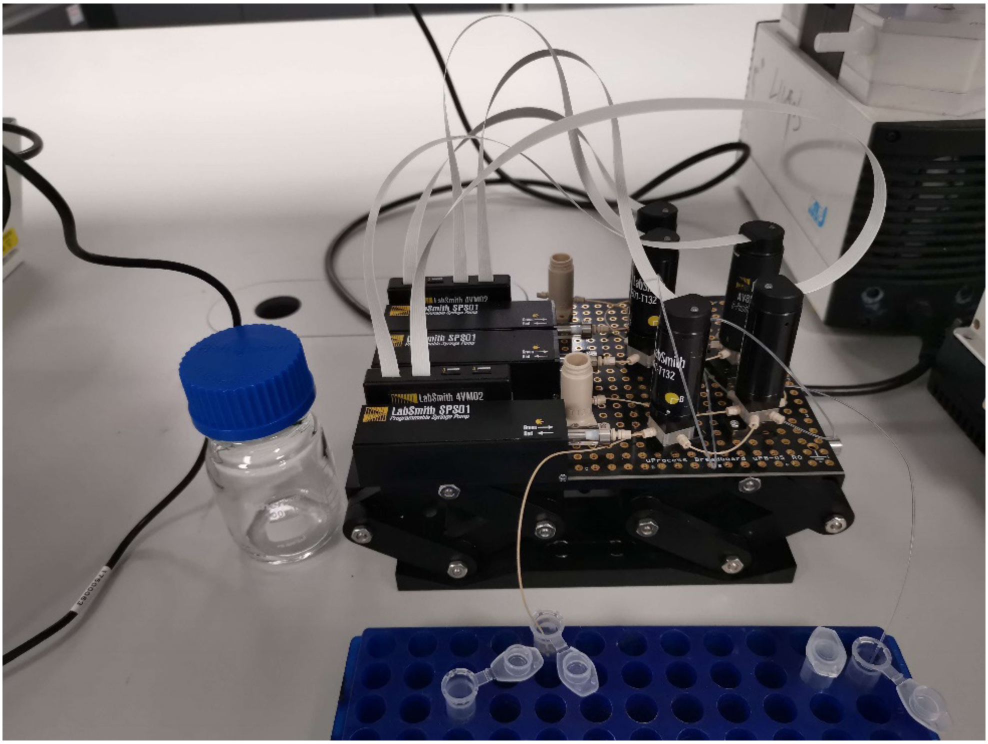

Figure 1. Liquid management system for the microfluidic separation device, including sample/reagent reservoirs that can be contained in an area of 13.4 × 18.5 cm. The overall footprint of the microdevice plus auxiliary systems can be contained within an area that is less than the area of a standard A4 paper.

39

Developments in actinide analytical chemistry at AWE

Matthew A. Higginson[*], *Thomas Shaw, Sarah Crooks, Louise Ingman, Stuart Dunn,*
Sam Cross and Philip Kaye

AWE, Aldermaston, RG7 4PR
[*]E-mail: matthew.higginson@awe.co.uk

Keywords: non-destructive analysis, plutonium, gamma spectrometry, x-ray fluorescence, spectroscopy, actinide analytical chemistry, automation, radiochemistry

The precise analysis of plutonium materials for process development, fundamental research, regulatory and specification requirements currently rely on destructive, wet chemistry methodologies. These processes add considerable complexity and cost to plutonium analysis as well as generating waste.

We will present innovations to this conventional approach. [1][2][3] Analytical developments are specifically aimed at reducing the process hazard and improving efficiency. Recent work using portable gamma spectrometry and process automation will be discussed as well as applying non-destructive techniques to solid actinide samples underpinned by wet chemistry.

A scalable sample containment system will be discussed to allow multiple analysis techniques to be applied to a sample non-destructively prior to wet chemistry. The sample can be cleared in this containment from the glovebox and can be handled in the open laboratory. Actinide samples were consistently produced and prepared to a precise geometry to enable calibration approaches to reference standards to be established. Radiometric, X-ray fluorescence, spectroscopic and microscopic techniques can then be applied to the same sample. We will present recent results on measurement of trace elemental impurities and other key analytes compared to quality assured wet chemistry methods.

Overall, these developments allow us to work faster and in a safer and more efficient manner.

Acknowledgments

Lav Tandon, Angela Olsen and Jung Rim (Los Alamos National Laboratory) are thanked for guidance and supporting this work.

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48

Results of americium and curium analyses in a series of radioactivity measurement proficiency tests

Simon Jerome[*], *Lindis Skipperud*

Fakultet for miljøvitenskap og naturforvaltning, Norges miljø- og biovitenskapelige universitet,
1433 Ås, Norway
[*]E-mail: simon.mark.jerome@nmbu.no

Keywords: americium, curium, proficiency tests, data analysis, method bias

Proficiency test exercise data are a valuable resource for analysing trends in analytical capabilities of the measurement community, particularly when such data is available over an extended time period. This presentation uses data from a series of proficiency exercises for radioactivity measurement where traceable assigned values for ^{241}Am and ^{244}Cm were available. The data was used to determine whether biases exist in the analysis of these nuclides, whether they are statistically significant and the general state-of-the-art for such measurements.

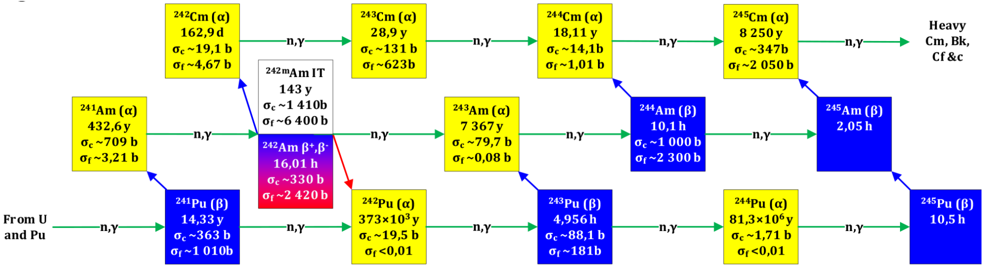
Americium and curium isotopes are formed both in the civil nuclear fuel cycle and from military use of nuclear fission through successive neutron capture and radioactive decay in uranium and plutonium. As such, americium and curium isotopes are widely distributed in the environment, where ^{241}Am, ^{242}Cm, ^{243}Cm and ^{244}Cm are the nuclides most often measured. In this work, two aspects of americium and curium analysis are considered:

- Bias between α-spectrometry and γ-spectrometry in ^{241}Am measurements, and
- Bias between americium and curium measurements by α-spectrometry

In determining the difference between α-spectrometry and γ-spectrometry measurements for ^{241}Am, the data used considered exercises where both measurement techniques were used, where $n = 243$ for α-spectrometry and $n = 97$ for γ-spectrometry. A difference of ~2,6% is observable between the two techniques. When considering the differences between americium and curium analysis by α-spectrometry, only results where both nuclides were measured by participants on the same sample were considered. In this case, $n = 203$ for both nuclides. A difference of ~8,7% is observable between ^{241}Am and ^{244}Cm.

In this presentation the data analysis will be explained, and the underlying reasons for the differences in (i) ^{241}Am measurements, and (ii) americium and curium analysis will be discussed, and means of reducing these biases examined.

Figure



Formation of americium and curium

Acknowledgments

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159

Evaluation of methods for analysing oxygen in plutonium materials at Los Alamos National Laboratory (LANL)

John Matonic[*], *Shauni Williams*[**]

Los Alamos National Laboratory, Los Alamos, NM, USA
E-mails: [*]shauni@lanl.gov, [**]matonic@lanl.gov

Keywords: plutonium, plutonium oxide, interstitial, inert gas fusion, oxygen

Plutonium metal's high affinity for even small amounts of oxygen can cause major material impacts to plutonium metal. As such, careful analysis of plutonium metal materials is important to assess the plutonium production process. The analysis of samples for oxygen in plutonium is challenging not only because of the very air sensitive nature of plutonium and it radioactive properties, but also the method needs to be able to reliably analyse for oxygen that is strongly bound to plutonium. LANL has recently installed a commercially available instrument for oxygen analysis in a glovebox within the plutonium facility and is routinely performing analyses. This presentation will explore the methods currently being used at LANL for oxygen analysis in plutonium metal materials. This will include sample handling, instrumentation, methods and will also discuss methods for assessing total oxygen content in plutonium oxides using current inert gas fusion instrumentation.
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74

Summary of plutonium and iron analysis capabilities at Los Alamos National Laboratory

T. Gannon Parker[*], *Justin Cross, Mary Knaak, Lisa Colletti, Angela Olson, Lav Tandon*

Actinide Analytical Chemistry, Los Alamos National Laboratory, Los Alamos, NM, USA
[*]E-mail: tgparker@lanl.gov

Keywords: plutonium, assay, titration, iron, spectroscopy, corpel

The capabilities for the assay of plutonium using a Corpel titration method at Los Alamos National Laboratory will be detailed, along with the complementary technique for measuring iron in plutonium materials. The Corpel titration method is designed to determine the plutonium content in metals, oxides, alloys, and other plutonium materials. Typical samples are less than 300 mg Pu. The solid Pu sample is dissolved and the solution is diluted with sulphuric and nitric acids, treated with sulfamic acid, reduced with Ti(III) over-titrated with excess Ce(IV) and back titrated with Fe(II), and the endpoints are determined potentiometrically using a plutonium electrode. Since iron is an interferent in the assay measurement, a separate analysis is performed for this element (along with measurements for Np and U, not detailed here) in order to perform corrections for the plutonium assay value. In this method, aliquots of the dissolved plutonium material are treated with hydroxylamine hydrochloride to reduce Fe(III) to Fe(II), followed by precipitation of the plutonium in the form of its oxalate, and subsequent isolation of Fe(II). The iron is then complexed with o-phenanthroline and analysed by UV-Vis spectrophotometry. These techniques are being developed for new facilities at the Lab to complement current methods in labs with aging infrastructure that have been in use since the era immediately following the Manhattan Project.

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198

Production and characterization of NBL plutonium isotopic standard CRM137A

Tashi Parsons-Davis[1*], *Josh Wimpenny*[1], *Cassandra King*[1], *Roger Henderson*[1],
Kiel Holliday[1], *Ross Williams*[1], *Pete Mason*[2], *Anna Tourville*[2], *Michael Holland*[2],
Robert Watters[2]

[1]Lawrence Livermore National Laboratory, Livermore, CA, USA
[2]New Brunswick Laboratory Program Office, Oakridge, TN, USA
[*]E-mail: parsonsdavis1@llnl.gov

Keywords: plutonium, isotopic standard, reference material

Lawrence Livermore National Laboratory (LLNL) and the NBL Program Office (NBL PO) are collaborating on production of purified sub-units of the aging plutonium isotopic reference materials formerly called NBS 936, 937 and 938, which will be distributed as certified reference materials (CRMs) CRM 136A, CRM 137A, and CRM 138A, respectively. Here we describe production and characterization of CRM 137A, the first of the series to be completed. An original unit of CRM 137 (formerly NBS 937) was purified in a new glovebox at LLNL via two-stage anion exchange chromatography to significantly reduce the quantities of U, Am, and Np in the source material. The purified plutonium was dispensed in nitric acid into individual units containing 1 mg Pu in 30 mL FEP bottles. Solution was gently evaporated to dryness and the units were packaged for distribution. The concentrations of Pu, U isotopes, 241Am, and 237Np in three analytical units were measured to provide informational values via isotope dilution (ID) multicollector–inductively coupled plasma–mass spectrometry (MC-ICP-MS). Results indicate the anion exchange procedure completely removed 241Am and U, while the Np concentration was reduced to 11.18 ± 0.15 ppm. High-precision measurements of the Pu isotopic composition have been made at LLNL, and units have been shipped to four other DOE laboratories for independent isotopic characterization. The NBL PO evaluation of isotopic data will be used to issue a certificate for CRM 137A as well as a new certificate for the CRM 137 source material.

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16

Application of controlled potential coulometry for plutonium mass fraction measurement in reference materials at the CETAMA

Sébastien Picart[*], *Ygor Davrain, G. Canciani, C. Rivier, M. Crozet*

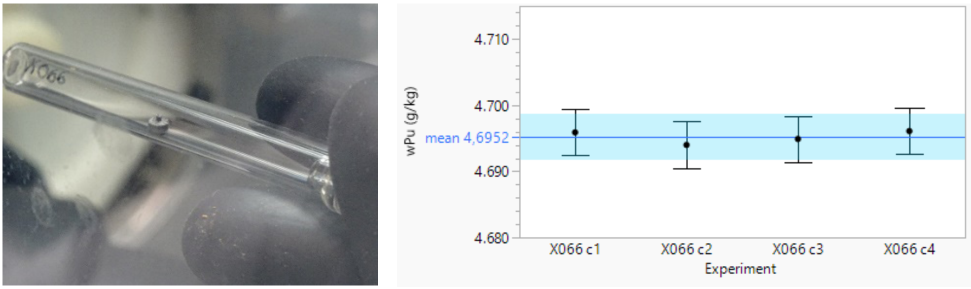
CEA, ISEC, DMRC, CETAMA, Univ. Montpellier, Marcoule, Bagnols-sur-Cèze, France
[*]E-mail: corresponding.sebastien.picart@cea.fr

Keywords: coulometry, plutonium, reference material, pure metal

Controlled Potential Coulometry (CPC) is an analytical technique used for the accurate determination of the amount content of an electroactive species in a solution by measuring the quantity of electricity required for this species to undergo a quantitative electrochemical reaction [1, 2]. The quantity of electricity involved in the studied reaction, Q, is then related to the mass of the element in solution, m, by applying Faraday's law. The technique is then defined as a primary method [3] because it provides a measurement of a quantity (mass of the element) without relation to a standard of the same kind as it is only related to physical standards of time (s) and current (A), both SI units (International Units System).

In the case of the measurement of plutonium (Pu) mass fraction, CPC can attain a high accuracy with uncertainties close to, or below, 0.1% even on small quantities of matter (typically a few milligrams) [1]. In light of these good performances, CPC has been successfully adopted for decades at the French Committee for the Establishment of Analytical Methods (CETAMA) for the determination of the Pu amount content in certified reference materials (CRM) [4,5].

Recently, CPC was applied to measure the Pu amount content in the CETAMA's new MP4 pure Pu metal reference material, which is currently (2022-2023) undergoing certification. The Pu mass fraction of the material was determined from the mean of four replicate measurements on a single piece of metal dissolved in nitric acid (Figure 1). The standard uncertainty of measurement was calculated by using the Monte Carlo Method and was found to be 0.037% which is below the International Atomic Energy Agency's 2020 International Target Values for the analysis of Pu mass fractions of pure compounds of Pu by CPC (0.14%) [6].



(a) (b)

Figure 1: (a) a piece of MP4 Pu metal RM in its ampoule under argon; (b) a four-replicate measurements of the Pu mass fraction of a MP4 dissolution sample by coulometry.

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212

First measurement of ^{236}U/^{238}U isotope ratios with MILEA AMS system in the Czech Republic

*Tomáš Prášek**, *Mojmír Němec*

Department of Nuclear Chemistry, Czech Technical University in Prague, Prague, Czech Republic
*E-mail: tomas.prasek@fjfi.cvut.cz

Keywords: 236U, accelerator mass spectrometry, environmental analysis, nuclear safeguards

Over the past few years, anthropogenic ^{236}U has become an established isotopic tracer with applications in both nuclear safeguards and environmental analyses, particularly in oceanography where its conservative chemical behaviour allows for reliable tracking of deep ocean currents. Due to trace concentrations of this radionuclide in environmental samples, accelerator mass spectrometry (AMS) is used almost exclusively for this purpose, enabling precise determination of ^{236}U/^{238}U ratios routinely down to 10^{-14}. The very first such facility in the Czech Republic has recently been built in Řež near Prague [1], based on 300 kV compact multi-isotope system MILEA from the Swiss manufacturer Ionplus AG. After initial tuning of the beamline using ^{236}U-labelled uranium oxide and KkU standard material, a pilot series of environmental samples taken from the Bohemian region were measured for ^{236}U content, including pitchblende uranium ore, borehole water from an area with uranium-rich bedrock and pre-war iron material, processed before the 1940s. The results obtained successfully confirmed the possibility of ^{236}U determination in environmental samples at the new facility.

Acknowledgments

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252

Application of a stripped isotope dilution approach to the analysis of nuclear material samples containing low levels of uranium and plutonium: The IAEA Safeguards Analytical Laboratory

Urska Repinc[*], *Monika Sturm, Dante Nakazawa, Andras Toervenyi, Georges Duhamel*

IAEA, Department of Safeguards, Office of Safeguards Analytical Services (SGAS), Vienna, Austria
[*]E-mail: u.repinc@iaea.org

Keywords: isotope dilution analysis, uranium, plutonium, isotope stripping

Although the standard analytical procedures used in the Safeguards Analytical Laboratory (SAL) of the International Atomic Energy Agency (IAEA) are sufficient for application to most routine nuclear material inspection samples, a new approach was needed for processing and analysis of samples with complex matrixes and very low amount contents of uranium and/or plutonium (several mg U, ng Pu total content). The application of standard procedures in SAL to these samples required time consuming treatments and often resulted in multiple rounds of mass spectrometric measurements before passing quality control checks. The isotope dilution analysis (IDA) technique using a stripping calculation was investigated as an alternative to the standard approach for such samples. The stripped isotope approach offers the advantage of being able to derive isotope amount ratios for the sample from isotope amount ratio measurements of the sample-spike blend using only a few simple calculation steps. This approach is applied as an alternative to the standard IDA method, as direct isotope ratio measurements do not need to be performed if the same sample is used for assay analysis for the element of interest. The calculation principle is based on the use of an artificial spike isotope that is (1) ideally not present in the sample, and (2) has a high atom abundance. The spike should also not be monoisotopic spike (containing only U-233 or Pu-244), since measurements are to be performed using thermal ionization mass spectrometry (TIMS), therefore at least two isotopes should have sufficient atom abundances to obtain reliable isotope ratio measurements.

The consistency of the results obtained using the stripped isotope dilution approach was tested on various quality control materials and safeguards samples (containing uranium and plutonium). Typical samples that the approach has been applied to are (1) down-blended materials declared as scrap or waste, (2) plutonium samples that contain very low amounts of uranium, and (3) for samples in which Pu/U age determinations are requested. The stripped isotope approach is also being evaluated for isotope ratio analysis of mg-size UF_6 samples, and for the analysis of plutonium in high-activity liquid waste samples.

255

Surface science investigations at JRC Karlsruhe

Alice Seibert[1*], *Thomas Gouder*[1], *Frank Huber*[1], *Hicham Idriss*[1,2]

[1]European Commission, Joint Research Center, JRC Karlsruhe, Karlsruhe, Germany
[2]Karlsruhe Institute of Technology (KIT), Institute of Functional Interfaces (IFG), Karlsruhe, Germany
[*]E-mail: alice.seibert@ec.europa.eu

Keywords: uranium oxides, metallic nanoparticles, photoemission spectroscopy, KPFM

There is a growing need for innovation in societal applications such as energy production, environmental safety or health. Solutions generally emerge from underpinning research. Our investigated systems, at the JRC Karlsruhe, are mainly based on thin films and nanomaterials. In particular, we valorise the unique material properties of actinides in testing them as novel materials for hydrogen production and nano-scaled materials with specific properties. The development of model surfaces represented by sputter deposited thin films of actinide compounds is a long standing technique at JRC KA [1,2]. Actual investigations look into the surface reactions of UO_2 thin film samples with metallic particle additions. This is of particular interest in the frame of photocatalytic production of hydrogen (e.g. when using suspended Au nanoparticles, for their electron capture properties [3] and surface plasmon resonance [4] effects or concerning Pd particles to simulate ε-particles in an UO_2 surface in corrosion investigations. After production these films are usually characterised by XPS (X-ray Photoemission Spectroscopy) and AFM (Atomic force microscopy) and where possible SEM/EDX (Scanning Electron Microscopy with energy dispersive X-ray Spectroscopy). In addition, KPFM (Scanning Kelvin Probe Force Microscopy) can be used. Recent results will be described in the contribution.

This and additional Research Infrastructures at JRC Karlsruhe are open to researchers in EU member states free of charge through the JRC Open Access activity ActUsLab [5] and helps maintaining a high level of nuclear competence through education and training.

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Advances in radiochemistry supporting the nuclear fuel cycle

180

Practical considerations to sourcing fit for purpose proficiency test materials

Lawrence Jassin

Eckert & Ziegler Isotope Products, Atlanta, GA
E-mail: larry.jassin@ezag.com

Keywords: proficiency testing, isotopes, reference materials, calibration, standards, decomissioning

Laboratories supporting all facets of the nuclear fuel cycle depend on a proficiency test (PT) materials/samples that are fit for the work they currently do and in support of their accreditation. This presentation will outline key considerations in acquiring traceable PT materials/samples that cover a broad range of matrices and isotopes. Examples will be given of new materials which support everything from incident response to decommissioning. These are available to both individual laboratories/facilities and in collaboration with governmental laboratories for their own distribution and administration.

6 Key Considerations:

- The Role of Stakeholders?
- What does ISO 17043 ask of PT participants?
- What the US DOE and DoD requires for proficiency tests?
- Method, Matrix, Analyte, why is this critical?
- Proficiency Test Material Considerations? Assigning values, traceability to national standards, grading criteria.
- What is currently available from Eckert & Ziegler Analytics?
- Eckert and Ziegler Analytics (EZA), Atlanta, GA, USA, routinely supports the nuclear fuel cycle laboratories with a variety of effluent and environmental PT's delivered quarterly to comply with regulations.
- ISO/IEC 17043:2010, Competence in the field of Proficiency Testing Provider, reminds us that it is the responsibility of the participant to select the appropriate proficiency test scheme and to evaluate results correctly. EZA provides both routine PT's and the resources to customize more complex materials to deliver what is needed around the world.

Figures

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235

o-Disulfonamide and *o*-sulfonamidophenol derivatives for f-element sensing and separation in caustic high level waste

Rene Panzer[1], *Leigh D. Ruddock*[1], *Oluwaseun W. Adedoyin*[1], *Xinrui Zhang*[1], *Emily J. Martinez*[1], *Indranil Chakraborty*[1], *Alexander N. Morozov*[1], *Alexander M. Mebel*[1], *Ingrid Lehman-Andino*[2], *David P. DiPrete*[2] *and Konstantinos Kavallieratos*[1*]

[1]Department of Chemistry and Biochemistry, Florida International University, Miami, FL, USA
[2]Savannah River National Laboratory, Aiken, SC, USA
*E-mail: kavallie@fiu.edu

Keywords: solvent extraction, f-elements, high-level-waste, actinides, NG-CSSX

Legacy waste processing[1] and decontamination of the Savannah River Site (Aiken, SC; US) concentrates on the generation of a low activity waste (LAW) stream for saltstone disposal and a high activity waste (HAW) stream for vitrification. Basification and concentration of the tank waste over the years has yielded three layers: (i) the high activity sludge, (ii) the saltcake, and (iii) the supernatant. The liquid supernatant, currently is being processed in SRS via two sequential steps: The Actinide Removal Process (ARP), where strontium and minor actinides are adsorped on monosodium titanate (MST), followed by the Next-Generation Caustic-Side Solvent Extraction Process (NG-CSSX), selectively separating Cesium, thus isolating the main contributor of the overall radiotoxicity.[2] NG-CSSX compatible f-element chelators, such as the ones presented herein could achieve simultaneous separation of Cs and An in a one integrated solvent extraction process, thus, decreasing the need for extensive contact time and amount of titanate sorbent during the ARP step, contributing to a more efficient, faster and cost-effective processing. *o*-Disulfonamide (**dsa**) and *o*-sulfonamidophenol (**msa**) derivatives have been shown to be stable under highly alkaline conditions and were tested by our group as possible extractants and sensors for f-elements. A library of **dsa** and **msa** ligands were synthesized (Fig. 1) and tested. Remarkably high Sm(III) recovery values of >90% at pH = 14 in dichloromethane[3] with the first-generation **msa** and 30.4 (+/–3.7)% into a non-polar NG-CSSX with the highly-lipophilic dodecyl-substituted **msa** derivatives at up to 2.5 M NaOH concentrations were obtained. Furthermore, by using these ligands as additives in the NG-CSSX we have also revealed the sensing potential of dansyl- and nitro-substituted analogs. Those were shown to act as optical sensors in UV-Vis and fluorescence studies, respectively. Deprotonation-induced electronic structure changes, spectroscopic effects, and extraction thermodynamics were investigated by DFT theoretical calculations.

Figures

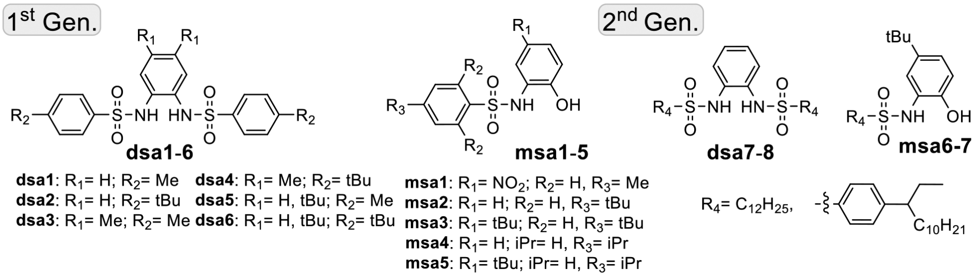

Figure 1. Investigated **dsa** and **msa** chelators for f-element extraction and recovery from alkaline solutions.

Acknowledgments

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171

Methyl-glutarimidedioxime *vs*. glutarimidedioxime: A methyl attached to piperidine cycle generate different coordination modes with uranyl

Xingliang Li[*], *Zhuoxi Li, Yuyu Liang*

Institute of Nuclear Physics and Chemistry, China Academy of Engineering, Mianyang, China
[*]E-mail: xingliang@caep.cn

Keywords: glutarimidedioxime, uranium, complex mode, thermodynamics

The ocean contains an abundant supply of uranium that could be used to meet the world's future energy demands. Despite a high abundance, uranyl (UO_2^{2+}) is found in low concentration (3ppb) in seawater. Materials deployed to harvest UO_2^{2+} must be designed with high affinity, selectivity over competing metals, and retain adsorption capabilities over multiple cycles in order to make uranium mining from seawater economically feasible. The most widely utilized approach to extract uranyl out of seawater is amidoxime polymers. In the amidoxime-based sorbents, the cyclic glutarimidedioxime (H_2A, Figure 1) is the preferred configuration for sequestration of uranium from seawater. However, varying structures coexist in these polymer sorbents, and the corresponding coordination modes of binding uranyl ions remain unclear. To improve the efficiency of uranium extraction, it is necessary to systematically evaluate the binding ability and complex mode, so that the conditions of the preparing sorbents could be optimized to achieve the maximum yield of the configuration with the highest binding ability towards uranium. Here, we report a methyl-glutarimidedioxime (H_2Q, Figure 1) to demonstrate how minor structural changes generate major consequences in the binding ability and complex mode.

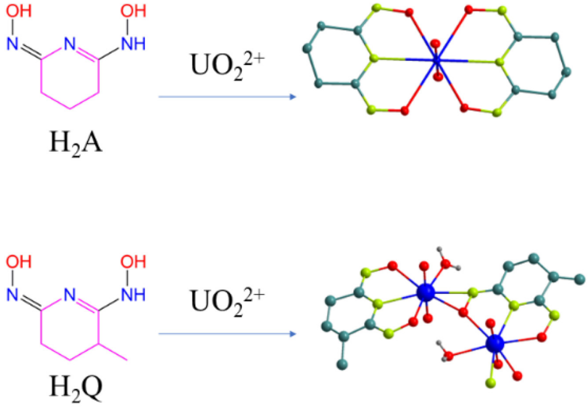

Figure 1. Structures of imidedioxime and corresponding uranyl complexes

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227

Aggregation behaviour of radiolytically degraded DGA based solvent systems

Narayanan Parvathy[1,2], *Jammu Ravi*[1], *T. Prathibha*[3], *K.A. Venkatesan*[1,2*]

[1]Reprocessing Research and Development Division, Reprocessing Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India
[2]Homi Bhabha National Institute, Anushakti Nagar, Mumbai 400094, India
[3]Fuel Chemistry Division, Material Chemistry and Metal Fuel Cycle Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India
[*]E-mail: kavenkat@igcar.gov.in

Keywords: gamma irradiation, aggregation, third phase formation, FTIR Sspectroscopy, Nd(III) extraction

N,N,N',N'-tetraoctyl diglycolamide (TODGA), being a versatile extractant for the minor actinide partitioning from the high level liquid waste, possess certain shortcomings such as early third phase formation, when contacted with trivalent metal ions. To avoid this event, the organic phase was modified with phase modifier such as dioctyl hydroxyacetamide (DOHyA), one of the degradation products of TODGA. The binary solution of TODGA+DOHyA in *n*-dodecane (Fig 1) exhibits good extraction behaviour and higher third phase formation limits. For instance, during the separation of trivalent actinides from HLLW by solvent extraction procedure, the organic phase is exposed to various ionizing radiations leading to the formation of several degradation products. Extensive studies on the radiolytic degradation behaviour of diglycolamides in *n*-dodecane medium has proven that the distribution ratios and aggregate sizes were decreased with increase of absorbed gamma dose. However, the detailed study on the radiolytic degradation of the diglycolamide in the presence phase modifier is not available. In the present study, the radiolytic degradation of 0.1 M TODGA + 0.2 M DOHyA in *n*-DD at various dose levels was studied under different conditions. The organic phase subjected to irradiation was classified into four different cases (Table 1). The extraction behaviour of Nd(III) from nitric acid and the aggregation behaviour of the degraded solution of 0.1 M TODGA + 0.2 M DOHyA/*n*-DD was probed by dynamic light scattering technique and ATR-FTIR spectroscopy. The results thus obtained were compared with the those obtained in the corresponding individual systems. The results revealed that the presence of *n*-DD along with extractants during irradiation enhanced the degradation of extractant, due to sensitization effect, which leads to the reduction in the aggregate size. Furthermore, this study rejected the popular notion of deleterious effect of gamma radiation on solvent system, but confirmed that irradiation shifts the third phase formation limit to higher values by the minimizing the aggregation. It is proposed to described the complete results in the presentation.

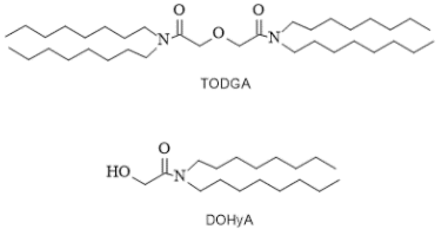
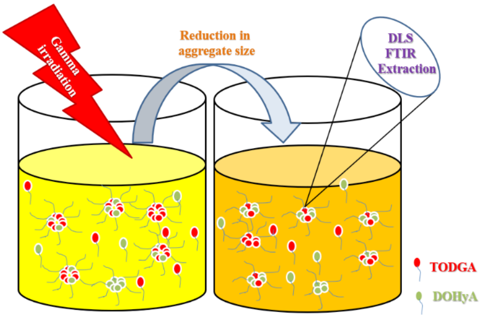


Fig 1. Chemical structures of extractants

Table 1. Various cases performed in this study

Case 1	Extractant + *n*-dodecane was irradiated to various dose levels for performing the studies.
Case 2	Neat extractant was irradiated alone to various absorbed dose levels & was mixed with unirradiated *n*-dodecane to obtain final solution for performing the studies.
Case 3	The irradiation of *n*-dodecane alone to various absorbed dose levels & mixed with unirradiated extractant to obtain final solution for performing the studies.
Case 4	The extractants and *n*-dodecane were taken separately and irradiated to various absorbed dose levels & mixed to obtain final solution for performing the studies.



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157

Investigating the sorption of relevant organic molecules in cement-based nuclear waste containment

Marko Štrok[*], *Tamara Gajšt, David Heath, Ester Heath*

Jožef Stefan Institute, Ljubljana, Slovenia
[*]E-mail: marko.strok@ijs.si

Keywords: EDTA, NTA, PEG, cement

In the disposal of nuclear waste, most disposal strategies involve cement, either as a stabilising agent or in the form of different barriers preventing radionuclides from entering the geosphere. Additionally, radioactive waste can contain various organic molecules from different technological processes, which can decrease or, more importantly, increase the mobility of radionuclides and, consequently, the risk that they will reach the biosphere within the disposal timeline needed for the radionuclides to decay to environmental levels. Organic molecules are also subject to radiolysis and hydrolysis, which can lead to the formation of various degradation products that could also affect radionuclide mobility.

This study investigated two types of organic molecules: complexing agents, generally used for decontamination purposes, such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), and radiolytic and hydrolytic degradation products (polyethylene glycol PEG) from polycarboxylate and polyaryl ether superplasticisers, which are used as concrete admixtures to improve their workability. The goal was to evaluate and compare the sorption capacity of complexing agents on degraded hardened cement pastes and to analyse the effect of organic molecules on radionuclide mobility in cement matrices. Batch sorption experiments were conducted on two degraded hardened cement pastes, one of which had reached degradation state II and the other degradation state III. After grinding, cement samples were characterised using X-Ray Diffraction (XRD) and Brunauer-Emmett-Teller (BET) techniques. Sorption experiments were performed in a nitrogen atmosphere with a solid-to-liquid ratio ranging from 0.3 to 100 g/L and organics ranging from 1E-2 to 1E-4 M concentrations.

Preliminary results showed that NTA had much stronger sorption than EDTA, with more than 80% sorption at a concentration of 1E-4 M and a solid-to-liquid ratio of 100 g/L, whereas only about 20% of EDTA had been adsorbed under such conditions. Sorption of PEG 1500 was intermediate between EDTA and NTA, with approximately 40% adsorption.

Acknowledgements

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50

Uptake of ^{85}Sr and ^{137}Cs onto cementious materials and synthetic geopolymer

Václav Znamínko[1,2*], *Petr Večerník*[2], *Martin Člupek*[1], *Pavel Řezanka*[1]

[1]Department of Analytical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology, Prague, Technická 5, 166 28 Praha 6, Czech Republic
[2]ÚJV Řež, a. s., Hlavní 130, 250 68 Husinec-Řež, Czech Republic
[*]E-mail: znaminkv@vscht.cz

Keywords: strontium, caesium, radioactive waste, sorption, infill materials, cement, synthetic geopolymer

In a few years there will be a large amount of high-level radioactive waste produced by decommission of nuclear facilities. This type of radioactive waste is allowed to be stored only in deep geological repository. The aim of the ALMARA project is to find infill materials that will make deep geological repository safe for long period of time and to test those materials.

The subject of this work is strontium and caesium sorption on three cementious materials and one synthetic geopolymer, finding the equilibrium time needed for their sorption. Sorption experiment was batch type, synthetic granitic water (SGW) with addition of $^{85}SrCl_2$ or $^{137}CsCl$ was used as liquid phase. Hardened cement paste (C), cement mixed with 20 wt.% of bentonite (AFM), cement mixed with 1 wt.% of nano iron particles (NNM) and synthetic geopolymer (GP) were used as solid phases. Those materials were used after curing (28 days) or after interaction with SGW. Two different grain sizes were used (mesh fraction smaller than 0.5 mm and mesh fraction between 1 and 2 mm) and two different solid-liquid ratios were used (1/10 and 1/5 g/ml). Distribution coefficients (R_d) were calculated to compare those materials.

For the fresh material, best results were obtained for GP, with equilibrium time being one week for both radionuclides. For other materials, equilibrium time was one week for caesium and about two months for strontium. The R_d values decreased for strontium as follows GP>>AFM>NNM>C and decreased for caesium as follows GP>>AFM>C≈NNM.

Acknowledgments
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Collaborative material excercise

46

Age and elemental impurities determination in nuclear materials by Single Quadrupole ICP-MS

Andreea Elena Serban[1], *Florin Albota*[1*], *Erhan Ionuz*[1,2], *Catalin Tuta*[1], *Andrei Apostol*[1], *Marian Virgolici*[1]

[1]National Institute for Physics and Nuclear Engineering (IFIN-HH), Bucharest – Magurele, Romania
[2]Department of Science and Engineering of Oxide Materials and Nanomaterials, Faculty of Applied Chemistry and Material Science, Politehnica University, Bucharest, Romania
[*]E-mail: florin.albota@nipne.ro

Keywords: nuclear materials, micro destructive analysis, age determination, elemental impurities, Single Quadrupole ICP-MS

In the context of the Collaborative Materials Exercise 7 (CMX-7), organized by the International Working Group on Nuclear Forensics, also referred to as ITWG, four sample of uranium materials were analysed by the National Institute for Physics and Nuclear Engineering, IFIN-HH Bucharest, Romania. In order to fulfil the exercise's requirements, the following tests have been performed: SQ ICP-MS micro destructive analysis at 24-hours; FT-Raman non-destructive analysis and SQ ICP-MS destructive analysis at 1 week and 2 months stages. The presented work is focused on presenting the step-by-step analytical process, decision making framework, the challenges encountered and the lesson learned while adapting a Single Quadrupole ICP-MS to the CMX-7, such that to be used for determining fingerprints of the nuclear material of interest. The results of the "in-house" protocol developed within this exercise, along with adjusting key operating parameters in the instrument, made possible the determination of the uranium isotopic ratio of the samples in the 24h time-frame, without the use of chemical separation. Moreover, the developed protocol was further upgraded such that to be used in the 1 week and 2 months stages, thus the laboratory being able to provide accurate results regarding the concentration of the trace elements in the materials of interest. Based on these results, it was computed a PCA statistical analysis and the REE pattern of the samples, in order to establish the mineralogy origin. Also, the Pb and Sr isotopic ratios were calculated. The present method developed by the laboratory in CMX-7 was used for the age determination for the samples of interest, that was computed based on the ^{230}Th/^{234}U chronometer, also without the use of chemical separation.

91

Phase investigation of uranium-vanadium alloy using multiple techniques

Michal Brandis[1], Gregory Gershinsky[1], Arnon Rubinshtein[2], Yevgeni Zakon[1], Maor Assulin[2,4], Amiram Moyal[2], Eyal Elish[2], Arnon Grafit[3], Aldo Shemesh[4], Assaf Bolker[1], Ofer Aviv[1], Noa Fruchter[2], Nir M. Yitzhak[1], Sagi Nissim[1], Zohar Yungrais[1], Alexander Zinger[3], Lena Plastovez[3], Noam Gonen[3], Itzhak Sedgi[2], Itzhak Hershko[1], Itzhak Halevy[2], Ruth Yam[4], Tzah Mackmal[1], Tal Riemer[1], Yinon Ben David[1], Sapir Shunkur[1], Daniel Kurtzer[1], Yosi Ben Ishay[1], Dan Breitman[1], Dan Berkovits[1], Boaz Assaf[2], Hanan Datz[1]*

[1]Soreq Nuclear Research Center, Yavne 818000, Israel
[2]Nuclear Research Center Negev, P.O. Box 9001 Beer Sheva 8419000, Israel
[3]Division of Identification and Forensic Science, Israel Police, Jerusalem, Israel
[4]Department of Earth and Planetary Sciences, Weizmann Institute of Science, 76100 Rehovot, Israel
[*]E-mail: michalas@soreq.gov.il

Keywords: nuclear forensics, CMX7, uranium alloy

Four unknown samples were investigated by the Israeli National Nuclear Forensics laboratory (INNFL) during Collaborative Material Exercise 7 (CMX-7). The unknown samples, identified as depleted uranium, were marked ES-1, ES-2, ES-3 and ES-4. The extensive characterization of the samples included over 30 different analytical techniques, several of which were used for the first time in a nuclear forensics investigation in Israel. The nuclear forensics investigation also included conventional forensics analysis of related materials - fingerprints, DNA, digital evidence etc.

ES-2 was identified as different from the other exercise samples by its isotopic composition -samples ES-1, ES-3 and ES-4 have an identical isotopic composition (0.300±0.003% U-235, 0.0017±0.0001% U-234, 0.0108±0.0001% U-236) while ES-2 had a different isotopic composition (0.200±0.004% U-235, 0.0007±0.0001% U-234, 0.0018±0.0001% U-236). It also contained a significant vanadium concentration (app. 3000 ppm).

ES-2 phase was not metallic and hard to determine. It presented a metallic density and initial appearance but showed non-metallic behaviour during sampling and dissolution. To determinate ES-2 phase and origin a series of analyses was carried out, indicating that the vanadium was present in porosive areas on the surface. The surface contained non-homogenous U oxide layer typical of metal in an uncontrolled environment, while the bulk of ES-2 was determined to also contain crystalline uranium. The oxygen isotope ratios pointed to thermal processing under environmental conditions. Uranium isotopic ratio were homogenous over ES-2 surface and particle analysis.

92

Linking UK radiochronometry measurements of CMX-7 exhibits to material processing conditions

James A. Dunne[*], *Matthew A. Higginson, Samuel T. J. Cross, Chris R. D. Gilligan, Stuart Dunn, Josh King*

AWE, AWE Aldermaston, RG7 4PR, UK
[*]E-mail: james.dunne@awe.co.uk

Keywords: nuclear forensics, radiochronometry, uranium, Seventh Collaborative Materials Exercise (CMX-7)

Radiochronometry has become an important nuclear forensic signature for assessing the process history of unknown nuclear material. Together, multiple chronometric pairs (e.g. ^{230}Th/^{234}U, ^{231}Pa/^{235}U) may be used to obtain a model production date of a material. Modern analytical techniques can measure these atom ratios to high accuracy and precision. However, recent work suggests that measurement uncertainties can underestimate the variability of this signature [1]. This issue is exacerbated where nuclear industry processes chemically fractionate uranium decay progeny, ^{230}Th and ^{231}Pa, to yield discordant model ages: A phenomenon that is common to the nuclear fuel cycle. To inform our understanding of this signature's behaviour in representative materials, it is key to study specimens with well-defined processing histories. Such materials are often challenging to obtain given the complexities of the fuel cycle. The seventh Collaborative Materials Exercise (CMX-7) provided several candidate materials representative of feed, intermediate and product stages of the fuel cycle. Here we present the UK radiochronometry results and their application to the CMX-7 materials. We relate these data to the sample history shared by the organising committee to inform future interpretation of radiochronometric data.

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221

Conventional forensics boosting of the nuclear forensics investigation in CMX7

Eyal Elish[1*], *Michal Brandis*[2], *Aldo Shemesh*[3], *Arnon Grafit*[4], *Ludwik Halicz*[5]

[1]Nuclear Research Center Negev (NRCN), Beer Sheva, Israel
[2]Soreq Nuclear Research Center (SNRC), Yavne, Israel
[3]Weizmann Institute of Science (WIS), Rehovot, Israel
[4]Israel Police - CSI, Rehovot, Israel
[5]The Geological Survey of Israel (GSI), Jerusalem, Israel
[*]E-mail: eyalel@nrcn.gov.il

Keywords: nuclear forensics, conventional forensics, Collaborative Material Exercise

The Collaborative Material Exercise 7 (CMX7), included for the first time, a conventional forensics package prepared by the FBI. Conducting a parallel conventional investigation was voluntary, hence was not applied by all the CMX7 participants. The Israeli police is operating a professional, highly experienced CSI teams all over the country, 24/7. The specific team operating in the vicinity of SNRC, was asked to join forces with the nuclear forensics team in the Israeli National Nuclear Forensics Laboratory (INNFL) and participate in the CMX7. Conducing a parallel forensics investigation, involving both conventional and radioactive exhibits, by two different teams, was challenging, and required adequate assessment in the laboratory. The intimate real time collaboration, between the two teams, was found to be most fruitful, yielding significant findings, within relatively short investigation time. A typical example is concluding rather fast about the connection between ES-1, ES2 and ES3, by understanding the order in which they were rapped by the discovered tape, and the radiography of the exhibits package. The methodology of conducting parallel inquiry in a small laboratory, involving two expert's disciplines, radiological and conventional, and its benefits, will be described in detail.

Figure 1 – Radiography of the closed package

Figure 2 – Tape matching

179

Analysis of the CMX-7 samples at the Canadian Nuclear Laboratories

Anaïs Fourny[*], *Ike Dimayuga, Dan Cluff, Liqian Li, Aditya Ayyagari, Youqing Shi*

Canadian Nuclear Laboratories, Chalk River Laboratories, Chalk River, ON, Canada K0J 1J0
[*]E-mail: anais.fourny@cnl.ca

Keywords: CMX-7, nuclear forensics, SEM-EDX, Raman, XRD, mass spectrometry

The Canadian Nuclear Laboratories participated in the Seventh Collaborative Materials Exercise (CMX-7) organized by the International Technical Working Group on Nuclear Forensics (ITWG). The exercise started with the receipt of the materials at CNL on 2022 March. The initial physical examination and observations of the four CMX-7 samples were completed for the 24 hours-report first, followed by non-destructive and destructive analyses for both the seven day- and two month-reports. The morphology of the two powder samples (ES-1 and ES-3) and the surface characteristics of the two metallic samples (ES-2 and ES-4) were examined by Optical and Scanning Electron Microscopic (SEM) techniques. SEM-Energy Dispersive X-ray (EDX) analysis provided information on their chemical composition. Raman spectroscopy and X-ray diffraction (XRD) were also used on the two powder samples to identify their composition. Immersion density performed on the metallic samples helped to identify their possible composition. The trace element compositions of the four samples were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), and their uranium isotopic composition by Thermal Ionization Mass Spectrometry (TIMS). The data analysis of all sample measurements from this CMX-7 exercise led CNL to identify that one of the metal samples (ES-2) was not related to the other three samples. The non-destructive and destructive analyses performed at CNL will be presented and discussed along with the lessons learned for future nuclear forensics exercises.

47

Development in rapid non-destructive analysis tools for solid actinide samples for nuclear forensics

Matthew A. Higginson[*], *Thomas Shaw, Sarah Crooks, Stuart Dunn, Sam Cross, Christopher Gilligan, James Dunne, Olivia Marsden, Darrell Knight, Phill Scivier*

AWE, Aldermaston, RG7 4PR
[*]E-mail: matthew.higginson@awe.co.uk

Keywords: non-destructive analysis, gamma spectrometry, x-ray fluorescence, radiochronometry, spectroscopy, nuclear forensic analysis

The rapid non-destructive measurement of material parameters of an unknown nuclear material is crucial to inform analytical planning, assess public health impact and to answer initial law enforcement questions for nuclear forensics. Optimising and underpinning these workflows to quality assured standards is key to underpin a robust and iterative capability to address the urgent law enforcement need.

We will report developments in our approaches to develop solid, non-destructive actinide analysis tools using examples from relevant materials measured for nuclear forensics, including the recent International Technical Working Group (ITWG) on Nuclear Forensics Collaborative Materials Exchange 7 (CMX-7) exercise. [1]

We will present the use of a sample containment system allowing for maximal exploitation of multiple samples within 8 hours of sample receipt, allowing for a wide series of measurements to be undertaken without compromise of the customer exhibit. [2] Key to this effort was development of solid actinide analysis approaches for radiometric analysis. We will show that measurement of a sample rapidly by multiple techniques allowed for radioisotope, assay, isotopes, radiochronometry and major elemental content can be readily measured for initial assessment.

Acknowledgments
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230

Non-destructive characterization of nuclear materials for the CMX-7 International Exercise

Kim B. Knight[*], *Ashley Cocciadiferro, Zurong Dai, Dana Drew, Charlotte Eng, Amy Gaffney, Victoria Genetti, Narek Gharibyan, Matthew Gonzales, Patrick Grant, Greg Klunder, Rachel Lindvall, Naomi Marks, Ken Moody, Eric Oerter, Tashi Parsons-Davis, John Rolison, Mike Sharp, Joseph Swider, Todd Wooddy, Paul Spackman*

Lawrence Livermore National Laboratory, Livermore, CA, USA
[*]E-mail: knight29@llnl.gov

Keywords: nuclear forensics, uranium, CMX-7

In 2022, the 7th Collaborative Materials Exercise (CMX-7) of the Nuclear Forensic International Technical Working Group presented an opportunity to practice the handling and characterization of a suite of four physical samples associated with a nuclear forensics context and back story. The four samples were received in a range of primary containers. The samples included two primary forms, with two as powders and two as solids. In-exercise analyses identified the powder materials as uranium oxide and uranyl nitrate hydrates, and the solid samples as uranium metals with an oxide coating, in the forms of foils and a bar. Sample forms (powders vs. solids) dictated distinct analytical sequences and decisions with respect to sample aliquoting and planning for subsequent destructive analyses. Initial non-destructive characterization was performed prior to any aliquoting of materials or destructive analyses (i.e., methods requiring dissolution or other compromise of sample form or characteristics). In this early stage of the exercise investigation, analytical planning addressed multiple challenges including the number of samples, their distinctive forms, the presence of radionuclides, and variations in sample quantity. Additional non-destructive analyses were performed on sample sub-aliquots. Non-destructive methods applied included gamma spectrometry, mensuration, optical characterization, X-ray diffraction, UV/Vis/Near IR spectroscopy, thermogravimetric analyses, and electron microscopy.

Throughout this exercise, sample observations and exercise-derived questions and constraints guided our approach, with the goal of maximizing information gained through non-destructive analysis of these materials while striving for efficient processing and ensuring materials would be available for subsequent destructive analysis. Sample handling and non-destructive characterization, as well as creation of sample aliquots, were performed with considerations to ensure dissolution-based radiochemistry would not be impacted (or that any effects can be appropriately accounted for). This presentation highlights a selection of observations, challenges, and benefits from working with this unique suite of nuclear forensic exercise samples.

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56

Isotopic, structural, and elemental characterization of uranium nuclear forensic samples within the 7th Collaborative Material Exercise

Jan Lorincik[1*], *Kristina Sihelska*[1,3], *Daniela Vesela*[1], *Ivan Elantyev*[1,3], *Klara Rezankova*[1],
Claudia Aparicio[1], *Thi Minh Do*[1], *Jan Kucera*[2], *Jan John*[3], *Mojmir Nemec*[3],
Miriam Mindova[3], *Vlastimil Miler*[4], *Daniel Gotz*[4], *Jiri Janda*[5], *Alena Kelnarova*[6]

[1]Research Centre Rez, Husinec-Rez, Czech Republic
[2]Nuclear Physics Institute, Academy of Sciences of the Czech Republic, Prague, Czech Republic
[3]Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, Prague, Czech Republic
[4]Nuclear Research Institute, Husinec-Rez, Czech Republic
[5]NBC Defence Institute, University of Defence, Vyskov, Czech Republic
[6]National Radiation Protection Institute, Prague, Czech Republic
[*]E-mail: jan.lorincik@cvrez.cz

Keywords: nuclear forensics, uranium, uranium compounds, trace elements in uranium compounds, uranium isotopic composition, CMX-7

This paper aims to describe the nuclear-forensic characterization of materials provided by the Nuclear forensic international technical working group (ITWG) within the 7th Collaborative Material Exercise (CMX-7). The characterized materials were two powdered uranium-compound samples labelled ES-1 and ES-3 and two uranium metal samples labelled ES-2 and ES-4.

A combination of several analytical and radiometric techniques was used by a group of Czech laboratories to the identification of chemical compounds, the determination of the uranium isotopic composition and the elemental composition of all four samples. Those results allowed for an unambiguous conclusion that the ES-1 is depleted uranium trioxide, ES-2 is depleted uranium-vanadium alloy, ES-3 is depleted uranium nitrate, and ES-4 is depleted uranium metal. A further conclusion was that ES-2 cannot originate from the same source as the other three samples and that ES-1, ES-3, and ES-4 had a common source material.

After excluding the ES-2 sample from the association with the other ones, the next task was the search for any other characteristics, besides the isotopics, linking the remaining three samples ES-1, ES-3, and ES-4 with each other through a chemical technological process. Though chemical reactions leading to the transformation of one sample into the other one (ES-4 uranium metal into ES-3 uranium nitrate powder and this powder into ES-1 uranium trioxide powder) could have been quickly proposed, the experimental proof at a high level of confidence turned out to be difficult to obtain. Available elemental screening methods of Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy (SEM-EDX) or Energy Dispersive X-Ray Fluorescence (EDXRF) did not provide conclusive results.

Therefore, additional elemental survey method - Neutron Activation Analysis with pre-separation (PS-NAA) to remove uranium by extraction chromatography resin UTEVA^{TM} was used to obtain information about a possible linkage among ES-1, ES-3, and ES-4 samples. The use of the PS-NAA for trace-element screening provided concentrations of more than

10 elements at ppm levels for all four samples. The cluster analysis of the PS-NAA data revealed short linkage distance between the ES-4 metal and the ES-3 powder, which supported the conclusion that the uranium nitrate powder ES-3 was created from the uranium metal ES-4. The other powdered sample ES-1 had long linkage distance to both ES-3 and ES-4, therefore the proposed reaction path between the uranium nitrate powder and the uranium trioxide powder remained neither confirmed nor excluded. Though the potential of PS-NAA for survey analysis has not been fully explored in this work, it can be already concluded that PS-NAA could be a useful tool for trace level elemental screening of samples with high content of uranium and its application potential in nuclear forensics deserves further exploration.

76

The experience of the 7th Collaborative Materials Exercise of the Nuclear Forensics (CMX-7) and future tasks

Yoshiki Matsui[*], *Yoshiki Kimura, Yuji Umino, Masaharu Hosoi, Tetsuya Matsumoto,*
Nobuo Shinohara, Hitoshi Yamazaki and Tomoki Yamaguchi

Japan Atomic Energy Agency (JAEA), Ibaraki, Japan
[*]Email: matsui.yoshiki@jaea.go.jp

Keywords: nuclear security, nuclear forensics, CMX-7

The Integrated Support Center for Nuclear Nonproliferation and Nuclear Security (ISCN) of the JAEA is developing technologies for nuclear forensics to identify the origin and intended use of nuclear and radioactive materials. The Nuclear Forensics International Technical Working Group (ITWG) regularly holds the Collaborative Materials Exercise (CMX) to share the experience on nuclear forensics analysis and to improve analytical methods in the international community. The ISCN participated in the 7th exercise (CMX-7) this time. This paper discusses the experience of the ISCN during the CMX-7 including the results of laboratory analysis and nuclear forensics interpretation, as well as future challenges for laboratory capability at the ISCN.

In the CMX-7, under the hypothetical case scenario (illegal transferring of nuclear materials), uranium samples and other conventional forensics evidence were provided for the exercise. During the exercise, participants reported the analytical results according to the timeframes recommended by the Nuclear Forensics Guidelines of the IAEA [1] (24 hours, 1 week, and 2 months from sample receipt). The ISCN reported the physical characteristics and the results NDA analysis on the uranium samples at the first two timeframes, and the results of mass spectrometry with the data interpretation as the 2 months report. The results of uranium isotope ratio and trace elements measurements were exceedingly good, but the results of age dating were significantly deviate from the overall average. Reducing the time for destructive analysis that allows timely provisions of the results, as well as the improvement of the confidence in age dating are future tasks for the nuclear forensics analysis of the ISCN laboratory.

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Education in radiochemistry

105

The ISOradioLAb project devoted to students of high schools of minor Italian islands: The radon measurements to introduce them to STEM subjects

Flavia Groppi[1,2*], *Fabrizio Ambrosino*[3], *Giuseppe La Verde*[3,4], *Mariagabriella Pugliese*[3,4], *Michele Colucci*[1,2]

[1]Department of Physics, University of Milan, via Celoria 16, I-20133 Milan, Italy
[2]LASA, University of Milan and INFN-Milano, via F.lli Cervi 201, I-20090 Segrate, MI, Italy
[3]University of Napoli Federico II, Dipartimento Fisica Ettore Pancini, Naples, Italy
[4]INFN-Napoli, Istituto Nazionale di Fisica Nucleare, Naples, Italy
[*]E-mail: flavia.groppi@unimi.it

Keywords: radon-222 measurements, education, citizen science, STEM, risk perception, ionizing radiations, radioprotection

ISOradioLAb is an INFN (Italian National Institute of Nuclear Physics) citizen science project, mainly devoted to high school students, but also with a broader engagement to middle school student and the population in general. It was born in 2021 as a complementary part of the National RadioLAB INFN project devoted to the indoor radon -222 concentration that involved 9 Italian Reagions but also Albania and Ecuador schools[1,2,3]. Both projects are devoted to the students of High Schools to bring them more confident with the items of radioactivity, by presenting and discussing good reasons to acquire and conserve expertise and knowledge in the nuclear field as important contribution to the society.

The students are involved in the in the experimental measurements of the radon-222 concentration by CR-39 solid state nuclear track dosimeters (SSNTD) and with electrete ion chambers inside different places such as their school, home or other indoor sites of their interest. They conduct the experiences in a way that allow to realize that a LAB is not just a physical place but a METHOD of "KNOW" through the "KNOW-HOW".

The preliminary results of this study, together with the evaluation of the knowledge and the risk perception associated to the ionizing radiations are presented. Moreover, this work can be seen as a model to implement the citizen science protocol to map at national scale the radon concentration or every other physical quantity of interest in confined spaces, starting from schools but also in homes, public places, public administrations and so on.

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137

A radiochemistry laboratory exercise: Estimation of uranium in tap water by solvent extraction and liquid scintillation counting

Eros Mossini[*], *Gabriele Magugliani, Francesco Galluccio, Andrea Santi, Marco Giola, Elena Macerata, Mario Mariani*

Department of Energy - Nuclear Engineering Division, Politecnico di Milano, Milan, Italy
[*]E-mail: eros.mossini@polimi.it

Keywords: laboratory exercise, natural radioactivity, uranium, liquid scintillation counting, co-precipitation, solvent extraction

Several challenges related to the civil use of nuclear technologies can be addressed by Radiochemistry. In this perspective, it is important to develop the knowledge background of future nuclear scientists, for instance by means of experimental laboratory experiences on radiochemistry and nuclear chemistry topics. In this work, an original hands-on activity has been designed and tested with the students of the Applied Radiochemistry course at Politecnico di Milano, who autonomously carried out the experiment under the guidance of a tutor.

The scope of this hands-on activity is the determination of U in tap water by Liquid Scintillation Counting (LSC). The sample consists of half a litre of tap water acidified to pH 1. Dealing with low activity environmental samples, the execution of some preliminary radiochemical steps is required before performing the measurement. The sample pre-concentration could be performed by exploiting the well-known Ca phosphate co-precipitation efficacy for actinides. The students conduct the experiment by adding calcium nitrate, dibasic ammonium phosphate and adjusting the pH to 9-10 on medium heat to favour crystal growth [1]. The supernatant is discarded, while the precipitate containing the analyte is washed with water and dissolved with nitric acid. Due to the scarce selectivity of the co-precipitation, a radiochemical purification is needed to remove interfering radionuclides like Th and U daughters, that may interfere with the LSC measurement. Solvent extraction with tributyl phosphate (TBP) is chosen as separation method selective for uranium. A lipophilic LSC cocktail is used as diluent for TBP, so that the extracting system can be directly measured via LSC, thus reducing the processing time and maximising the loading factor [2]. Given that no tracer is used, the students should perform the extraction twice for achieving an optimal recovery yield. Afterwards, the recovered organic phases are transferred to a LSC vial and measured. The pulse length index (PLI) and other measuring parameters are previously optimised to allow proper alpha/beta discrimination according to the different decay constant of alpha- and beta-induced voltage pulses. The measuring efficiency is assumed to be equal to the triple-to-double coincidence ratio (TDCR) [3]. The students are requested to estimate the characteristic limits, the activity and the concentration of U-238 and U-234, under the hypothesis of secular equilibrium. In order to verify the reliability of the proposed method, a promisingly confirmatory analysis has been performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Accuracy and precision within 5% are easily obtained by assuming ICP-MS results as reference.

The proposed exercise successfully aims at getting the students familiar with the concepts and best practices of the environmental radiological characterization, such as sample preconcentration, radiochemical separation, alpha measurement by LSC, and data analysis.

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272

Mesoporous nanoceria column-based separation of high-purity $^{99m}TcO_4^-$ from low specific activity ^{99}Mo for radiopharmaceutical applications

Mohamed F. Nawar[1,2*], *Alaa F. El-Daoushy*[2], *Metwally Madkour*[3], *and A. Türler*[1]

[1]Department of Chemistry, Biochemistry, and Pharmaceutical Sciences (DCBP), Faculty of Science, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland
[2]Radioactive Isotopes and Generators Dept., Hot Laboratories Center, Egyptian Atomic Energy Authority, P.No. 13759, Cairo, Egypt
[3]Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat, 13060, Kuwait
[*]E-mail: mohamed.nawar@unibe.ch

Keywords: ^{99m}Tc, ^{99}Mo/^{99}Tc generators, nano-materials, column chromatography, radiopharmaceuticals

Diagnostic interventions in nuclear medicine strongly rely on ^{99m}Tc-radiopharmaceuticals. ^{99m}Tc is commercially available from low-pressure column chromatographic ^{99}Mo/^{99m}Tc generators that use acidic alumina as a sorbent matrix. However, the limited sorption capability of alumina asks for high specific activity ^{99}Mo, which poses serious production challenges and raises proliferation concerns. Therefore, many ideas aimed at using low specific activity (LSA) ^{99}Mo. Nonetheless, the main roadblock is the low sorption capacity of the used alumina. This work demonstrates the feasibility of using different nano-sorbents developed in our laboratory as potential column material for developing ^{99}Mo/^{99m}Tc generators by using low specific activity ^{99}Mo.

First, several cerium oxide nano-sorbents were synthesized using a simple preparation method. Then, their structural characterization was performed using different techniques. Additionally, we evaluated the distribution ratios (K_d) of ^{99}Mo and ^{99m}Tc, the ^{99}Mo breakthrough profile, and the sorption capacity of the synthesized sorbents for carrier-added ^{99}Mo. Eventually, we prepared a ^{99m}Tc generator, and its elution performance was repeatedly evaluated.

Our findings indicate that the materials synthesized are mesoporous and possess a large surface area. Furthermore, The K_d values prove that the parent, ^{99}Mo, is selectively retained on the prepared sorbents, and its daughter, ^{99m}Tc, can be readily collected by using 0.9% NaCl solution. Moreover, the eluted daughter exhibits high chemical, radiochemical, and radionuclidic purity suitable for clinical applications. The payoff for the successful investment of the proposed approach will open up a new possibility to supply onsite, clinical-grade ^{99m}Tc for millions of cancer patients worldwide independently of the fission-produced ^{99}Mo.

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161

A CINCH-HUB: Portal for nuclear- and radiochemistry education and awareness

Martin Sacha[*], *Mojmir Nemec*

Department of Nuclear Chemistry, Czech Technical University, Prague, Czech Republic
[*]E-mail: martin.sacha@fjfi.cvut.cz

Keywords: CINCH, A-CINCH, nuclear, radiochemistry, education, CINCH-HUB

The Cooperation In education and training in Nuclear and radioChemistry (CINCH) project series with the latest project A-CINCH ("Augmented Cooperation in education and training In Nuclear and radioCHemistry") since 2010 produced and developed many tools and materials dedicated to teaching and training nuclear and radiochemistry (NRC) of the target groups ranging from secondary and high school students and teachers, to university levels from bachelor to Ph.D. study, and up to vocational and educational training for professionals or public awareness. One of the long-term aims of the project is to create a single, widely accessible, guidepost pointing the visitors to all the available education materials and related tools in a structured and easily updatable way.

This presentation summarizes the activities and outputs which have been done during the A-CINCH project duration, in particular the development of the so-called CINCH HUB, which is going to integrate all the education activities governed by the CINCH consortium. The hub interconnects already existing and newly created education tools like the Virtual Laboratory, Moodle courses, RoboLabs, Hands-on Trainings, Massive Open On-line Courses (MOOCs), Teach the Teacher package and much more.

Each referenced education tool will be briefly discussed as well as possibilities how to join as a participant, or contribute as an educated professional.

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Mass spectrometry

144

Contribution of mass spectrometry to the enhancement of objectives of radiological characterization in environmental samples

Céline Augeray[1], *Azza Habibi*[1], *Hugo Jaegler*[1], *Coralie Carrier*[1], *Anaëlle Magre*[2], *Béatrice Boulet*[2]

[1]Institut de Radioprotection et de Suûreté Nucléaire (IRSN), PSE-ENV, SAME, LERCA, 781160 Le Vésinet, France
[2]Institut de Radioprotection et de Suûreté Nucléaire (IRSN), PSE-ENV, SAME, LMRE, 91400 Orsay, France
*E-mail: celine.augeray@irsn.fr

Keywords: ICP-MS, environmental analyses

Turnaround time and performances of standard analytical protocols may not be compatible with the objectives (contributing to knowledge of the radiological state, detecting an abnormal rise in radioactivity as early as possible…) and the levels of radioactivity present in the environment. Research and expertise programs, implemented to explain or predict radioactivity transfers between the different compartments of the environment, require a rapid and consistent identification of isotopes (U, Pu, Th) in order to allow experts to determine the origin of radionuclides.

Developments engaged by environmental analyses and metrology department (SAME) at IRSN in order to meet these requirements have made possible to develop reliable methods for the rapid processing and analysis of solid matrices, including chemical treatment – separation and measurement by mass spectrometry. Some of these techniques have been automated and can be used for emergency response. Others have been deployed as part of regular monitoring metrology, where they help to increase productivity and sensitivity.

This communication will be focused on various examples to compare the performances of standard methods with those of the new techniques of preparation and analysis by ICP-MS. This overview of new methods will explain how IRSN's needs are met through faster, more precise and more exhaustive characterizations of environmental samples, both routinely and during radiological emergencies.

141

Quantification of ^{129}I and ^{129}I/^{127}I in environmental samples by ICP-MS/MS

<u>Coralie Carrier</u>[1], Azza Habibi[1], Céline Augeray[1], Denis Maro[2], Lucilla Benedetti[3]*

[1]IRSN/PSE-ENV/SAME/LERCA, Le Vésinet, France
[2]IRSN/PSE-ENV/SRTE/LRC, Cherbourg-Octeville, France
[3]Univ. Aix-Marseille, CNRS, IRD, INRAE, Coll. France, UM 34 CEREGE, Aix-en-Provence, France
[*]E-mail: coralie.carrier@irsn.fr

Keywords: environment, iodine, mass spectrometry

Iodine is an extremely volatile element naturally present under various organic or inorganic forms with different oxidation states (–1, 0, +1, +5 and +7) [1]. These physico-chemical characteristics complicate its extraction and quantification. Among the 37 iodine isotopes, ^{127}I is the only stable one and ^{129}I is the radioisotope with the longest half-life (16.1 x 10^6 y [2]). ^{129}I is chronically and regulatory released by fuel reprocessing plants e.g. La Hague (France). For environmental monitoring and radioecological studies, particles, organic and inorganic gas ^{129}I is often trapped in filter and active charcoal.

To analyse ^{129}I in environmental samples, an extraction step allows the extraction of iodine from solid matrix. Then, the purification is essential to eliminate the matrix components and interfering isotopes. This step could also allow the improvement of detection limits by a concentration of a large quantity of sample. Solvent extraction is the most used technique to isolate iodine from the matrix components. However, it is time consuming and often requires the handling of hazardous substances. Liquid chromatography and more specifically extraction chromatography appears to be a more convenient technique than solvent extraction [3].

Despite the efficiency of γ-spectroscopy and LSC to quantify ^{129}I in contaminated samples, the detection limits provided are often higher than the environmental background. Furthermore, none of these techniques allows the determination of ^{129}I/^{127}I isotopic ratio.

Mass spectrometry (e.g. ICP-MS* and AMS**) is an excellent alternative for the determination of ^{129}I and ^{129}I/^{127}I isotopic ratio [4].

In this work, a safe and innovative method to quantify ^{129}I and ^{129}I/^{127}I in charcoal and air filters samples was developed. It is based on an acid digestion, optimized by DOE***, followed by a purification with solid phase extraction, usually meant to be used with LSC. It was adapted to ICP-MS measurement and the elution medium was meticulously studied with the aim to be compatible with ICP-MS measurement while minimizing spectral and non-spectral interferences. The isobaric interference due to ^{129}Xe was drastically reduced by reaction gas using ICP-MS/MS.

Excellent figures of merits including a signal gain > 20 and the memory effect elimination were obtained. The achieved performances allowed decreasing the detection limit for ^{129}I (2 mBq for solid sample) and ^{129}I/^{127}I (10^{-9}) [5] with excellent accuracy and precision. This method was successfully applied to analyse particulate and gaseous ^{129}I sampled on air filters and charcoal near La Hague reprocessing plant in France.

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93

Fluoride target material for ^{26}Al measurements by ion-laser-interaction mass spectrometry

Kateřina Fenclová[1*], *Tomáš Prášek*[1], *Mojmír Němec*[1], *Martin Martschini*[2], *Peter Steier*[2]

[1]Department of Nuclear Chemistry, Czech Technical University in Prague, 115 19 Prague 1,
Czech Republic
[2]VERA Laboratory, Faculty of Physics, University of Vienna, 1090, Vienna, Austria
[*]E-mail: katerina.fenclova@fjfi.cvut.cz

Keywords: accelerator mass spectrometry, AMS, ion-laser-interaction mass spectrometry, 26Al, fluoride matrix

Determination of ^{26}Al with accelerator mass spectrometry (AMS) finds use in several fields of interest, for example isotopic characterization of meteorites and rocks, especially for their age determination, or in paleoclimate studies for polar ice dating. Routine AMS measurements of ^{26}Al/^{27}Al isotopic ratios are often performed by using Al_2O_3 target material and subsequent extraction of negative Al^- ions from ion source. In such case, interfering ^{26}Mg isobar is suppressed, as magnesium does not form sufficiently stable negative ions, however the intensity of $^{26}Al^-$ currents is significantly lower compared to molecular ions like $^{26}AlO^-$ or $^{26}AlF_4^-$ from the fluoride sample material [1]. These molecular ions are unfortunately not suitable for the analysis with common AMS systems due to the MgO^- based molecular isobaric interference formation on the corresponding masses. For this reason, performance of fluoride materials using a superhalogenide ion AlF_4^- extracted from Na_3AlF_6 based targets was analysed with ion-laser-interaction mass spectrometry (ILIAMS) at VERA Laboratory (University of Vienna) [2] with the aim to eliminate the magnesium interference at the mass of $^{26}AlF_4^-$ by using the laser techniques, while maintaining high yields of aluminium ions. A possibility of fluoride matrix utilization for ^{26}Al measurements was investigated previously with a standard AMS system MILEA at ETH Zürich where the ^{26}Al/^{27}Al measurements failed due to the strong magnesium interference [1]. In both studies, AlF_4^- current was used to evaluate performance of the Na_3AlF_6 and additives as PbF_2 were tested to increase the extracted ion currents. Besides, samples containing MgF_2 were used to investigate the presence of isobaric ions. In this study the signal of $^{26}Mg^{3+}$, while injecting the mass of $^{26}AlF_4^-$, was investigated with the gas ionization detector and was affected with different kind of lasers and cooling gases to successfully remove the magnesium interference.

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203

Boron isotopic analysis *via* MC-ICPMS in zirconium-rich and lithium-rich matrices

Timothy Gregory[*], *Daniel Stubbs, and Simon Woodbury*

National Nuclear Laboratory Ltd., Central Laboratory, Sellafield, UK
[*]E-mail: timothy.gregory@uknnl.com

Keywords: boron, MC-ICPMS, isotopic, neutron poison, control rod, mass spectrometry.

Boron has two naturally occurring isotopes: ^{10}B and ^{11}B. Boron-10 is an effective neutron poison because of its large neutron capture cross section [1]. The ^{10}B/^{11}B of natural materials [2] is ~ 0.25 (~ 19.8 atom% ^{10}B and ~ 80.2 atom% ^{11}B), and, as a boron-bearing neutron poison is irradiated with neutrons, the ^{10}B is consumed *via* a ^{10}B(n,α)^{7}Li reaction. Therefore, with increasing neutron irradiation, the mass of ^{10}B decreases, the mass of ^{7}Li increases, and the mass of ^{11}B remains constant. In principle, the ^{10}B/^{11}B in a control rod can range from 0.25 (no burn-up) to 0 (complete burn up), and the concomitant [Li]/[B] can range from 0 (no burn up) to 0.25 (complete burn up). It is therefore useful to be able to measure the boron isotopic composition of neutron poisons to high-precision to assess the degree of burnup. Multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) is well suited to making such measurements.

Prior to MC-ICPMS analysis, boron is usually separated from matrix elements *via* ion-exchange chromatography [3] or micro-sublimation [4] to eliminate isobaric interferences and plasma matrix effects. However, chemical separation is time consuming, expensive, hazardous, increases operator radiation dose, and has the potential to introduce blank and isotopic fractionation to the sample. Boron's volatility in acid media [5] complicates matters by increasing the chance of sample loss and isotopic fractionation. It would therefore be advantageous to measure boron isotopic ratios *via* MC-ICPMS without chemical separation.

To this end, we established a boron isotopic analysis capability *via* MC-ICPMS in our active laboratory. Our instrument is a 'nuclearised' NuPlasmaII able to measure solutions with an activity of up to 3.7 MBq alpha and 170 MBq beta. We introduced our samples in a solution of 0.3 M hydrofluoric acid–0.5 M nitric acid using a perfluoroalkoxy alkane spray chamber as a 'wet plasma'. We measured ^{10}B and ^{11}B in static mode using Faraday cups equipped with 10^{11} Ω feedback resistors. The boron concentration in our solutions was typically 200 ng mL^{-1}. We employed strict data rejection criteria based on the interquartile range of repeat measurements rather than the conventional standard deviation criteria.

We measured the isotopic composition of a reference solution to high-precision (typically ~ 0.5 ‰, 2sd for ^{10}B/^{11}B) doped with varying amounts of zirconium (to simulate cladding) and lithium (to simulate lithium ingrowth). We varied the [Zr]/[B] in our solutions from 0 to 200 and the [Li]/[B] from 0 to 0.25. We saw no perturbation in our ability to measure boron isotopic ratios accurately and there was no impact on precision. Thus, we demonstrated that we are able to measure boron isotopic ratios in zirconium-cladded control rods over a wide range of chemical matrix concentrations over a range of [Li]/[B] ratios.

Acknowledgments

We thank Joe Stewart (Bristol Isotope Group) for his advice when we were setting up our instrument.

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146

Field of applicability of triple quadrupole mass spectrometry (ICP-MS/MS) for the measurement of radioactivity in the environment

Azza Habibi, Hugo Jaegler, Coralie Carrier, Céline Augeray, Danièle Dias Varela, Isabelle Baconet, Delphine Haloche*

Institut de Radioprotection et de Suûreté Nucléaire (IRSN), PSE-ENV, SAME, LERCA,
781160 Le Vésinet
*E-mail: hugo.jaegler@irsn.fr

Keywords: ICP-MS/MS, environmental analyses

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is an analytical method based on the separation, identification and quantification of the isotopes of a sample according to the value of mass/charge ratio. When ICP-MS is quadrupole, it is based on the coupling of a plasma torch generating ions, a collision reaction cell, a quadrupole mass spectrometer and a detector allowing the conversion of the ion beam into a quantifiable electrical signal.

Since its commercialization in the 1980s, ICP-MS has been adopted for the simultaneous analysis of trace and ultra-trace elements (isotopes less than 10^{-6} g/g) and for the determination of isotope ratios in biological and environmental samples. Indeed, this technique, fast and multi-elemental, allows the analysis of 20 to 30 different isotopes in about ten minutes.

During the last decade, triple quadrupole ICP-MS devices (ICP-MS/MS), containing two mass filters that surround the collision reaction cell, have been introduced on the market. This new technology has extended the applicability of this technique and improved the performance of the instruments including sensitivity, abundance sensitivity, instrumental background and accuracy on isotopic ratios.

These improvements have made this new technology, the ICP-MS/MS, an essential piece of equipment in the field of radioactivity measurement in environmental samples. This measurement technique can now be an alternative to some less accessible mass spectrometry methods such as the Accelerator Mass Spectrometer (AMS) for many radionuclides (^{129}I, ^{226}Ra, ^{234}U, ^{235}U, ^{236}U, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{241}Pu...).

The applicability of ICP-MS/MS for the quantification of a given isotope and its competitiveness with AMS depends essentially on the period of the isotope, its interferents and its ionization potential. The objective of the work carried out by IRSN is therefore to compare the analytical performances of ICP-MS/MS and AMS (detection limit, precision and analysis times). This comparison will make it possible to evaluate the extent to which ICP-MS/MS can constitute an alternative to the use of AMS in the context of quantifying radioactivity in environmental matrices (water, aerosols, mineral and biological matrices), both in routine situations and in the context of control, monitoring, expertise and research programs.

131

Recent developments of radiopurity measurements by mass spectrometry for the LEGEND experiment

Jakub Kaizer[1*], *Marek Bujdoš*[2], *Miroslav Ješkovský*[1], *Ivan Kontuľ*[1], *Jakub Zeman*[1], *Pavel P. Povinec*[1]

[1]CENTA, Faculty of Mathematics, Physics and Informatics, Comenius University, 841 48 Bratislava, Slovakia
[2]Faculty of Natural Sciences, Comenius University, 84215, Bratislava, Slovakia
[*]E-mail: kaizer@fmph.uniba.sk

Keywords: thorium, uranium, AMS, ICPMS

Large-scale experiments which have been established in order to answer some fundamental questions of nuclear physics, such as LEGEND (Large Enriched Germanium Experiment for Neutrinoless *ββ* decay), have been recently arising the need for precise and reliable radiopurity measurements on the nBq g^{-1} scale. The LEGEND collaboration has been developing a ^{76}Ge-based double-beta decay experimental program which proceeds to a discovery potential at a half-life beyond 10^{28} years [1]. One of the main contributors to the background of any nuclear physics underground experiment includes natural thorium (^{232}Th) and uranium (^{238}U). The content of thorium and uranium in construction materials of a detector can be determined by advanced mass spectrometry methods, such as inductively coupled plasma mass spectrometry (ICP-MS) and accelerator mass spectrometry (AMS). ICP-MS offers relatively quick and inexpensive analysis down to 10^{-15} g per sample of a small size (<0.5 g) [2]. However, it requires separation of radionuclides of interest from original sample due to possible unwanted matrix and isobaric (monoatomic and polyatomic) interferences. These steps, which are crucial for radiopurity measurements at the ultra-trace levels, enable their pre-concentration, resulting in further improvement of detection limits.

Although AMS is expected to reach better detection limits for ^{232}Th and ^{238}U than ICP-MS, sample preparation is even more complicated. AMS typically utilizes sputtering of a target by cesium ions, thus thorium and uranium must be co-precipitated from dissolved sample on a solid matrix (ferric oxide) prior to analysis. This material is then pressed in a target holder which is installed in an ion source of the AMS system. Because AMS determines isotopic ratio, it is important to add tracers during sample preparation. The presentation will cover recent developments in thorium and uranium determination by ICPMS and AMS, together with basics of separation chemistry applied in order to process different sample matrices. The new possibility to measure ^{232}Th and ^{238}U by ICP-MS and development of AMS at the Comenius University in Bratislava will be also discussed.

Acknowledgments
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130

Complexation effect on the radiolytic stability of DOTA ligand: An experimental and theoretical approach

Ilyes Mahti, Dominique Guillaumont, Xavier Hérès, Georges Saint-Louis,
*Laurence Berthon**

CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France
*E-mail: laurence.berthon@cea.fr

Keywords: radiolysis, complexation, computational chemistry, nuclear medicine

For both diagnostic and therapeutic purposes, radioisotopes are increasingly used in nuclear medicine. To reach the target cells in the biological environment, these elements are attached to a vector via a chelating molecule. In contact with radioisotopes, the chelating molecule is subjected to the effects of radiation, which can lead to its degradation and induce an alteration of its complexing properties. Therefore, it is important to study the impact of radiolysis on the speciation of "radioisotope-chelating molecules" complexes.

The ligand DOTA (1,4,7,10– tetraazacyclododecane -1,4,7,10-tetraacetic acid) has been studied for a long time because it is currently used for medical imaging, especially as a chelating molecule for gadolinium. Zirconium has a positron-emitting radionuclide, ^{89}Zr, which is an isotope of interest for medical PET imaging (Positron Emission Tomography). The complexes formed between the chelating molecules and the radioisotopes must be very stable in order to avoid the release of the metal in the body. Many clinical trials were done to find the best chelating molecule for ^{89}Zr. [1] More recently, a study showed that the DOTA ligand allowed the formation of the most stable zirconium complexes. [2]

Previous work has been done on the degradation of the DOTA ligand under alpha irradiation. The study revealed that the ligand is degraded preferentially by decarboxylation and cleavage of the acetate arm -CH_2-COOH. [3]

The aim of this study is to investigate the radiolytic stability of the DOTA ligand and the Zr-DOTA complex in aqueous solution. The degradation products obtained by gamma irradiation of our compounds were identified by Electrospray Ionization Mass Spectrometry (ESI-MS). Quantum chemistry calculations by DFT were also performed to determine binding dissociation energies (BDE) and calculate Fukui functions (Figure 1). Fukui indices indicates chemical reactivity of a particular atom towards radical attack whereas BDEs evaluate bond strength.

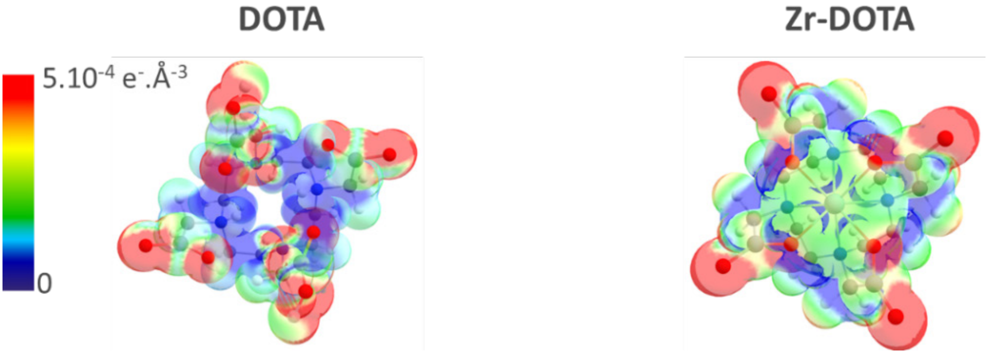

Figure 1. Radical Fukui function (R) calculated for DOTA and Zr-DOTA. Color scales the values of the Fukui function.

The degradation of the ligand when complexed with Zr is significantly less important than when it is free in solution, which indicates that the metal protects the ligand from degradation. Moreover, the degradation products are different within the complex. These results have been strengthened using theoretical chemistry calculations.

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153

Characterization of meteoric ^{10}Be in certified reference materials for use in internal control standards

Gerardo Rojas[1], *Grisel Méndez García*[2,3*], *Santiago Padilla*[4], *Corina Solís*[3], *Efraín Chávez*[3], *and Arcadio Huerta*[3]

[1]Facultad de Química, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico
[2]CONACyT - Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico
[3]Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico
[4]Centro Nacional de Investigación Humana (CENIEH), Burgos, España
[*]E-mail: griselmendez@fisica.unam.mx

Keywords: cosmogenic isotopes, sediments, particulate matter, AMS

In recent decades, interest in the measurement of ^{10}Be and ^{26}Al produced by cosmic rays has grown due to the many applications they have in various fields of science. Trace amounts of 10Be and 26Al produced from meteoric or atmospheric sources require sensitive accelerator mass spectrometry (AMS) measurements and robust sample preparation.

The extraction, separation, and preparation of the appropriate oxide form for AMS require extensive and careful laboratory processing and standard reference materials to validate the chemical performance of the protocols used, as well as the calibration of the AMS system in the measurement. In this work, the meteoric concentrations of ^{10}Be and ^{26}Al in three reference materials are characterized to establish their suitability for use as internal control standards for laboratory chemical preparation and AMS measurements of these radioisotopes in our laboratory. Preliminary results show high repeatability and low uncertainties (less than 10%) in particulate matter and sediment samples.

150

Measurement of ^{129}I/^{127}I isotopic ratios in sea and fresh water samples by MILEA

Miriam Mindová[1*], *Mojmír Němec*[1], *Martin Daňo*[1], *Christof Vockenhuber*[2], *Xiaolin Hou*[3]

[1]Department of Nuclear Chemistry, CTU, Prague, Czech Republic
[2]Laboratory of Ion Beam Physics, ETH Zürich, Zurich, Switzerland
[3]Department of Environmental and Resource Engineering, DTU, Roskilde, Denmark
[*]E-mail: miriam.mindova@fjfi.cvut.cz

Keywords: ^{129}I, AMS, seawater samples

The majority of ^{129}I (with a half-life of 15.7 My) in the environment comes from human nuclear activity, especially from reprocessing facilities of nuclear fuel. In this work seawater and freshwater samples collected by DTU (Technical University of Denmark) were used and processed. Iodine was separated from pre-treated water samples with solvent extraction and subsequent precipitation as AgI. Measurement of the iodine concentration in each sample by ICP-MS took place at DTU.

Within this work, the first batch of iodine samples were separated from environmental water samples in Denmark and prepared as AgI which were then pressed in copper target cathodes and measured at the MILEA (Multi Isotope Low Energy AMS) system at LIP, ETH Zürich, Switzerland. Measured ^{129}I/^{127}I atomic ratios range from 1×10^{-7} to 2×10^{-6}. Higher ^{129}I concentrations in seawater samples collected from the North Sea comparing to in the samples collected from the Baltic Sea was observed. This corresponds with the known dominant source of ^{129}I in this region - reprocessing plants at La Hague (France) and Sellafield (United Kingdom), which was discharged into the marine environment. Iodine-129 labeled water is transported by sea current to the north along the European coast. Small part also enters in the North Atlantic Ocean and causes increased concentration of ^{129}I there. The main part of ^{129}I in North Atlantic Ocean was originated from nuclear weapons fallout [1]. The measurements show that the ^{129}I/^{127}I ratios for seawater samples from Greenland seas varies from 2×10^{-8} to 4×10^{-9} and for seawater surrounding the Faroe Islands was $5\text{-}10\times10^{-10}$. The results show that ^{129}I serves as a good oceanographic tracer for monitoring water mass exchange [2]. Values for freshwater samples, specifically Danish rivers, reached ratios of 1×10^{-8} - 4×10^{-9}.

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158

Quo vadis, radioanalytics?

Pavel P. Povinec[*]

Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovakia
[*]E-mail: pavel.povinec @uniba.sk

Keywords: radionuclides, C-14, Be-10, U, Th, underground gamma-spectrometry, AMS, ICPMS

Many scientific investigations from very different fields have been crucially depended on the sensitivity, accuracy and precision of radionuclide measurements in various types of samples, as well as on the radionuclide contamination of instruments used for such investigations. We may mention, e.g., investigations of rare nuclear decays and processes in physics with large-scale underground experiments searching for neutrinoless double beta-decays of several isotopes with target masses reaching one ton, or even more (e.g., for Ge-76 [1] and Xe-136 [2]), as well as searchers for dark matter particles applying various techniques for registration of candidates either of low mass (<1 GeV/c^2) or high mass particles [e.g., 3,4]. These topics initiated new research on ultra-radiopure materials required for construction of detectors operating in deep underground laboratories. On the other hand, a direct radionuclide activity measurement with high precision in very small samples has been even more challenging process because it requires to fulfil both these requirements, i.e., a very low instrumental background and high efficiency of the radionuclide analysis in small samples. This has been well demonstrated in climate change studies using isotope archives, e.g., C-14 in tree rings [5], and Be-10 and Cl-36 in ice cores [6]. We shall review the present status of the ultra-sensitive radioanalytic technologies (underground gamma-spectrometry, AMS and ICPMS) and discuss possible improvements in the future.

Acknowledgments

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32

Sequential analysis of ^{36}Cl by ion chromatography-ICP-MS/MS with deuterium gas reaction via dynamic reaction cell

Yoshitaka Takagai[1,2*], *Makoto Matsueda*[1], *Makoto Furukawa*[1,3], *Tatsuya Shoji*[1],
Kyoko Kobayashi[3], *Tomohiko Kawakami*[4], *Yumi Suzuki*[4], *Nobuyuki Sekine*[5],
Hisashi Mikami[5], *Takahiro Matsuda*[6]

[1]Faculty of Symbiotic Systems Science, Cluster of Science and Technology, Fukushima University, Fukushima, Japan
[2]Institute of Environmental Radioactivity, Fukushima University, Fukushima, Japan
[3]PerkinElmer Japan Co., Ltd., Kanagawa, Japan
[4]Kaken Inc., Ibaraki, Japan
[5]Fuji Electric Co., Ltd., Kanagawa, Japan
[6]The Japan Atomic Power Company, Tokyo, Japan
[*]E-mail: s015@ipc.fukushima-u.ac.jp

Keywords: chlorine-36, beta particle emitter, ICP-MS/MS, dynamic reaction cell, deuterium, hydrogen

Chlorine-36 (^{36}Cl; half-life = 3.01 × 10^5 years) is produced by neutron activation reaction ^{35}Cl(n, γ)^{36}Cl and has a long half-life with high mobility in environment. Whereas most of the generated ^{36}Cl remains inside in reactor, a small amount of ^{36}Cl has been released into environment *via* the decommissioning process. In spite of the monitoring of ^{36}Cl is important, the literature regarding effective measurement means of ^{36}Cl was little reparted. Meanwhile, inductively coupled plasma mass spectrometry (ICP-MS) as typical rapid analysis has a problems concerning isobaric interferences in ^{36}Cl analysis. The coexistence of ^{36}Ar (0.34%) and ^{36}S (0.02%) has not been allowed in the mass-spectrometric analysis of ^{36}Cl, and polyatomic ions have been further caused by the generation of ^{35}Cl^{1}H. As another interferences, the peak tailing arising from large amounts of ^{35}Cl would be always caused. The significant number of separation efficiency exceeding ten to the power of 9 would be required to overcome the problem for the discrimination. There are no literature concerning ICP-MS analysis of ^{36}Cl, whereas ICP-MS has great advantages in the rapidity compared with other analytical method.

In this study, we have approached deuterium gas reaction *via* dynamic reaction cell (DRC) in ICP-MS/MS technology. Utilizing hydrogen gas is very classical means in ICP-MS. In spite of little differences in chemical properties between of these hydrogen isotopes has been thought, the rapid and sequential quantification of ^{36}Cl using ICP-MS/MS with deuterium gas reaction via DRC overcame various problems in ^{36}Cl analysis rather than use of hydrogen (H_2) in DRC. In addition, to achieve the desired analysis, the proposed ICP-MS/MS analysis connected with ion-chromatography (IC) was also proposed in this study. Furthermore, addition/recovery experiments were conducted on actual samples.

Neutron activation analysis

200

Simultaneous determination of 21 elements in microgram quantities of marine suspended particulate matter by instrumental neutron activation analysis

Asoka I. Kulathilake, 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: a.chatt@dal.ca

Keywords: marine suspended particulate matter, conventional instrumental neutron activation, cyclic instrumental neutron activation, epithermal instrumental neutron activation

Suspended particulate matter (SPM) in ocean water is frequently conglomerates of various components. Sizes of individual components vary from less than 1 µm up to several mm; the majority by number of particles is less than 10 µm. In practice, SPM is commonly defined with reference to a minimum diameter, depending on the pore size of the filter being used for collecting them. Fraction retained on Nuclepore polycarbonate membrane filters with a pore size of 0.4 µm was considered as SPM in the work reported here. Natural marine SPM consists of a large number of components: inorganic material such as sand, clay and minerals; living organisms such as phytoplankton, zooplankton, bacteria and fungi; and organic detritus. It is of much interest to determine the mass fractions of various elements in SPM to understand their origin as well function. In the present study, 22 samples of SPM were collected from 5 different locations in the Cabot Strait and Gulf of St. Lawrence of the Atlantic Ocean. A conventional instrumental neutron activation analysis (INAA), a cyclic INAA (CINAA), and an epithermal INAA (EINAA) methods were developed for the simultaneous determination of up to 21 elements in these samples using the Dalhousie University SLOWPOKE-2 reactor (DUSR) facility at a neutron flux of $5x10^{11}$ cm^{-2} s^{-1}. The samples were irradiated in normal and cadmium-shielded sites for various lengths of time, allowed to decay, and counted using coaxial Ge(Li) and low-energy photon detectors. The list of elements determined included Al, Au, Ba, Br, Ca, Ce, Cl, Fe, Hg, I, K, La, Mg, Mn, Na, Sc, Sm, Sr, Ti, V and Zn. An elaborate quality assurance scheme was designed to check the precision and accuracy of measurements. Details of methods along with results will be presented.

264

Total fluorine quantification by INAA at SLOWPOKE NAA Laboratory of Polytechnique Montréal

Darren R. Hall, Cyril Koclas, Cornelia Chilian[*]

Department of Engineering Physics, Polytechnique Montréal, Canada
[*]E-mail: cornelia.chilian@polymtl.ca

Keywords: fluorine determination, instrumental neutron activation analysis, plastics, per- and polyfluoroalkyl substances, PFAS, hydrocarbons and organic samples

This paper presents a new instrumental neutron activation method based on the $^{19}F(n, \gamma)^{20}F$ reaction using the SLOWPOKE-2 reactor of Polytechnique Montréal at thermal neutron fluence rates varying between 10^{10} cm^{-2}s^{-1} and 10^{12} cm^{-2}s^{-1}. The calibrator standards were prepared from 10 up to 10 000 µg/mL NaF certified solutions on filter paper, or from 99.9% KF anhydrous powder. The method was validated with certified or custom reference materials. The calibrators, reference materials and samples were encapsulated in 1.4 or 5 mL HDPE vials and irradiated using a fast pneumatic transfer system with transit times below 5 s. The nuclear interference from the reaction $^{23}Na(n,\alpha)^{20}F$ was corrected using certified NaOH solutions on filter paper irradiated and counted under the same conditions. We present results for fluorine quantification in organic matrices having fluorine concentrations varying from trace level up to 60 wt% fluorine content. The limit of quantitation of this method is the concentration of the lowest calibrator standard.

107

A calculator for gamma-ray yield analysis of neutron activation with arbitrary neutron beam

Tongyuan Cui[1,2], *Yigang Yang*[1,2*]

[1]Department of Engineering Physics, Tsinghua University, Beijing, P. R. China
[2]Key Laboratory of Particle & Radiation Imaging, Tsinghua University, Ministry of Education, Beijing, P. R. China
[*]E-mail: yangyigang@mail.tsinghua.edu.com

Keywords: neutron activation analysis, delayed gamma-ray, isomeric ratio, arbitrary neutron spectrum

A calculator aiming to evaluate the quantities of the delayed gamma-rays released by samples irradiated by user given arbitrary pointwise neutron spectrum was developed to address the problem that existing calculators could only accepts the neutron flux with limited parameters, typically, the thermal neutron flux, the Cd ratio and the fast to thermal neutron ratio. With the aid of the evaluated nuclear databases and carefully calculation of isomeric ratios in the activation process, this calculator shows the smallest error to the experimental results[1] comparing to online calculators from NCNR[2] and WISE[3] on calculating the specific delayed gamma-ray yields of neutron irradiated samples with elements from oxygen to lead (Z=8-82), as is shown in Fig. 1. This calculator is written by MATLAB and we named it CYANUS (the Calculator for Yield Analysis of NeUtron Activations). At present, it could be downloaded from https://cloud.tsinghua.edu.cn/f/2132e9c880bf4a1eb067/

Figure

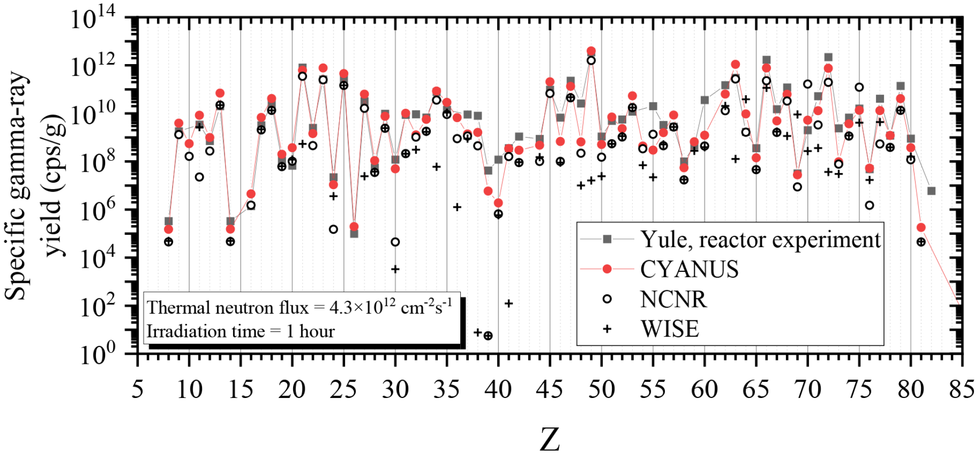

Fig.1 Comparison of the calculated and experimental specific gamma-ray yields of elements with Z=8-82 at the end of 1-hour irradiation with neutrons of 4.3×10^{12} cm^{-2}s^{-1}.

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128

User access opportunities at the Neutron Activation Analysis laboratory of the Budapest Neutron Centre (BNC)

Katalin Gméling[*]*, László Szentmiklósi*

Nuclear Analysis and Radiography Department, Centre for Energy Research, Budapest, Hungary
[*]E-mail: gmeling.katalin@ek-cer.hu

Keywords: instrumental neutron activation analysis, user laboratory

Neutron activation analysis (NAA) is a highly appreciated technique for the non-destructive and bulk-representative elemental composition measurement of samples. However, the recently experienced decline in the number of operational reactor-based neutron sources in Europe, both for foreseen and unexpected reasons, limited the access possibilities to NAA measurements.

The Budapest Neutron Centre's (BNC) NAA laboratory, in addition to its significant contributions to method developments (e.g. the k_0-NAA method), to its in-house research programs, and to internal services to the reactor operation, has been increasingly utilized in the past decade as an NAA service provider to our domestic and international user community. From 2004 to 2016, the NMI3 access program, a pan-European coordination action of neutron research activities integrated all research infrastructures in these fields within the European Research Area. After the termination of this funding scheme, BNC's own user program, as detailed on the website www.bnc.hu, became more emphasized. Further, our lab became a partner in several topic-oriented transnational access programs. Notable examples are the series of EU-funded projects in heritage science (CHARISMA, IPERION CH, IPERION HS, E-RIHS), the central European collaboration in material science (CERIC-ERIC), and the nuclear training activities coordinated by the IAEA. In 2022, BNC offered beamtime to the users of other European neutron facilities, where their accepted proposals were delayed due to prolonged downtimes (BNC LENS beamtime initiative).

The high level of service for the user community requires technical and organizational considerations. External users propose measurements in different disciplines, so the matrices and the elements of interest show large diversity. The lab needs operation flexibility and a deep understanding of the method to realize these experiments. As the user needs to submit a formal measurement proposal, where irradiation and measurement conditions must be reasonably well estimated in advance, prediction tools of NAA (e.g. NAAPro) or even Monte Carlo calculations (e.g. MCNP) must be extensively used.

Unlike other neutron beamline instruments, the NAA measurement procedure is lengthy and may need up to 4-6 weeks to complete the analytical workflow and report the results. The timing is crucial, as the irradiation shall be harmonized with the other activities of the reactor, while measurement must take place in given periods following the irradiation. The user therefore can typically attend only part of the procedure, either during sample preparation, or the gamma spectrometry measurements. In all cases, the discussion, the interpretation, and the publication of the results are done together with the user.

The recent COVID-19 pandemic forced many labs to follow new operation routines. The rise in remote access, i.e. the collaborative measurements without the personal presence of the user, could be facilitated by the intense use of modern online communication tools. The difficulties in accessing the labs called for a higher level of automation of the measurement process as well as the data evaluation.

The third main pillar of collaboration is the form of joint research projects, where the analytical service is provided for the project members. This activity, from a lab management point of view, is easier to schedule, and the scope of the measurement is better known. Two recent flagship collaborations are in nuclear-grade concrete engineering (V4-Korea RADCON) and the circular economy (ReMade@ARI).

We will present research highlights made in collaborations to illustrate the prosperity of this operational model.

241

Comparison of EDXRF and k_0-INAA methods used for analysis of organic and inorganic materials

Radojko Jacimovic[1]*, *Marijan Necemer*[2]

[1]Department of Environmental Sciences, Jozef Stefan Institute, Ljubljana, Slovenia
[2]Department of Low and Medium Energy Physics, Jozef Stefan Institute, Ljubljana, Slovenia
*E-mail: radojko.jacimovic@ijs.si

Keywords: EDXRF, k_0-INAA, multi-element analysis, environmental samples, comparison

In this work, we focus on the comparison of two non-destructive analytical techniques, Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) and the k_0-method of Instrumental Neutron Activation Analysis (k_0-INAA), for multielement determination in organic and inorganic materials. The EDXRF enable fast and cheap screening of multielement content of various types of a sample with minimum sample preparation requirement. The method is especially suitable as well as reliable for studies where the distinction among a larger number of samples is investigated. On the other hand, the k_0-INAA technique is more accurate and sensitive and can be used to determine major, minor and trace elements in various samples, but is more time-consuming. In general, the method is widely spread in laboratories, which have nuclear research reactors and absolutely calibrated HPGe detectors.

Performance characteristics of both methods such as sample preparation, analytical results, limits of detection of elements (LOD), cost/sample, available range of elements for analysis, cost of analytical instrument etc., will be investigated and compared. In addition, some examples of internal comparison of the results of analysis between methods for various organic and inorganic materials will be presented and discussed. In the case of interlaboratory comparison (ILC) samples, the performance of both methods will be evaluated by the organizer's criteria.

Acknowledgments

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175

INAA of sands from the Badain Jaran Desert in search of the parent impact crater for Australasian tektites

Jiří Mizera[1,2*], *Vladimír Strunga*[1], *Martina Havelcová*[2]

[1]Nuclear Physics Institute, Czech Academy of Sciences, Husinec-Řež, Czech Republic
[2]Institute of Rock Structure and Mechanics, Czech Academy of Sciences, Praha, Czech Republic
[*]E-mail: mizera@ujf.cas.cz

Keywords: Badain Jaran Desert, WEDP02 drill core, INAA, Australasian tektite, impact crater

The Badain Jaran Desert (BJD), Northwest China, is a place of geological mysteries such as existence of sand megadunes and lakes, hydrothermal activity, and abrupt paleoenvironmental changes during the Mid-Pleistocene transition. We have proposed a hypothesis connecting the mysterious features of BJD with a meteoritic impact which at 788 ka produced Australasian tektites (AAT), with strewn field covering one sixth of the Earth's surface and unknown parent crater [1]. The suggested location of the AAT impact to BJD, an alternative to the consensus location in Indochina, has been supported by multiple lines of evidence: 1) suitability and sufficient supply of pre-impact BJD sediments as AAT source material, anticipated from close geochemical match between AAT and Chinese loess, and from paleoenvironmental proxies in the WEDP02 drill core situated at the edge of the supposed impact crater; 2) ideal conditions for crater burial under Holocene sand megadunes, and relatively small ecological consequence of the AAT impact consistent with impact into an area surrounded by mountains; 3) gravity data indicating existence of a large circular structure in the BJD megadune area centered at 39.7°N, 102.2°E; 4) specific features of this location possibly attributable to post-impact effects including formation and maintenance of megadunes and lakes, with signs of hydrothermal activity; 5) recovery of possible products the impactor ablation and other impact-related features in Chinese loess layer coeval with the AAT impact; 6) agreement with principles of distal ejecta ballistic transport and distribution of various morphological and constitutional AAT types.

In 2021 and 2022, sand samples from the WEDP02 drill core (from depth range dated to Lower to Middle Pleistocene) have been acquired from the Lanzhou University for geochemical analysis, mainly by instrumental neutron activation analysis (INAA). The analyzed coarse sand samples show less geochemical similarity with AAT than, e.g., loess samples or modern sands from BJD and neighbouring Tengger Desert, probably due to lower clay and higher carbonate fractions. On the other hand, a pronounced Ba anomaly (identified as sulphate) was determined in a sample dated around the impact; similar anomalies have been described in connection with the Cretaceous–Paleogene impact and extinction event (Chicxulub crater). A possibility that the analyzed BJD sands represent fallback ejecta depleted in the fine clay fraction is discussed, among others in view of recently reported stable isotope record from the WEDP02 drill core showing several anomalies within the analyzed depth range. Other new indicators of the impact in BJD found recently in literature will also be presented.

Acknowledgments

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36

High spatial and energy resolution for alpha particles using a Timepix detector chip

<u>Jeroen Plomp</u>, Antonia Denkova, Joep Hoefsloot, Erik van Lieshout,

Delft University of Technology, The Netherlands
*E-mail: j.plomp@tudelft.nl

Keywords: Timepix, alpha radiation, alpha spectroscopy, apatial resolution

Alpha radionuclide therapy is very promising in the treatment of metastasised tumours. One of the most applied radioisotopes in this therapy is ^{225}Ac which is a part of a decay chain having daughter radionuclides that also emit alpha radiation making it a very potent treatment. However, upon decay the newly formed daughters are released and can damage healthy tissue. It is therefore of an importance to detect the location and activity of these daughters in model systems to be able to determine possible adverse side effects of current and new treatments using 225Ac but also other alpha emitters. This requires an alpha spectrometer with tens of µm position sensitivity and good energy resolution. The energy resolution is still missing in the classical alpha camera systems.

Here, we present a new detection method based on the Timepix detector. The Timepix detector, developed by CERN, is a 256 x 256 pixilated detector chip with 55 µm size pixels with an energy determination per pixel. When the alpha particle hits the Timepix chip it will deposit its energy and distribute this over several pixels, typically 4 to 20. From this event the total energy can be calculated as well as the sub-pixel position of the alpha. In our experiments, we have shown to reach a sub-pixel resolution of 10 µm with the help of a special microchannel plate collimator and a ^{241}Am source, as well as achieving an energy resolution of 10 keV. This enables us to image small quantities of ^{225}Ac with high spatial resolution and at the same time to identify the alpha emitting daughters of ^{225}Ac. This method opens exciting new opportunities but still has several challenges that need to be overcome..

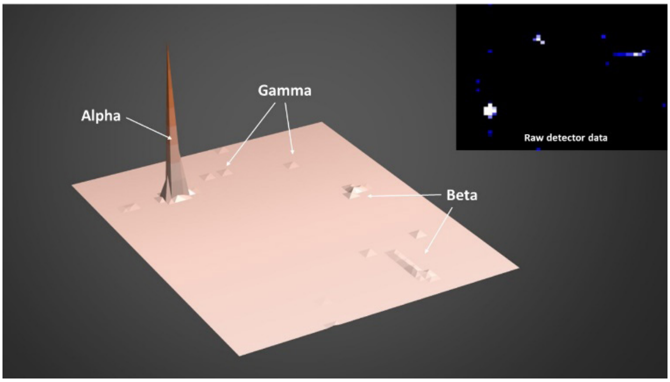

Figure 1; Raw detector image of the TimePix with in plane the position (x,y with 55µm/pixel) and energy in z (peak height). The alpha is clearly distinguishable from the Beta and gamma hits.

223

Keeping the legacy – a NAA database spanning three laboratories and multiple reactors

Johannes H. Sterba[1*], *Hans Mommsen*[2]

[1]Center for Labelling and Isotope Production, TRIGA Center Atominstitut, TU Wien, Vienna, Austria
[2]Helmholtz-Institut für Strahlen- und Kernphysik, University of Bonn, Bonn, Germany
[*]E-mail: johannes.sterba@tuwien.ac.at

Keywords: interlaboratory comparison, archaeometry, NAA

In the late 1960ies, Perlman and Asaro [1] started routine chemical analysis of archaeological ceramics by Neutron Activation Analysis at the Lawrence Radiation Laboratory in USA, California. Irradiation was done at the Berkeley TRIGA reactor. In the late 1980ies, Mommsen established his laboratory for NAA on archaeological ceramics in Bonn, Germany, based on the same procedures [2]. Irradiation of samples for Bonn was initially done at Reactor FRG-1, GKSS Geesthacht. In both cases, the main goal of analysis was to establish provenance of the ceramic samples under investigation. Very soon it became clear that the provenancing of ceramics is only possible if a sufficiently large database of chemical fingerprints of other samples is available. NAA's major strength, the very high achievable precision makes it possible to see very subtle differences between the chemical fingerprints of ceramic groups. At the same time, this strength becomes challenging when data from different laboratories are to be compared. Experience shows that even a change in neutron source, as had to be done in Bonn several times due to the shutdown of research reactors, requires careful recalibration of spectral analysis.

Several areas of potential differences in analytical procedures exist:

- Neutron energy spectrum: Especially when interference corrections are to be made, a change in the ratio of thermal to epithermal and fast neutrons can significantly impact total neutron capture cross sections for interfering reactions. This requires experimental work to re-calibrate against a new neutron source.
- Gamma spectroscopy regimes: several measurements after different decay times allow for 30+ elements to be characterized. Decay times and energy regions can have significant influence on the reduction of measurement errors and have to be weighed against high throughput. Peak fitting versus fixed channel summation also impacts measurement errors.
- Data evaluation: Due to the high precision of NAA measurements and available information on individual measurement errors, specialized statistical evaluation algorithms should be used for data evaluation. This becomes even more important when comparison with the existing corpus of NAA data is planned.

In the 2000s, NAA of archaeological ceramic was started at the Center for Labelling and Isotope Production (CLIP) at the TRIGA Center Atominstitut [3]. From the beginning, procedures were set up in a way to provide highest compatibility with the databases from Bonn and Berkeley.

The current setup and the calibration measurements done at the CLIP to provide full compatibility with the aforementioned databases will be described and lessons learned will be discussed. Provisions for a potential move to a new neutron source are described.

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193

Neutron Activation Analysis – Projects and data analysis at MLZ

Christian Stieghorst[*], *Zsolt Révay*

Heinz Maier-Leibnitz Zentrum (MLZ), Technical University of Munich, Garching, Germany
[*]E-mail: christian.stieghorst@frm2.tum.de

Keywords: NAA, data analysis, instrument and method development, AI

Heinz Maier-Leibnitz Zentrum (MLZ) in Garching offers Neutron Activation Analysis (NAA) for scientific and industrial users. The irradiation positions in the FRM II reactor are well-thermalized with thermal-to-epithermal ratios up to 12,000 and fluxes in the rage of 10^{13}–10^{14} $cm^{-2}s^{-1}$. We present the characteristics of the instrumentation and discuss some typical applications. FRM II is currently on an extended maintenance break (until beginning of 2024), thus we also report on the experiments at the research reactors in Budapest and Mainz. Currently, most applications are from the fields of cultural heritage, geology, and recycling technologies. A particular focus is on the characterization of reference materials for the use in other analytical methods. Furthermore, we will report on instrument and method developments for NAA at MLZ: (1) A prototype of a cyclic in-beam NAA has been developed as an additional setup at the PGAA instrument. (2) Improved automation is planned for the classic NAA. (3) For data analysis in PGAA, NAA and related methods, a new project has been initialized. It includes AI/ML-assisted evaluation of gamma-ray spectra and is funded by the German Federal Ministry of Education and Research (BMBF). Its concept and first results will be discussed in the presentation.

124

Defining “k_f-factors” for threshold reactions

R. van Sluijs[1*], *M. Blaauw*[2]

[1]k0-ware, Schaesbergerweg 25, 6415 AB Heerlen, The Netherlands
[2]Reactor Institute Delft, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands
[*]E-mail: robbert.van.sluijs@hetnet.nl

Keywords: neutron activation analysis, k0-method, fast neutron spectrum, threshold reactions, ENDF/B-VIII.0

The k_0-method [1] was developed solely for the use (n, γ) nuclear reactions in neutron activation analysis. For this, a definition of only the thermal and epi-thermal flux was needed. The fast flux of the fission neutrons was not taken into account although it was considered for primary interferences in [1]. The energy distribution of the fission neutrons can be rather well described by a Watt distribution but is reactor dependent. To complicate things, the activation cross-section behaviour is nuclide dependent. In order to incorporate threshold reactions in the k_0-method we propose to use predefined k_f-factors, measuring the fast flux using a Ni-58 monitor, and to introduce an h-factor that accounts for all deviations for a specific reaction and irradiation facility. It is shown, based on data from Verheijke [2], that there are useful correlations for Ni-58, Ti-47 and Ti-48. Activation cross section functions indicate that there are possible more relations that might allow h-factors to be predicted.

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Nuclear forensics

101

Stable element doping of sol-gel toward production of nuclear forensic benchmarking materials

Justin Cooper[1*], *Mathew Snow*[1], *George Diehl*[2]

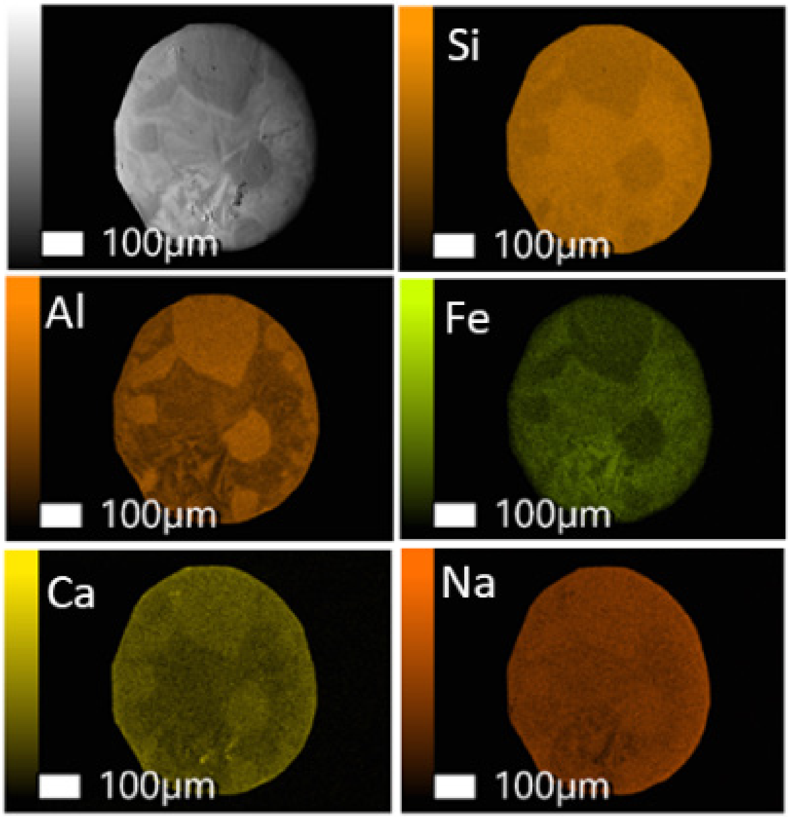
[1]Idaho National Laboratory
[2]University of Utah
[*]E-mail: justin.cooper@inl.gov

Keywords: nuclear forensics, benchmarking materials, surrogates, sol-gel

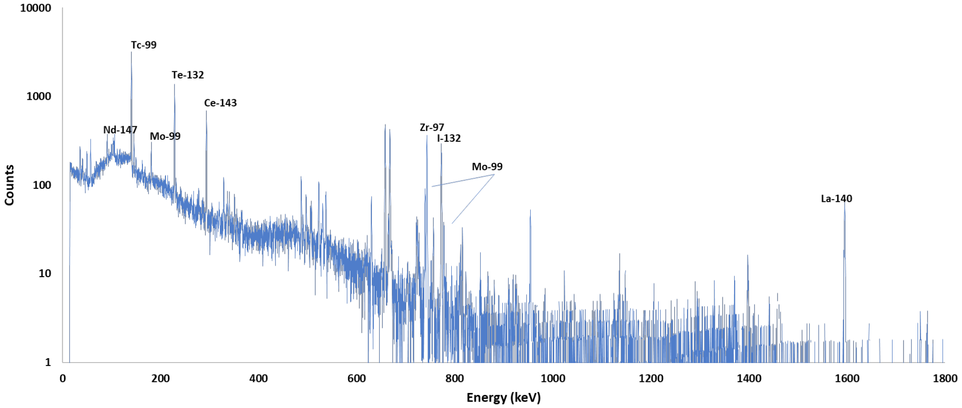
Post detonation nuclear forensic materials which resemble the size, color, elemental composition, and radionuclide content of real nuclear debris would be valuable for developing and validating new nuclear forensic techniques. As nuclear fallout types vary significantly, the ability to tailor each of these parameters accurately is desired to produce materials capable of testing analytical methods under a wide array of forensic scenarios.

Sol-gel synthesis techniques can provide tunability of size, shape and composition for producing a wide variety of solid nuclear forensics benchmarking materials. The sol-gel process consists of forming a metal oxide material, often silica, through polymerization of a metal-alkoxy precursor. In this work, we characterize the ability to load sol-gel particles with secondary elemental components such as iron, aluminum, and calcium toward producing benchmarking materials approximating the elemental composition of historic nuclear debris from the Nevada National Security Site. We also demonstrate quantitative radionuclide encapsulation toward producing benchmarking materials with controllable radionuclide content. Finally, we employ these techniques to produce nuclear debris benchmarking materials with controllable elemental matrix composition and radionuclide content and compare these samples with the composition of a historic fallout sample previously reported from the Nevada National Security Site.

Figures



Example of SEM/EDS of doped sol-gel



Example of gamma-ray spectrum of radionuclide encapsulation in sol-gel

42

Nuclear forensics – Fission Track Analysis – Simulation for training

Rami Babayew[1], *Lorincik Jan*[2], *Orion Itzhak*[3], *Halevy Itzhak*[1,3,*]

[1]Physics Department, Nuclear Research Centre Negev, Beer-Sheva, Israel
[2]Nuclear Fuel Cycle Department, Research Centre Rez, Czech Republic
[3]Unit of Nuclear Engineering, Faculty of Engineering Sciences, Ben-Gurion University of the Negev, Israel
[*]E-mail: halevy.itzhak.dr@gmail.com

Keywords: FTA, simulation, forensics

To answer the nuclear forensics questions, we are developing new techniques and new approaches to make this analysis more reliable and more accurate. Till now the images from the microscope were analyse by a trained researcher. Since the analysis is done by human skills, it is clear that different researchers will give a bit different result. The Certification to a new worker is long and must cover a lot of examples that were measured before and even some that we can only predict.

A good simulation can help in training and can give a tool to grade a new researchers. [1,2]

The fission tracks were simulated by Monte-Carlo software, GEANT4, which uses all the physics behind the nuclear fission tracks - thermal neutrons flux, fission cross-section, radiation time, particle size, enrichment, etc. The full software is written by MatLab code.

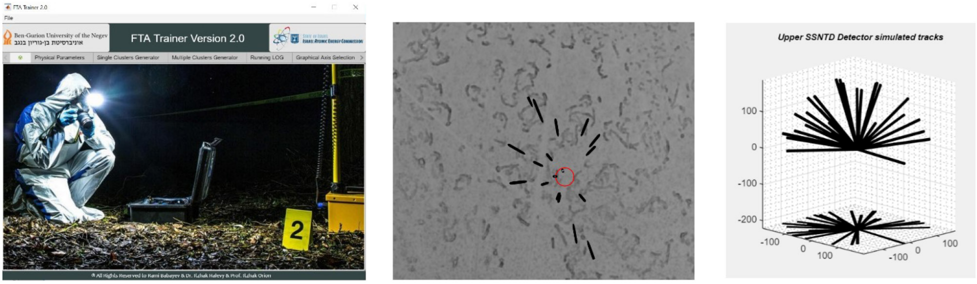


Fig. 1. The new software (left), Simulated star of 1.5 μm diameter U with natural enrichment (center), simulated tracks on upper detector (left).

We can simulate an extreme condition and learn new aspect in the fission track technique.
From the simulation we can learn about the proper amount of material to use as a sample in the FTA technique. The simulation can give as a large database of fission tracks images that are used for artificial analysis (AI) [3]. The simulation can predict and compared to the mini-bulk and the micro-bulk analysis.
The software will be published soon as an open source.

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52

Application of deep metric learning model to microscope images analysis for the determination of UOC samples in nuclear forensics analysis

Yoshiki Kimura[1*], *Tetsuya Matsumoto*[2], *Tomoki Yamaguchi*[1]

[1]Integrated Support Center for Nuclear Nonproliferation and Nuclear Security, Japan Atomic Energy Agency, Tokai-mura Ibaraki, Japan
[2]Faculty of Environmental and Life Science, Okayama University, Okayama, Japan
[*]E-mail: kimura.yoshiki@jaea.go.jp

Keywords: nuclear forensics, deep metric learning, uranium ore concentrate, microscope image

Nuclear forensic analysis is a technical means to determine the origin and intended use of nuclear and other radioactive materials by characterizing them and by the interpretation of the material characteristics called as nuclear forensics signatures. Many analytical approaches including destructive and non- destructive analysis for the material characterization, as well as the statistical analysis and expertise for the interpretation can contribute as the effective means for determination of the materials of interests in nuclear forensic analysis. Application of a machine learning model, represented by a convolutional neural network (CNN) model, to electron microscopic image analysis has been proposed as one of the novel approaches for the determination of uranium materials in nuclear forensics application [1]. In this study, application of deep metric learning model based on CNN to microscope images analysis for the determination of UOC samples was proposed and discussed. The ArcFace model [2] used in this study can automatically analyze the surface patterns of the UOC samples captured by scanning electron microscope (SEM) with its convolutional layers, and it can make classification of UOC samples with high performance, similar to the proposed methodology in the past study [1]. One of the unique and additional benefits of the model is that it can also determine if a sample is unknown or known one. In general, most of the machine learning models can make the classification of samples, but it is difficult to determine whether samples that comes from outside of the range of the training data are unknown. In the proposed technique, sample images of surface patterns captured by a trained embedding network are embedded into a feature space, and unknown samples are detected based on the distance between samples in that space. It was confirmed by the test for UOC standard reference materials with cross-validation that the present technique can detect hypothetical unknown samples with greater than 0.8 of average AUC values. This can be an effective technique to provide preliminary observations in nuclear forensics analysis, where its basic approach is the comparative analysis of a sample with known substances. Future work should discuss the robustness of the present approach with respect to the setting parameters of the SEM for image acquisition and the number of material types to be used for the model trainings, to develop an analytical technique with high confidence for nuclear forensics application

Acknowledgments

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234

Application of retrospective dosimetry in nuclear forensics

Jovana Nikolov[1], Milos Travar[1], Andrej Vranicar[1], Natasa Todorovic[1], Ziv Arazi[2], Erez Gilad[3], Eyal Elish[2], Naomi Porat[4], Shahar Segal[2], Andras Kovacs[5], Andras Klemen[5], Viven Sos[5], Peter Volgyesi[5], Zsolt Varga[6], Maria Wallenius[6], Klaus Mayer[6]*

[1]University of Novi Sad, Faculty of Sciences, Novi Sad, Serbia
[2]Nuclear Research Center Negev, Beer Sheva, Israel
[3]Ben Gurion University of the Negev, Beer Sheva, Israel
[4]The Geological Survey of Israel, Jerusalem, Israel
[5]Centre for Energy Research, Budapest, Hungary
[6]EC Joint Research Centre, Karlsruhe, Germany
[*]E-mail: jovana.nikolov@df.uns.ac.rs

Keywords: nuclear forensics, retrospective dosimetry, MORC

In order to link a suspect with a MORC sample, or a malicious act involving radioactive material, indicators are sought which allow to retrospectively determine if an individual has been close to a radiation source. Solid State Dosimetry using everyday objects might provide such information. Materials suitable for that purpose should exhibit properties similar to compounds used e.g. in thermoluminescence dosimetry. Components such as semiconductors or electric resistors\capacitors (as contained in micro-circuits used in mobile phones, USB keys, Credit cards, etc.), displays of mobile phones, etc. might be potential candidate materials. Additional promising materials for such purpose, might include various building materials containing silicates, or other radiation sensitive agents.

The present research collaboration aims at elaborating a comprehensive study to investigate the potential usefulness of Solid State Dosimetry in Nuclear Forensics. Current studies have been performed in the range of relatively high doses; one of the aims of the proposed investigation is to examine the potentiality for lower doses. Ultimately, this might contribute to enlarging the nuclear forensic toolbox.

For the purpose of applicability of every-day used items as dosimeters for nuclear forensics investigation we designed a simple experiment to “calibrate” simulation code. The simulations are performed using Geant4 toolkit. The results of initial experiments and simulations will be presented in this paper and they will serve as a starting point for the use of Monte Carlo simulations for the applications in the retrospective dosimetry. After initial verification the simulation code, with some adjustments, may be used in the future investigations to test the possibilities of using different types of materials as retrospective dosimeters.

Nuclear instrumentation and methodology

162

The low activity investigation room at the Event Verification and Identification Laboratory (EVIL LAIR) at Los Alamos National Laboratory

M. Boswell[*]*, D. Cox, S. Elliott, D. Flanagan, S. Lamont, and S. Meijer*

Los Alamos National Laboratory, Los Alamos, NM, USA
[*]E-mail: mitzib@lanl.gov

Keywords: low-background assay, gamma spectroscopy, environmental radioactivity, nuclear forensics

The Los Alamos National Laboratory Nuclear & Radiochemistry Countroom has a distinguished history of nuclear forensics dating back to the 40’s. Over the years the Countroom has evolved to serve many programs, processing over 55,000 measurements a year. In this talk, I will discuss our new facility for specialized applications like nuclear forensics. I will primarily focus on our new low-background laboratory being constructed in an historic Manhattan-project era tunnel in the Los Alamos canyon. The tunnel at TA-41 was built between June 1948 until May of 1949. The tunnel is lined with concrete and extends approximately 250 feet into the north side of Los Alamos Canyon, providing roughly 300 ft of rock overburden. Such a facility is a prime location for a low-background laboratory, and is currently home to 4 HPGe detectors, with a plan to expand that to include 4 more detectors along with several low-background beta chambers. I will present data from our current detectors operating in the facility, as well as discuss our future plans for additional detectors in the facility, and discuss the challenges in setting up such a facility in an historic location.

122

Development of analytical method and device for free acidity titration in liquid-liquid extraction spent nuclear fuel treatment processes

Sylvain Costenoble[*], *Sylvain Broussard, Johann Sinot, Fabien Lengrand*

French Alternatives Energies and Atomic EnergyCommission, CEA, DES, ISEC, DMRC, Univ. Montpellier, Marcoule, France
[*]E-mail: sylvain.costenoble@cea.fr

Keywords: free acidity, titration, oxalic acid, liquid-liquid extraction

In the back-end of nuclear fuel cycle, the PUREX liquid-liquid separation process is used for UOX (uranium oxide) spent fuel reprocessing. After their coextraction in the organic phase, uranium and plutonium separation is achieved by reduction of Pu(IV) to Pu(III) with the use of redox reagents. New processes are currently developed to perform the uranium/plutonium separation by decreasing the nitric acid concentration thanks to the use of branched alkyl-monoamides extractants instead of TBP.

That is why, the accurate knowledge of free acidity in the process is essential to manage the uranium/plutonium partition flowsheet. A new method and device called CALIS [1-2] (see figure 1) were developed in order to perform free acidity measurements (with or without uranium and plutonium in the solution) closer to the process. This work was also performed to drastically reduce the response time, the amount of sampling and the liquid waste produced for the analysis.

In the first part of this work, the method and the device will be introducted and described. In the second part, as this new apparatus was used in the framework of experimental liquid-liquid extraction process demonstration in glove-boxes (with surrogate feed solutions) and shielded lines (with genuine feed solutions) at the ATALANTE facility, the results will be presented and compared with data obtained by off-set measurement.

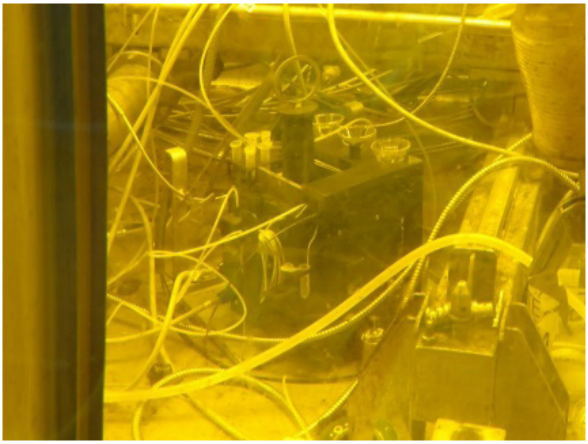

Figure 1: the CALIS device in the shielded process line CBP at the ATALANTE facility

Acknowledgments

The system described in this paper was designed with the financial support of Orano.

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17

Radiation monitoring of surface waters in the Czech Republic: Advances in development of instruments for real-time measurements of gamma and beta activity and their potential

Michal Fejgl[*], *Miroslav Hýža*

National Radiation Protection Institute, Prague, Czech Republic
[*]E-mail: michal.fejgl@suro.cz

Keywords: real-time measurements, radiation monitoring, Cs-137

Ordinary procedure for both normal and emergency radiation monitoring of water environment is to perform water sampling on monitoring sites and their subsequent laboratory analyses.

These procedures and their requirements are defined mainly by Regulation 360/16 [1]. Despite frequency of sampling is in case of emergency situation increased and, at the same time, detection sensitivity requirements are significantly eased, [1] doesn't take in account any of the in situ measurements options for purpose of water radiation monitoring. Although the legislative position on the use of these tools is unfavourable, the monitoring department of the National Radiation Protection Institute (NRPI) is developing several different types of real-time monitoring stations.

Until present, activity concentration of artificial radionuclides in water samples (surface and drinking waters are object of regular monitoring within [1]) are very low in the Czech Republic (^{137}Cs with mean activity concentration of ~1 mBq/L is the main contributor). In next years a huge boost of outpatient applications of radio pharmaceutical treatment is expected, with consequent increase and fluctuations of activity concentration of artificial Gamma in surface waters of the Czech Republic. Determination of reference levels of such activities by collected samples analyses would be rather complicated. At the same time, functionality of emergency monitoring in case of radiation accident is dubious.

Under these circumstances a research project TK02010064 was launched with the aim to propose innovations of surface waters radiation monitoring and subsequent system of contamination dissipation simulation. The basic point of the proposed innovations is endeavour to improve time coverage of the monitoring system. An abundant involvement of the monitoring systems including devices working in real-time mode are preferred.

In the conference contribution a basic framework of proposed innovations of the monitoring system will be presented. But the main object of presentation will be a presentation of the monitoring stations which are in recent years being developed in NRPI. Thee structure types will be presented:

1) Autonomous monitoring station for gamma activity determination employing sophisticated software. This kind of monitoring station was launched in operation in the Czech Republic already [2].

The other two groups are in stage of developing concepts based on rapid development of technological components occurring in recent years, namely solid scintillators and silicon diodes (SiPM) under some conditions capable to replace traditional solid scintillators and photo multiplier tubes (PMT).

2) Device for continuous measurements of beta activity using device utilising scintillation crystals (under development)

3) Device for continuous measurements of gamma activity utilising a low-budget probe working alternatively either with GAGG+ or with CsI:Tl detector assembled with SiPM.

Acknowledgments

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60

A novel Lab on Chip device for in-situ detection for difficult-to-measure radionuclides

Sarah E. Lu[1*], *Geraldine Clinton-Bailey*[2], *Matthew C Mowlem*[2], *Philip E Warwick*[1]

[1]School of Ocean and Earth Sciences, Faculty of Environmental and Life Sciences,
University of Southampton, University Rd, Highfield, Southampton SO17 1BJ, UK
[2]National Oceanography Centre, European Way, Southampton SO14 3ZH, UK
[*]E-mail: sarah.lu@soton.ac.uk

Keywords: Lab on Chip, LoC, in-situ, microfluidics, pure β-emitting radionuclides

In-situ microfluidic radiochemical analysis has the potential to offer an alternative to traditional manual sampling in industrial, environmental and nuclear forensic applications. Pure β-emitting radionuclides are typically monitored via discrete manual sampling followed by destructive analysis at an off-site laboratory, leading to delays in data availability and response times. The development of an *in-situ* microfluidic Lab on Chip (LoC) device with an integrated detection system capable of detecting pure β-emitting radionuclides presents an alternative to manual sampling and the technical challenges that accompany this method. The advantages of a LoC device include the ability to reduce occupational exposure, reagent usage and production of contaminated waste. In-situ detection also enables shorter lead times for initial analytical data, whilst providing improved temporal resolution through near real-time data acquisition. Pure β emitting radionuclide measurement often relies on the counting of photons arising from the Cherenkov Effect (for high energy beta emitters) or via liquid scintillators. Therefore photon transport through a microfluidic system is a key area to target for improvement and development to reduce analysis time and achieve the best limit of detection. Numerical modelling, coupled with non-radiogenic and radiogenic testing has been used to assess the impact of bulk design features on photon transmission and detection through microfluidic systems; enabling improved designs to realise better counting efficiency and overall platform design. A prototype radioanalytical LoC system integrated with a detection system has been developed, manufactured and undergone early evaluation with ^{90}Sr. Finally, we employed the prototype LoC system for the analysis of additional β-emitting radionuclides. Our work established the capability to reduce material consumption and the requirement for specialist facilities needed for handling radioactive materials during the initial characterisation process. This constitutes a proof of concept and the first step toward robust *in-situ* microfluidic detection for pure β-emitting radionuclides that is capable of integration with autonomous platforms to enable remote detection and monitoring.

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164

Heterogeneous isotope exchange in the study of phosphorous forms of soils

Noémi M. Nagy[*], *Dóra Buzetzky, Eszter Mária Kovács, Zoltán János Vörös, József Kónya*

Imre Lajos Isotope Laboratory, Department of Physical Chemistry, University of Debrecen, Debrecen, Hungary
[*]E-mail: nagy.noemi@science.unideb.hu

Keywords: heterogeneous isotope exchange, ^{32}P tracer, phosphate species, soil

Phosphorus plays an important role in plant development and also influences yield. In plant cultivation, the recent quantity of water soluble and exchangeable phosphate is an important factor. Its value and changes under different conditions can be examined by heterogeneous isotope exchange using radioactive phosphorous isotopes.

In this study, six types of soils were investigated (Chernozem, Calcaric Arenosol (Humic), Dystric Arenosol (Humic), Calcic Vertisol (Gleyic), Rendzic Phaeozem (Hyperhumic), Calcic Gleysol(Arenic, Humic)). The changes of phosphate fractions (water-soluble (Pw), isotopically exchangeable (PIE), ammonium lactate soluble phosphorus (PAL), and tightly sorbed phosphorus (Ptightly)) in soil were determined as a function of P supply, incubation time and the plant culture. The soil samples were incubated at different times (1, 3, 13 weeks) and phosphate quantities. 0, 40, 80, 160, 320 mg P/kg soil doses of P fertilizer were added to the soils. After incubation, perennial ryegrass (Lolium perenne L.) was sown. A significant correlation was found between the sum of Pw and PIE and Puptake of plant proving that these values can be good indicators of plant available phosphorus. During plant culture, the Pw and PIE values always decrease showing that plant directly utilizes these phosphate forms. The transformation of added phosphate to tightly sorbed phosphate is the highest for soils with great humus content.

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226

The role of gamma-ray spectrometry and Monte Carlo simulation in the characterisation of meteorites

Riccardo Rossini[1,2,3,*], *Oliviero Cremonesi*[3], *Daniela Di Martino*[3], *Matthias Laubenstein*[4], *Massimiliano Clemenza*[3]

[1]Department of Physics and local INFN Division, University of Pavia, Pavia, Italy
[2]ISIS Neutron and Muon Source, Science and Technology Facilities Council (STFC), Didcot, UK
[3]Department of Physics and Local INFN Division, University of Milano-Bicocca, Milan, Italy
[4]Laboratori Nazionali del Gran Sasso (LNGS), INFN, Assergi, L'Aquila, Italy
[*]E-mail: riccardo.rossini@infn.it

Keywords: meteorite, low-background gamma spectrometry, aluminium-26

The characterisation of meteorites is a process typically carried out with an invasive set of procedures. In particular, the attribution of a sample as a meteorite requires the cutting of a thin section and a campaign of petrological observations.

We proposed a fully non-destructive method for the characterisation of meteorites[1] which entails many nuclear techniques. Among those, low-background gamma spectrometry is used to identify a sample as a meteorite and potentially to date its fall. In fact, there are some radionuclides of cosmogenic origin and lifetime shorter than the age of the atmosphere, whose presence testifies the meteoric origin of a sample. The longest-living of these isotopes is ^{26}Al ($t_{1/2} = 7.17 \cdot 10^5$ years).

The method implemented in this protocol is carried out on the sample as it is[2], therefore it requires the estimation of the full-energy-peak efficiencies by means of Monte Carlo simulation. In fact, meteorites can come in different shapes and samples could also be portions of a full meteorite. Furthermore, many meteorites have a highly inhomogeneous texture, which can result in regions where gamma-ray self-absorption is enhanced.

By measurements with calibrated and certified radioactive sources compared with Monte Carlo simulations, it is possible to carry out a fine tuning of the equivalent dead layers of the detector, which need to be optimised periodically from the ones declared in the detector datasheets. This procedure acts also as a validation process for the Monte Carlo geometry, which is fundamental for the confidence in the protocol. The flexibility of a Monte Carlo approach in describing geometries enables to estimate the efficiencies also in the case of meteorites, which are samples with complex shapes and possible inhomogeneities. As a consequence, our method is a feasible strategy to compute and compare single-radionuclide activities from a range of samples with different composition and structure without any damage.

Some samples, the bigger and most active ones, were measured in the radioactivity laboratory of the University of Milano-Bicocca and INFN Milano-Bicocca, whereas some of them were measured at the STELLA facility for low background gamma spectrometry at the underground Laboratori Nazionali del Gran Sasso (LNGS-INFN). This enabled us to gain some conclusions about how to proceed for such measurements depending on the age of the meteorite, its type, and its size. Monte Carlo simulations were performed with the Arby interface to the Geant4 toolkit.

Acknowledgments

The STELLA facility at the Laboratori Nazionali del Gran Sasso (INFN) is acknowledged for performing gamma measurements on their HPGe detectors.

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225

Multilayer foils to enhance the α/β discrimination capabilities of PSkits

X. Mendo[1], *H. Bagán*[1], *A. Tarancón*[1,2,3*]

[1]Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, Martí I Franqués 1-11, Barcelona, Spain
[2]Serra-Húnter Programme, Generalitat de Catalunya, Barcelona, Spain
[3]Institut de Recerca de l'Aigua, University of Barcelona, Spain
[*]E-mail: alex.tarancon@ub.edu

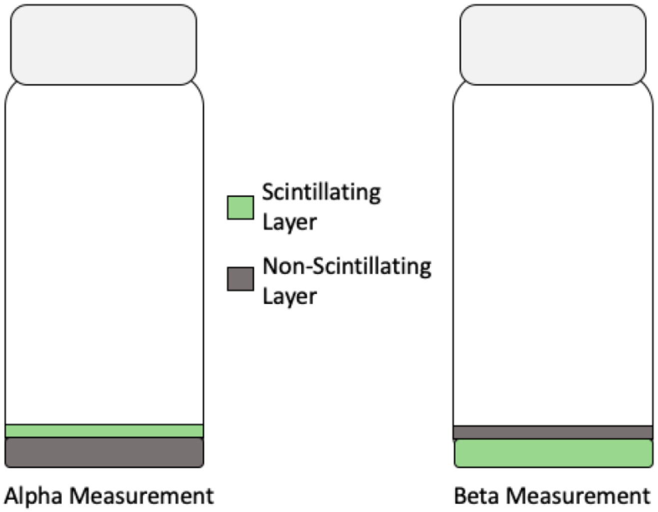
Keywords: decommissioning, PSkits, alpha-beta discrimination, scintillation

Nowadays, around 400 nuclear reactors are operative. However, 200 reactors (being Europe the most affected region) will have reached the end of their operational life and will have to be decommissioned. Decommissioning leads to huge amounts of liquid radioactive waste that have to be characterised and treated and disposed according to their composition. Therefore, new screening methods rise as a necessity to do an effective classification while reducing the number of samples to be fully characterized. These new methods have to be simple, fast and selective. Plastic scintillators fit the idea due to their versatility, as they can have multiple forms (e.g, microspheres, foils) and an enhanced resistivity to difficult matrices, as nuclear decommissioning samples are. Moreover, their surface can be modified by adding a selective extractant to make the system selective to a target radionuclide. Therefore, a new system for the screening measurements of decommissioning samples can be prepared by the polymerisation of plastic scintillators in form of foils and the settlement of a selective extractant on their surface, all inside a plastic vial, generating a PSkit.

The coexistence of alpha and beta emitters is quite common in decommissioning samples. Their analysis requires and acceptable alpha-beta discrimination characteristics in addition to a previous selective extraction. Alpha-beta discrimination is usually based on the analysis of the duration of the pulse originated in the scintillations by alpha and the beta disintegrations. The discrimination can be enhanced by the addition of diisopropylnaphtalane, which delays alpha scintillation pulses because of a higher population of the triplet states. Moreover, alpha-beta discrimination can have another approach based on the attenuation of their emissions, due to their different penetration capability.

In this work, the traditional discrimination by pulse shape analysis is backed with the attenuation of alpha and beta emissions based on their penetration capability. A multilayer PSkit with a specific distribution of a scintillating layer and a non-scintillating layer is used for total or partial attenuation of the alpha or beta emissions depending on the needs. With the combination of these two strategies (penetration and pulse delay) a better alpha-beta discrimination can be achieved. Moreover, a selective extractant can be settled on the upper layer facilitating the extraction of the desired radionuclide and facilitating analysis in case that a big disproportion between radionuclides takes place. After developing the synthesis method, scintillating and non-scintillating layers of different thicknesses and composition have been studied in different configurations. Scintillating signal of each PSkit configuration for several alpha (e.g. ^{241}Am, ^{238}Pu) and beta emitters (e.g. ^{90}Sr, ^{99}Tc) was evaluated. Also, the coating by some extractants addressed to ^{99}Tc or actinides was studied . The results were evaluated in terms of the effect of the different variables on the radionuclide retention, detection efficiency and alpha/beta discrimination (with and without pulse shape discrimination).

Figures



Nuclear methods in material structure studies

197

Iron(III) citrate complexes at physiological pH

Maria Gracheva[1,2*], *Zoltán Homonnay*[1], *Zoltán Klencsár*[2], *Krisztina Kovács*[1]

[1]Department of Analytical Chemistry, Institute of Chemistry, Eötvös Loránd University,
Pázmány P. s. 1/A, Budapest, 1117, Hungary
[2]Centre for Energy Research, Konkoly-Thege Miklós út. 29-33, 1121, Budapest, Hungary
[*]E-mail: gracheva@student.elte.hu

Keywords: iron citrate, Mössbauer spectroscopy, EPR spectroscopy, iron metabolism

Iron is known to be an essential micronutrient for all living organisms because it plays an important role in cells construction and metabolic processes such as DNA synthesis, respiration, and photosynthesis. Iron(III) citrate is a collective term for a large group of carboxylate complexes containing ferric ions and citrate ligands with various degrees of protonation. Due to the ability of citric acid to bind metal ions, these complexes play an important role in the iron metabolism of living beings. Citric acid is known to facilitate the bioavailability of iron and enhance its transport through the cell membranes [1,2], therefore, some bacteria species possess a transport system specific for iron citrate, while in the plant xylem sap iron was found in the form of ferric citrate complex [3]. In pharmaceutical sciences, iron(III) citrate was approved in the European Union and in the United States for improving hemoglobin response and iron parameters for adult patients with iron deficiency anemia and chronic kidney disease [4].

Despite the crucial role of iron(III) citrate systems in iron metabolism, the coordination chemistry of ferric citrate in aqueous solutions remains a matter of debate, especially for the physiological pH values. By applying Mössbauer and electron paramagnetic resonance spectroscopies, we performed detailed analysis of iron environment in solutions prepared with various iron to citrate ratios and pH values. The formation of both polynuclear and mononuclear species was observed in the presence of citrate excess at physiological pH, while when iron and citrate are present at equimolar concentration, the ratio of iron incorporated into the monomeric species was negligible. Comparative evaluation of both EPR and Mössbauer spectra exhibited the presence of several mononuclear species with different structure and allowed to assume the ratio between them. The stability of the polynuclear complexes of iron(III) citrate was additionally checked in the presence of several organic solvents showing high coordination ability to Fe^{3+} and compared with the stability of the dimers of iron(III)-EDTA. The results provided a novel quantitative and qualitative information on iron speciation in the presence of citrate excess which has high relevance for the understanding of iron citrate chemistry in biological systems.

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257

Mössbauer Spectroscopy analysis of iron(VI) to iron(III) ratio in electrochemically produced potassium ferrate(VI) for waste water treatment

Zoltán Homonnay[1*], *Ernő Kuzmann*[1], *Kende Attila Béres*[1], *Miklós Kuti*[1,2], *Győző G. Láng*[1], *Gyula Záray*[1], *József Lendvai*[2]

[1]Eötvös Loránd University, Budapest, Hungary
[2]IMSYS Engineering Service Ltd., Budapest, Hungary
[*]E-mail: homonnay.zoltan@ttk.elte.hu

Keywords: ferrate(VI), water treatment, anodic oxidation, Mössbauer Spectroscopy

Ferrate(VI) has long been known as a realistic alternative for waste water treatment, not using chlorine gas or hypochlorite. Characterization and preparation methods have been reviewed, e.g., in [1]. The stability of the high oxidation state of iron in normal environment is an important issue. Even if no reducible reactant is around, in aqueous systems, the insufficiently high pH (i.e., 9-10) is enough for the decomposition of the otherwise thermodynamically stable iron(VI) species.

Even the solid dry potassium ferrate(VI), K_2FeO_4, has a tendency to decompose when exposed to moisture and CO_2. The method of production can be an important factor for the stability of the ferrate product.

We have developed a specially designed electrochemical cell for ferrate(VI) production in which an iron metal anode is oxidized. The ferrate (K_2FeO_4 or a mixed $(K,Na)_2FeO_4$) forms in a high pH aqueous solution containing concentrated NaOH. The solid end product is kept wet after filtration. The thin high pH film on the ferrate crystallites helps stabilize the iron(VI) state. The samples sealed in polyethylene bags were stored in a regular refrigerator at ~5°C and showed negligible decomposition over a one year period [2].

The decomposition end product of ferrate(VI) is iron(III) in various forms, in many cases yet without explored identity. For monitoring of the stability, the iron(VI) to iron(III) ratio can be reasonably estimated using Mössbauer spectroscopy. The molar ratio of iron(III) and iron(VI) species is affected by the different Mössbauer-Lamb factors and also, the tendency of temperature dependent magnetic ordering makes the spectrum evaluation complicated. We present in this work how these factors may be taken into account for an accurate quantitative analysis of the iron content of the ferrate product.

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248

Free volume analysis of Nafion for proton exchange membrane in hydrogen fuel cell by positron annihilation spectroscopy

Jaegi Lee[1], Young Su Jeong[1,2], Young Rang Uhm[1], and Gwang-Min Sun[1]*

[1]HANARO Utilization Division, Korea Atomic Energy Research Institute, Daejeon, Republic of Korea
[2]Daegu Catholic University, Daegu, Republic of Korea
*E-mail: jgl@kaeri.re.kr

Keywords: positron annihilation lifetime spectroscopy, coincidence Doppler broadening spectroscopy, Nafion, proton exchange membrane, hydrogen fuel cell

Positron annihilation spectroscopy (PAS) is a spectroscopic technique that uses positrons to probe the properties of matter. It measures the lifetime and electron momentum of annihilated positrons, allowing for the analysis of nano-structural properties of materials. This information can provide insight into the behaviour of materials, including the presence of free volume, impurities, and defects. In this study, proton exchange membrane, Nafion, was analyzed by positron annihilation spectroscopy.

Four kinds of Nafion samples with different thickness (15, 25, and 50 μm) were prepared to analyze the free volume. Each sample was cut by a 1 × 1 cm^2, and piled up until 1 mm to annihilate all positrons from the source. A Na-22 encapsulated positron source with a 5-μm titanium window (POSN-22, Eckert & Ziegler) was centered at two identical Nafion samples. Two photomultiplier tubes (PMT) (R329-02, Hamamatsu Photonics K. K.) with fast timing plastic scintillation crystals (BC-422Q, Saint Gobain Crystals) were connected to PMT bases (265A, Ortec). A high voltage of 2.1 kV was applied to two PMTs (556, Ortec). Two constant fractional differential discriminators (CFDDs) (418, Ortec) selectively processed 1.27-MeV gamma rays from the beta decay of Na-22 and 0.511-MeV gamma rays from positron annihilation. A time-to-amplitude converter (TAC) (566, Ortec) generated time different logic signals from two gamma rays within 50 ns. An analog-to-digital converter/multi-channel analyzer (927, Ortec) sent digitized signals to a personal computer. The PALS spectra were analyzed by the *PALSfit3* software to analyze positron lifetime. For coincidence Doppler broadening spectroscopy (CDBS), two identical HPGe detectors (10% efficiency) were located at a 10-cm distance from the samples in a 180 degree. Two scientific amplifiers (672, Ortec) were connected to each detector. A coincidence module (Labo NT24-DUAL) collected coincident annihilated gamma-rays within 1 μs. The CDBS spectra were analysed by the *MePASto* software.

The positron lifetimes and relative intensity of Nafion with a thickness less and equal than 25 μm were 2.45-2.48 ns and 10.2-10.5%, respectively (Table 1). However, a 50-μm Nafion sample (NR-212) showed different positron lifetime and intensity. The free volume size of NR-212 was smaller than the other Nafion samples. Even though the relative intensity of NR-212 was larger than those of the others, the fractional free volume calculated by Tao-Eldrup model was less than those of the others. Therefore, Nafion with a thickness larger than 25 μm is not recommended to use proton exchange membrane in hydrogen fuel cell.

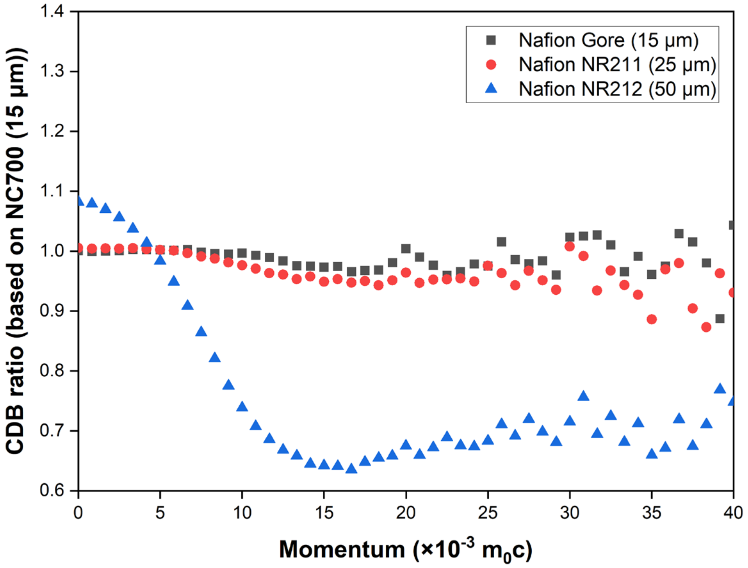

Figure 1. Coincidence Doppler broadening ratio curve of Nafion samples

Table 1. Positron lifetime (τ3), intensity (I3) and fractional free volume (Vf) of Nafion samples

	τ_3 (ns)	I_3 (%)	V_f (mm^3)
#G (15 μm)	2.45	10.2	0.14
#NC-700 (15 μm)	2.46	10.5	0.14
#NR-211 (25 μm)	2.48	10.4	0.14
#NR-212 (50 μm)	1.67	15.7	0.07

Acknowledgments

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245

Study of Mössbauer spectroscopy for ^{57}Fe-N/C electrocatalysts synthesized using e-beam irradiation for oxygen reduction reaction

Young Rang Uhm[*], *Chaewon Lee Hyunkyung Choi, Gwang Min Sun, and Jaegi Lee*

HANARO Utilization Division, Korea Atomic Energy Reasearch Institute, Daejeon, Rep. of Korea
[*]E-mail: uyrang@kaeri.re.kr

Keywords: Mössbauer Spectroscopy, 57Fe-N/C, e-beam irradiation

Mössbauer spectroscopy is a method of analyzing gamma-ray resonance absorption of atomic nuclei by irradiating samples with gamma-rays with specific energy generated from radioisotopes. An analysis method is good for improving Oxygen reduction reaction (ORR) performance by distinguishing the active points of the catalyst and comparing the presence and proportion of various iron species in the catalysts.^{57}Fe-N-C catalysts synthesized using e-beam irradiation pyrolysis of ^{57}Fe-Chloride and N precursors have been studied due to their remarkable activities for the electrochemical oxygen reduction reaction (ORR). The condition for the formation of Fe-Nx was confirmed at irradiation of 80 kGy using e-beam energy of 10 MeV and beam current of 800μA. Coordination between Fe and phenanthroline isomer was effectively controlled by the molecular structure of bidentate coordination (1,10-phenanthroline). The pyrridinic in N % was revealed 68 % for ^{57}Fe(1,10-phenanthroline)/KB prepared e-beam irradiation ptrolysis. This is exhibited superior ORR activity and stability in alkaline half-cell. The use of precursors with bidentate coordination is important to obtain the effective derivation of ^{57}Fe-Nx active sites for active catalysts during ORR. The various ^{57}Fe-N digits that can be present after after heat treatment in ^{57}Fe-N-C catalysts are divided into low spin spin state (Doublet Doublet 1 or D1), intermediate spin state (Doublet 2 or D2), and high spin state (Doublet3 or D3). The difference difference the ratio of the active point , ^{57}Fe, ^{57}Fe –N$_4$ moieties, directly affects the activity activity of ORR.

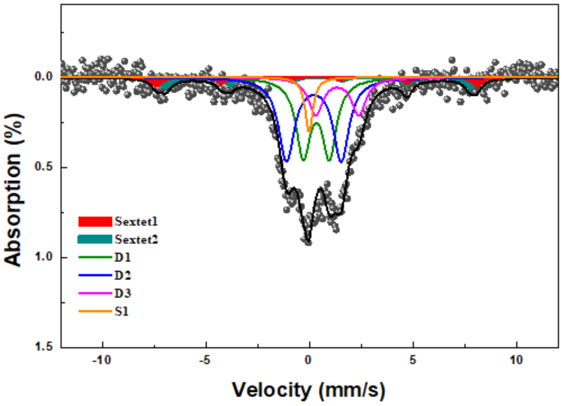

Figure 1. Mössbauer sextets, doublets, and single line assignment for sample (Fe-based catalyst prepared using e-beam) at 4.2 K.

Acknowledgments

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Production of radionuclides

88

Study of production of Sc isotopes using natural Ca compounds

Arshiya Anees Ahmed[*], *Ryszard Misiak, Mirosław Bartyzel, Jerzy W. Mietelski, Bogdan Wąs*

H. Niewodniczański Institute of Nuclear Physics Polish Academy of Sciences, Cracow, Poland
[*]E-mail: arshiya.ahmed@ifj.edu.pl

Keywords: medical radionuclides production, scandium, reaction cross-sections, proton induced reactions, SPECT

The nuclear decay data and the nuclear reaction cross sections are the two main categories of nuclear data relevant to medical radionuclides. While accurate reaction cross sections are crucial for the optimization of a production process and radionuclide quality control, i.e., maximizing the yield of the desired product while minimizing the level of impurities, whereas decay data are used to evaluate a radionuclide's suitability for medical applications. In terms of nuclear decay data, continuous experimental and evaluation efforts are being made with sufficient accuracy. In contrast, nuclear reaction cross sections, particularly charged particle induced ones, require more consideration for optimizing established nuclear reactions and expanding new routes [1,2].

Scandium-47 ($T_{1/2}$ = 3.35 d) is a relatively new medical radionuclide with excellent nuclear decay properties that can be produced in both a nuclear reactor and a cyclotron by irradiating titanium and calcium targets for potential use in cancer theranostics. The ^{47}Sc could be used in single photon emission computed tomography (SPECT) imaging due to its ideal gamma ray energy of 159.381 keV, and it is also suitable for targeted therapy of small tumors due to its favourable beta-emission. Other short-lived scandium isotopes (^{43}Sc and ^{44}Sc) have recently received a great deal of attention , as ^{47}Sc in combination with either ^{43}Sc or ^{44}Sc, could be a potential theranostic radionuclide pair for radiotherapy and PET scanning. Because ^{47}Sc can easily form stable complexes with a wide range of bifunctional chelators (BFCs), it can be easily utilized in radiopharmaceuticals production [3].

A thorough review of the literature reveals that various production pathways for ^{47}Sc via charged particle irradiations on a natural (and/or enriched) calcium, titanium, and vanadium target have been investigated [4]. However, significant discrepancies were discovered among the reported cross sections. A comparison of the cross sections for all of the above- mentioned nuclei reveals that the reaction with the Ca nucleus promises significantly higher production efficiency.

We have carried out proton-induced reactions on natural CaO and $CaCO_3$ targets using a 60 MeV proton beam in order to obtain precise reaction cross-section data and to resolve the discrepancies in the available data. The outcomes of the above experiments will be discussed thoroughly in this presentation. Radionuclide impurities were also evaluated along with ^{47}Sc.

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67

TTY and RNP calculations for the production of ^{155}Tb using the precursor technique ^{nat}Dy(d,x)^{155}Dy(ε,β^{+})^{155}Tb

Michele Colucci[1,2*], *Flavia Groppi*[1,2], *Ferid Haddad*[3,4], *Etienne Nigron*[4], *Simone Manenti*[1,2]

[1]Department of Physics, University of Milan, via Celoria 16, I-20133 Milan, Italy
[2]LASA, University of Milan and INFN-Milano, via F.lli Cervi 201, I-20090 Segrate, MI, Italy
[3]Laboratoire Subatech, IN2P3-CNRS, IMT Atlantique, Nantes Université, 4 rue Alfred Kastler, 44307 Nantes, France
[4]GIP Arronax, 1 rue Aronnax, 44817 Saint-Herblain, France
[*]E-mail: michele.colucci@unimi.it

Keywords: terbium, theranostic, radionuclide production, thick-target yield, radionuclidic purity

Four of the terbium radioisotopes have great potential as theranostic radionuclides [1]. This work mainly focuses on ^{155}Tb (I_{ec}=100%, $T_{1/2}$=5.32 d). It emits gamma rays with energies suitable for SPECT studies and the absence of β^{+}/ β^{-} emissions reduces the radiotoxicity of this radionuclide. The effectiveness of ^{155}Tb for the diagnostic in nuclear medicine has been preclinically proved [1].

It has been demonstrated that ^{155}Tb can be produced using the precursor technique ^{155}Dy(ec,β^{+})^{155}Tb [2]. ^{155}Dy, in turn, can be produced exploiting the nuclear reaction induced by deuterons on natural dysprosium targets. The cross-section of this reaction has been experimentally measured [3,4]. Here, the Thick-Target Yield (TTY) as a function of the irradiation conditions and of the thickness of the dysprosium target has been determined. EMPIRE-3.2.3 simulation tool has been used to decuple the cumulated cross-sections of ^{1xx}Dy and ^{1xx}Ho when the experimental values are not present. The double step radiochemical separation process that permits to extract ^{155}Tb in no-carrier added condition has been theoretically optimised and maximum RadioNuclidic Purity (RNP) obtainable has been determined. A simplified scheme is reported in Figure 1. The possibility to exploit the optimised production and the subsequent separation process to obtain high purity ^{155}Tb for clinical applications has been discussed.

Figures

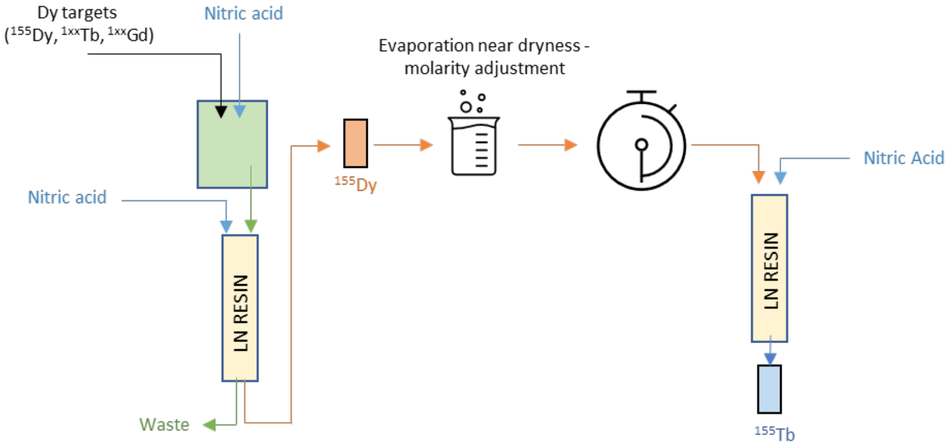

Figure 1. Simplified scheme of a double step radiochemical separation to realise a theoretical precursor for the production of ^{155}Tb starting from ^{nat}Dy targets irradiated with deuterons.

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97

Recent evaluations of production cross sections of a few positron emitters under Pak-German collaboration for medical application

Mazhar Hussain[1,2*], *M. Naveed Aslam*[3], *Nouman Amjed*[4], *Ingo Spahn*[2], *Bernd Neumaier*[2], *Syed M Qaim*[2]

[1]Department of Physics, Government College University Lahore, Lahore 54000, Pakistan
[2]Institute of Neuroscience and Medicine: INM-5(Nuclear Chemistry), Forschungszentrum Jùlich, 52428 Jùlich, Germany
[3]COMSATS University, Defence Road, Lahore 54000, Pakistan
[4]Division of Science and Technology, University of Education, College Road, Lahore 54000, Pakistan
[*]E-mail: dr.mazharhussain@gcu.edu.pk; presently Alexander von Humboldt Fellow at FZJ

Keywords: cross section, evaluation, positron emitter, PET, nuclear model calculation

Non-standard positron emitters require a deep knowledge of nuclear data for their production and clinical application. Although their experimental databases are limited, the available findings have supported to calculate complete excitation functions of nuclear reactions leading to their formation.

The Jùlich Group has fostered a large number of scientists of Asia, Europe, America and Africa to carry out significant research projects of international importance. The cooperation between Pakistan and Germany (Pak-German collaboration) on measurement and evaluation of production cross sections started 20 years ago. Over this long period a wide variety of diagnostic and therapeutic radionuclides were studied. In recent years, the focus has been on non-standard positron emitters including ^{86}Y, ^{73}Se and ^{89}Zr. In this work we summarize the evaluations of cross sections of those radionuclides.

For each radionuclide the existing experimental data were examined and standardized as per recommendations of the International Atomic Energy Agency (IAEA). To generate the recommended sets of the data, a theory-based approach was adopted. This involved extensive nuclear model calculations, using the modern codes ALICE-IPPE, EMPIRE and TALYS [1]. In the case of ^{86}Y, significant discrepancies were found in the existing cross section data [2]. The evaluation motivated a new measurement under international cooperation [3]. Now the status of the database is well established for the ^{86}Sr(p,n)^{86}Y reaction. Similarly, ^{73}Se has been recently investigated in detail up to 70 MeV. ^{89}Zr is the most important radionuclide for immunoPET. Evaluation of excitation functions of ^{89}Y(p,n)^{89}Zr and ^{89}Y(d,2n)^{89}Zr reactions for the production of ^{89}Zr has also been done under Pak-German collaboration. The thick target yields of these two radionuclides calculated from the new evaluated excitation curves are closer to the experimental yields than from older evaluations. The availability of these non-standard positron emitters is opening new pathways in medical research, e.g. labelling of monoclonal antibodies in high specific activities, theranostic approach etc. Additionally, production of these radionuclides at small cyclotrons located in hospital environments in Pakistan is also underway.

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69

Practical yield of ^{99m}Tc obtained by irradiation of enriched ^{100}Mo sample in small medical cyclotron

Ihor Kadenko[1]*, *Borys Bondar*[2,3], *Borys Leshchenko*[3], *Yaroslav Kmetyuk*[2]

[1]Department of Nuclear Physics, Taras Shevchenko National University of Kyiv, Ukraine
[2]Radiopharmaceutical Production Department, Clinical Hospital «Feofaniya», Kyiv, Ukraine
[3]National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine
*E-mail: ndef.office@gmail.com

Keywords: technetium production, cyclotron, gamma-spectrum, isotope yield

There are more than 70 medical radioisotope laboratories in Ukraine. Among them there are 3 PET-centers with 2 medical cyclotrons, and the others are SPECT diagnostics departments utilizing ^{99m}Tc. The existing 2 cyclotrons are low-energy accelerators (11-MeV Eclipse RD (Siemens) and 16-MeV PETtrace (GE)), that nowadays are operated only for ^{18}F production [1]. This routine production takes up to 2 hours per day and fully covers 3 PET-scanners, while for ^{99m}Tc tracer there is no any production center in Ukraine despite its higher demand. Therefore, the existing cyclotrons are considered to be potentially used for ^{99m}Tc production in line with the accelerator-based approach [2]. It gives lower yield in comparison with reactors, but it has advantages such as absence of contamination, low cost and decentralization in supply.

According to nuclear data on excitation functions of (p,x) reactions and theoretical predictions [3], the production of ^{99m}Tc is feasible via ^{100}Mo(p,2n) nuclear reaction on enriched molybdenum, which is commercially available in a form of powder. Thus, the implementation of ^{99m}Tc production technology was started with the development of new target assembly, allowing solid samples irradiation in carousels, dedicated for liquid and gas targets. The new target assembly was designed, manufactured and successfully tested in a proton beam [4]. Then molybdenum solid sample was prepared by pressing the Mo powder with enrichment of 92,2% by ^{100}Mo isotope into the pellet with size of Ø15 mm x 3 mm. This sample was irradiated applying new target assembly in 11-MeV Eclipse RD cyclotron during 5 min under the proton beam of 6 μA. The gamma-spectra of irradiated sample were measured using NaI(Tl) and HPGe spectrometers. The conditions of irradiation process and sample measurements were precised based on MCNP simulations. The produced activity of ^{99m}Tc appeared to be 14,9±0,7 MBq and accompanied by impurities of ^{95}Tc (6.9 ± 3.6 kBq) and ^{96}Tc (2.1 ± 0.3 kBq) isotopes. The neutron flux over the sample was analyzed taking into account the construction elements of the target module and cyclotron self-shielding. The contribution to the ^{99m}Tc yield by indirect production via ^{98}Mo(n,γ)^{99}Mo→^{99m}Tc reactions was also estimated. The obtained results were compared with theoretical calculations and data of other authors in similar energy ranges.

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96

Preparation of highly radioactive targets for nuclear data measurements

Veronika Mocko[1*], *Brad J. DiGiovine*[1], *Cecilia Eiroa-Lledo*[1], *Michael E. Fassbender*[1], *Paul E. Koehler*[1], *Stosh A. Kozimor*[1], *Sean A. Kuvin*[1], *Hye Young Lee*[1], *Artem V. Matyskin*[1,2], *Ellen M. O'Brien*[1], *Athanasios Stamatopoulos*[1], *C. Etienne Vermeulen*[1]

[1]Los Alamos National Laboratory, Los Alamos, NM, USA
[2]Pennsylvania State University, University Park, PA, USA
[*]E-mail: vmocko@lanl.gov
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Keywords: nickel-56, zirconium-88, radioactive target, nuclear data

Nuclear data for neutron induced reactions on short-lived radioisotopes are critical for a wide range of applications spanning from radiochemical diagnostics, nuclear reactor designs to nuclear astrophysics. In this contribution, fabrication of two different targets: (1) ^{56}Ni electroplated on gold foil and (2) ^{88}Zr-filled tungsten cannister within a hot cell will be described. Tools developed to accomplish these unique experiments by remote handling techniques will be highlighted.

Nickel-56 ($t_{1/2}$ = 6.075 days) was produced by medium energy proton-induced reaction on natural cobalt target at Isotope Production Facility (IPF) at Los Alamos Neutron Science Center (LANSCE). After target dissolution, approximately 100 mCi of ^{56}Ni was separated from bulk of cobalt by cation-exchange chromatography. The final step involved electroplating of isolated and purified ^{56}Ni on a 6 µm-thick gold foil mounted on a metal frame. This sample was studied using the fast neutron beams available at the Weapons Neutron Research (WNR) facility at LANSCE [1,2].

The second project involved production of ^{88}Zr ($t_{1/2}$ = 83.4 days) via low-energy proton irradiation of natural yttrium target at IPF. The yttrium target was dissolved and several curries of ^{88}Zr were isolated utilizing hydroxamate-based extraction chromatography resin. Zirconium-88 was concentrated to very small volume in hydrochloric acid. An automated dispensing unit was designed and installed inside a hot cell to dispense samples of ^{88}Zr ranging from 4 to 8 microliters into tungsten cannisters and enclosed using lead plugs. Neutron transmission measurements were performed on these ^{88}Zr-filled samples at LANSCE utilizing the Device for Indirect Capture Experiments on Radionuclides (DICER) [3,4].

Acknowledgments

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83

Molybdenum nanoparticles for the production of high specific activity ^{99}Mo by the recoil effect

Pablo Serra Crespo[1*], *Andrea Tsinganis*[2], *Francesco Fumagalli*[3], *Stephan Oberstedt*[2], *Arjan Plompen*[2], *Ana Ruiz Moreno*[3]

[1]European Commission, Joint Research Centre. Westerduinweg 3, 1755 LE Petten, The Netherlands
[2]European Commission, Joint Research Centre (JRC), Retieseweg 111, B-2440 Geel, Belgium
[3]European Commission, Joint Research Centre Via E. Fermi, 2749. TP 281, I-21027 Ispra (VA), Italy
[*]E-mail: Pablo.SERRA-CRESPO@ec.europa.eu

Keywords: molybdenum-99, generator, radionuclide separation

A new route to produce high specific activity molybdenum-99 is proposed. The route includes the production of nanoparticle agglomerates of molybdenum oxide by spark ablation, their irradiation to produce molybdenum-99 and the extraction method to separate the produced molybdenum-99 from the nanoparticle agglomerates.

Spark ablation technology provides an easy method to produce nanoparticles. It consists of a physical process in which nanoparticles are produced by spark ablation of molybdenum electrodes followed by gas-phase nucleation and growth in an inert gas flow. We observed that the size of the nanoparticle agglomerates mainly depended on the inert gas flow. As can be seen in figure 1, at an argon flow of 1 L/min big agglomerates of more than 200 nm are formed, meanwhile at 2 L/min the agglomerates are about half this size. At 5 L/min, still smaller agglomerates are mixed with small particles. When the gas flow applied was 10 L/min, no agglomerates are visible and only nanoparticles are produced. In contrast to discrete nanoparticles, the agglomerates can be easily separated by centrifugation and were chosen for the further experiments.

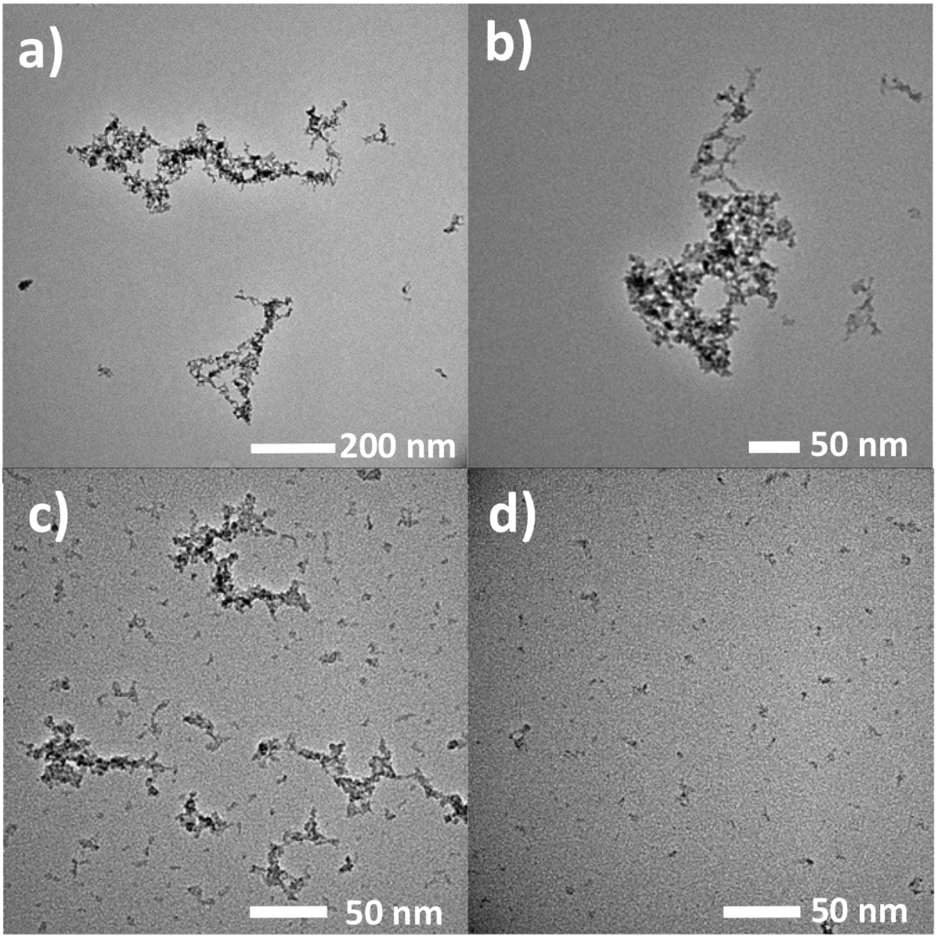

Figure 1. Molybdenum oxide nanoparticles produced by spark ablation. Argon flow of a) 1 L/min, b) 2 L/min, c) 5 L/min and d) 10 L/min.

Several samples were irradiated with fast neutrons in the MONNET light-ion accelerator in JRC Geel. Upon absorption of an incident neutron by naturally present molybdenum-100 the nucleus recoils, with the recoil energy further modified by the emission of two fast neutrons. If the nanoparticle is small enough compared to the range of the recoiling molybdenum-99, then the latter may exit the nanoparticle facilitating extraction.

After irradiation, the samples were dispersed in different extraction solutions, which included typical metallurgy extracting agents. However, the solvent used for the solid-liquid extraction had to be carefully chosen to prevent any dissolution of the nanoparticle agglomerates that would result in a decrease of the final specific activity. Under some of the selected extraction conditions, a selective isotopic separation of molybdenum-99 was accomplished, resulting in an increased specific activity.

114

Radiation resistant chromium metal-organic frameworks for the production of ^{51}Cr by the recoil effect

Chao Ma[1], *Iván Sánchez-García*[2], *Hitos Galan*[2], *Antonia G. Denkova*[3], *Pablo Serra Crespo*[4*]

[1]Zhongyuan Critical Metals Laboratory, Zhengzhou University, Zhengzhou 450001, China
[2]Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Avda. Complutense 40, 28040, Madrid (Spain)
[3]Applied Radiation and Isotopes, Delft University of Technology, 2629 JB Delft, Mekelweg 15, The Netherlands
[4]European Commission, Joint Research Centre. Westerduinweg 3, 1755 LE Petten, The Netherlands
[*]E-mail: Pablo.SERRA-CRESPO@ec.europa.eu

Keywords: radionuclide production, recoil effect, metal-organic frameworks, radiation stability

Chromium-51 is an attractive radionuclide in clinical application for labelling of red blood cells, diagnosis of gastrointestinal bleeding and assessing life span of red cells. This work reports on the stability of two chromium-based metal-organic frameworks (MOFs) (MIL-100 and MIL-101) upon gamma radiation and their application as radiation targets to produce high specific activity ^{51}Cr utilizing the Szilard-Chalmers effect.

First, the radiation stability of two MOFs under high gamma doses was determined. For these experiments two different facilities were utilized, for a low rate dose the ^{60}Co facility in TU Delft was used(1) and for high dose rate the facility Nayade at CIEMAT was applied. After a thorough characterization that included XRD, FTIR and Raman spectroscopy, TGA and N_2 adsorption, the results showed that MIL-100 (Cr) and MIL-101 (Cr) exhibited excellent radiation stability after exposure to gamma radiation dose up to 5 MGy, not showing a dose rate dependency.

Subsequently the Cr-MOFs were irradiated in the HOR reactor at TU Delft. The ^{51}Cr yield and specific activity were determined at different irradiation times, extracting agents and extraction times. The most optimal results show that high enrichment factor (>500) and yield (>50%) can be achieved, appearing to be a promising ^{51}Cr production route for nuclear medicine.

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Prompt gamma activation analysis

49

Elemental abundances of archaeological pottery using Prompt Gamma Activation Analysis

Andrey Yu Dmitriev[1], Wael Badawy[2], Sergey Barzakov[1]*

[1]Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 6 Joliot-Curie St, 141980 Dubna, MR, Russian Federation
[2]Radiation Protection and Civil Defense Department, Nuclear, Research Center, Egyptian Atomic Energy Authority, (EAEA) 13759 Abu Zaabal, Egypt
[*]E-mail: wmbadawy@gmail.com

Keywords: elemental composition, PGAA facility, statistical analysis, archaeological ceramics

The present work was carried out to validate the facility of Prompt Gamma Activation Analysis at the pulsed reactor IBR-2, Frank Laboratory of Neutron Physics (FLNP) - Joint Institute for Nuclear Research (JINR). Therefore, the first experiments were carried out to study the elemental composition of archaeological ceramics using PGAA. The activity concentration was measured using a radiation resistant n-type High Purity Germanium (HPGe). A total of 14 elements were determined as the preliminary results and namely; Al, C, Ca, Fe, Gd, H, K, Mn, Na, P, S, Si, Sm, and Ti. For comparison purposes; the obtained results were compared with those analyzed by other analytical techniques INAA (Instrumental Neutron Activation Analysis) and portable X-ray fluorescence (XRF) for the same archaeological fragments. These findings will improve the PGAA installation and automation of the data obtained, which in turn will improve the quality of analysis.

66

Neutron-based elemental composition analysis of electronic waste items

Noémi Anna Buczkó[*]*, Boglárka Maróti, Katalin Gméling, László Szentmiklósi*

Nuclear Analysis and Radiography Department, Centre for Energy Research, Hungary
[*]E-mail: buczko.noemi@ek-cer.hu

Keywords: neutron activation analysis, prompt gamma neutron activation analysis, electronic waste

The recycling of waste electrical and electronic equipment (WEEE) is an important aspect of the circular economy. The elemental composition of such waste is frequently unknown. An appropriate analytical methodology is required for the determination of the valuable and/or hazardous elements in WEEE. The aim of this work is a comprehensive elemental analysis of memory cards from legacy personal computers. Our ambition with this research is to establish a validated analytical methodology for the comprehensive analysis of WEEE. A combination of different neutron-based techniques, such as prompt gamma neutron activation analysis (PGAA), instrumental neutron activation analysis (INAA), and in-beam neutron activation analysis (in-beam NAA), was used to determine the elemental composition of memory cards. The elements measured by more than one technique were used for the cross-validation of the methods. The components of the memory cards were measured after mechanical separation, grinding, and homogenization with the three different techniques. PGAA and in-beam NAA measurements also were performed on the intact, structured memory cards, without any sample preparation. The applicability of the faster, cheaper, and more available handheld X-ray fluorescence spectroscopy (hhXRF) was also investigated.

Each method typically provided complementary information about the elemental composition. The combination of the techniques was found to be suitable to quantify most of the valuable and/or hazardous elements present in memory cards (e.g. Au, Ag, La, Ce, Eu, Gd, Tb, Yb, Sb, Sc, Hf, Br, Cd, etc.). The raw concentrations measured with PGAA were systematically higher compared to INAA. The reasons for the differences were identified, and corrections were worked out. One of the reasons identified is the non-negligible thermal neutron self-shielding of the samples, which caused an underestimation of the concentration of all elements in INAA measurements. The boron content of the samples, which was the main reason for the thermal neutron self-shielding, was measurable solely with PGAA and the thermal neutron self-shielding was successfully corrected based on boron results obtained from PGAA. Another identified reason was the distorting effect of undetected main components on the PGAA measurements. Oxygen, the presumed main component of memory cards, was not detectable with PGAA under typical measurement conditions. For the correction, an oxygen concentration was calculated based on the known chemical formula. The absolute concentrations were also measured with in-beam NAA with the measurement of the effective neutron flux, these results also were used to the corrections of PGAA results. The results of different techniques were in agreement after applying the corrections. Concentrations measured with hhXRF differed significantly from those measured by neutron-based techniques, even for ground samples. The identified reason for this is the lack of a matrix-matched factory cali-

bration method in the evaluation software of the hhXRF device. The establishment of a new matrix-matched calibration is planned.
Beyond the memory chips, other pieces of electronics, such as LEDs, liquid-crystal displays, solar panels, etc. were also analyzed in this study.

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73

Prompt Gamma Activation Analysis for ^{239}Pu characterization

Conny Egozi[1*], *William S. Charlton*[2], *Sheldon Landsberger*[2]

[1]Los Alamos National Laboratory, Los Alamos, USA
[2]University of Texas at Austin, Austin, USA
[*]E-mail: cegozi@lanl.gov

Keywords: Prompt Gamma Activation Analysis, ^{239}Pu, compton suppression

Prompt Gamma Activation Analysis (PGAA) is a non-destructive method that produces characteristic gamma rays of much higher energy than decay gammas. In situations where the gamma rays may be attenuated, such as a nuclear material storage container, the use of PGAA would be highly beneficial. An isotope of particular interest for quantification through a nuclear material storage container is ^{239}Pu. Accountability of this radionuclide is of utmost importance for safeguards and verification. It is often not possible to remove ^{239}Pu from containment, and therefore performing PGAA on the isotope for yield determination would have great value. Currently, the IAEA has a database of PGAA gamma rays and yields for numerous radionuclides, but not for ^{239}Pu. A preliminary PGAA determination and yield determination was performed at the Nuclear Engineering Teaching Laboratory at the University of Texas with a 1.81E6 Bq ^{239}Pu foil. A different ^{239}Pu source of 10 kBq electrodeposited on stainless steel was used in this study to perform quality control for the yields of the 12 gamma rays previously identified. The system used for these measurements was a combined PGAA and Compton suppression setup. The suppressed spectrum had better net areas for the peaks and so could better be applied for yield determination. The source was counted for 4 hours with PGAA, then the neutron source was blocked and the source was counted for 8 hours. In this way, it was possible to eliminate fission product gamma rays and identify the gammas of interest. With these gamma rays, it will be possible to enhance current safeguards techniques and enable ^{239}Pu detection even through attenuating nuclear material storage container.

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103

Progress in Neutron Activation Analysis in China - From delay gamma to prompt gamma

Daqian Hei[1], *Zhifang Cai*[2]

[1]School of Nuclear Science and Technology, Lanzhou University, No.222 Tianshui South Street, Lanzhou, China
[2]Institute of High Energy Physics, China Academy of Sciences, 19B Yuquan Road, Shijingshan District, Beijing, China
*E-mail: heidq@lzu.edu.cn

Keywords: NAA, PGNAA, DGNAA, element analysis

As one of the most important research interests in the field of nuclear science and technology, Neutron Activation Analysis (NAA) technique is an effective nuclear analysis technology, playing an important role in the nuclide identification. Compared with the other elemental analysis techniques, NAA technique has the characteristics of high analytical accuracy and strong capacity of anti-interference, and has been widely used in geochemistry, cosmic science, environmental science and many other fields. As the parts of the important branches in NAA, Prompt Gamma Neutron Activation Analysis (PGNAA) technique and Delayed Gamma Neutron Activation Analysis (DGNAA) technique also have the advantages of high sensitivity, non-destructive inspection and non-essential sample pretreatment, and it can meet the needs of in-situ and bulk sample analysis, etc.

With the development of other analytical methods and instruments, NAA technique was greatly challenged. However, it still plays an irreplaceable role in detecting the internal components of bulk samples. In China, NAA technique has been developed and applied in many field in recent years. Based on the large scientific facilities (such as reactors and spallation neutron sources) and low-yield neutron sources (neutron generator, isotopic neutron source, etc.), many researches have been carried out in Chinese institutes, including the detection of trace elements in alloy, the distribution of internal elements in cultural relics, measurement of cross-sections of nuclides, etc. With the new challenges and opportunities, the developement of NAA technique in China is fully discussed in this presentation.

261

pyEGAF: Modernization of the EGAF database

Aaron Hurst[*], *Rick Firestone*

Department of Nuclear Engineering, University of California, Berkeley, California, 94720, USA
[*]E-mail: amhurst@berkeley.edu

Keywords: prompt gamma activation analysis, thermal neutron capture cross sections, python implementation

Signatures from neutron-induced reactions are key for a wide array of applications ranging from nuclear nonproliferation and national security to fossil fuel and space exploration. Although neutrons are often born at high energy, upon thermalization neutron capture is frequently the most probabilistic interaction leading to formation of a residual compound nucleus in an excited state just above the neutron-separation energy. Under these conditions the most likely decay mode of the compound nucleus is through electromagnetic emission. The emitted gamma rays are then described with energies equivalent to the unique recoil-corrected energy difference between initial and final states of the associated transitions. Accordingly, the produced pattern of emitted gamma-ray energies and intensities provide distinct fingerprints of isotopes present in an unknown assembly, making the thermal neutron-capture reaction particularly useful for nondestructive-assay applications.

One of the most comprehensive resources for thermal neutron-capture data is the Evaluated Gamma-ray Activation File (EGAF), containing data from Prompt Gamma Activation Analysis (PGAA) measurements carried out in a consistent manner at the Budapest Research Reactor for 245 isotopes [1]. Although these valuable datasets have been freely available for many years, one of the drawbacks is the outdated and cryptic Evaluated Nuclear Structure Data File (ENSDF) format [2] that is currently adopted for dissemination, making it difficult for users unfamiliar with ENSDF to utilize the data contained therein. Furthermore, the ENSDF format does not readily lend itself to modern computational technologies and a parser is required to interpret the complicated mixed-record format. To help overcome these challenges, we have developed a translator to convert the ENSDF-formatted data sets into an open standard JavaScript Object Notation (JSON) format enabling accessibility to applications using different programminng languages running in different environments. Additionally, we have developed an open-source software package implemented in Python, pyEGAF, that is designed to interact with the JSON data structures for general purpose access, manipulation, and rapid assessment of the capture-gamma data in EGAF. An overview of the new format and utilization of pyEGAF will be presented.

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30

Development of industrial device for coal analysis based on PGNAA technology

Jiatong Li[1*], *Daqian Hei*[1], *Wenbao Jia*[2], *Zeen Yao*[1]

[1]School of Nuclear Science and Technology, Lanzhou University, No.222 Tianshui South Street, Lanzhou, China
[2]Institute of Nuclear Analytical Technology, Nanjing University of Aeronautics and Astronautics, Nanjing, China
[*]E-mail: lijt@lzu.edu.cn

Keywords: PGNAA, Monte Carlo simulation, Signal-to-Noise Ratio (SNR) optimization method, industrial analysis, spectra analytical method

Prompt Gamma-ray Neutron Activation Analysis (PGNAA) is a real-time, online and non-destructive elemental analysis method which is widely applied in environment, health sciences, and industry, etc. In the industrial application, a set of on-line fixed devices were developed for coal analysis. To improve the performance of device, a SNR optimization method was proposed for the design of PGNAA device [1], and a fixed coal online analysis system was optimized based on the mentioned optimization method in our research (Fig.1), with a D-T neutron generator and scintillator detector was as the core in the system [2]. Combined with the Library least squares method (LLS) for element analysis, the small deviations were found, which indicated a good performance of the designed system (Fig.2).

Further, faced to the high cost, installation difficulties and the other shortcomings of fixed devices, the on-line PGNAA device was updated, and a built-in device with a small volume was designed in MCNP code and built for measurement (Fig.3). Because of a small number of modules used in device, a higher SNR value (514.86%) was acquired compared with that of the previous fixed device (16.01%), which benefited to the performance of the device. In addition, to improve the performance of the device from the view of analytical method, the weighted library least squares method (WLLS), instead of LLS method, was furtherly used. Compared with the results of LLS method, because of the smaller standard deviations of elements in different coal samples were found (Fig.4), the feasibility of WLLS method for coal analysis was investigated.

Figures

Fig.1 Coal on-line analysis system

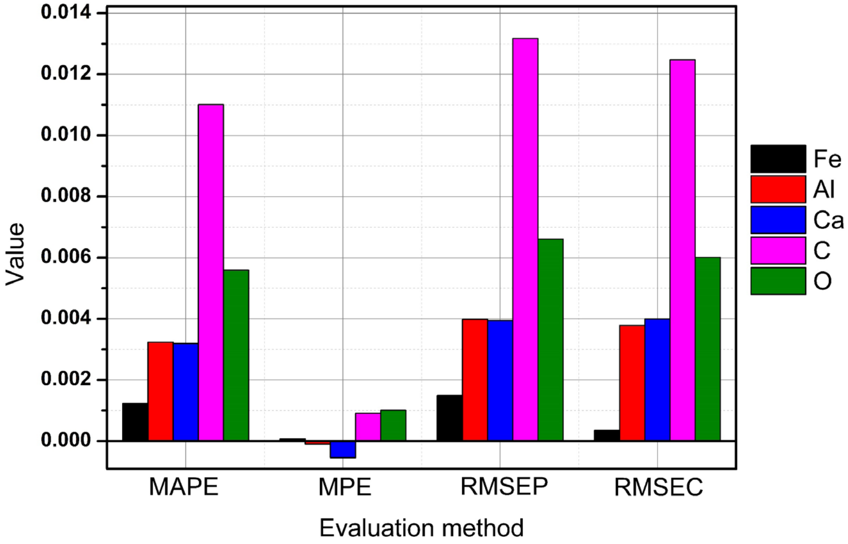

Fig.2 Analytical accuracy of elements by different evaluation method

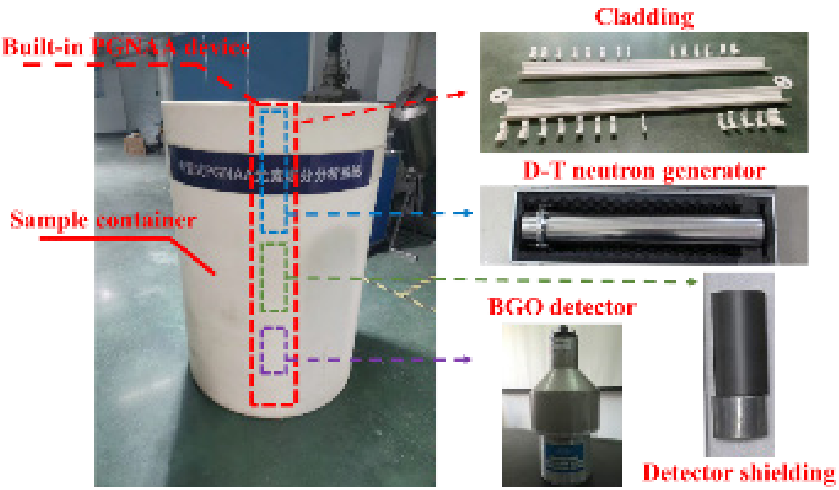

Fig.3 Built-in device

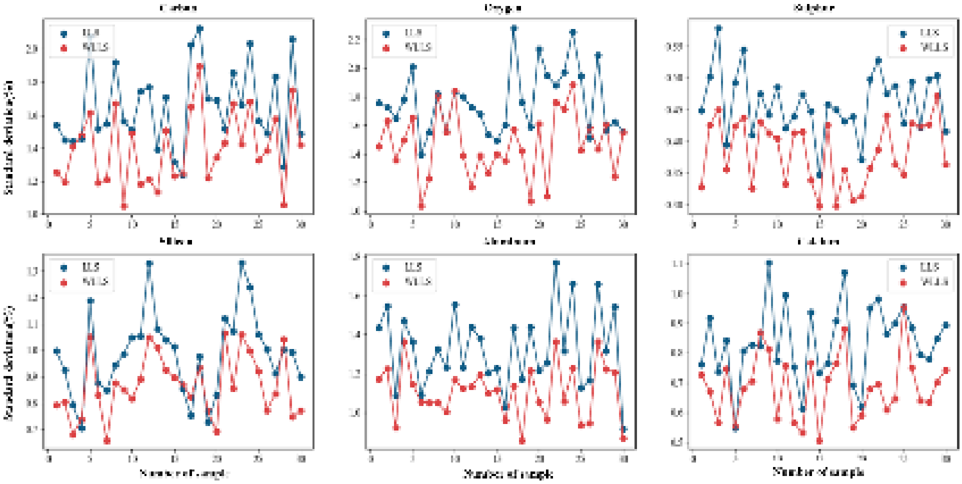

Fig.4 Standard deviations of different elements based on LLS and WLLS method

Acknowledgments

This work was a project funded by National Natural Science Foundation of China (12205131), China Postdoctoral Science Foundation (2022M711444).

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99

Reverse engineering of concrete composition by cold neutron PGAA

Richard Livingston[1*], *Neal Berke*[2], *Heather Chen-Mayer*[3]

[1]Department of Materials Science & Engineering, University of Maryland, College Park, MD, USA
[2]Tourney Consulting Group, LLC., Kalamazoo, MI, USA
[3]Materials Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA
[*]E-mail: rliving1@umd.edu

Keywords: concrete, petrography, constituents, prompt gamma, chlorides

The scientific analysis of a concrete sample for its constituents and contaminants such as chlorides is known as concrete petrography [Poole and Sims, 2016]. This is an important topic in the condition assessment of concrete structures. The conventional approach involves crushing the sample to a powder which is then analyzed by X-ray methods and wet chemistry. To evaluate the feasibility of prompt gamma neutron activation analysis (PGAA) as an alternative method, batches of concrete were prepared with either limestone or granite coarse aggregate. Several batches were mixed with various levels of Cl. The concrete batches were then cast into cylinders from which samples were taken and crushed according to the standard procedure [ASTM C2004]. The powders were analyzed at the Cold Neutron PGAA (CNPGAA) facility at NIST. Counting time was typically10 to 15minutes. The analyzed elements were usually H, C, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Mn, Fe and Sr. To correct for local variations in the neutron flux, the calculated masses of the individual elements were normalized by the mass of the dominant element, either Ca or Si. For Cl the levels measured by CNPGAA agreed to within 6% of the values measured by wet chemistry. The Cl minimum level of detection (LOD) is estimated at 100 ppm. The elements Ca, Si, H and S were also used to estimate the mass fractions of the constituents (coarse aggregate, fine aggregate, water and cement) in the original mix design by the matrix inversion method. The estimated composition was within 3% of the actual, rather than nominal, value. This analysis also led to the serendipitous discovery that the PGAA data could be used to estimate the degree of progress of the cement hydration reaction. This was possible because the free water content was lost from the sample during the grinding process, leaving only the chemically bound H which was detected by the CNPGAA. Degree of hydration is difficult to measure by conventional techniques. This loss of water did shift the mass fractions of the constituents from the nominal mix design values by a scale factor. Thus PGAA measured the actual re-scaled constituent mass fractions rather than the nominal ones. This effect likely only occurs with sample destruction, and can be eliminated by using the PGAA in a scanning mode to measure intact samples, thus avoiding the crushing step entirely. The conclusion is that CN PGAA would be a feasible method for concrete petrography.

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118

Non-destructive analysis of complex cultural heritage objects

Boglárka Maróti[1*], *J. Gábor Tarbay*[2], *Zoltán Kis*[1], *László Szentmiklósi*[1]

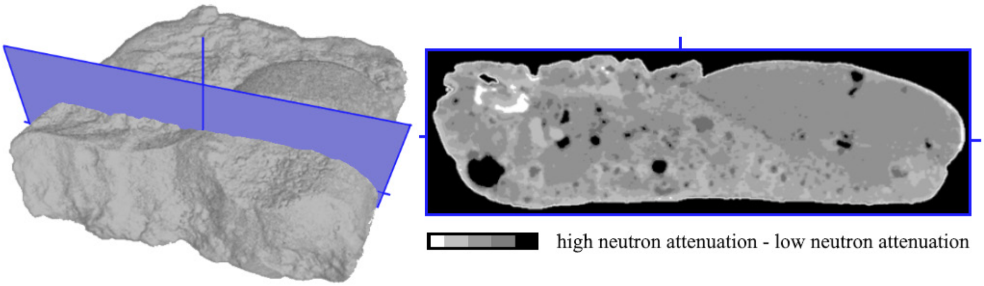
[1]Nuclear Analysis and Radiography Department, Centre for Energy Research, Budapest, Hungary
[2]Department of Archaeology, Scientific Directorate, National Institute of Archaeology, Hungarian National Museum, Budapest, Hungary
[*]E-mail: maroti.boglarka@ek-cer.hu

Keywords: prompt gamma activation analysis, neutron imaging, non-destructive, complex shape, bronze

One of the major application fields of the Budapest PGAA laboratory is the non-destructive analysis of cultural heritage objects. In the framework of a project "Non-destructive, spatially-resolved element analysis of structured samples", our aim was to establish a workflow enabling the reliable chemical composition determination of large, irregularly-shaped or structured objects in a completely non-destructive way.

A generally applicable matrix correction procedure based on MCNP Monte Carlo simulation software was developed for comprehensive analysis. The steps to validate the MCNP code included the analysis and simulation of plate-like, layered model samples [1], homogeneous but irregular-shaped bulky objects [2], and lastly, a cube prepared using 3×3×3 pieces of unit cubes of different materials [3]. The geometrical input data required to the simulation came from 3D optical scanning or from X-ray/neutron tomography.

The elaborated method has been applied to the more in-depth analysis of real cultural heritage objects, e.g. on a Late Bronze Age spearhead and a casting ingot from the collection of the Hungarian National Museum. Data obtained by the neutron tomography, XRF and PGAI measurements of the objects are presented, together with combined interpretation of the MCNP results.



Neutron tomogram and virtual cross-section of the cuboid ingot from Velem-Szent Vid site. The cross-section reveals the two distinct materials (different hues of gray) of the ingot, while air inclusions (black) and inclusions containing materials with high neutron absorption are also present.

Acknowledgments

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133

Characterization of rare-earth elements in magnetic materials by fast neutron inelastic scattering for industrial applications

*I. Meleshenkovskii**, *E. Mauerhofer, T. Brückel*

Juelich Center for Neutron Science, Forschungszentrum Juelich GmbH, 52425 Juelich, Germany
*E-mail: i.meleshenkovskii@fz-juelich.de

Rare-earth magnets (such as NdDyFeB, SmCo, etc.) are a critical component of modern technologies and their recycling is of strategic importance in view of sustainable handling of valuable resources. An efficient recycling requires in front end a sorting of the magnets according not only to their type but also to their rare-earth elements content. In industrial scale this is a new challenge to take up because the analysis needs to be done rapidly and on bulk materials. The traditional methods used for determination of rare-earth elements content, such as ICP-MS or –OES, XRF, LIPS or PGNAA with cold or thermal neutrons reach their performance capabilities in such applications. These limits are attributed to either the necessity to dissolve part of the sample or due to attenuation of the interrogation beam in bulk and dense material flows. In this presentation, we propose a concept for rapid and accurate non-destructive characterization of magnet samples of various composition, geometry and thickness based on fast neutrons as a source of interrogation radiation and measurement of the element specific prompt gamma-rays induced by the inelastic scattering of fast neutrons due to the (n,n´γ) reaction (PGA-INS). The analytical technique is based on detection of element specific prompt gamma-rays using a spectrometer, allowing to unfold qualitative and quantitative information about the magnet elemental composition. We describe the physical principle of the method physics and its advantages, discuss on the detection methodologies and data analysis routines.

115

Fast Neutron-induced Gamma-ray Spectrometry (FaNGaS)

Niklas Ophoven[1,2*], *Zeljko Ilic*[2], *Eric Mauerhofer*[1], *Tsitohaina H. Randriamalala*[1], *Egor Vezhlev*[1], *Christian Stieghorst*[4], *Zsolt Révay*[4], *Thomas Brückel*[1,3], *Jan Jolie*[2], *Erik Strub*[2]

[1]Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
[2]Mathematisch-Naturwissenschaftliche Fakultät, Universität zu Köln, 50923 Cologne, Germany
[3]Lehrstuhl Für Experimentalphysik IVc, RWTH Aachen University, 52056 Aachen, Germany
[4]Heinz-Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstraße 1, 85748 Garching, Germany
[*]E-mail: n.ophoven@fz-juelich.de

Keywords: inelastic scattering, fast neutron, cross section, gamma ray, detection limit

Prompt Gamma Neutron Activation Analysis (PGNAA) based on cold or thermal neutron capture is well established as a powerful technique for non-destructive elemental analysis of small and thin samples. However, due to limited penetration and attenuation effects, PGNAA is not suited for a precise investigation of large objects. The general possibility to analyse large samples by measuring prompt gamma rays from fast-neutron-induced reactions was already demonstrated several decades ago [1]. The FaNGaS (Fast Neutron-induced Gamma-ray Spectrometry) instrument, installed at Heinz Maier-Leibnitz Zentrum (MLZ) in 2014, advances this unique technique in nuclear analytical chemistry and makes it valuable for a broad community of industry and research [2-7]. It uses the intense fission neutron beam delivered by the SR10 channel (Strahlrohr 10) of the research reactor FRM II (Forschungs-Neutronenquelle Heinz Maier-Leibnitz) to investigate fast-neutron induced prompt gamma-ray emission. It offers new possibilities for the chemical analysis of large or small samples as a complementary method to conventional thermal- or cold-neutron based PGNAA. The dominating reaction channel of fast neutrons at FaNGaS is the (n,n'γ) inelastic scattering reaction, currently with only one existing database: the "Atlas of Gamma-rays from the Inelastic Scattering of Reactor Fast Neutrons", published in 1978 by Demidov et al. [8]. This data compilation is valuable and a relational database has been recently developed based on this Atlas [9]. However, it was yet never validated and previous measurements with FaNGaS show the need for a critical and meticulous validation [3-6]. Apart from building up a comprehensive catalogue of (n,n'γ) reactions another main objective is a continuous optimization of the instrument to achieve a further peak-to-background reduction resulting in enhanced sensitivity and lower detection limits.

In this contribution the complementarity between fast-neutron-induced gamma-ray spectrometry with FaNGaS and conventional PGNAA will be addressed. The experimental set-up of the instrument will be presented, including details in shaping of the neutron beam from its creation to the sample and shielding design. The use of our instrument will be demonstrated based on several measurements. Special attention is dedicated to the reliability and agreement of obtained nuclear data to existing literature.

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190

ProSpeRo – Updated software for quantitative analysis in Prompt Gamma Activation Analysis

Zsolt Révay[1*], *László Szentmiklósi*[2], *Boglárka Maróti*[2]

[1]Technical University Munich, Research Neutron Center Heinz Maier-Leibnitz, Garching, Germany
[2]Center for Energy Research, Budapest, Hungary
[*]E-mail: zsolt.revay@frm2.tum.de

Keywords: prompt gamma activation analysis, spectroscopy data, data evaluation

ProSpeRo (Prompt Gamma Spectrum Rover) is Excel-based expert system for the determination of elemental composition of irradiated samples based on prompt gamma-ray spectra. It is based on a statistical comparison of the evaluated spectra to the spectroscopy data library of prompt gamma lines.

The library project started about 25 years ago in Budapest after it was recognized that no reliable database of prompt gamma lines existed for analytical purposes. The new database contains energies and the so-called partial gamma-ray production cross sections for the detectable lines of the chemical elements. In the first measurement campaign lasting until 2004, elements and their compounds were measured in the thermal- and cold-neutron beam of BNC. Pure elements (or their oxides, sometimes other simple compounds with low-cross-section elements) were measured first. The actual line energies were determined in the presence of chlorine (irradiating chlorides or adding a PVC foil to the elemental sample), low- and high-energy lines of the unknow element were calibrated to well-known chlorine lines whose energies were determined using crystal spectrometer with high accuracy. The intensities were then standardized using stoichiometric compounds and the counting efficiency. The database has been successfully used in thousands of analyses in Budapest and Garching, also at NIST and University of Texas [1].

This database has been regularly updated with improved data from higher-precision measurements mainly performed at the Garching PGAA facility. The latest library and program updates were released in 2022.

The analysis is based on the detailed comparison of the efficiency-calibrated peak areas to the partial cross sections of the elements. ProSpeRo calculates a set of statistical parameters, mainly Z-scores and χ^2 values to quantify the similarity of the line pattern in the database to the peak list. The program's recommendation can be adjusted manually. It also corrects for the spectral background, interferences and also for the neutron self-shielding and the gamma-ray self-absorption. It also determines the detection limits of all the elements based on the characteristics of the spectra.

The tests of the latest version were performed together with the Nuclear Analytical Laboratory in Budapest. We checked the reliability of the analyses in the case of the updated spectroscopy data. The influence and reliability of the refined interference correction was also thoroughly tested.

The further improvement of the analytical method and of the data library is an ongoing project.

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178

Alloys of West Hungarian Late Bronze Age spearheads

János Gábor Tarbay[1*], *Boglárka Maróti*[2]

[1]Department of Archaeology, Scientific Directorate, National Institute of Archaeology, Hungarian National Museum, Budapest, Hungary
[2]Nuclear Analysis and Radiography Department, Centre for Energy Research, Budapest, Hungary
[*]E-mail: tarbay.gabor@hnm.hu

Keywords: Sn, Pb, Sb, prompt gamma activation analysis, neutron imaging, non-destructive, use-wear

Offensive weaponry during the Late Bronze Age (1450–850 B.C.) went through specialization and a development of new forms and shapes applied to different combat scenarios. During this period, it was common for objects to be alloyed with an optimal Sn alloying ratio between 8 and 12 wt%. With the aid of cold hammering and/or annealing, this alloy type made the weapons resilient to endure, with proper maintenance, multiple throwing, thrusting, and slashing actions throughout their use-lives.

The recent prompt gamma activation analyses (PGAA) of nine hoarded spearheads from the territory of West Hungary revealed that the ratio of bulk tin varied between 0.7 and 12 wt% in the studied samples. Objects also have a relatively high Sb content, between 1.3 and 13 wt%. Two spearheads had an Sn content below the detection limit of the applied method, and one had extremely low wt% of Sn and high wt% of elements like Sb and Pb: Celldömölk (Sn < D.L., Sb 6.4 wt%, Pb < D.L.), Budakeszi X (Sn < D.L., Sb 13 wt%, Pb 5 wt%), Budakeszi Y (Sn 2.7 wt%, Sb 9.1 wt%, Pb 21 wt%).

The more pronounced appearance of Sb and Pb in the copper matrix of Late Bronze Age metal products is a phenomenon observed mostly between 1140 B.C. and 900 B.C. This is the period where most of the studied finds are dated, and this elemental composition pattern may be related to the extraction of ore sites in the territory of Slovakia, Austria, and the Northern Balkans. Ag and As also appear in the studied samples in combination with Sb content, which suggest the smelting of Fahlore according to the work of Z. Czajlik. It appears likely that during this period, craftsmen began experimenting with new alloying materials (Pb) other than tin and special raw material with high Sb content to improve product quality and become less reliant on tin, which is more difficult to obtain in this region.[1] The Sb-Sn spearheads with 5.2 wt% Sn content were already functional, according to the use-wear analysis.[2] The above-mentioned extreme cases from the Celldömölk and Budakeszi hoards can be explained in a different way. It is possible that they were intentionally alloyed with Sb, particularly in the case of the Celldömölk spearhead. According to the use-wear analysis carried out on the artifacts, these weapons were not or hardly used at all. One spearhead from Budakeszi is a dysfunctional, defective product. Its 21 wt% Pb content would have made its material so soft that even if the casting had been well done, it could not have been used as a functional weapon. The Celldömölk spearhead lacked wear traces completely, while the other Budakeszi spearhead showed only one try-out mark, after which it was intentionally broken into two pieces. All three were selected almost directly from the foundry for larger ritual hoards. In these cases, it seems that the absence or low percentage of Sn (around 2 wt%) may be more indicative of prehistoric objects that were intentionally not made for everyday use.

Acknowledgments

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33

Fast neutron measurement system using prompt gamma neutron activation convertor: Monte Carlo simulations

Jonathan Walg, Itzhak Orion[*]

Department of Nuclear Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel
[*]E-mail: iorion@bgu.ac.il

Keywords: PGNA, KCl, radiation, MCNP, accelerator, convertor

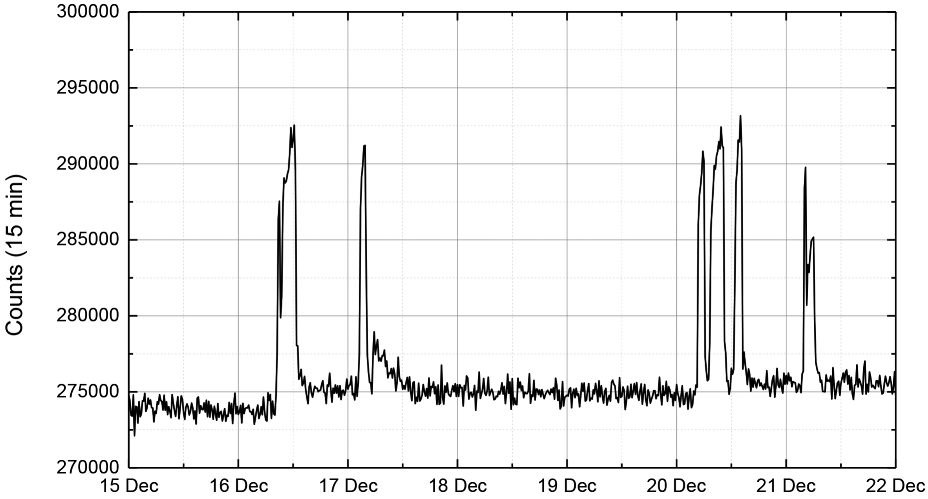
Measuring fast neutron emission around accelerators is important for environmental monitoring and for radiation safety. It is necessary to detect two types of neutrons: thermal and fast. There are several types of detectors for thermal neutrons, such as BF_3 ion-chamber and LiI(Eu) scintillator. Fast neutron spectroscopy is commonly used by a hydrogen-recoil proportional-counter; however, its threshold is 2 MeV.

In our previous research we established a counting system composed of a large convertor of KCl with a NaI(Tl) gamma radiation spectrometer. The system was placed next to an 18-MeV proton cyclotron. The KCl convertor is efficient for fast neutron prompt gamma emission due to the Cl-35 cross section magnitude (PGNA). The potassium naturally includes a K-40 radioisotope that emits 1.460 MeV gamma rays. The presence of the constant level of 1.460 MeV gamma rays counts gives an advantage by providing a stable background to the detector [1]. Fig. 1 shows the prompt gamma radiation peaks from Cl-35 above the K-40 count level for each fast neutron's emission peaks.

The aim of this current study is to expand PGNA convertors based on KCl to fulfil the need to detect neutron energies from 0.02 MeV up to 3 MeV. The study was carried out using MCNP simulations of the counting system with a variety of PGNA convertors that include Ca, Zn, In, Ti and Sc.

We conclude that KCl mixtures with other elements, such as PGNA converters, using an NaI(Tl) detector showed improved detection performance for fast neutron emissions.

Figures



NaI(Tl) prompt gamma counts measurement results of fast neutron emitted during cyclotron operations.

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Radioanalytical methods of long-lived radionuclides

168

Application of automatic fusion for decommissioning samples

Maya Jäggi[*], *Martin Heule, Fabian Köhler, Nick Walter, Sabine Mayer*

Paul Scherrer Institute, Department of Radiation Safety and Security, Radioanalytics,
5232 Villigen PSI, Switzerland
[*]E-mail: maya.jaeggi@psi.ch

Keywords: automatic fusion, decommissioning, radionuclides

The range of the decommissioning samples from nuclear facilities include materials, such as barite concrete, concrete, sludge samples from waste water basins, asbestos containing materials (ACM), mortar and wall paint etc. Thereby, a variety of decommissioning samples have to be analysed for radionuclides before disposal.

To cover the radionuclide vector necessary for fulfilling waste specifications, the analysis of pure alpha- and beta-emitters has to be included. These decommissioning samples have therefore to be dissolved completely. In addition, a fast and reliable chemical separation procedure is necessary.

For full dissolution of the decommissioning samples, the borate-fusion method was chosen. The method even allows to dissolve refractory particles during the hot melt phase at more than 1000 °C. The borate-fusion process was automated for an increased sample throughput and for safety reasons. To tackle the problematics of Si-O_2 gelation after fusion, polyethylene glycol was added to the 4.5 M nitric acid solution to promote the flocculation of SiO_2-gel, which can be filtrated. The chemical separation of the radionuclides was done using the resin cartridges TEVA-UTEVA-DGA-Sr-Resin (Triskem, international) in series for the analysis of Am, Pu and Sr.

Some matrices were fused and the radionuclides Am, Pu and Sr chemically separated. In general as shown in table 1, the tracer recoveries were 69 % or higher. It was observed that HF (hydrofluoric acid) treated ACM material before fusion showed much inferior recoveries with ^{243}Am. The lowest recovery of the test series with ^{242}Pu tracer was observed to reach 55 % only. Testing the fusion on ACM material, followed by SiO_2-gel flocculation using polyethylene glycol, however, the recovery of ^{85}Sr tracer in 4 samples was 97 % ± 6 %.

Table 1: Am, Pu and Sr tracer recoveries of various decommissioning matrices.

Sample matrix	243**Am [%]**	242**Pu [%]**	85**Sr [%]**
Radioactive sludge (0.3 g – 0.5 g), N = 19	69 ± 17	84 ± 8	72 ± 7
Barite concrete (0.3 g), N = 6	88 ± 7	83 ± 3	75 ± 16
Barite concrete (3.0 g), N = 2	98 ± 1	77 ± 3	74 ± 2
*ACM HF-treated (1.0 g), N = 5	<30	55 ± 12	-
ACM (0.14 g), N = 4	80 ± 10	105 ± 6	

*The RCM material was treated with HF before fusion, thus no polyethylene glycol was added.

In conclusion, all the decommissioning samples with their variety in composition could be dissolved completely by applying the same automated borate-fusion procedure with subsequent SiO_2-gel flocculation induced by polyethylene glycol. The chemical separation worked well for material masses of 0.14 g – 3.0 g. The combined procedure lasted only 2.5 d – 3 d for a group of 4 samples. In the future, additional different decommissioning samples, such as linoleum, or mortar and wall paint will be analysed.

Acknowledgments

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167

Towards a quantitative Cl-36 PVC tracer for radioanalytical investigations of decommissioning samples

F. Köhler[*], *M. Heule, M. Jäggi, P. Dutheil, P. Zimmermann, N. Walter, S. Mayer*

Paul Scherrer Institute (PSI), Forschungsstrasse 111, 5232 Villigen PSI, Switzerland
[*]E-mail: fabian.koehler@psi.ch

Keywords: chlorine-36, polyvinylchloride, PVC, reference material, decommissioning

As part of the decommissioning of nuclear facilities, removal of kilometers of electric cables has to be addressed. In addition, in the second half of the 20th century PVC has been widely used as part of the polymer mixtures for insulation and jacket materials in electric cables. Exposure to strong neutron fields can lead to activation of PVC, producing long-lived Cl-36 ($T_{1/2}$: 300.000 a). Nuclear waste regulations increasingly demand the analysis of cable waste for Cl-36. The fact that Cl-36 is a pure beta-emitter results in the requirement for chemical separation of the chloride from PVC, which will be subject to losses during the process. In order to be able to quantify these losses, efforts aimed at producing a suitable PVC/Cl-36 reference material.

First batches of pure PVC reference pills were created from powdered pure PVC reference material. Irradiation of the material was performed at the spallation neutron source (SINQ) at the Paul Scherrer Institute (PSI). In addition to this, a first comparison was made with unplasticized PVC. Activation of 200 mg PVC pills over 600 s (total neutron fluence of 5.6E15 neutrons/cm^2 per sample) yielded approx. 250 Bq/g of Cl-36. However, the interfering reaction pathway Cl-35(n;p)S-35 produced relatively high beta activities of S-35 with $T_{1/2}$ = 87 d (400 – 500 kBq in each irradiated PVC pill). First tests consisted of dissolving the PVC pill in tetrahydrofuran (THF) and heating the solution to complete decomposition at 450 °C with release of predominantly HCl. While dissolution in THF is ideally suited for the reference pills, plasticized PVC contains additives that create insoluble precipitates as well as colored solutions. These result in additional quenching during LSC measurements. The second option for PVC treatment utilizes heat to destroy the matrix. Yet, the disadvantage was a low recovery (<30 %) of Cl-36 from the fumes when captured using gas wash bottles.

LSC measurements were performed with Ultima Gold LLT and a HIDEX instrument. Even though the interfering S-35 activity is up to four orders of magnitude higher, the detection of Cl-36 is achievable when the measurement windows are set correctly. In addition to the preparation procedure, the results of both direct dissolution and thermal degradation will be presented.

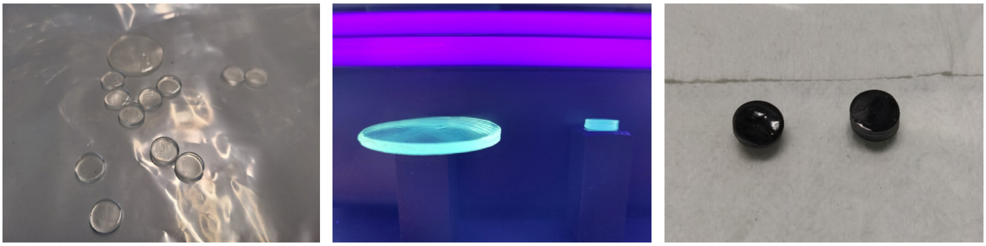

Figure 1: Images of PVC pills. Left: PVC pills after dissolution and preparation with acetone. Middle: PVC pills before irradiation under UV light. Right: PVC pills after neutron irradiation.

Acknowledgments

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53

Determination of the ^{210}Po analytical method in environmental samples for investigation of phosphate fertilizer facility

Hyeon-Woo Lee, Ji-Eun Lee, Eun-ju Choi*

Department of NORM Analysis, Korea Institute of Nuclear Safety, Yuseong-gu, Daejeon,
Republic of Korea
*E-mail: hwlee@kins.re.kr

Keywords: polonium-210, phosphogypsum, alpha spectrometry, acid digestion, spontaneous deposition

Naturally occurring radioactive material(NORM) contains natural radionuclides such as ^{238}U, ^{232}Th, ^{226}Ra, and ^{210}Po, and the potential risk of radiation exposure has been reported when natural radionuclides are concentrated in the NORM industrial process.[1] Especially, in a phosphate fertilizer facility, radium is separated and concentrated by a chemical process using sulfuric acid, and pipe scale with high radium concentration and a large amount of phosphogypsum are produced as by-products. Recycling of pipe scrap and outdoor storage of phosphogypsum piles can cause leakage of natural radionuclides into the external environment. Therefore, in Korea, the level of radioactive contamination around facilities is being investigated in accordance with the "Act on protective action guidelines against radiation in the natural environment"(Nuclear Safety and Security Commission, 2013). ^{210}Po, one of the major radionuclides in environmental investigations, is a decay series nuclide of ^{226}Ra which is concentrated in phosphate fertilizer facilities and exists in all environments through the release of ^{222}Rn($t_{1/2}$=3.8days) into the atmosphere. ^{210}Po emits high alpha energy of 5.304 MeV and has a relatively long half-life, causing continuous internal exposure when ingested or inhaled, making it the most concerning within the polonium group. Additionally, due to its characteristic of being well absorbed in minerals, particles, and colloids, it plays an important role in tracking the behavior of polonium in the environment. In order to evaluate the contamination of the environment around a facility, it is essential to use accurate radioactivity data and develop validated analytical method.

In this study, analytical methods for ^{210}Po determination in environmental samples were compared and optimized for the environmental investigation of phosphate fertilizer facilities. For validation of the analysis process, certified reference materials of similar medium such as IAEA-385(Irish sea sediment), IAEA-434(phosphogypsum), IAEA-446(Baltic sea seaweed), IAEA-447(Moss soil) were used. Then, ^{208}Po and ^{209}Po were spiked as yield tracers to confirm the loss of polonium in each pretreatment process. The polonium detection source was prepared through acid digestion, extraction chromatography, and spontaneous deposition under optimized conditions.[2] Specifically, in order to prevent volatilization of polonium and optimize the decomposition of the sample, open and pressure vessels were used to compare the sample decomposition rate and polonium recovery rate according to the mixed ratio of various acids such as HNO_3, HCl, HF, H_2O_2 and $HClO_4$. After that, polonium was purified by extraction chromatography using Sr-resin, and a detection source was made by spontaneous deposition method using a newly manufactured polonium deposition kit. The activity concentration of ^{210}Po in the certified reference materials were calculated based on the recovery rate of tracers, and the result is compared with the certificate value.

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111

For the determination of ^{41}Ca in concrete samples: Comparison of different counting efficiency calibration methods for liquid scintillation counting

Inés Llopart-Babot[1,2*], *Mirela Vasile*[1], *Andrew Dobney*[1], *Sven Boden*[1], *Katrien Smits*[1], *Michel Bruggeman*[1], *Martine Leermakers*[2], *Jixin Qiao*[3]

[1]SCK CEN, Boeretang 200, 2400 Mol, Belgium
[2]VUB, AMGC, Pleinlaan 2, 1050 Brussels, Belgium
[3]Department of Environmental and Resource Engineering, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark
[*]E-mail: ines.llopart@sckcen.be

Keywords: ^{41}Ca, efficiency calibration, CIEMAT NIST, TDCR

One of the largest low level nuclear waste streams produced during Nuclear Power Plant decommissioning is the biological shield. Usually, it is a massive reinforced concrete structure that surrounds the reactor, shielding against external doses during reactor operation by absorbing neutrons emitted from the reactor. During operation of the reactor this biological shield is subject to neutron activation thus producing several radionuclides in this material. These radionuclides have to be quantified when decommissioning the reactors at their end of life. Amongst the different radionuclides present in this material, ^{41}Ca is relevant with respect to radiation protection, related to the disposal of the biological shield, because of its long half-life ($T_{1/2}$ 10^5 year). ^{41}Ca is produced by the activation of ^{40}Ca, which is a major element in biological shield concrete and can also be an impurity in graphite samples (International Atomic Energy Agency, 1998).

The challenges for the determination of ^{41}Ca are: (1) the long and complex radiochemical separation procedures in order to obtain a pure fraction (Hou, 2007; Lee et al., 2020); (2) the lack of reference materials for development and validation of the analytical procedures; (3) the limited availability (only at JRC-Geel with a certified ratio of ^{40}Ca:^{41}Ca) of reference solutions for calibration of measurement instruments. Liquid scintillation counting (LSC) has been used mostly for the quantification of ^{41}Ca despite the low counting efficiency. Moreover, effects such as adsorption on the walls of labware or precipitation of calcium salts must be considered (Hampe et al., 2013; Hou, 2007; Lee et al., 2020). The long half-life of ^{41}Ca makes possible its measurement by mass spectrometric techniques, such as accelerator mass spectrometry (AMS) or triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS) (Hampe et al., 2013; Russell et al., 2021).

This work reports the comparison of different methods to perform the counting efficiency calibration for ^{41}Ca measurement by LSC. The first approach is based on the use of quench curves set up with a certified reference solution with a known ratio of ^{40}Ca/^{41}Ca. The second approach relies on the CIEMAT NIST efficiency method by using a ^{3}H reference solution (Günther, 2002; Rodriguez Barquero and Los Arcos, 1996). The third method uses the triple to double coincidence ratio (TDCR) technique available in a Hidex counter which uses two independent coincidence counting rates to compute the actual counting efficiency (HIDEX, 2022). The advantages and disadvantages of the three methods applied to the quantification of ^{41}Ca in samples from the biological shield concrete from Belgian Reactor 3 (BR3) will be presented in this paper.

Acknowledgments
We would like to thank ENGIE for sponsoring this project.

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211

Comparative study of preparation methods in radiocarbon dating of bones

Mirela Mihon[1*], *Oana Gaza*[1], *Alexandru Petre*[1], *Cristian Manailescu*[2]

[1]Department of Applied Nuclear Physics, Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, Magurele, Romania
[2]Department of Nuclear Physics, Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, Magurele, Romania
[*]E-mail: mirela.mihon@nipne.ro

Keywords: pretreatment, bone, ^{14}C AMS dating, quality assurance

The aim of this comparative study was to optimize the chemical treatment methods used for extraction of Type I collagen from bones and teeth. Bones are one of the most common materials analysed by the ^{14}C Accelerator Mass Spectrometry (AMS) dating method in RoAMS laboratory from IFIN-HH. The standard pretreatment method used to remove contamination was acid-acid (AA) method [1, 2]. A modification of this method, acid-base-acid-acid (ABAA) method has been previously studied [3]. In this study bones and teeth samples were pretreated by three methods: AA, ABAA and optimised AA method for poorly preserved samples.The C/N atomic weight ratio of the untreated and pretreated bones was a useful indicator for the most suitable processing method in removing contaminants [4].

The results of this study demonstrate the usefulness of the pretreatment method prior to ^{14}C AMS dating to ensure accurate radiocarbon ages.

Acknowledgments
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100

Determination of actinides and ^{93}Zr in radioactive waste and mineral samples

István Papp[1,2*], *Nóra Vajda*[1,3]

[1]University of Debrecen, Doctoral School of Chemistry, Debrecen, Hungary
[2]ISOTOPTECH Zrt., Bem tér 18/C, 4026 Debrecen, Hungary
[3]RADANAL Ltd., Konkoly-Thege M. út 29-33, 1121 Budapest, Hungary
[*]E-mail: pappistvan@isotoptech.hu

^{93}Zr is an important radionuclide in radioactive waste and decommissioning samples of NPPs. It is a long-lived, difficult-to measure nuclide, and its accurate determination requires separation techniques prior to analysis.

Separation of ^{93}Zr is usually challenging because complete separation of the matrix and the possible interferences (stable Nb, ^{93}Mo in ICP-MS) is required, and is especially difficult in case of mineral samples (e.g., soil, concrete) due to their complex chemical and mineralogical composition. Complete dissolution with acids or alkali fusion is necessary, and pre-concentration of analytes is often needed prior to chromatographic separation.

A couple of years ago we developed a sequential separation procedure based on a single DGA resin column for the determination of actinides (i.e., U, Pu, Am) in radioactive waste, and later improved the procedure for treating soil and sediment samples [1]. Due to the chemical similarities between Zr and tetravalent Np and Th we extended the procedure for the separation of Zr, and applied it for the analysis of liquid radioactive waste and mineral samples.

In this presentation we will show the process of method development for determination of ^{93}Zr. Batch uptake experiments were made in order to determine the equilibrium distribution coefficients of Zr on DGA and TEVA resins (products of TRISKEM International) in HCl and HNO_3 media. The separation procedure was optimized by chromatographic experiments where DGA resin was used to separate U, Pu and Am, while Th, Np and Zr were stripped together and finally separated on a TEVA column. The method was successfully tested by analyzing radioactive wastes (evaporation concentrates from an NPP) after applying a HF/HCl/HNO_3 destruction procedure.

To analyze ^{93}Zr in mineral samples alkali fusion with NaOH was used, and the pre-concentration procedure developed for co-precipitation of actinides (CaF_2 and $Mg(OH)_2$) was thoroughly tested/modified in order to make it adequate for the pre-concentration of Zr.

The performance parameters of the procedure will be discussed in the presentation.

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75

Rapid faecal and urinary bioassay of multiple actinide isotopes by mass and alpha spectrometric techniques

Guosheng Yang[*], *Eunjoo Kim, Jian Zheng, Munehiko Kowatari, Osamu Kurihara*

National Institutes for Quantum Science and Technology, Chiba, Japan
[*]E-mail: yang.guosheng@qst.go.jp

Keywords: ICP-MS, alpha spectrometry, actinides, bioassay, PROCORAD

To provide timely information for prompt decision-making in emergency radiation therapy, simple and rapid urinary and fecal bioassays has been developed to determine ultra-trace actinide isotopes, combining mass and alpha spectrometric methods. To measure Pu and ^{237}Np isotopes in 20-mL urinary samples by sector field - inductively coupled plasma mass spectrometry (SF-ICP-MS) and triple-quadrupole inductively coupled plasma–mass spectrometry (ICP-MS/MS), organic matter decomposition, LaF_3/CaF_2 coprecipitation, and chromatographic purification using 2 mL of AG MP-1M anion exchange resin column were performed [1]. Using ICP-MS/MS with low background provided the method detection limits (MDLs) for ^{237}Np, ^{239}Pu, ^{240}Pu, and ^{241}Pu of 0.025, 0.025, 0.015, and 0.020 fg mL^{-1}, respectively. To measure U isotopes in a 2-mL urinary sample by ICP-MS, organic matter decomposition and chromatographic purification using 2 mL DGA extraction resin cartridge were performed. The MDLs of ^{234}U, ^{235}U, and ^{238}U were 0.319, 0.217, and 2.80 fg mL^{-1}, respectively. To measure U, Pu, Np, and Am isotopes in a 150-g synthetic faecal sample by ICP-MS/MS, ashing, borate fusion, CaF_2 coprecipitation, and chromatographic purification using 2 mL of AG MP-1M anion exchange resin column and 2 mL DGA extraction resin cartridge were performed. The MDLs of ^{237}Np, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{243}Am were 0.003, 0.003, 0.002, 0.003, and 0.012 fg g^{-1}, respectively. Pu, U, and Am/Cm isotopes were also measured in a 500-mL urinary sample and a faecal matter ash by alpha spectrometry. Prior to analysis, organic matter decomposition, iron hydroxide coprecipitation, and chromatographic purification using 2 mL of TEVA and 2 mL of DGA resin cartridges were performed. The MDLs of Pu, U, and Am/Cm isotopes were ~ 1 mBq L^{-1} and ~ 0.15 mBq g^{-1} with a 24-h counting in urinary and faecal samples, respectively [2].

These radiometric and mass spectrometric methods were applied for participation in the annual intercomparison organized by the Association for the PROmotion of Quality COntrol in RADiotoxicological Analysis (PROCORAD), France, for method validations. Especially, the results that we submitted in the year 2022 intercomparisons was qualified as TOP LABO for the measurements of: Urine DTPA-actinides.

Acknowledgments
This work is partly supported by Japan Society for the Promotion of Science KAKENHI (22 K12384).

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Radioecology and environmental radioactivity

86

Dose assessment of ^{210}Po in total Kuwaiti diet

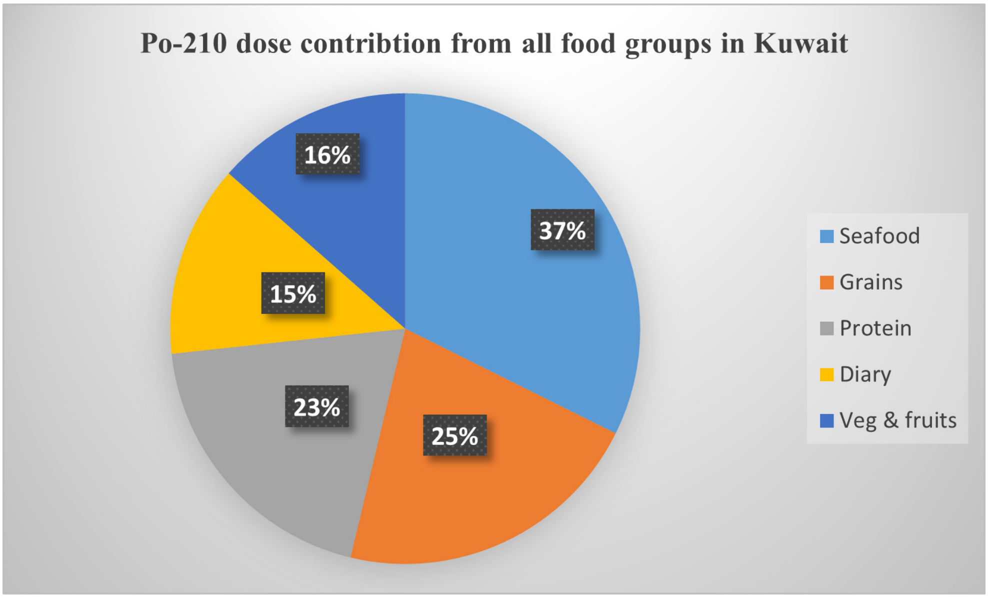
Aishah Alboloushi[*], *Omar Alboloushi, Abdulaziz Aba, Anfal Ismaeel, Sabeeka Al-Nuaimi*

Kuwait Institute for Scientific Research
Al-Jaheth Street, Shuwaikh, 13109, Kuwait
[*]E-mail: aboloushi@kisr.edu.kw

Keywords: type your, keywords here, separated, by commas

Food consumption is a key element contributing to the internal effective dose by ingestion of radioactive ingredients. More than half (70 µSv) of the total (110 µSv) annual committed effective dose from ingestion of food is coming from ^{210}Po radionuclide according to UNSCEAR data. Also, ^{210}Po/^{210}Pb activity ratio >1 in Kuwait air was recorded, thus, a possible enhanced ^{210}Po concentration in local cultivated foodstuff can result after deposition of air suspended solid particles. The importance of the study can be also linked to the probable nuclear releases of the current operating nuclear power plants in the region and in addition, to the high local consumption of imported different foods from different countries with different nuclear histories. This present study aimed to assess ^{210}Po and its associated dose in the total Kuwaiti diet including water and beverages. Activity concentration (Bq/kg), annual limits of intake (Bq/y), and committed effective dose due to the ingestion (µSv/y) were calculated and evaluated. The annual committed effective dose due to ^{210}Po ingestion was assessed to be 105.1±15.8 µSv. The highest ^{210}Po dose was due to seafood ingestion (39.3±3.1 µSv/y), while the lowest was due to ingestion of diary (16.0±4.8 µSv/y). Future studies will be done determining gamma emitters ^{210}Pb, ^{226}Ra, and ^{228}Ra in Kuwaiti diet and their doses.

Figures



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104

Monitoring of radioactive substances in water intended for human consumption according to Council Directive 2013/51/Euratom and Polish Regulation of the Ministry of Health

Izabela Chmielewska

Silesian Centre for Environmental Radioactivity, Central Mining Institute, Katowice, Poland
E-mail: ichmielewska@gig.eu

Keywords: monitoring, radioactivity, water intended for human consumption, indicative dose

In October 2013 European Commission issued Council Directive 2013/51/Euratom. It clearly defines the criteria which water intended for human consumption must meet concerning radioactive substances. The provisions of this directive have been introduced into Polish law and from December 7, 2017 are included in the **R**egulation of **M**inistry of **H**ealth. Requirements regarding radioactivity monitoring in drinking water apply to all drinking waters intakes in Poland.

According to RMH drinking water in Poland should be regularly monitored in terms of radioactivity, regardless the type of water intake (surface or underground), taking into account content of the following radionuclides:

- tritium ^{3}H
- radon ^{222}Rn
- radium isotopes: ^{226}Ra and ^{228}Ra.

Also RMH (after Directive 2013/51) inserts term: indicative dose. It means the committed effective dose for one year of ingestion resulting from all radionuclides which were detected in water intended for human consumption, no matter of origin (natural or artificial). Concentration of ^{3}H, ^{40}K, ^{222}Rn and short-lived radon daughter product shall not be taken into consideration while indicative dose is calculated.

During presentation, the requirements contained in the above mentioned regulation will be discussed in detail and research methods used in monitoring of drinking water will be presented. Also technical specifications and limitations of these methods in the context of monitoring principles will be described.

Additionally, the paper will present the results of two measurements campaigns for radioactivity determination in potable waters in Poland carried out by Silesian Centre for Environmental Radioactivity in years 2017 - 2018 and 2022.

191

Interaction of plutonium (IV) with calmodulin: Exploring the impact of amino acids variation in the metal binding loop

L. Daronnat[1*], *L. Berthon*[1], *N. Boubals*[1], *T. Dumas*[1], *P. Moisy*[1], *P. Guilbaud*[1], *D. Moreno Martinez*[1], *S. Sauge-Merle*[2], *D. Lemaire*[2], *C. Berthomieu*[2]

[1]CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France
[2]Aix Marseille Université, CEA, CNRS, BIAM, UMR7265, IPM, 13108 Saint Paul-Lez-Durance, France
[*]E-mail: loic.daronnat@cea.fr

Keywords: plutonium, calmodulin, coordination, reduction, hexanuclear cluster, XAS, UV-Vis spectroscopy

Pu is an actinide of major societal relevance due to its large stock worldwide and its key role in the cleanup challenges of legacy nuclear sites. Although its physiological impact has been widely investigated, understanding its interactions with biological molecules remains limited. The molecular mechanisms of Pu uptake and transportation, and in particular, the direct interaction of Pu with proteins is still unclear. Recent publications have revisited Pu interaction with transferrin1, an iron carrier of blood, and proposed that the transferrin Pu/Fe complex could be involved in its internalization in cells2. Pu interactions with the iron-storage protein ferritin3 were also studied, and high Pu affinity was measured for the liver-derived plasma protein fetuin that binds small clusters of calcium phosphate[4]. Other calcium-binding proteins were also identified as possible Pu targets[5]. As Pu, UO^{2+}, and Fe^{3+}, Ca^{2+} is a hard cation – strong Lewis acid, which forms electrostatic interactions with 7 to 8 ligands. This work aims at investigating the interaction of actinide elements, and more specifically plutonium, with the calcium-binding EF-hand motifs of calmodulin. Calmodulin is expressed in all eukaryotic cells and is involved in a large number of signal transduction pathways. We previously showed that native and engineered calmodulin calcium binding sites present a high affinity for uranyl[6,7]. In this study, we will study the interaction of Pu(IV), the main oxidative state of Pu present *in vivo*, with four variants of the calmodulin calcium binding site 1. The coordination loop containing 12 amino acids was modified at 3 different positions to modulate the charge of the metal binding loop and the number of carboxylate ligands. (see figure 1). The interactions between Pu(IV) and calmodulin variants were characterized using visible and X-ray absorption spectroscopies and showed multiple behaviors: stabilization of 1:1 complexes, or hexanuclear PuO_x clusters, and even plutonium reduction, depending on the nature of amino acids in the metal binding loop. Molecular dynamics simulations were used to rationalize these observations.

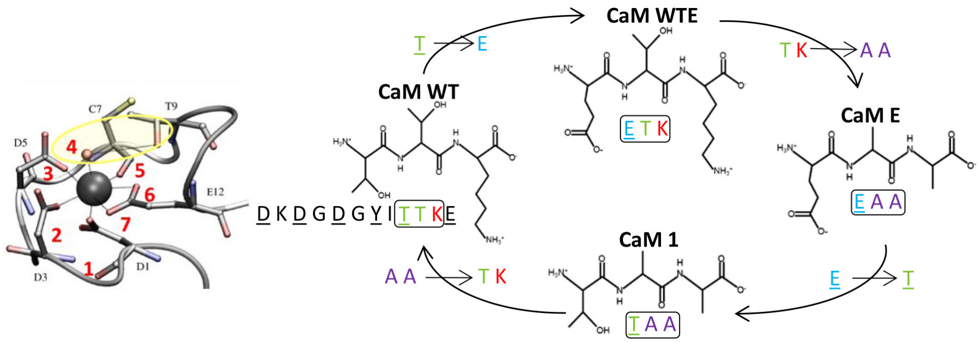

Figure 1. Scheme of the calcium-binding site (left), and sequences of the metal-binding loops (right). D: aspartate, K: lysine, G: glycine, Y: tyrosine, I: isoleucine, T: threonine, E: glutamate, A: alanine.

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126

Gross alpha and beta methodology as a screening measurement for decommissioning activities

Daniel Götz[*], *Radek Posvar, Vlastimil Miler*

UJV Rez, a.s., Hlavni 130, Husinec-Rez, Czech Republic
[*]E-mail: daniel.gotz@ujv.cz

Keywords: gross alpha, gross beta, decommissioning, waste management

Gross alpha and beta activity determination using a gas proportional detector is well established ISO methodology mainly for water quality assessment. However, this method is also effective for planning of sampling during the decommissioning of nuclear facilities and workplaces due to its speed and lower equipment requirements.

Radionuclides typically occurring during radioactive waste disposal can be divided into so-called "easy-to-measure" (ETM) and “difficult-to-measure” (DTM). ETM radionuclides such as Cs-137 or Co-60 emit usually high-energy gamma radiation with sufficient yield and can be easily determined non-destructively outside the package using gamma spectrometry. On the other hand, DTM radionuclides, which include e.g., Pu-238, Pu-239, Sr-90, or C-14 emitting predominantly only alpha, beta, or low-energy gamma radiation, must be determined by complex radiochemical techniques. These destructive methods usually first require time and financially expensive separation techniques, and then the isotopes are determined by alpha-spectrometry, liquid scintillation counting, or mass spectrometry.

The gas proportional counter used for gross alpha and beta activity determination allows to measure liquid (regardless of pH or color) or solid (ground or leached) samples quickly after evaporation or digestion. On the other hand, this method involves bottlenecks including different measurement efficiencies for individual radionuclides, higher detection limits, and crosstalk of alpha to beta region. Therefore, the results must always be interpreted carefully and serve primarily for a screening.

The obtained values of gross alpha and beta can be compared with results from the gamma spectrometry and reveal whether the activity is formed mainly by ETM radionuclides or whether further analyzes of DTM radionuclides also need to be done. Overall, it can thus contribute to significant time and cost reduction during nuclear decommissioning.

274

Characterization of niobium adsorption on clay rocks and granite by nonlinear heterogeneity-based isotherm models

Shih-Chin Tsai[1,2], Chuan-Pin Lee[2], Kuan-Ying Hsieh[3*], Hui-Min Chiu[1]*

[1]Nuclear Science and Technology Development Center, National Tsing Hua University, Hsinchu 30013, Taiwan (R.O.C)
[2]Radioactive Waste Disposal Technology Research and Development Center, National Tsing Hua University, Hsinchu 30013, Taiwan (R.O.C)
[3]Chemistry Division, Institute of Nuclear Energy Research, Atomic Energy Council, Taoyuan City 32546, Taiwan (ROC)
[*]E-mail: bennis6723@gmail.com

Keywords: niobium, granite, nonlinear isotherm, sorption capacity, Langmuir-Freundlich, generalized-Freundlich

The nonlinear heterogeneous adsorption behaviors of niobium (Nb) on clay rocks (bentonite and argillite) and granite in synthetic groundwater and seawater systems were evaluated by adsorption experiments, applying two heterogeneity-based isotherm models: the Langmuir–Freundlich (LF) and generalized-Freundlich (GF) models. According to the root mean square error (RMSE) between the experimental results and numerical simulation, the two heterogeneous sorption models (LF and GF), which correspond to a different heterogenous constant (β), were more adequate than Langmuir models for characterizing the Nb adsorption mechanism. The fitting results demonstrated that the sorption of Nb on granite, bentonite, and argillite exhibited a different adsorption affinity spectrum as a result of the heterogeneous mineral surface. Consequently, the Nb sorption capacity of bentonite and argillite was higher than that of granite and was estimated at 9.24E-01 mmol/g for bentonite, 8.44E-01 mmol/g for argillite, and 2.33E-02 mol/kg for granite.

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240

Status overview of gross activity measurements in water: “keep or replace?”

Viktor Jobbágy

Freelance researcher; European Commission-Joint Research Centre, Geel, Belgium
(until 30 April 2022)
E-mail: viktor.jobbagy@mail.com

Keywords: gross alpha beta activity, radionuclide specific analysis, water, trueness, repeatability

The presentation will give an overview on the gross alpha/beta activity determination in drinking water by introducing its past, current status and possible future applications. The current situation will be concluded from the results of two European wide proficiency tests (PT) organised for the European environmental radioactivity monitoring laboratories by the Joint Research Centre. The performances of many participants/methods from approximately 180 laboratories were not satisfactory. Sample preparation and measurement methods were reviewed focusing on method-dependency of the measurement results. It was an important aspect to confirm if best practices could be identified. It will be also presented how to improve the situation in this field but with the intention to initiate discussions whether the current situation of gross activity measurements in the analytical world is suitable.

Since gross methods are just referred to as screening methods it may suggest that they can just be considered as qualitative analytical technique in a sense that indicating whether an activity concentration threshold is exceeded. Then the whole interpretation of the gross alpha/beta activity analytical results should be revised fundamentally.

As it was identified, the majority of gross-counting methods suffer from trueness and repeatability issues. Furthermore, gross-counting methods without supporting radionuclide specific measurements of water samples can not provide true quantitative analytical results or even qualitative information (except liquid scintillation counting). Radionuclide specific methods have undisputable advantages over gross-activity counting: 1) clear identification of analytes, 2) metrological traceability can be established, 3) calculation of indicative dose from the individually determined radionuclides. Therefore, the inaccurate gross activity measurement methods should be used a complimentary method or replaced by rapid radionuclide specific screening procedures where qualitative and quantitative analytical data can be obtained with turnaround times comparable to the gross-counting methods.

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106

Accelerator Mass Spectrometry as a tool to reveal nuclear sources in the Baltic Sea

Mercedes López-Lora[1*], *Grzegorz Olszewski*[1,2], *Elena Chamizo*[3], *Per Törnquist*[1], *Håkan Pettersson*[1,4], *Mats Eriksson*[1]

[1]Department of Health, Medicine and Caring Sciences (HMV), Linköping University, Linköping, Sweden
[2]Microscopy Inc., Department of Environmental Chemistry and Radiochemistry, University of Gdańsk, Gdańsk, Poland
[3]Centro Nacional de Aceleradores (CNA), Universidad de Sevilla, Sevilla, Spain
[4]Department of Medical Radiation Physics, Linköping University, Linköping, Sweden
[*]E-mail: mercedes.lopez.lora@liu.se

Keywords: Accelerator Mass Spectrometry (AMS), actinides, minor Pu isotopes, Baltic Sea, radioactive liquid discharges, Studsvik Nuclear Facility

The Baltic Sea is a semi-enclosed and shallow sea with an increased accumulation of radioactive materials compared to open oceans due to the impact of multiple local/regional sources: i) fallout coming from Chernobyl accident (1986), ii) liquid releases form Sellafield and La Hague nuclear reprocessing facilities transported through the North Sea, iii) authorized radioactive discharges occurring during the routine operation of nuclear installations in the Baltic Sea region, and iv) possible leakages from the multiples radioactive wastes dumping sites within this marine region [1]. Moreover, all these reginal inputs coexist with the baseline radioactivity levels imposed by the global fallout (GF) from the atmospheric nuclear tests (1945-1980) [2]. Although, the Baltic Sea has been one of the most studied areas regarding the distribution of radioactive radionuclides, long-lived actinides such us ^{236}U, ^{237}Np or Pu isotopes (^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu), have been scarcely investigated and there are still many open questions about their sources in this marine region [3]. Accelerator Mass Spectrometry (AMS) has demonstrated competitive limits of detection for the study of such family of radionuclides in environmental samples [4].

In this context, the radioecology group at Linköping University (LiU, Sweden), in collaboration with the Centro Nacional de Aceleradores (CNA, Spain), is working to investigate unknown inputs to the Baltic Sea. Specifically, this work is focused on the study of the Tvären Bay, directly impacted by the liquid releases from Studsvik Nuclear facility (east coast of Sweden), whose actinide isotopic composition have not been documented. The Pu isotopic distribution was studied in an undisturbed sediment core, including the most minor isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, ^{244}Pu), allowing us to establish the Pu origin in this area and to reconstruct Studsvik aquatic release history [5]. The results show high enriched ^{239}Pu, probably originating from the Swedish nuclear program in the 1960s-1970s and the handling of high burn-up nuclear fuel in later years. The ^{244}Pu/^{239}Pu atomic ratio was used to unravel the GF from the Studsvik's local input. The ^{244}Pu/^{239}Pu atomic ratio for the GF period between 1958-1965 is suggested to be $(7.94 \pm 0.31)\cdot 10^{-5}$. In addition, a higher value of $(1.51 \pm 0.11)\cdot 10^{-4}$ was detected in the bottom of the sediment (i.e. dated to 1953-1957), indicating the possible impact of the first US thermonuclear tests. This work is now being expanded to study other radionuclides (^{233}U, ^{236}U, ^{237}Np). Moreover, seawater samples have been collected in the area to understand the circulation patterns of those radionuclides and their paths into the Baltic Sea.

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140

Monitoring of natural radionuclides and toxic metals contamination in tubers grown in the vicinity of a Nigerian cement factory

Jolayemi Oluwafemi Gbenga[1], *Gabriele Magugliani*[2*], *Eros Mossini*[2], *Marco Giola*[2], *Ibrahim Umar*[3], *Rose Ada Onoja*[4], *Francesco Galluccio*[2], *Andrea Santi*[2], *Elena Macerata*[2], *Mario Mariani*[2]

[1]Nigerian Nuclear Regulatory Authority, Nigeria
[2]Department of Energy - Nuclear Engineering Division, Politecnico di Milano, Milan, Italy
[3]Department of Physics, Nasarawa State University, Keffi, Nigeria
[4]Centre for Energy Research and Training (CERT), A.B.U. Zaria, Nigeria
[*]E-mail: gabriele.magugliani@polimi.it

Keywords: environmental analysis, contamination, natural radionuclides, toxic metals

The natural radionuclides ^{232}Th, ^{235,238}U and ^{40}K with their progenies are uptaken by plants roots along with other minerals and nutrients and accumulate in their edible parts. Upon consumption, *e.g.,* by food ingestion, the accumulated radionuclides contribute to the internal radiation dose to humans. Beside natural origin, some human activities may involuntarily enrich the soil with these radionuclides, for example by using fertilizers or by contamination from nearby mining or industrial operations. In this work, a characterization of soil and crop samples collected in proximity of the Dangote cement plant in Obajana was undertaken, to determine whether the industrial activity may have had a radiological impact on the surrounding area.

Five sampling points were identified in proximity of the cement plant, while two additional locations far from Obajana were selected as a reference. Samples of soil and of three crops (sweet potato, yam, cassava) were collected from each sampling point and from the two control locations.

Soil samples were conditioned according to EPA methods 3051A and 3052 [1,2]. After collection, they were dried at 105 °C overnight and then sifted at 2 mm. Microwave assisted acid digestion was employed to achieve complete sample dissolution. Crop samples were cleaned, processed, and dried at 105 °C to a fine dry residue. Incineration at 600 °C was carried out afterwards, and residual ashes were dissolved in acid. Soil and crop samples were then analyzed via ICP-MS (for ^{232}Th and ^{238}U) and ICP-OES (for K). Other elements - like Ni, Cr, Pb, As, and Cd - were monitored to ascertain whether toxic metal pollution had occurred. Results in terms of concentration were determined with respect to dry masses for both soils and crops.

The average measured concentrations in soil samples collected near the cement plant for ^{232}Th, ^{238}U and K amounted to 11.9 ppm, 1.9 ppm and 2.9% respectively. For corresponding crop samples, an average concentration of 0.1 ppm, 0.03 ppm and 1.2% on dry weight was measured for the three analytes. The measured concentrations have been used to calculate the soil to plant radionuclide transfer according to ICRP publication 114 [4]. No statistically significant increase in concentration was noted between samples collected in proximity of the cement plant with respect to control positions, therefore neither a toxic nor a radiological impact deriving from the industrial activity can be ruled out. As a further confirmation, the measured concentrations of ^{238}U, ^{232}Th and K in the soils sampled around the cement factory are comparable with the world average reported by UNSCEAR [3], that are 30 Bq/kg (7.39 ppm) for ^{232}Th, 35 Bq/kg (2.83 ppm) for ^{238}U and 400 Bq/kg (1.51 ppm) of ^{40}K, equivalent to 1.3% of K. Hence, any radiological health concern is not expected.

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229

Radioactivity in Hungarian drinking waters and mineral waters

Szabolcs Osváth[*]*, Bálint Izsák, Tibor Málnási, Márta Vargha*

National Public Health Center, Budapest, Hungary
[*]E-mail: osvath.szabolcs@osski.hu, osvath.szabolcs@nnk.gov.hu

Keywords: drinking water, mineral water, indicative dose, total alpha activity, uranium, radium

In accordance with the 2013/51/Euratom directive, radioactivity in Hungarian drinking waters (tap waters) has been intensively studied since 2016. Approximately 8000 water samples have been analyzed. Activity concentrations of radon and tritium have been determined and the indicative dose (characterizing the radiation exposure via water consumption) was estimated. Results of the analyses by accredited testing laboratories have been uploaded into the National Drinking Water Quality Database.

Although high quality tap water is available practically everywhere in the country, bottled mineral water is also quite popular (their consumption is ca. 120 L in a year). Therefore radioactivity in different brands of bottled mineral water was also studied – although the directive mentioned above does not apply to natural mineral waters.

In the tested samples, activity concentrations of tritium have been below the detection limit (10 Bq/L).

Activity concentrations of radon have been over the parametric value (100 Bq/L) in very few drinking water samples only.

To estimate the indicative dose, several measurement techniques can be used. As a primary approach, waterworks generally have been chosen measurements of total alpha and total beta activity concentrations. In the tested drinking water samples, total beta activity concentrations have been below the screening level (1 Bq/L). However, in 11.7% of the samples the total alpha activity concentrations have been over the (quite strictly set) screening level (0.1 Bq/L).

In cases of some non-complying water samples, activity concentrations of some individual alpha emitting radionuclides have been determined by nuclide-selective methods. Activity concentrations of U-238, U-234 and Po-210 have been determined by alpha spectrometry after radiochemical separations; while activity concentrations of Ra-226, Ra-228 and Pb-210 have been determined by gamma-spectrometry after evaporating large volume samples. The indicative dose values calculated on the bases of individual activity concentrations of these radionuclides have been below the parametric level (0.1 mSv in a year).

U concentrations of drinking water samples from areas of elevated alpha activity concentration have been measured by ICP-MS. A slight correlation has been found between total alpha activity concentration and U concentration.

Total beta activity concentrations of some mineral waters have slightly exceeded the 1 Bq/L screening level. This can be explained by their high concentrations of K. Total alpha activity concentrations have reached even 1200 mBq/L.

In the analysed mineral waters, activity concentrations of U-238 and U-234 have been below 25 mBq/L and 37 mBq/L, respectively. Therefore their dose consequence is at most

2 μSv in a year. However, the highest activity concentration of Ra-226 that has been measured (430 mBq/L) has a dose consequence of 86 μSv in a year.

However, these data do not explain all the high total alpha activity concentration results. Further investigation (determination of activity concentration of other alpha-emitting radionuclides, such as Po-210) is needed to get a better assumption of dose consequences of consumption of mineral water. But it can be concluded that the consumption of tap water in Hungary does not pose a radiological risk to the consumers' health.

26

Determination of radionuclides in soils in the Czech Republic

Pavel Řezanka[*], *Lenka Filipiaková*

Department of Analytical Chemistry, Faculty of Chemical Engineering, University of Chemistry
and Technology, Prague, Technická 5, 166 28 Praha 6, Czech Republic
[*]E-mail: pavel.rezanka@vscht.cz

Keywords: Czech Republic, environment, radionuclides, soil

The subsoil in the Czech Republic is very rich in radioactive elements, which is also evidenced by the uranium mining that took place there for many decades. There are also radioactive springs whose water contains a significant concentration of radon. Another source of radionuclides can be tailings and ash from thermal power plants. From these sources, radionuclides can then enter the soil. Knowing the content of radionuclides in the soil can thus provide information about the state of the environment.

The subject of this work is the determination of the content of radionuclides in the soil. For this purpose, soil was sampled in several locations in the Czech Republic in order to represent locations with different sources of radionuclides (see above). The soil was taken from three different depths so that the influence of the soil profile on the content of radionuclides could also be monitored.

The measurement was carried out on a semiconductor gamma detector and by measuring the alpha radiation of radon present in the air above the sample, which was stored for one month in a closed container. The amount of radionuclides was determined by adding radionuclide standards (^{137}CsCl and KCl) of known concentration.

Radionuclides of all three natural decay series and surprisingly also ^{137}Cs were detected in the soil samples. The results indicate that the amount of radionuclides decreases with the depth of soil sampling.

45

Speciation and characterization of Ra(II) in the human digestive system and synthesis of potential complexing agents

A. Shamoun[*], *L. Holtmann, B. Riebe, C. Walther*

Institute for Radioecology and Radiation Protection, Leibniz Universität Hannover, Germany
[*]E-mail: shamoun@irs.uni-hannover.de

Radionuclides ingested with food may accumulate in the human body and pose a potential health risk. To remove these radionuclides, decorporation agents are used. One of these radionuclides is the naturally occuring radium, which may be present in drinking water and in certain foods in larger quantities up to ca. 10 Bq kg^{-1} [1]. Daily consumption of only a few Brazil nuts, which can have activity concentrations of > 200 Bq kg^{-1} caused by radium [2], may lead to an additional committed dose in the mSv range, while consumption of drinking water high in uranium progenies, such as the Disi Aquifer in Jordan, can lead to even higher doses [3]. For risk assessment, precise knowledge of the radionuclides biokinetics is needed. This is also important for development and application of decontamination procedures after accidental incorporation of very high radium quantities. In this project, artificial biofluids produced according to the UBM protocol (BARGE) are used to investigate the interaction of radium in the alimentary tract of humans. In preliminary experiments, the non-radioactive homologue barium is used to determine compounds being formed in these biofluids. The speciation of radium in biofluids, i.e. in the digestive system, are determined by ESI-MS and gamma-spectroscopy. Subsequently, the decorporation agent is added, and the Ra-containing complexes are analyzed again with ESI-MS, and additionally with NMR and IR. The influence of complexation agents on Ra(II) speciation under physiological conditions is investigated. Potential decorporation strategies will be tested in further work. The experimental determination of the speciation of Ra(II) is corroborated by thermodynamic modelling using appropriate tools (e.g.PHREECC).

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5

Preliminary studies of naturally occurring radionuclides (NORM) in fertilizers produced in Poland

Grzegorz Szaciłowski[*], *Marta Konop, Małgorzata Dymecka, Grażyna Kaczyńska, Jakub Ośko*

Radiation Protection Measurements Laboratory, National Centre for Nuclear Research, 7 A.
Soltana Str, 05-400 Otwock – Świerk, Poland
[*]E-mail: grzegorz.szacilowski@ncbj.gov.pl

Keywords: fertilizers, natural radioactivity, radium equivalent, gamma spectrometry

Agriculture is one of the most important branch of food production. The constant growth of human population increasing demand for food, rapid urbanization leading to shrinking of agricultural lands and shortages of manpower imply strong pressure on farmers to increase yields of crops per unit area of land. Those problems are solved mainly by increasing land productivity by fertilization. The ongoing public debate about balance between bonuses and disadvantages of fertilizers has been even more ignited as more and more studies show, that selected types of fertilizers may introduce additional radioactivity to global food chain. The naturally occurring radioactive elements (NORM) are materials found in the environment that contain radioactive elements of natural origin. Due to industrial processing of those materials natural radioactivity can be enhanced, posing potential risk to the public and the environment.

The aim of this study was to perform preliminary assessment of the concentration of gamma-emitting radionuclides in selected fertilizers suspected to contain NORM. In order to compare the results radium equivalent activity (Ra_{eq}) has been calculated. Upon the recommended dosage of fertilizers the theoretical annual dose increment has been assessed.

Two groups of fertilizers have been selected for this study, namely designed for industrial and home use. Industrially used fertilizers were obtained directly from the farmers, as they come in large quantities. The ones intended for home gardens were obtained from several local markets and hardware shops. All studied fertilizers were produced by Polish chemical industry. In total 13 fertilizers were tested among which 6 were intended in particular for home gardens, 6 for industrial use and one was of universal use. For the analysis high purity germanium (HPGe) detector and the geometry of Marinelli vessels were used. All samples were packed into vessels, airtightly closed and stored for at least 21 days prior to measurement. The results showed concentrations reaching up to 13.8 ± 1.4 kBq kg^{-1}, 2.12 ± 0.37 kBq kg^{-1}, and 34.5 ± 4.4 Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th respectively. In several samples quantitative concentrations of ^{235}U were also present, reaching concentration of 69.3 ± 7.4 Bq kg^{-1}. The calculated radium activity equivalent was between <5.6 and 2155 Bq kg^{-1}.

19

Environmental radioactivity in bulk deposition samples (rainwater and dust) from Northern Algeria: Radiological monitoring and radionuclides behavior

D. Taieb Errahmani[1*], *A. Noureddine*[3], *M. Boulahdid*[2], *A. Hammadi*[1], *M. Maache*[1]

[1]Radioecology and Environmental Monitoring Department, Nuclear Research Center of Algiers (CRNA) .02 Bd. Frantz Fanon, Box.399, Algiers, Algeria
[2]National Higher School of Marine Sciences and Littoral Managment (ENSSMAL), BP 19, Campus universitaire de Dely Brahim, Bois des Cars, 16320, Alger, Algeria
[3]Retired
[*]E-mail: d.taieberrahmani@crna.dz

Keywords: bulk deposition, Gamma spectrometry, radionuclides, complementary techniques

Bulk deposition samples were collected on monthly basis using 1 m^2 collector from the roof of the CRNA's building at a 162 m of altitude during the period ranging from june 2014 to june 2018.

Regarding wet deposition, dusts particles were separated from the rainwater. They were dried at 70 °C in an oven, frozen and homogenized before analysis.

For rainwater samples, ten (10) liters were concentrated by evaporation in order to determine the natural radioactivity level while more than 80 liters were concentrated by coprecipitation with Ammonium Molybdophosphate (AMP) in order to determine the ^{137}Cs level.

All Samples were analyzed by direct counting making use of HPGe gamma spectrometry.

The hydrochemical composition of rainwater was measured by ionic chromatography using Dionex –DX120. Major and trace elements in some dust samples were measured by the XRF technique.

Similar studies were conducted in Spain (Lozano et al.,2011; Dueñas et al.,2011).

The results found clearly showed the absence of ^{137}Cs in rainwater and the presence of ^{137}Cs in some dust samples. The mean activity concentration of ^{210}Pb, ^{7}Be, and ^{137}Cs were found 2.80 Bq.g^{-1}, 18.81 Bq.g^{-1} and 0.013 Bq.g^{-1}, respectively.

Monthly depositional fluxes of ^{210}Pb, ^{7}Be, and ^{137}Cs were found to be in the range of (0.25-69.22 Bq.m^{-2}.month^{-1}, 3.06-487.45 Bq.m^{-2}.month^{-1} and 0.016-0.68 Bq.m^{-2}.month^{-1}, respectively.

Correlations between specific activity concentrations and some meteorological parameters were examined.

Results of complementary techniques (XRF and ionic chromatography) help one to understand the behavior of the surveyed radionuclides in the atmosphere for the sake of radiological monitoring purposes.

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Radiolabeled compounds and radiopharmaceuticals

79

Investigating several reaction factors and methodologies for the radiosynthesis of N-succinimidyl 4-[^{18}F]fluorobenzoate ([^{18}F]SFB)

Mohammed Al-Qahtani

Cycloron and Radiopharmaceuticals Department, King Faisal Specialist Hospital and Research Centre, Riyadh, Saudi Arabia
*E-mail: mo1500@hotmail.com

Keywords: [^{18}F]SFB, reaction factors, methodologies

The interest in labeling development methods for organic and biological molecules with positron-emitting radionuclides is becoming highly demandable as a wide range of uses of Positron Emission Tomography (PET) imaging applications are increasing dramatically. For example, peptides labeled with positron-emitting radionuclides are of outstanding interest for radiotracers development that allows imaging of cellular functions in vivo. Small radiopharmaceutical molecules are labeled with fluorine-18, by displacement of a leaving group with [^{18}F]fluoride, using well-established radiochemical reactions. However, this strategy is not viable for radiolabeling larger biologically sensitive species such as proteins. In such cases, fluorine-18 is typically introduced by reacting the bioactive molecule with a pre-formed, [^{18}F]-labeled, bifunctional prosthetic group. Numerous prosthetic groups were developed for such applications and to date, N-succinimidyl 4-[^{18}F]fluorobenzoate (S[^{18}F]FB) remains one of the most widely used due to its in vivo stability.

S[^{18}F]FB can react with primary amines of biomolecules; it demonstrates a suitable and versatile ^{18}F-prosthetic group to radiolabel peptides, proteins, and antibodies in terms of in vivo stability and radiolabeling yield. The reaction of S[^{18}F]FB with four biologically relevant resin-bound peptides was studied and optimized. For comparison, each peptide was ^{18}F-fluorobenzoylated in solution under different conditions, and the product distribution was analyzed, confirming the advantages of the solid-phase approach. Moreover, the method's feasibility for a selective radiolabeling process, was investigated for both the N-terminus and the lysine side chain. Labeling on solid phase with S[^{18}F]FB resulted in crude ^{18}F-fluorobenzoyl peptides whose radiochemical purities were typically greater than 90%. The drawback of fluorine-18 labeling with biomolecules (antibodies, proteins and peptides) (S[^{18}F]FB) involved a long synthesis time applying the manual methodology. However, several studies reported modifications to the manual procedure of the S[^{18}F]FB radiosynthesis, and semi-to-full automated approaches were investigated using different synthesizer modules.

A fully optimized and configured reaction factors were investigated, and a built program was designed for the synthesis and has been modified several times to end by a smooth automated synthesis program consisting of multiple steps that run in ~38 min. Good to Comparable radiochemical yields (~ 40 % ± 7%, n = 10) to both reported and manual procedures are achieved with shorter time and higher radiochemical purity (> 98%).

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134

Preparation of radiolabeled sulfamoyl fluorides by SuFEx $^{18}F/^{19}F$ isotopic exchange and assessment of their *in vivo* stability

Jan Bertram[1*], *Heike Endepols*[1,2], *Bernd Neumaier*[1,2,3], *Boris Zlatopolskiy*[1,2,3]

[1]Forschungszentrum Jülich GmbH, Institute of Neuroscience and Medicine, Nuclear Chemistry (INM-5), Wilhelm-Johnen-Straße, 52425, Jülich, Germany
[2]University of Cologne, Faculty of Medicine and Cologne University Hospital, Institute of Radiochemistry and Experimental Molecular Imaging, Kerpener Straße 62, 50937, Cologne, Germany
[3]Max Planck Institute for Metabolism Research, Gleueler Straße 50, 50931, Cologne, Germany
[*]E-mail: j.bertram@fz-juelich.de

Keywords: fluorine-18, SuFEx click chemistry, isotopic exchange, amino acid tracer

Objectives: Aryl fluorosulfates (FO_2S-O-) and disubstituted sulfamoyl fluorides (FO_2S-N-) often possess high hydrolytic stability and are widely used in chemical biology and drug design. Recently we reported a protocol for convenient preparation of radiolabeled aryl fluorosulfates with high molar activity via fast $^{18}F/^{19}F$ isotopic exchange.[1] The aim of the present work was to study the suitability of this procedure for radiofluorination of sulfamoyl fluorides. To this end, the procedure was applied to *N*-sulfamoylated indole and carbazole as well as to three protected amino acids (Boc-Trp(SO_2F)-OMe **1**, Boc-His(SO_2F)-OMe **2** and Boc-2,3-DH-Trp(SO_2F)-OMe **3**). Additionally, the *in vivo* stability of the radiolabeled tryptophan derivative Boc-Trp([^{18}F]SO_2F)-OMe (**[**18**F]1**) was evaluated.

Methods: Aqueous [^{18}F]fluoride was loaded onto an anion exchange QMA cartridge and eluted with Et_4NOH (10 µmol) in MeOH (1 mL). MeOH was evaporated, a solution of the corresponding substrate (31-125 nmol) in MeCN (500 µL) was added and the reaction mixture was stirred for 7 min at 40 °C. Thereafter, H_2O (1 mL) was added and radiochemical conversions (RCCs) were determined by radio-HPLC. **[**18**F]1** was isolated by solid phase extraction using a StrataX C18 cartridge. The tracer was formulated in Tween® 20 (200 µL) and 1 mm sodium phosphate buffer (2 µL; pH 7.2) and subjected to a preclinical evaluation in healthy mice using µPET.

Results: Radiolabeled *N*–sulfamoyl fluorides of carbazole and indole were prepared in RCCs of 72±2% and 86±2%, respectively. FO_2SN-functionalized protected tryptophan **1** (RCC: 68±5%), histidine **2** (RCC: 3±1%) and 2,3-DH-tryptophan **3** (RCC: 34%; 60°C, 14 min), were also successfully radiofluorinated. Boc-Trp([^{18}F]SO_2F)-OMe **[**18**F]1** was isolated in activity yields of 24±2% with a radiochemical purity of 99% (n = 3) within 70 min using 12.5 µg (31 nmol) of precursor. In µPET experiments, the radiolabeled product showed very low radioactivity accumulation in bones, indicating a lack of significant *in vivo* defluorination. The study also demonstrated almost exclusive hepatobiliary elimination of the tracer, presumably owing to its very high lipophilicity.

Conclusions: The SuFEx protocol developed for radiolabeling of fluorosulfates was successfully applied for the simple and fast preparation of ^{18}F-labeled sulfamoyl fluorides. High metabolic stability of Boc-Trp(SO$_2$[^{18}F]F)-OMe underlines the suitability of this class of radiolabeled compounds as PET-probes for *in vivo* imaging.

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27

Radiolabeling of micelles for combined chemo- and radionuclide therapy

Antonia G. Denkova, Huanhuan Liu, Elizabeth Carroll, Robin Nadar, Rienk Eelkema

Delft University of Technology, The Netherlands
[*]E-mail: a.g.denkova@tudelft.nl

Keywords: polymeric micelles, radiolabeling chemo-radionuclide therapy, tumour spheroid, cell viability

Combining therapies such as radiation therapy and chemotherapy often provides much better outcome for patients, provided side effects can be minimized. Here, we investigated the opportunity to combine chemotherapy with radionuclide therapy using polymeric micelles. The micelles were composed of the biodegradable polymer poly(ε-caprolactone-b-ethylene oxide) (PCL-PEO) micelles and loaded with the chemotherapeutic drug paclitaxel (PTX). Simultaneously, we radiolabelled the micelles with ^{177}Lu(III) using a novel and simple radiolabeling method, which only requires adding the radionuclide to the micelles. Radiolabeling efficiency above 90 % could be achieved, allowing further evaluation in vitro. The co-loaded micelles performance was investigated by first determining their distribution in 3D tumor spheroids composed of glioblastoma cells (U87). Light-Sheet Fluorescence Microscopy and confocal microscopy were used to determine the diffusion of the micelles, showing that they penetrated deep into the spheroid within 24 hours. Evaluation of the cell killing efficiency of the single (PTX or 177Lu(III)) versus combined treatment (PTX + 177Lu(III)) was carried out by determining the growth of the spheroids as well as by a cell-viability assay. The results showed that the combined therapy achieved much better therapeutic effect leading to much more pronounced cell growth inhibition and higher cell killing efficiency compared to the single treatments.

135

Novel mediators for highly efficient radiolabeling of aryl boronates and stannanes

Chris Hoffmann[1,2], *Niklas Kolks*[1,2], *Benedikt Gröner*[1,2], *Elizaveta A. Urusova*[1,2],
Heike Endepols[1,2,3], *Felix Neumaier*[1,2], *Bernd Neumaier*[1,2*], *Boris D. Zlatopolskiy*[1,2]

[1]University of Cologne, Faculty of Medicine and University Hospital Cologne,
Institute of Radiochemistry and Experimental Molecular Imaging, Kerpener Straße 62,
50937 Cologne, Germany
[2]Forschungszentrum Jülich GmbH, Institute of Neuroscience and Medicine,
Nuclear Chemistry (INM-5), Wilhelm-Johnen-Straße, 52428 Jülich, Germany
[3]University of Cologne, Faculty of Medicine and University Hospital Cologne,
Department of Nuclear Medicine, Kerpener Straße 62, 50937 Cologne, Germany
[*]E-mail: b.neumaier@fz-juelich.de

Keywords: alcohol-enhanced, automation, Cu-mediated, PET-tracer, radiofluorination

Objectives: Cu-mediated radiofluorination is a versatile tool for the preparation of radiofluorinated (hetero)aromatics from readily accessible precursors like (het)aryl boronates [-B(OH)$_2$, -Bpin] and trialkylstannanes (-SnR$_3$). However, large amounts of precursor and Cu mediator are often needed to achieve high radiochemical conversions (RCC), which can complicate purification of radiolabeled products. In this work, we prepared a series of copper(II) complexes and evaluated their suitability as radiolabeling mediators. In addition, we performed one-parameter optimizations of the reaction conditions (solvent, temperature and time), and confirmed the practical applicability of the modified protocol by production of several PET tracers.

Methods: Cu(II)-complexes were prepared by reaction of Cu(X)$_2$ (OTf, ClO$_4$, ClO$_3$, Cl, Br, OAc, SO$_4$) (1 eq.) and different *N*-heterocyclic ligands (6 eq.) in hot $_i$PrOH or MeOH. For radiosyntheses, [^{18}F]fluoride ([^{18}F]F$^-$) was loaded onto a QMA-CO$_3$ cartridge and eluted with Et$_4$NOTf (1 mg) in *n*BuOH (400 µL) directly into a solution of the respective boronate precursor (≤10 µmol) and Cu-complex (10 µmol) in DMA, PC, or DMI (800 µL). For stannyl substrates, [^{18}F]F$^-$ elution was performed with Et$_4$NOTf (1 mg) in MeOH (500 µL) followed by removal of MeOH and addition of a solution of the respective stannyl precursor (≤10 µmol) and Cu-complex (10 µmol) in the respective solvent. The reaction mixtures were heated at 110 °C for 10 min and radiochemical conversions (RCCs) were determined by radio-HPLC. 4-Ph- and 4-Ac-Ph-X [X= B(OH)$_2$, Bpin, Bneo, and SnMe$_3$] were used as model substrates. Results of the screening experiments were statistically evaluated using GraphPad Prism software. For further optimization, reactions were performed at different temperatures (60–150 °C) and reaction times (1–40 min). The optimized conditions were used for manual or automated (AllinOne, Trasis) synthesis of seven known PET tracers (precursor amount: ≤10 µmol).

Results: From a total of 36 prepared Cu-complexes, especially Cu(4-PhPy)$_4$(ClO$_4$)$_2$ and Cu(3,4-Me$_2$Py)$_4$(OTf)$_2$ in *n*BuOH/DMI or DMI provided considerably higher RCCs than

conventional $Cu(Py)_4(OTf)_2$ [≥57% for Ar-$B(OH)_2$/BPin/Bneo; ≥47% for Ar-$SnMe_3$; previous protocols: 2–30%]. Furthermore, for radiolabeling experiments with $Cu(4\text{-}PhPy)_4(ClO_4)_2$, high and reproducible RCCs of up to 84% were obtained over a broad range of temperatures (80–130 °C) and reaction times (5–20 min). At reaction temperatures < 80 °C, a longer reaction time of 40 min enabled radiolabeling of 4-Ph-Ph-$B(OH)_2$ in RCCs of 69–80%. The optimized protocol was successfully applied for preparation of the PET tracers [^{18}F]R91150, [^{18}F]ALX5407 and (*S*)- and (*R*)-3-[^{18}F]FPhes in activity yields (AYs) of 23–41% (Lit.: 10–17%). Production of (*S*)-3-[^{18}F]FPhe and 6-[^{18}F]FDOPA using precursor amounts as low as 2.5 µmol resulted in RCCs of up to 75% and AYs of 23–30%. (*S*)-3-[^{18}F]FPhe was prepared in an automated synthesis module from 2.5 µmol precursor afforded the desired PET-probe in AYs of 18±3%.

Conclusions: Our screening study led to discovery of several novel mediators for Cu-mediated radiofluorination, which enabled highly efficient ^{18}F-labeling of different boronate and stannyl substrates, especially when performed in *n*BuOH/DMI or DMI. The practicality of the method was demonstrated by preparation of several radiotracers, including 6-[^{18}F]FDOPA, in improved radiochemical yields and/or using significantly lower precursor loadings.

Acknowledgments:

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139

Application of quaternary 1,4-diazabicyclo[2.2.2]octane (DABCO) salts for S_N2 “minimalist” radiofluorination

Yannick Keuthen[1,2*], *Boris D. Zlatopolskiy*[1,2], *Bernd Neumaier*[1,2]

[1]University of Cologne, Faculty of Medicine and University Hospital Cologne,
Institute of Radiochemistry and Experimental Molecular Imaging
[2]Forschungszentrum Jülich GmbH, Institute of Neuroscience and Medicine,
Nuclear Chemistry (INM-5), Wilhelm-Johnen-Straße, 52428 Jülich, Germany
*E-mail: Yannick.keuthen@uk-koeln.de

Keywords: ^{18}F, minimalist, inductive heating, piperazine

Objectives: The piperazine scaffold is a privileged structural motif present in many therapeutic drugs and several PET-tracers. The aim of this work was to evaluate quaternary 1,4-diazabicyclo[2.2.2]octane (DABCO) salts as potential precursors for preparation of probes containing an *N*-(2-[^{18}F]fluoroethyl)piperazyl fragment by the “minimalist” approach, which enables radiofluorination of onium salts using [^{18}F]fluoride without external bases, other additives or azeotropic drying[1].

Methods: Quaternary DABCO salts were prepared by direct alkylation, (het)arylation, benzoylation or tosylation of DABCO, followed by anion metathesis if necessary. For radiofluorination, [^{18}F]fluoride was eluted from an anion exchange resin with a solution of the corresponding DABCO salt in MeOH and the MeOH was evaporated at 60 °C for 8 min under reduced pressure in a stream of argon. The residue was taken up into a suitable solvent, heated for a given time in a Monowave 50 synthesis reactor, and the radiochemical yields (RCYs) were determined by HPLC. Radiolabeling conditions were optimized with respect to reaction time, temperature, solvent and DABCO salt counter ion. Radiolabeled compounds prepared from alkyl-substituted DABCO salts were isolated by solid phase extraction (SPE). Following SPE isolation, *N*-(2-[^{18}F]fluoroethyl)-*N*'-pentynyl-piperazine ([^{18}F]**1**) was coupled with benzyl azide (**2**) using a Cu-catalyzed “click” cycloaddition to prepare a ^{18}F-fluorinated model triazole ([^{18}F]**3**).

Results: Radiofluorination of quaternary alkyl DABCO salts under “minimalist” conditions furnished the corresponding *N*-alkyl-*N*'-(2-[^{18}F]fluoroethyl) piperazines as ring opening products in RCYs of 48–93% and, after isolation by SPE, activity yields of up to 31%. Reaction of [^{18}F]**1** with **2** afforded [^{18}F]**3** in quantitative RCYs. (Het)arylation, benzoylation and tosylation of DABCO afforded the respective *N*'-substituted piperazyl-*N*-ethyl DABCO salts (addition products of two DABCO molecules) in up to 90% yields as single isolable products. ^{18}F-Fluorination of these substrates mainly proceeded via Sn2 substitution of the DABCO group, leading to formation of the corresponding *N*-substituted *N*'-(2-[^{18}F]fluoroethyl)piperazines in RCYs of 28–46%.

Conclusions: Quaternary DABCO salts are efficient precursors for the rapid preparation of probes containing an *N*-(2-[^{18}F]fluoroethyl)piperazine motif by the “minimalist” protocol.

Acknowledgments

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259

^{18}F-labeled S(VI)-F-based probes for positron emission tomography (PET): Promises and pitfalls

Bernd Neumaier[1,2,3]

[1]Forschungszentrum Jülich GmbH, Institute of Neuroscience and Medicine, Nuclear Chemistry (INM-5), Wilhelm-Johnen-Straße, 52425, Jülich, Germany
[2]University of Cologne, Faculty of Medicine and Cologne University Hospital, Institute of Radiochemistry and Experimental Molecular Imaging, Kerpener Straße 62, 50937, Cologne, Germany
[3]Max Planck Institute for Metabolism Research, Gleueler Straße 50, 50931, Cologne, Germany
E-mail: b.neumaier@fz-juelich.de

Keywords: fluorine-18, SuFEx click chemistry, isotopic exchange, PET-imaging

In the era of personalized precision medicine, positron emission tomography (PET) and hybrid techniques like PET/CT and PET/MRI have become indispensable tools for clinical diagnostics. A more widespread adoption of these imaging modalities in clinical practice critically depends on the availability of established and emerging PET-tracers, which in turn requires the development of simple, reliable, and efficient radiolabeling approaches.

Certain non-carbon atoms like B, Al, Sc, Si or S can rapidly form strong bonds with fluorine, which has been exploited for the preparation of ^{18}F-labeled PET-tracers. B-^{18}F, Si-^{18}F and Al-^{18}F-based tracers have all been the subject of numerous preclinical studies and some of them, which demonstrated high metabolic stability and favorable pharmacokinetics, have already been translated into the clinic. In contrast, compounds containing an ^{18}F-label attached to S(VI) remain underexplored, even though they represent a promising class of rapidly accessible candidate probes.

The aim of this lecture is to summarize existing methods for the preparation of S-^{18}F-containing radiotracers, to give an overview of preclinical studies with these tracers and to discuss their suitability for clinical applications.

224

Mitsunobu mediated access to ^{18}F-labeled 1,2,4,5-tetrazines and other structurally diverse derivatives

Veronika Rosecker[1,2], *Martin Pressler*[1,2], *Tori Demuth*[1,3], *Martin Wilkovitsch*[1],
Christoph Denk[1,3], *Hannes Mikula*[1]

[1]Institute of Applied Synthetic Chemistry, TU Wien, 1060 Vienna, Austria
[2]Institute of Atomic and Subatomic Physics, TU Wien, 1020 Vienna, Austria
[3]Center for Labelling and Isotope Production, TRIGA Center Atominstitut, TU Wien, 1020 Vienna, Austria
*E-mail: martin.pressler@tuwien.ac.at

Keywords: bioorthogonal chemistry, click chemistry, mitsunobu reaction, PET, fluorine-18, radiofluorination

As bioorthogonal chemistry has become indispensable in nuclear medicine, new radiolabeling strategies for bioorthogonal building blocks gained significant importance. Especially the inverse electron demand Diels–Alder reaction (IEDDA) with its outstanding kinetics is most appropriate for *in vivo* pretargeting applications. Therefore, interest in effective radiolabeling of 1,2,4,5tetrazines and *trans*-cyclooctenes is increasing. Additionally, the stability of the tetrazine itself and a stable linkage between host molecule and tag is essential for most applications. In this work we describe a Mitsunobu reaction-based one-pot method for ^{18}F-labeling a 1,2,4,5-tetrazine group forming a stable ether linkage. This versatile method uses an easily accessible tetrazine building block (**1**) which can be linked to a variety of OH-bearing substrates. To the best of our knowledge, modification of 1,2,4,5 tetrazines as well as ^{18}F-labeling using a Mitsunobu based approach has not been reported so far.

Tetrazine **1** was synthesized in our group and showed promising ligation kinetics and stability in biological media.[1] Due to the high acidity of the phenolic OH group O alkylation via SN reactions with various alkylating agents (R-X) was not feasible. Utilizing the high acidity, we used Tetrazine **1** as substrate for Mitsunobu based reactions. The fast one-pot reaction involving triphenylphospine and a diazocompound takes place under mild conditions and is well suited for ^{18}F-labeling. Moreover, this reaction tolerates different functional groups and allows simple tuning of lipophilicity by choosing an adequate alcohol precursor. Furthermore, the ether linkage created is more stable than frequently used amides, which is advantageous for many biomedical applications. Tuning of lipophilicity can easily be achieved by varying the linker (e.g. the PEG chain length). To demonstrate our ^{18}F labeling approach we choose water soluble PEG4, which was sequentially protected and tosylated prior to radiolabeling (see Figure 1). Radiosynthesis of the ^{18}F alcohol was straightforward and yielded the ^{18}F-synthon in excellent yields. Subsequent Mitsunobu reaction gave the ^{18}F labeled tetrazine within 20 min in 80% RCY.

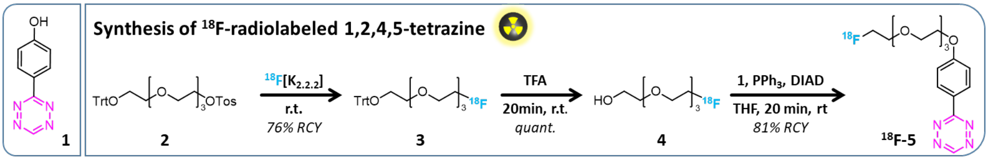

Figure 1. Tetrazine 1 and the ^{18}F-labeling strategy[3] to achieve ^{18}F-PEG4-tetrazine in high RCY.

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Radionuclide separation

199

Investigation of the applicability of baker's yeast to the uranium liquid waste treatment process

Yoichi Arai[1*], *Kenta Hasegawa*[1], *Sou Watanabe*[1], *Masayuki Watanebe*[1], *Haruaki Mastuura*[2], *Naoto Hagura*[2], *Yasuhiro Konishi*[3]

[1]Japan Atomic Energy Agency, Muramatsu, Tokai-mura, Naka-gun, Ibaraki, Japan
[2]Tokyo City University, Tamazutsumi, Setagaya-ku, Tokyo, Japan
[3]Osaka Metropolitan University,Gakuen-cho, Naka-ku, Sakai-shi, Osaka, Japan
[*]E-mail: arai.yoichi@jaea.go.jp

Keywords: baker’s yeast, STRAD project, U recovery, radioactive liquid waste

Radioactive aqueous and organic liquid wastes contaminated by U are generated by solvent extraction of nuclear fuel materials in experiments of reprocessing technologies. Although incineration and denitrification/conversion processes are promising for treating such liquid waste, the installation of large equipment is essential. Radioactive liquid waste containing the nuclear fuel materials and chemical reagents is stored in the nuclear facilities. To give appropriate treatment procedures for radioactive liquid waste generated in nuclear facilities, STRAD (Systematic Treatments of RAdioactive liquid wastes for Decommissioning) project was started by Japan Atomic Energy Agency (JAEA) with several organizations [1]. Treatment of liquid wastes generated from the reprocessing experiments is one of important tasks of this project, and the recovery technologies of nuclear materials from the spent solvent has been developed [2, 3]. However, recovery of trace amounts of nuclear fuel material from aqueous solutions with wide pH range is still a challenging task.

We are focusing on baker's yeasts for their excellent metal ions adsorption characteristics, easy handling and low prices. In a previous study, baker's yeast showed excellent adsorption performance of Mo(VI), Zr(IV), and Pd(II) from nitric acid solutions [4]. Moreover, affinity of the baker’s yeasts to anions was also suggested. Since chemical form of U in nitric acid solution depends on acidity, and U is possilbe to take anion form under alkaline environment. The baker’s yeast has a potential for treatment both of acidic and alkaline solutions. In order to optimize adsorption performance and operation procedures as the liquid waste treatment technology, adsorption performance of U has to be precisely investigated. In this study, adsorption performance of U and anion from nitric acid solution was investigated by batch-wise adsorption experiments.

The dry baker's yeast (Oriental yeast co., ltd.) was put into nitric acid solution containing U(VI) and Tc(VII), and shaken at 298 K or 308 K for 30 to 180 min. The baker’s yeast was separated from the solution by centrifugation. The collected supernatant liquid was measured by ICP-AES or gamma spectrometer. Baker’s yeast showed the adsorption performance of about 10% of U in 2M HNO_3, while Tc could not be adsorbed in the weak to strong acid region at pH 4 to 1 and 2M HNO_3. In our previous study, Mo was confirmed to be adsorbed as a metal ion ($[MoO_2]^{2+}$), and it is speculated that U is also adsorbed to baker's yeast by the same mechanism. On the other hand, Tc is known to exist stably as an anion (TcO_4^-). The adsorption behaviour of Tc is different from that of U, which exists as UO_2^{2+} in nitric acid solution. Currently, investigation of structural analysis of baker's yeast and recovery of baker's yeast dispersed in solution with a gelling agent underway.

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117

Development of recyclable decontamination medium for decommissioning

Kateřina Čubová, Mojmír Němec, Tereza Šobová, Barbora Drtinová

Department of Nuclear Chemistry, Czech Technical University in Prague, Prague, Czech Republic
*E-mail: katerina.cubova@fjfi.cvut.cz

Keywords: decommissioning, decontamination, corrosion layer

Decommissioning of nuclear facilities has become one of the most topical issues. The experience from decommissioning of some nuclear power plants has shown that different operating chemistry and/or different composition of the construction materials play a very important role and can cause unexpected problems. It is well known that the key process for metal decontamination is dissolving of the surface corrosion layer and removing radionuclides released. Technology based on application of a low-temperature decontamination medium was developed and tested. The experiments aim at dissolving the most resistant chemical present in corrosion layers, chromium (III) oxide containing compounds, using redox chemistry. Further tests applied found redox systems on stainless steels and corrosion layers of the primary circuits present at VVER type NPPs.

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65

Single-atom gas chromatographic adsorption studies of short-lived lead and bismuth atoms on SiO_2 surfaces supported by advanced Monte Carlo simulations

Dominik Dietzel[1,2*], *Alexander Yakushev*[2], *Christoph E. Düllmann*[1,2,3], *Jörg Krier*[2], *Jadambaa Khuyagbaatar*[2], *Egon Jäger*[2]

[1]Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany
[2]GSI Helmholtzzentrum für Schwerionenforschung GmbH, 64291 Darmstadt, Germany
[3]Helmholtz-Institut Mainz, 55099 Mainz, Germany
[*]E-mail: dietzel@uni-mainz.de

Keywords: radionuclide separation, gas chromatography, adsorption, Monte Carlo simulation

In preparation of gas phase chemical experiments with element 115, we studied the chemical behavior of single short-lived ^{211}Bi atoms in rare gases (helium and argon) and in oxygen atmosphere. For that purpose, we performed off-line isothermal gas chromatography experiments at room temperature. The short-lived volatile ^{219}Rn precursor, provided from an ^{227}Ac-source, was transported into the miniCOMPACT setup (mini **C**ryo-**O**nline **M**ulti detector for **P**hysics **a**nd **C**hemistry of **T**ransactinides), using different carrier gases. The alpha-detectors making up the inner surface of the chromatography column within the miniCOMPACT allowed measuring internal chromatograms as a function of carrier gas type and gas flow rate, thus characterizing the miniCOMPACT detector array. All measured species deposited on the SiO_2 surface of the miniCOMPACT via diffusion-controlled deposition. The chromatograms were modeled by Monte Carlo simulations, which account for the precursor effect of beta-decaying ^{211}Pb that decays to the detected alpha-decaying ^{211}Bi, and compared them to experimental results to determine a lower limit of the adsorption enthalpy of bismuth on silicon dioxide. These studies aid to optimize the conditions for future experiments with superheavy elements.

59

Development of a chemical separation strategy for Pu, Am and Cm from rare-earth rich geological archives

Sebastian Fichter[1*], *Dominik Koll*[1,2], *Anton Wallner*[1,2]

[1]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany
[2]Nuclear Physics and Accelerator Applications, Research School of Physics, Australian National University, Canberra, Australia
[*]E-mail: s.fichter@hzdr.de

Keywords: actinide separation chemistry, nuclear astrophysics, accelerator mass spectrometry

The understanding of the formation of the elements has been an intriguing topic within the last decades. It is now approved that the heaviest naturally occurring elements on earth, the actinides, are produced in the astrophysical *r*-process. However, the exact site of this process is still debated. Recently, the amount of interstellar ^{244}Pu ($T_{1/2}$ = 81.3 Myr) in various geological archives like deep-sea ferromanganese crusts and sediments has been investigated by applying highly sensitive accelerator mass spectrometry measurements (AMS).[1,2] Correlation of the influx of ^{244}Pu with ^{60}Fe ($T_{1/2}$ = 2.6 Myr) which is produced by the weak s-process in massive stars and ejected into the interstellar medium by supernovae could point to a possible origin of the *r*-process in the universe. To further prove this hypothesis, recent investigations focus on the determination of other long-lived radionuclides which are also produced in the *r*-process, e.g. ^{247}Cm ($T_{1/2}$ = 15.6 Myr) and ^{182}Hf ($T_{1/2}$ = 8.9 Myr). However, the separation of the expected ultra-trace amounts of these nuclides (a few 100 atoms per gram) from huge amounts of matrix and interfering elements represents a major analytical challenge. Thus, this contribution aims to probe existing chemical treatment strategies for the determination of minute amounts of actinides and Hf from various geological archives. The separation method is based on anion exchange for Pu separation and extraction chromatography for Cm and Hf, respectively.[3] The yield of the different elements is monitored by a combination of AMS, γ-counting and ICP-MS measurements. The effective separation strategy of different actinides and Hf from major matrix elements allow for processing multi-gram amounts of different geological samples. This is a prerequisite for the detection of live interstellar ^{247}Cm and ^{182}Hf in geological archives. Furthermore, this adapted method can be used for the analysis of environmental samples regarding their content and isotopic ratio of anthropogenically produced Pu, Am and Cm which holds potential for nuclear safeguards and nuclear forensics studies.

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209

First approach of a scintillating imprinted polymer for the fast and simple determination of ^{55}Fe

Isaac Giménez[1*], Héctor Bagán[1], Alex Tarancón[1,2,3]

[1]Department d'Enginyeria Química i Química Analítica, Universitat de Barcelona, Marti i Franqués, 1-11, ES-08028, Barcelona, Spain
[2]Serra-Húnter Programme, Generalitat de Catalunya, Barcelona, Spain
[3]Institut de Recerca de l'Aigua, Universitat de Barcelona. Montalegre, 6, ES-08001, Barcelona, Spain
[*]E-mail: Isaacgimenez@ub.edu

Keywords: iron-55, imprinted polymer, scintillation, low energy beta-emitting radionuclide

Over the following years, several nuclear power plants will reach the end of their operational life. That means that a huge amount of analyses will need to be performed in order to ensure an adequate classification of the wastes, during the decommissioning process, and therefore the protection of the workers, environment and the whole population. One radionuclide of major concern is Fe-55. It is a fission product formed as result of the neutron activation of the stable iron and its activity could be very high in certain samples (i.e. spent resin). The two main techniques used for its analysis are x-ray spectrometry and liquid scintillation. For the x-ray spectrometry even though the pre-treatment step might be simpler, the detection efficiency is near to zero and the detection limit is too high. For liquid scintillation, the most used, the determination is long, tedious, and complex, as several steps as co-precipitation and separation are carried out to remove interferences. Moreover, detection efficiency is found to be around a 15% because of the low energy of the beta particles emitted and the presence of colour quenching due iron species. For that reason, the current methods could be improved in order to satisfy better the requirements needed in terms of analysis time and reliability of the results.

One possible solution to improve Fe-55 analysis may be found on an already existing material and procedure for the analysis of stable iron isotopes such as the iron ion imprinting polymers (Fe-IIP). Fe-IIP consist on a rigid matrix of a monomer, (i.e. styrene or methyl acrylic acid), a crosslinker (i.e. divinylbenzene or EDGMA) and a polymerizable complexing agent molecule that is coordinated with a template in order to leave a specific cavity for the element to be analysed, iron in this case. Fe-IIP present a high selectivity for Fe and therefore would allow the specific retention of iron with practically no previous sample treatment. Therefore, in this challenging work, it is presented a first approach based on a newly scintillating Fe ion imprinted polymer (SC-Fe-IIP) for the analysis of ^{55}Fe. The SC-Fe-IIP combines both characteristics: selective separation of Fe-55 based on its cavity and scintillation measurement thanks to the scintillating compounds trapped on the polymer structure (Figure 1). To achieve that, a balance between the rigidity provided by the crosslinked and the scintillating capacities of the monomer are needed. The different SC-Fe-IIP prepared presented an iron specific capacity from 10-25 mg Fe^{+3}/g of Sc-Fe-IIP and a detection efficiency for ^{14}C and for ^{55}Fe between 20-60% and >1% respectively. Those properties make possible the analysis of Fe-55 though this strategy.

Figures

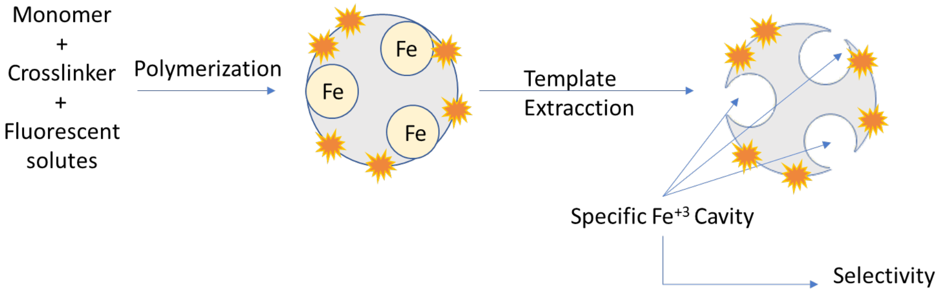


Figure 1 Fe-IIP scheme

204

Uranium-plutonium separation from irradiated nuclear fuel *via* ion exchange prior to MC-ICPMS isotopic analysis

Timothy Gregory[*], *Daniel Stubbs, and Simon Woodbury*

National Nuclear Laboratory Ltd., Central Laboratory, Sellafield, UK
[*]E-mail: timothy.gregory@uknnl.com

Keywords: uranium, plutonium, actinide, separation, ion exchange, isotopic analysis, MC-ICPMS

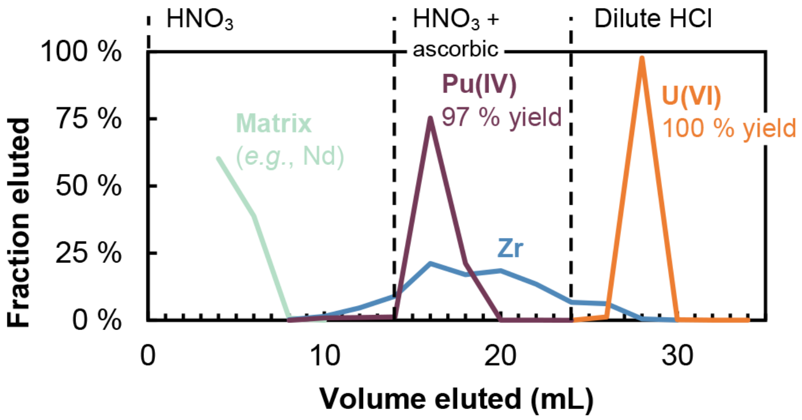
Accurately measuring uranium and plutonium isotopic ratios is important for post-irradiation fuel analysis. One of the best analytical techniques to make these measurements is multi-collection inductively coupled plasma mass spectrometry (MC-ICPMS), owing to its high-precision and high sample throughput. When twinned with isotope dilution, MC-ICPMS also allows absolute masses for each isotope to be quantified.

Before uranium and plutonium are measured *via* MC-ICPMS, they must be quantitatively separated from matrix elements and each other. This eliminates (1) isobaric interferences (*e.g.*, $^{238}U^+$ and $^{238}Pu^+$; $^{241}Am^+$ and $^{241}Pu^+$), (2) plasma matrix effects, and (3) isotopic fractionation, all of which can introduce measurement inaccuracy. Traditionally, uranium and plutonium have been separated *via* ion exchange [1] or liquid-liquid extraction [2]. Ion exchange offers numerous advantages, namely that it produces less waste and does not generally use flammable reagents. With this in mind, we are designing a separation procedure with the following criteria: isobaric interferences eliminated such that they do not measurably perturb our isotopic measurements; matrix elements must not exceed the concentration of uranium or plutonium by a factor of more than ~ 100; and quantitative (> 99 %) yields for uranium and plutonium.

Since its discovery in 1940 [3], plutonium has been found to exist in seven oxidation states (0, +2, +3, +4, +5, +6, and +8; [4]), at least four of which (+3 to +6) can exist in solution simultaneously. This complicates its ion exchange behaviour. Perfect sample-spike equilibration requires all the plutonium in a sample-spike mixture to exist in a single oxidation state at some point prior to separation. Therefore, the oxidation state of plutonium must be carefully conditioned prior to ion exchange.

Using UTEVA and TEVA resin, we experimented with separating uranium and plutonium from simulated irradiated fuel using several pre-column redox and column elution procedures. For redox conditioning we used: hydroxylamine hydrochloride and ascorbic acid as reductants; and nitric acid, sodium nitrite, hydrogen peroxide, and *aqua regia* as oxidants. For the elution procedure, we experimented with nitric acid, ascorbic acid, hydrofluoric acid, and hydrochloric acid eluents.

So far, we have had success achieving quantitative yields for uranium with various elution procedures. We also achieved high yields (> 97 %) of plutonium using a nitric acid + ascorbic acid elution procedure but faced difficulties in separating zirconium. Work is ongoing to streamline the pre-column redox and to recover plutonium without zirconium contamination. When complete, this separation procedure will form the basis for our new uranium and plutonium isotopics capability.



An example of a U-Pu elution profile using UTEVA resin.

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215

Separation and characterization of ^{229}Th from historical ^{228}Th sources of Union Minière

<u>Stephan Heinitz</u>[1], Dominic Maertens[1], Jasper Mermans[1], T. Cardinaels[2]*

[1]Target Radiochemistry Group, NURA, Belgian Nuclear Research Centre, Mol, Belgium
[2]Radiochemistry Group, NMS, Belgian Nuclear Research Centre, Mol, Belgium
*E-mail: stephan.heinitz@sckcen.be

Keywords: Union Minière, separation, ^{226}Ra, ^{227}Ac, ^{229}Th, radon

Between 1969 and 1974, Union Minière, the world biggest producer of radium at that time, has engaged with SCK CEN in a large scale commercial production of ^{227}Ac by neutron irradiation of ^{226}RaCO$_3$ targets in the BR2 reactor at Mol, Belgium. This project aimed to produce, isolate and integrate 20 grams of ^{227}Ac into a radioisotope thermoelectric generator (RTG) to be used for space applications [1]. More than 300 g of ^{226}Ra were made available for 43 cyclic irradiation and separation campaigns, resulting in historic legacy material of ^{226}Ra, ^{227}Ac and ^{228}Th still partly present at SCK CEN in the 21st century. While ^{227}Ac from that project enabled the birth of Xofigo, the historic capsules of Union Minière once containing ^{228}Th were identified and analysed in 2015 using the ISOCS calibrated gamma spectrometry technique [2]. It revealed that these legacy sources still contain significant quantities of ^{229}Th, an isotope of interest for targeted alpha therapy (TAT) as generator for ^{225}Ac and ^{213}Bi. However, substantial quantities of ^{227}Ac and ^{226}Ra also present in these capsules require handling in a glove box or a hot cell due to the emanation of radon (^{219}Rn and ^{222}Rn) and the considerable dose rate.

In this work, we describe the chemical extraction and purification of ^{229}Th from these historical sources of Union Minière that occurred in 2016 and 2022. A description is given of the special tools and procedures developed to achieve this task and the challenges associated with processing 50 year old legacy sources of alpha-emitters with a complex decay chain. It is shown that extraction chromatographic resins such as TEVA and DGA are suitable agents to purify ^{227}Ac and ^{229}Th from a complex matrix of corrosion and decay products that accumulated in the capsules. We were successful in extracting 6.3 and 10 MBq of ^{229}Th from capsules B and C reported in [2] which are currently used as in-house ^{225}Ac (and ^{213}Bi) generators for radiopharmaceutical research [3]. Characterization of the isotopic composition of the purified Th fraction using ICP-MS revealed that the obtained product constitutes 95% of ^{229}Th and 4% of ^{230}Th for capsule B. Additionally, emanation techniques have been employed in order to quantify the residual quantity of ^{228}Th that persisted since 1973 using measurements of the ^{220}Rn volumetric activity concentration above the ^{229}Th source. It is shown that the result correlates well with the activity of 300 GBq ^{228}Th reported at that time for capsule B.

This contribution aims to share the experience in processing legacy material of Union Minière and to show past expertise and new developments at SCK CEN in handling radon-emanating alpha emitters in a hot-cell environment that are required for large quantities of ^{226}Ra, ^{227}Ac and ^{228}Th .

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98

Towards cyclotron independence – ^{44}Ti/^{44}Sc radiochemical generator development

Jan Klouda, Natalie T. Rice, J. Connor Gilhula, Ida D. Piedmonte, Stosh A. Kozimor, Michael E. Fassbender, Veronika Mocko[*]

Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM, USA
[*]E-mail: vmocko@lanl.gov
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Keywords: inorganic substrate, radiochemical generator, scandium-44, titanium-44, ZR resin

Positron emitting ^{44}Sc is a radioisotope with exciting properties for innovative approaches to medical imaging using positron emission tomography (PET). The versatility of ^{44}Sc is apparent when combined with β^- emitting ^{47}Sc, making up a viable theranostic couple. A half-life of 3.97 h renders ^{44}Sc suitable for following processes with slower kinetics compared to more established ^{68}Ga with a half-life of 67.71 min. Although relatively long lived amongst diagnostic radioisotopes, the ^{44}Sc half-life still limits its availability to the general vicinity of production sites equipped with particle accelerators. This limitation can be overcome by constructing a radiochemical generator using its parent radioisotope – ^{44}Ti with a half-life of 59.1 years. In a column generator setting, the ^{44}Ti is retained on a solid support that allows for high-yield recovery of the continuously ingrowing ^{44}Sc daughter. This contribution evaluates the feasibility of two solid supports for generator development purposes: organic ZR resin and a novel inorganic substrate.

Commercially available ZR resin possesses a hydroxamate functional group that strongly binds Ti^{4+} while allowing Sc^{3+} to pass effortlessly over a wide $HCl_{(aq)}$ concentration range. Herein, performance of two 81 µCi (3 MBq) generators based on ZR resin over the period of approximately one year is evaluated. Their performance is on par with generators described in the literature within the one-year time frame. Nevertheless, due to the long half-life of the parent, a ^{44}Ti/^{44}Sc generator may function for years and even decades. On this time scale, with medically relevant millicurie activities, radiolysis of the organic substrate might compromise its long-term stability. To develop a generator with enhanced stability, an approach using a novel inorganic solid substrate was tested. Proof-of-concept experiments show that the inorganic substrate is well suited for generator development using dilute $HCl_{(aq)}$. Moreover, X-ray absorption fine structure experiments were conducted to characterize Ti speciation under $HCl_{(aq)}$ concentrations relevant to generator development. Binding modes of Ti on both solid supports used in this study were also investigated using the same technique.

Both generator concepts described in this contribution show favorable properties for eluting ^{44}Sc with stable yields in a matrix compatible with radioconjugation efforts, $HCl_{(aq)}$. Constructing a well-functioning and reliable ^{44}Ti/^{44}Sc radiochemical generator has positive implications for PET imaging facilities. It will provide a steady supply of ^{44}Sc without the need to purchase and maintain a cyclotron. Therefore, it has the potential to lower the cost of the imaging procedure and make it more accessible to patients around the world.

Acknowledgments
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15

Studies of selenium and arsenic with a variety of extraction chromatography resins in HCl and HNO_3 media

Kelly N. Kmak[*], *John D. Despotopulos, Nicholas D. Scielzo*

Lawrence Livermore National Laboratory, Nuclear and Chemical Sciences Division, Livermore, CA, USA
[*]E-mail: kmak1@llnl.gov

Keywords: isotope production, arsenic, selenium, isotope generators

There is considerable interest in the production of radioactive arsenic isotopes for medical, biological, nuclear security, and environmental applications. There are numerous methods to produce radioarsenic isotopes for these studies including reactor, charged-particle, and heavy-ion irradiations. Furthermore, there are plans to harvest ^{72,73}Se and ^{77}As at the recently commissioned Facility for Rare Ion Beams (FRIB) for use in biochemistry, medical, astrophysics, and nuclear security experiments. All of these production routes require chemical separations to purify radioarsenic from the target material and any co-produced radioisotopes. Arsenic/selenium separations are particularly important as isotope generators based on the parent-daughter pair ^{72}Se/^{72}As have the potential to provide a convenient, portable source of radioarsenic. As many isotope-production and isotope-harvesting methods are under investigation to produce radioarsenic isotopes, fully characterized arsenic/selenium separations under a variety of chemical conditions are important for further development in this field.

The uptake behaviour of arsenic and selenium on a variety of extraction chromatography resins was studied from HCl and HNO_3 media. Batch uptake, kinetics, and column studies were performed with ^{75}Se and ^{73}As on commercially available resins as well as resins fabricated in-house. All the commercially available resins (TEVA resin, TRU resin, DGA resin, Pb resin, and CL resin) studied had uptake of selenium at high HCl concentrations and there was uptake of ^{75}Se on CL resin at all concentrations studied (~0.6 M to 11 M). Based on blank studies with XAD-7 resin, a significant amount of the ^{75}Se extraction from HCl can be attributed to backbone extraction, rather than extraction via the extractant molecules on the resin. From HNO_3 media, CL resin had weak uptake of selenium over a wide concentration range (0.1 to 4 M), while the other resins had no uptake. There was no significant uptake of ^{73}As on any of the resins in either acid media. Column studies were performed to demonstrate separations of ^{75}Se and ^{73}As on these resins with high yields and high radiopurity for ^{73}As. Selenium does not readily elute from these resins.

Based on these results, further resins were made in-house to optimize these separations with the goal of developing rapid, high yield separations. In particular, trioctylamine (TOA) and dimethyl sulfide (DMS) resins had high uptake (D_w >1000) of selenium from HCl solutions and no arsenic uptake at any concentration. TOA resin behaves similarly to TEVA resin, with ^{75}Se extraction at high HCl concentrations (≥10 M); in column studies, arsenic has no affinity for the resin and is immediately eluted with high yields and high radiopurity while selenium is difficult to elute once retained. Unlike the other resins, DMS resin has a peak extraction at lower HCl concentrations (6 M) and further studies are being conducted to assess whether other simple sulphur compounds may be suitable for separations of arsenic and selenium in more mild conditions than what is possible on the other resins studied.

With TOA, TEVA and TRU resins, multi-day column studies were conducted to assess if these resins may have the potential for use in isotope generator systems, and it was demonstrated that ^{75}Se can be retained on these resins with repeated elutions for time periods >18 days.

Acknowledgments

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110

Sequential determination of ^{79}Se, ^{151}Sm and ^{147}Pm in samples coming from nuclear activities

Inés Llopart-Babot[1,2*], *Mirela Vasile*[1], *Andrew Dobney*[1], *Sven Boden*[1], *Michel Bruggeman*[1], *Martine Leermakers*[2], *Jixin Qiao*[3], *Steffen Happel*[4], *Lesley Adriaensen*[1]

[1]SCK CEN, Boeretang 200, 2400 Mol, Belgium
[2]VUB, AMGC, Pleinlaan 2, 1050 Brussels, Belgium
[3]Department of Environmental and Resource Engineering, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark
[4]TrisKem International SAS, 3 Rue des Champs Géons ZAC de L'Éperon, Brittany, Bruz, 35170, France
[*]E-mail: ines.llopart@sckcen.be

Keywords: ^{79}Se, ^{151}Sm, ^{147}Pm, liquid scintillation counting, CIEMAT NIST, DTM

^{79}Se, ^{151}Sm and ^{147}Pm are fission products that are difficult to measure (DTM) and critical radionuclides that need to be determined due to their long half-lives, in samples originating from nuclear activities. Selenium's high mobility in the environment and its complex chemistry, driven by the different oxidation states in which selenium can be present, highlights the need for ^{79}Se quantification in samples from radioactive waste disposal (Frechou et al., 2007; Herrero Latorre et al., 2013). ^{79}Se has been analysed previously by using liquid scintillation counting (LSC) (Frechou et al., 2007; Jörg et al., 2010) and the challenge of Q-ICP-MS analysis for ^{79}Se has been described as ^{79}Br is an isobaric interference (Aguerre and Frechou, 2006). The lanthanides ^{151}Sm and ^{147}Pm might also be present together with ^{79}Se in decommissioning nuclear waste samples (Ashton, 2000; Martin, 1998; Miranda et al., 2018). Their chemical separation is hampered by the similarity in chemical properties with other lanthanides (europium, gadolinium or neodymium) (Ashton, 2000; Evans et al., 1984; Miranda et al., 2018). Warwick et al. 2022 recently reported an analytical method to successfully separate Sm and Pm from each other (Warwick et al., 2022). ^{151}Sm and ^{147}Pm can be measured also by LSC technique due to their beta-particle emissions (Sumiya et al., 1993). A challenge is evaluating the chemical recovery of promethium during separation due to the lack of a stable promethium carrier or the high cost of using a Pm radioisotope tracer (*e.g.* ^{148m}Pm) (Adriaensen et al., 2007; Yoshida et al., 1995).

In this work, we report the optimization of a sequential radiochemical separation procedure to determine ^{79}Se, ^{147}Pm and ^{151}Sm. A comparison of 2 resins, namely, Ln and DGA resins, for complete lanthanide separation is discussed together with the separation of the selenium fraction performed with a new Se resin (under development by Triskem). LSC is used to measure the activity of ^{147}Pm, ^{151}Sm and ^{79}Se in each fraction relying on ICP-MS for chemical recovery evaluation. Quench curves are used for the efficiency calibration of ^{147}Pm and ^{151}Sm, while CIEMAT-NIST software is applied for ^{79}Se calibration.

Acknowledgments
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70

Radioanalytical method for the separation of trace plutonium and neptunium from uranium

Zsuzsanna Macsik[1*], *Stephen P. LaMont*[1], *Joel R. Maassen*[1], *Will S. Fisher*[1], *Lisa A. Hudston*[1], *Matthew E. Sanborn*[1], *Kimberly A. Hinrichs*[1], *Jeremy D. Inglis*[1], *Ivis F. Chaple*[2], *Michael E. Fassbender*[2], *Robert E. Steiner*[1]

[1]Nuclear and Radiochemistry Group, Los Alamos National Laboratory, Los Alamos, USA
[2]Inorganic, Isotope, and Actinide Chemistry, Group, Los Alamos National Laboratory, Los Alamos, USA
[*]E-mail: macsik@lanl.gov

Keywords: neptunium, plutonium, uranium, ion exchange, alpha spectrometry, TIMS

A radioanalytical method was developed for the determination of trace plutonium and neptunium in samples composed primarily of uranium. The procedure uses a neodymium oxalate co-precipitation and a two-column separation on BioRad™ AG® 1-X4 anion exchange resin to achieve high uranium decontamination, quality plutonium and neptunium separation factors and low impurity levels. The separation of the three actinides from each other relies on their oxidation-reduction chemistry. Various measurement techniques can be applied to determine plutonium and neptunium in the purified fractions: i.e., alpha spectrometry, thermal ionization mass spectrometry and multi-collector inductively coupled plasma mass spectrometry.

During the method development, several anion exchange resins were tested. The behaviour of neptunium was studied and compared to the behaviour of uranium and plutonium at each stage of the separation process. The optimized method was applied to various analyses, such as a nuclear forensic examination of a highly enriched uranium material, characterization of irradiated highly enriched uranium, and plutonium analysis of highly radioactive samples.

20

Determination of ^{226}Ra in urine and water samples and sequential separation of ^{228}Ra and ^{90}Sr in drinking water

Dolores Arginelli[1], Paolo Battisti[2], Maria Chiara Botta[1], Sandro Ridone[1], Salvatore Zicari[3]*

[1]Integrated Laboratory of Radioactivity Measurement and Monitoring, Radiation Protection Institute of ENEA, Saluggia, Italy
[2]Integrated Laboratory of Radioactivity Measurement and Monitoring, Radiation Protection Institute of ENEA, Bologna, Italy
[3]Integrated Laboratory of Radioactivity Measurement and Monitoring, Radiation Protection Institute of ENEA, Rotondella, Italy
[*]E-mail: sandro.ridone@enea.it

Keywords: radium, strontium, liquid scintillation counting, urine, drinking water

Among natural radionuclides ^{226}Ra and ^{228}Ra are important for high radio-toxicity and widespread diffusion. Once absorbed to blood from gastrointestinal tract or lungs, they follow the general behavior of calcium with a substantial deposition and retention in bone and soft tissues. Radium intake can contribute considerably to radiological dose affecting human health, for its direct effect and for the local production of short-living daughters with high specific activity. According to Council Directive 2013/51/EURATOM the derived concentrations for the Indicative Dose of 0.1 mSv/y for ^{226}Ra and ^{228}Ra in water for human consumption are respectively 0.5 and 0.2 Bq/L. In order to develop a reliable and sensitive method of analysis, liquid scintillation counting (LSC) offers a good solution for their measurement in environmental (water) and biological (urine) matrices. While the determination of ^{226}Ra in water is quite simple and little time consuming, ^{226}Ra determination in urine requires a suitable radiochemical separation, in order to isolate it from interferents, till dissolution and transfer in a vial. The addition of a scintillation cocktail immiscible to water lets ^{222}Rn drift from the aqueous solution to the organic phase. The measurement of ^{222}Rn, ^{218}Po and ^{214}Po, in secular equilibrium with their mother allows to determine the activity of ^{226}Ra. Sometimes it might be necessary to evaluate the activity of both natural and anthropogenic radionuclides in the same matrix.

By the use of chromatography we investigated the possibility to optimize a sequential radioanalytical method for the determination of ^{228}Ra and ^{90}Sr in drinking water, as they are chemically similar, both belonging to Alkaline Earth group. Starting from secular equilibrium condition the daughters ^{228}Ac and ^{90}Y have been separated from possible interferents and isolated in the same vial. Thanks to their suitable β emission, their decay has been followed by Cherenkov effect and, through a three parameter fitting curve, it was possible to distinguish the contribution of each radionuclide to the total count, in order to determine the parent activity.

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78

Ion chromatographic separation of ^{45}Ti for routine production of PET-Tracers

Jonas Strecker[1*], *Tobias Wachten*[1], *Ingo Spahn*[1], *Bernd Neumaier*[1,2]

[1]Forschungszentrum Jülich GmbH, Institute of Neuroscience and Medicine, Nuclear Chemistry (INM-5), 52425 Jülich, Germany
[2]University of Cologne, Faculty of Medicine and University Hospital Cologne, Institute of Radiochemistry and Experimental Molecular Imaging, 50937 Cologne, Germany
[*]E-mail: j.strecker@fz-juelich.de

Keywords: titanium-45, ion-chromatography, PET

Introduction: ^{45}Ti ($T_{1/2}$ = 3.1 h, $E_{\beta^+_{max}}$ = 1.04 MeV) is a promising PET radionuclide that can be produced by proton bombardment of natural Sc targets. However, more widespread application of ^{45}Ti for PET imaging has been hampered by the hydrolytic instability of Ti(IV) in aqueous medium, which complicates recovery from the irradiated Sc target.[1] While various separation methods like cation exchange chromatography with citrate as eluent[2], liquid-liquid extraction[3] or thermochromatography[4] have been described, their applicability for routine tracer production is still limited. Since clinical application of ^{45}Ti requires a fast and simple approach that can be adapted to GMP-compliant routine production processes, we have focused on optimizing the cation exchange chromatography method based on Zr hydroxamate resin and evaluated ^{45}Ti recovery with different eluents.

Materials and Method: 45Ti was produced via the ^{45}Sc(p,n)^{45}Ti nuclear reaction using 16.5 MeV protons. Separation from the target material was performed by ion-chromatography using columns packed with 135±10 mg Zr hydroxamate resin (Triskem, France). To this end, the target material was dissolved in 10 m HCl (10 mL) and 1 mL fractions of the resulting solution were loaded onto the ion-exchange columns. Each column was then washed with 10 m HCl (5 mL) and H_2O (5 mL) before elution studies were conducted with the following eluents (2.5 mL): 0.1 m oxalate, 0.1 m citrate, 0.1 m tartrate, 0.65 m hydrogen peroxide, 30% acetonitrile in phosphate buffer (pH=8) and pure acetonitrile. Following elution, 1 mg of the complexing agent trans-1,2-diaminocyclohexane-N,N,N‘,N‘-tetraacetic acid (CDTA) was added to the ^{45}Ti containing solutions, the mixtures were stirred at room temperature for 45 min, and the radiochemical conversions (RCCs) to [^{45}Ti]Ti(CDTA) were determined by radio-TLC while the radionuclide purity was determined by γ-ray spectroscopy.

Results: The best combination of ^{45}Ti recovery and RCC was obtained with 0.1 m oxalate, with a decay corrected ^{45}Ti recovery of 69±2% (n=4). The subsequent radiolabeling of CDTA resulted in a RCC of 73±3% (n=3) with only 0.1% of ^{44}Sc impurity. The whole separation process could be completed within 20 min, suggesting that it is well suited for routine production of ^{45}Ti-labeled PET tracers for clinical application.

Conclusion: The optimized separation method enables recovery of ^{45}Ti in yields suitable for research and clinical use.

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216

Hafnium separation for high-precision isotopic abundance analysis

Daniel Stubbs[*], *Timothy Gregory, and Simon Woodbury*

National Nuclear Laboratory Ltd., Central Laboratory, Sellafield, UK
[*]E-mail: daniel.stubbs@uknnl.com

Keywords: hafnium, isotope composition, ion exchange chromatography, mass spectrometry

Hafnium has long been of interest to the nuclear industry owing to several of its key chemical and physical characteristics. It has several non-radioactive isotopes, all of which have relatively large neutron capture cross sections and transmute to higher mass hafnium isotopes with neutron irradiation. Combined with its high corrosion resistance, this ability to absorb neutrons over prolonged operational timescales places it as an ideal candidate as a neutron absorber.

An essential part of post irradiation examination is measurement of the atomic abundances of individual hafnium isotopes [*e.g.*, 1, 2, 3]. This can be achieved *via* multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS), a technique which discriminates between isotopes according to their mass-to-charge ratio. Given that during irradiation some hafnium isotopes transmute to other elements with the same mass as key hafnium isotopes (*e.g.*, ^{177}Lu *vs*. ^{177}Hf), chemical separation of hafnium from interfering elements is an essential prerequisite for analysis. Moreover, any impurities in the starting material require separation if accurate isotopic abundances are to be determined.

There are many published procedures that detail separation of hafnium for MC-ICPMS analysis [*e.g.*, 4, 5]. However, an important consideration for our method is the exposure time for operators given the significant dose associated with the metastable ^{178m2}Hf isomer (31-year half-life).

We designed a two-stage ion exchange chromatography procedure for hafnium separation, where in both procedures the hafnium is immediately eluted during sample loading with no interaction with the resin. First, we used published distribution coefficient data for DGA-N resin [6] to create a column for separation of hafnium from lutetium, ytterbium, and tantalum. Given that hafnium metal readily dissolves in nitric – hydrofluoric acid mixtures, we designed this procedure such that the sample is loaded in 3 M HNO_3 – 0.2 M HF, eliminating the need for a matrix conversion following digestion. In this reagent, ytterbium and lutetium adsorb strongly to the resin, and only minor quantities of tantalum bleed through with hafnium. Tungsten elutes alongside hafnium during loading. Next, the sample is loaded onto TRU resin in 6 M HCl – 0.02 M HF [7]; hafnium immediately elutes, whereas tungsten and the residual tantalum are retained.

In both columns the hafnium eluted during loading can be collected and immediately loaded back onto the column if further purification is required. Using this technique, decontamination factors of hafnium from ytterbium, lutetium, tantalum, and tungsten of 10^6 can readily be achieved, with > 99 % hafnium recovery. In these proportions, residual matrix in the measurement solutions does not perturb hafnium isotopic compositions outside the level of analytical uncertainty.

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28

Mixtures of active pharmaceuticals for studying behavior of medical radioisotopes

Evgeny E. Tereshatov[1*], *Charles M. Folden III*[1,2], *Sherry J. Yennello*[1,2]

[1]Cyclotron Institute, Texas A&M University, College Station, TX 77843, USA
[2]Department of Chemistry, Texas A&M University, College Station, TX 77843, USA
[*]E-mail: etereshatov@tamu.edu

Keywords: medical radioisotopes, active pharmaceuticals, separation, purification

A majority of active pharmaceuticals are solid at room temperature compounds with a limited solubility in water. However, their mixtures can form hydrophobic liquids with reasonable viscosities [1]. Such mixtures open an opportunity to study behavior of some medical radioisotopes, which are either widely used in nuclear medicine or undergoing preclinical studies. This approach allows for minimizing application of toxic and flammable compounds for isolation and purification of valued analytes. For example, we have studied ^{111}In extraction by means of binary and ternary mixtures of active pharmaceutical and food grade ingredients. In some cases the distribution ratio values were at a level of 100. Another medical radioisotope we have been working with is ^{211}At, which is one of the most promising α-emitting radionuclides for Targeted Alpha Therapy. This isotope is barely commercially available worldwide. However, we can produce it routinely at Texas A&M University via ^{209}Bi(α, 2n)^{211}At reaction at ~29 MeV beam energy to study its fundamental properties. Absence of any stable isotopes of astatine and relatively short ~7.2 h half-life require fast and efficient separation procedure performed at cyclotron facilities. Our group successfully developed one stage solid-liquid extraction method to isolate astatine from bismuth after the metallic target dissolution in nitric acid. Moreover, this process has been automated to minimize doze to personnel [2]. Astatine interaction with binary mixtures containing active pharmaceuticals was also investigated.

Acknowledgments
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268

Effect of different external metals of hexacyanoferrate on cesium removal

Junhua Xu

Nuclear Chemistry & Separation and Purification Technology Laboratory, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, Fujian Province, China
*E-mail: junhua.xu@fjirsm.ac.cn

The nuclear industry generates radioactive waste which cause a threat to the environment and human beings. In 2011, nuclear accidents at the Fukushima released large number of radioactive wastewaters into the environment. These radioactive radionuclides mainly contain ^{134}Cs, ^{137}Cs, ^{60}Co, ^{90}Sr and so on. Among these, ^{137}Cs is the most dangerous nuclide because of its high fission yield (6.09%), intense gamma radiation and relatively long half-life (30 years) [1-3]. Meanwhile, cesium has high solubility and will participate in the process of metabolism after entering the human body, which will pose a threat to human life [4], so radioactive wastewater must be strictly treated and discharged.

This study aims to investigate different external metal hexacyanoferrates [5], such as Co, Ni, and Cu towards Cs removal. The synthesized metal hexacyanoferrates adsorbents were prepared by conventional co-precipitation method. And the synthesized materials were systematically characterized by X-ray diffraction, Fourier transform-infrared spectrometry, thermogravimetry, scanning electron microscopy and X-ray photoelectron spectroscopy. This study investigated Cs adsorption behavior by the pH adsorption experiment, isotherm studies, kinetic studies, coexistence ions influence and NaOH potentiometric titration. We demonstrated that Cu-Fe PBA possessed the highest K_d value at ~pH 3 and the $7< \text{pH} <11$was proved to be the stable range for synthesized Co-Fe PBA, Ni-Fe PBA and Cu-Fe PBA. Cu-Fe PBA and Ni-Fe PBA were determined as the more selective adsorbents in coexisting ions. Finally, the mechanism was proposed by sodium hydroxide titration, X-ray photoelectron spectroscopy and ICP-AES characterizations. We proposed the mechanism that K in the interstitial sites and hydroxide group in vacancies as well as external metal within PBA contributed to the Cs adsorption. However, a clearer picture of the Cs adsorption mechanism needs more experimental and modelling work in the future study.

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269

Chemical behavior and concentration analysis of volatile iodine formed by gamma-ray irradiation

Jei-Won Yeon[*], *Minsik Kim*

Nuclear Chemistry Technology Division, Korea Atomic Energy Research Institute, Daejeon, Republic of Korea
[*]E-mail: yeonysy@kaeri.re.kr

Keywords: chemical behavior, concentration analysis, volatile iodine, gamma irradiation

The volatilization of iodine is affected by various environmental factors such as temperature, iodine concentration, solution pH, and redox condition as well as gamma irradiation dose. In our study, the chemical behaviour of iodine and iodine concentration analysis were investigated. Iodine volatilization was affected by the gamma dose, but the effect of the irradiation dose rate was relatively small. As the solution temperature increased, the reaction rate of gamma oxidation ($I^- + \cdot OH \rightarrow 1/2I_2$) decreased, but the evaporation rate from the liquid phase into the gas phase increased. As the solution pH increased, the reducing power of H_2O_2 activated from pH 6 and the disproportionation reaction of I_2 started from pH 10 affected the iodine volatility. The concentration of volatile iodine (I_2 or I_3^-) formed by gamma oxidation was determined by two different methods. One was measured by a UV-VIS (ultraviolet-visible) spectrophotometer without any chemical separation, and the other was extracted with toluene and measured by a UV-VIS spectrophotometer. Both analysis methods showed high accuracy compared to the total iodine concentration value determined by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer).

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Poster Presentations

Actinide analytical chemistry

22

The influence of water and carbon dioxide content in solvents on molecular-plating produced terbium thin films

Ernst Artes[1,2,3*], *Primiana Cavallo*[1], *Christoph E. Düllmann*[1,2,3], *Carl-Christian Meyer*[1,2], *Dennis Renisch*[1,2], *Evgenia Schaffner*[1]

[1]Department of Chemistry - TRIGA Site, Johannes Gutenberg University, Mainz, Germany
[2]Helmholtz-Institut Mainz, Mainz, Germany
[3]GSI Helmholtzzentrum für Schwerionenforschung GmbH, Darmstadt, Germany
[*]E-mail: erartes@uni-mainz.de

Keywords: thin films, molecular plating, scanning electron microscope, infrared spectroscopy, Raman spectroscopy

Molecular plating (MP) is an electrochemical deposition method to produce mechanically stable thin films of radioisotopes and the term was coined by Parker and Falk in 1962 [1]. The produced thin films find widespread applications in nuclear physics and chemistry experiments, e.g., as α-particle or recoil ion sources, or as targets for ion beam experiments [2].

To produce thin films via MP, the salt of the respective isotope is dissolved in a small volume of acid, diluted in alcohols, e.g., isopropanol or isobutanol and deposited at a constant current density <1 mA/cm^2, which corresponds to high voltages of up to >1000 V. Despite its long use, details of the MP process such as the exact nature of the deposited species are still not fully understood [3]. The deposition yields are only partially reproducible, and the films often suffer from organic residue [4,5] and cracking. To improve our understanding of MP f-element films, experiments were performed, in which the concentration of water and CO_2 in the plating solution was systematically changed using the controlled atmosphere inside an argon-filled glovebox. In the experiment series, Tb-nitrate was dissolved in an isobutanol/isopropanol mixture with <50 ppm water content. Observations show that changes in the water and CO_2 content affect the deposition yield and the quality of the films quite dramatically. Confirming earlier Raman spectroscopy results [4], our films contain organic residue, oxides, hydroxides, and carbonates [5]. The deposition yield was determined indirectly by performing neutron activation analysis (NAA) of the supernatant solution after the MP at the research reactor TRIGA Mainz. The layer morphology was studied using scanning electron microscopy (SEM). Raman and infrared (IR) spectroscopy were performed to characterize the anionic species in the thin film. The abundance of the different species in the films as a function of the water and CO_2 concentration of the solutions was determined.

At the conference the influence of water and CO_2 present in the solution on the MP process will be discussed.

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61

Development of TEVA resin extraction chromatography separation for Np determination in Pu materials using gamma spectrometry

Nicole A. DiBlasi[1*], *Sherrod Maxwell*[1,2], *Donivan R. Porterfield*[1], *Darlene Valdez*[1], *Jung Rim*[1], *Angela C. Olson*[1], *Lav Tandon*[1], *Kevin McCann*[1]

[1]Actinide Analytical Chemistry (C-AAC), Los Alamos National Laboratory, Los Alamos, New Mexico, USA
[2]Current Address: National Water Quality Laboratory, United States Geological Survey, Lakewood, Colorado, USA
[*]E-mail: ndiblasi@lanl.gov

Keywords: neptunium, plutonium, HPGe, gamma spectrometry, TEVA, extraction chromatography

^{237}Np is commonly present in Pu materials due to its production in nuclear reactors and being a decay product of Pu ($^{241}\text{Pu} \rightarrow \beta^- + {}^{241}\text{Am} \rightarrow \alpha + {}^{237}\text{Np}$). Quantifying low levels of ^{237}Np is complicated by the predominantly Pu matrix and high activity of ^{241}Am. Establishing effective redox control presents another considerable challenge for the separation of trace levels of ^{237}Np from a Pu matrix. Most methods of ^{237}Np analysis in Pu-materials utilize either mass spectrometry or radiochemical analysis. However, radiochemical analysis is generally only possible when paired with complex separations techniques to substantially eliminate any Am/Pu interferences. For example, one method involves both a cation exchange (IX) separation and a thenoyltrifluoroacetone (TTA)-methyl benzoate solvent extraction (SX) followed by measurement with gas flow proportional alpha counting, alpha spectrometry, and NaI(Tl) gamma spectrometry. This method often results in low chemical yields, requiring long count durations for sufficient data statistics and quality. In this study, we seek to develop and verify a rapid, robust separations technique to increase sample throughput and eliminate the need for multiple radiochemical analysis techniques, thus improving on the IX/SX method for routine ^{237}Np determination in Pu materials.

The approach investigated within this work couples vacuum-assisted TEVA Resin extraction chromatography with high-purity germanium (HPGe) gamma spectrometry. Similar approaches detailed within the literature have provided evidence for successful ^{237}Np separation and use of a single instrumental analysis [1-3]. TEVA Resin chemistry, when paired with appropriate valence control, retains Np(IV) on the resin while +III oxidation state actinides (e.g., Am, Pu) are largely eluted through rinsing. High chemical yields from the separation (~95%), determined through the use of a ^{243}Am/^{239}Np tracer, permit relatively short count durations. This study will compare the TEVA/HPGe method with both the IX/SX radiochemical analysis method and inductively coupled plasma mass spectrometry measurements on various Pu sample matrices. Additionally, a full uncertainty model will be generated for the TEVA/HPGe method. Ultimately, this work will expand upon current methodology through the investigation of the method's validity with Pu-material matrices, the use of a secular equilibrium tracer solution, the comparison to various analysis methods, and the development of the overall method uncertainties and detection limits for a new application of the TEVA/HPGe method.

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160

Current capabilities at LANL for measuring interstitial elements, (C, O, N & H) in plutonium materials

Shauni Williams[*], *John Matonic*[**]

Los Alamos National Laboratory, Los Alamos, NM, USA
E-mails: [*]shauni@lanl.gov, [**]matonic@lanl.gov

Keywords: plutonium, combustion analysis, interstitial, inert gas fusion, carbon, oxygen, nitrogen, hydrogen

High sample throughput and rapid turnaround results for the analysis of interstitial elements in plutonium containing material is imperative to support the rapid characterization of critical materials in the plutonium facility at Los Alamos National Laboratory (LANL). The Actinide Analytical Chemistry Group (C-AAC) recently installed adjacent instrumentation to analyse samples for trace amounts of Carbon, Hydrogen, Oxygen and Nitrogen in plutonium materials. The installation of this equipment in an existing nuclear facility was instrumental in overcoming multiple challenges. The poster will discuss some of these challenges and present the instrumental configuration that's been successful in supporting multiple programs. Routine analysis is currently being performed and we will present our challenges and limitations, in addition to our ability to support sample analysis for increased sample throughputs. In addition, we will present our continuing commitment to assessing the validity of the methods through the very important multi-organizational Pu Metal Standards Exchange Program.
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Advances in radiochemistry supporting the nuclear fuel cycle

185

Study on advection–dispersion behavior for simulation of HTO and Tc-99 transport in crushed granite of column experiments

Yu-Hung Shih[1*], *Kuan-Ying Hsieh*[1], *Liang-Cheng Chen*[1], *Tsuey-Lin Tsai*[1], *Neng-Chuan Tien*[2]

[1]Chemistry Division, Institute of Nuclear Energy Research, No. 1000, Wenhua Rd., Jiaan Village,
Longtan District, Taoyuan City 32546, Taiwan
[2]Nuclear Science and Technology Development Center, National Tsing Hua University,
Hsinchu 30013, Taiwan
[*]E-mail: kuan428@iner.gov.tw

Keywords: advection-dispersion experiments (ADE), breakthrough curves (BTCs), STANMOD simulation

For the safety assessment of deep geological repository for high-level radioactive waste, radionuclides transport behaviour in rock systems is necessary to clarify and establish a suitable model. Advection-dispersion experiments (ADE) were effectively designed for inadequate transport models through a calibration/validation process. HTO and Technetium (Tc) transport in crushed granite were studied using a highly reliable, dynamic column device in order to obtain the retardation factors (R) and the dispersion coefficients (D) by fitting experimental breakthrough curves (BTCs) for various path lengths. In order to conduct a safety assessment (SA) of a deep geological repository for high-level radioactive waste, radionuclide transport in rock systems is necessary to clarify and establish a suitable model. A dynamic column with a radiotracer HTO and Tc(VII) were applied to 20 cm path lengths using a STANMOD simulation. Moreover, it showed similar results between the BTCs of HTO and Tc(VII)by fitting an equilibrium model due to no retardation effect. In fact, there was relatively obvious sorption of Tc in the BTCs obtained by fitting a retardation factor (R) value higher than 1. In addition, the two sites non-equilibrium model with the lowest root mean square error (RMSE) were applied to realize Tc sorption mechanism on crushed granite of column experiments.

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38

A study of reduction reactions of Sm(II) and Eu(II) ions on inert W electrode in molten LiCl-KCl eutectic with Bi(III) ion

Byung Gi Park[1*], *Hwa Jeong Han*[1], *Beom Kyu Kim*[2]

[1]Department of Energy & Environmental Engineering, Soonchunhyang University, Asan, Republic of Korea
[2]FNC Technology Co. Ltd., Yongin, Republic of Korea
[*]E-mail: byunggi@sch.ac.kr

Keywords: samarium, europium, bismuth, LiCl-KCl, reduction, intermetallic compound

Pyrochemical process has been developed to recover uranium and transuranic elements in the spent nuclear fuel discharged from light water reactor. Recovery of uranium and transuranic elements leaves behind the contaminated molten salt. Lanthanide elements are the main source of contamination and should be removed if the salt is to be reused. Most lanthanide elements except Sm and Eu are dissolved as trivalent ions in molten LiCl-KCl eutectic and can be electrolytically extracted in the molten salt because they exhibit higher reduction potential than Li(I) and K(I) ions. Sm and Eu are stable as divalent ions in molten salt whose reduction potential to metal are similar or lower than Li(I) and K(I) ions. It is not possible to electrolytically extract Sm(II) and Eu(II) ions in LiCl-KCl eutectic but the addition of Bi(III) ion in the molten salt allows Sm(II) and Eu(II) ions to be electrolytically extracted by intermetallic compound formations of Bi-Sm and Bi-Eu, as shown in the cyclic voltammograms of LiCl-KCl-$BiCl_3$-$SmCl_2$ and LiCl-KCl-$BiCl_3$-$EuCl_2$ on inert W electrode. Disproportionate reactions of Sm(III)/Sm(II) and Eu(III)/Eu(II) exist in higher potential than that of intermetallic compound formation of Bi-Sm and Bi-Eu. Reduction signals between -1.7 V and -1.3 V indicate reduction of Sm(II) and Eu(II) ions by intermetallic compound formation with Bi. Reduction peak near -1.7 V indicates intermetallic compound formation of Li_3Bi. As a result of cyclic voltammograms, divalent ions of Sm and Eu could be electrolytically extracted by the intermetallic formation reaction with the addition of Bi(III) ion in the molten salt.

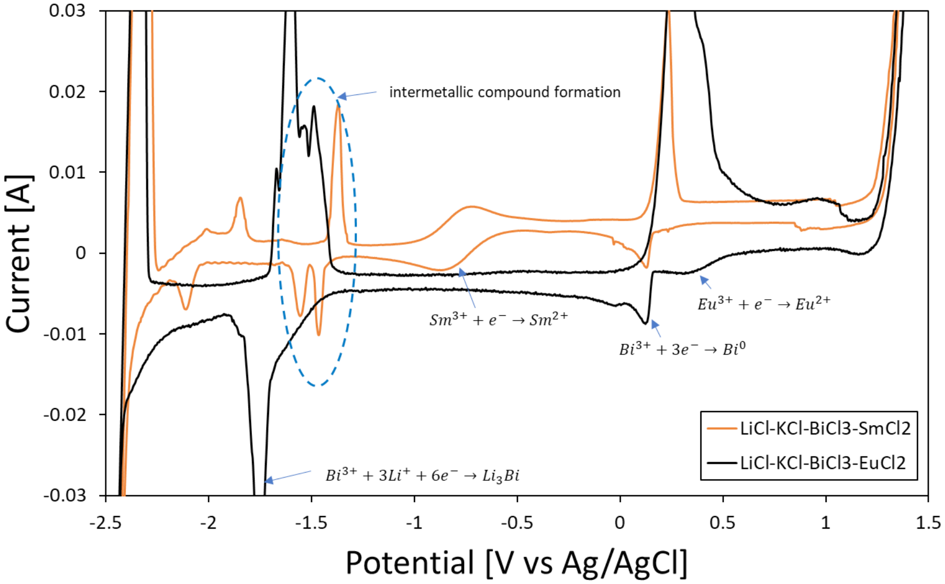

Fig. 1. Cyclic voltammograms of LiCl-KCl-BiCl$_3$-SmCl$_2$ and LiCl-KCl-BiCl$_3$-EuCl$_2$ on inert W electrode at 500

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Collaborative material excercise

156

An overview of non-destructive analysis of the Collaborative Materials Exchange exercise within the 24 hour reporting window

Samuel Cross[*], *Matthew A. Higginson, Thomas Shaw, Louise Ingman, Sarah Crooks, Stuart Dunn, Darrell Knight and Phill Scivier*

[1]AWE, Aldermaston, RG7 4PR, UK
[*]E-mail: sam.cross@awe.co.uk

Keywords: non-destructive analysis, sampling and containment, gamma spectrometry, x-ray fluorescence, microscopy, spectroscopy, nuclear forensic analysis

It is critical to be able to successfully extract the maximum quantity of analytical data from a nuclear forensic investigation in as short a time frame as possible. This is to inform the relevant law enforcement agencies to the immediate public health impact and to allow relevant police investigations to proceed. In addition being able to carry out rapid non-destructive analysis (NDA) of nuclear material helps to identify the best approach for higher fidelity destructive analysis. This information is critical to ensure the health and safety of radiological workers and to ensure analysis is adding investigative value. This must be achieved whilst preserving the integrity of the forensic exhibit [1].

Here we describe the initial 24-hour period of the Nuclear Forensics Collaborative Materials Exchange 7 (CMX-7) investigation at the Atomic Weapons Establishment, organised by the International Technical Working Group (ITWG).

Utilising recent developments such as the use of glovebags, particle sampling kit, and our bespoke universal sample holder facilitates rapid NDA analysis by High Resolution Gamma Spectroscopy, Scanning Electron Microscopy, Digital Light Microscopy, X-Ray Fluorescence and X-Ray Diffraction [2]. The approach also protects Nuclear Forensic exhibits from external contamination maintaining integrity. We will highlight the data gathered and initial observations seen.

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54

On the determination of uranium isotopic composition of nuclear forensic samples using Secondary Ion Mass Spectrometry

Ivan Elantyev[1,2*], *Jan Lorincik*[1], *Kristina Sihelska*[1,2], *Daniela Vesela*[1], *Vlastimil Miler*[3], *Daniel Gotz*[3]

[1]Research Centre Rez, Husinec-Rez, Czech Republic
[2]Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, Prague, Czech Republic
[3]Nuclear Research Institute, Husinec-Rez, Czech Republic
[*]E-mail: ivan.elantyev@cvrez.cz

Keywords: nuclear forensics, uranium, uranium isotopic composition, Secondary Ion Mass Spectrometry, SIMS, CMX-7

This paper aims to describe an advanced application of the Secondary Ion Mass Spectrometry (SIMS) to isotopic analysis of uranium in materials provided by the Nuclear forensic international technical working group (ITWG) within the 7th Collaborative Materials Exercise (CMX-7). It is becoming a common practice within the ITWG community to divide the analytical plan for analyses of nuclear forensic samples into a 24-hour phase, 1-week phase, and 2-month phase. Each of the phases has its preferred set of analytical methods and examination procedures, starting with fast non-destructive techniques in 24-hour phase, proceeding with commonly available microscopic and microanalytical methods (e.g., Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy, SEM-EDX) in 1-week phase, and with sophisticated, destructive, and time-consuming techniques in the 2-month phase. The SIMS is considered a destructive technique and a demanding method in many respects (cost, throughput, skill levels). Thus, it is usually employed in the 2-month phase or in the 1-week phase at best.

It will be shown in this paper, that SIMS can be used efficiently in the 24-hour phase and even considered a quasi-non-destructive technique. The procedure is based on the analysis of micrometer-size dust particles loosely bound to the inner surface of the sample container after their release from the sample surface. Those particles were collected onto a piece of clean particle-free piece of a cotton textile. Once the particles were on the swipe a similar SIMS analysis procedure was applied as it is used for analysis of environmental swipes within the Network of Analytical Laboratories of the International Atomic Energy Agency [1]. The particles are extracted onto a silicon planchet compatible with the SIMS sample holder. Then the SIMS performs two-dimensional image scans for ^{235}U and ^{238}U isotopes and an automated sample-stage movement in discrete steps to cover a major part of the planchet. The coordinates and preliminary enrichment of uranium particles is the result of that step. Next, several representative particles are chosen one by one and an accurate and precise measurement of isotopic composition, including minor isotopes ^{234}U and ^{236}U, of each individual particle is obtained. The main difference in the SIMS procedure used in this work compared to [1] was in speeding up the particle search and identification step by screening substantially smaller area of the planchet.

The characterized materials were two powdered uranium-compound samples labeled ES-1 and ES-3 and two uranium metal samples labeled ES-2 and ES-4. The particle swipes were taken from the inside of the glass bottles used for sample storage and transportation. The SIMS measurement for all four samples were completed within ~10 hours and the quality of the results allowed for a conclusion that ES-2 cannot originate from the same source as the other three samples and that ES-1, ES-3, and ES-4 had a common source material. This result was supported by a parallel gamma spectrometric measurement of the samples, which proved that isotopic composition of the collected particles from the samples and the bulk of the samples were identical.

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271

Advantages and limitations of four mass spectrometry techniques for uranium isotopic measurement. Case of the 7th collaborative material exercice of the International Technical Working Group

Anne-Laure Fauré[*], *Manon Cornaton, Amélie Hubert, Anne-Claire Humbert, Aurélie Ritt, Thibaud Sontag*

CEA/DAM Île-de-France, Arpajon, France
[*]E-mail: anne-laure.faure@cea.fr

Keywords: uranium isotopic composition, mass spectrometry

In the framework of the seventh collaborative material exercice (CMX-7) organized by the Nuclear Forensics International Technical Working Group (NF-ITWG), CEA/DAM Île-de-France applied a panel of mass spectrometry techniques to determine the uranium isotopic composition of the four samples. The sampling methodologies were different depending on the solid form of the sample (powder, crystallized or metallic), the scale of the applied mass spectrometry technique (particulate or bulk) and the timeliness required for the measurement during the course of the exercice.

Two mass spectrometry families can be considered: one requiring the sample to be in liquid form as inductively coupled mass spectrometry (ICP-MS), and one enabling the direct analysis of solid material as secondary ion mass spectrometry (SIMS) and laser ablation coupled to ICP-MS (LA-ICPMS).

For analysis at the particulate scale, ponderable amount of solid cannot be introduced in the instruments. Thus, particulate matter was collected either by wiping the surface with a cotton cloth or by diving a plastic tip into the powders. Beside the determination of the isotopic composition, particle analysis can provide information on the homogeneity of the samples. All samples were analyzed within one week and further characterizations were continued during the 2 months of the exercice.

For liquid mass spectrometry techniques, the solids were first divided in a few pieces and powdered samples were transferred into several vials by means of spatulas. These macroscopic sub-sampling aims at limiting the amount of nuclear material in the laboratory. Samples were then dissolved using concentrated nitric acid for subsequent analyses. Direct analysis of diluted solutions (µg range of U) were performed using quadrupole-based ICPMS to provide results within 1 week. After radiochemical purification on a part of the original digestion, analyses were then performed using multi-collector ICP-MS to get high precision isotopic ratios.

This poster will present the different techniques and sampling methodologies. The results obtained by the different techniques within one week and two months will be given. All isotopic ratios were in good agreement. Advantages and limitations of each technique will be discussed with a focus on response time and uncertainties.

233

Use of Laser Ablation Inductively Coupled Plasma Mass Spectrometry in the 7th Collaborative Materials Exercise

Tara Kell[*], *Slobodan Jovanovic*

Canadian Nuclear Safety Commission, Ottawa, Canada
[*]E-mail: tara.kell@cnsc-ccsn.gc.ca

Keywords: Laser Ablation, uranium, isotope ratio, radiochronometry, ITWG, CMX-7

The 7th Collaborative Materials Exercise (CMX-7) of the Nuclear Forensics (NF) International Technical Working Group (ITWG) was held in 2021-2022. The goal of CMX is to enable participating laboratories to exercise their NF capabilities and share experiences in an open forum. Our laboratory uses Laser Ablation triple-quadruple Inductively Coupled Plasma Mass Spectrometry (LA-QQQICP-MS) for NF examination of CMX samples through elemental and isotopic analyses [1]-[3].

In CMX-5 and CMX-6 we successfully utilized LA-ICP-QQQMS with an x-lens for uncalibrated trace element signal comparisons, quantitative uranium isotope ratio analysis, and radiochronometry (age-dating) [1]-[2]. In CMX-7, to increase sensitivity which is crucial for analysis of depleted uranium (DU) samples, we used an s-lens designed for semiconductor analysis by QQQICP-MS, which increases the sensitivity 2-3x over the broadly used x-lens, without the loss of accuracy. While the mass bias corrected uranium isotopic ratios were consistent with expected results, as revealed at the end of the exercise, the similarly corrected ^{230}Th/^{234}U ratios were inconsistent.

In the present work we investigated the possible sources of inconsistent LA-QQQICP-MS results. The observed deviations could be due to low ^{230}Th sensitivity and quadrupole instability over time. Low sensitivity was especially pronounced for the "youngest" DU metal sample, where the amplitude of the ^{230}Th signal was not sufficient for accurate determination of its age. To counter the issue of quadrupole instability, we used modified peak broadening instrumental conditions [similar to ref 4], which led to improved precision and accuracy of isotope ratio analysis. Higher than expected ^{230}Th/^{234}U ratio in the other DU metal sample seems to originate from heterogeneity due to suspected thorium migration to the surface [5] during the casting or rolling of the DU metal. The surface enrichment in ^{230}Th was established by probing the sample depth. The poster will highlight our efforts to investigate the cause of inconsistent ^{230}Th/^{234}U ratios and probe the thorium heterogeneity in the DU metal.

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247

CMX-7: A Los Alamos National Laboratory perspective

Robert E. Steiner[*], *Stephen P. LaMont, Theresa M. Kayzar-Boggs, Jacob E. Buettner, Rose A. Bloom, Melissa Boswell, Matthew Carpenter, Mark Croce, Joanna S. Denton, Mark A. Edwards, John R. Engel, Rebecca R. Foley, Alexa B. Hanson, Michael Harris, Lisa A. Hudston, Jeremy D. Inglis, Azim H.S. Kara, Kyle J. Krajewski, Joel R. Maassen, Daniel McNeel, Benjamin E. Naes, Matthew E. Sanborn, Matthew M. Schneider, Brian L. Scott, Eric L. Tegtmeier, Travis J. Tenner, Allison M. Wende, Kimberly N. Wurth*

Los Alamos National Laboratory, Los Alamos, New Mexico, USA
[*]E-mail: steiner@lanl.gov

Keywords: nuclear forensics, CMX-7, ITWG

Los Alamos National Laboratory participated in the Collaborative Material Exercise 7 (CMX-7), sponsored by the Nuclear Forensics International Working Group (ITWG) in 2022. This exercise focused on the forensic examination of four uranium materials and comparing the characteristics of the materials to identify relationships or similarities between them. Each of the four materials was thoroughly characterized for its chemical, isotopic, and morphological attributes, which revealed clear similarities and differences that helped to establish possible commonalities in the production history of each. For example, the UO_3, $UO_2(NO_3)_2$, and U-metal samples all shared a common depleted uranium isotopic composition, while a second U-metal sample was more depleted in ^{235}U and had less ^{236}U. Radiochronometry results for the four samples were statistically different for all samples, as were trace actinide concentrations. Physical differences revealed by optical microscopy and scanning electron microscopy were also helpful in identifying similarities and differences, especially for the two metal samples. Where possible, a univariate statistical approach based on calculating p-values was used to compare quantitative characteristics of the materials [1]. Overall, the CMX-7 exercise was useful for exercising our capability to perform forensics examinations on realistic materials and provided an opportunity to assess data and draw meaningful conclusions about how samples may be connected through a common process history.

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Education in radiochemistry

177

Optimizing decontamination procedures for educational applications

Alžběta Horynová[*], *Kateřina Čubová, Miroslava Semelová, Mojmír Němec*

Department of Nuclear Chemistry, FNSPE, Czech Technical University in Prague, Czech Republic
[*]E-mail: horynalz@fjfi.cvut.cz

Keywords: decontamination, decommissioning, chemical decontamination methods

For the purposes of practical training and topical research in decontamination procedures, a unique piece of laboratory equipment, the modular decontamination loop, was devised by the Department of Nuclear Chemistry, FNSPE, CTU in Prague. The system consists of multiple components that can be arranged in various ways depending on the experiment, including among others a stirred reactor, flow-through heaters, an electrochemical setup, a column for filtration, ion exchange or adsorption, a dual extraction module, and flow-through sensors of temperature, pH, activity and flow rate. A specific technique to be used in a laboratory task in the new study programme, Decommissioning of Nuclear Facilities, is being developed with the purpose of creating instructions for students and teachers. This includes assembly of the equipment by the student; selection, characterization and optimization of a chemical system consisting of a decontamination solution and a defined sample; preparation of the material for decontamination; and testing of the decontamination process and evaluation of its efficiency.

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138

A radiochemistry laboratory exercise: Estimation of Ba-137m half-life by its internal conversion electron

Eros Mossini[*], *Gabriele Magugliani, Francesco Galluccio, Andrea Santi, Marco Giola, Elena Macerata, Mario Mariani*

Department of Energy - Nuclear Engineering Division, Politecnico di Milano, Milan, Italy
[*]E-mail: eros.mossini@polimi.it

Keywords: laboratory exercise, very short-lived radionuclides, liquid scintillation counting, co-precipitation

Radiochemistry is a pivotal but complex discipline that addresses several challenges related to the civil use of nuclear technologies. Active and autonomous laboratory exercises could be helpful to foster students' engagement and their understanding of basic radiochemistry and nuclear chemistry topics. In this contribution, an original experimental activity has been conceived and tested with the Applied Radiochemistry lab class at Politecnico di Milano.

The aim of the activity is to experimentally estimate the half-life of Ba-137m. The radiometric measurement is performed by Liquid Scintillation Counting (LSC) to monitor the growth of the internal conversion electron peak after radiochemical separation of Cs-137 from Ba-137m. The starting sample is an aqueous solution spiked with few hundred Bq of Cs-137 at secular equilibrium with its daughter nuclide, Ba-137m. Several well-known methods exist to effectively separate Ba from Cs cations, owing to the different chemical behaviour of alkali and alkaline earth metals. In this work, the students co-precipitate Ba (and Ba-137m) as isomorphically substituted mixed crystals of Ca phosphate by adding Ca nitrate, ammonium hydrogen phosphate, and adjusting the pH to 9-10 [1]. Since Cs (and Cs-137) ions are not co-precipitated, a supernatant solution just containing Cs-137 is obtained. After quick centrifugation to enhance the deposition of the precipitate, the students collect a quantitative aliquot of the supernatant to be mixed with LSC cocktail and measured by LSC. The students set the region of interest (ROI) of the LSC multi-channel analyser to discard the beta spectrum of Cs-137 and just measure the internal conversion electron peak. By quickly performing a cycle of short measurements, the counts recorded in the ROI progressively increase and reach the saturation, that is the secular equilibrium with the parent nuclide. The triple-to-double coincidence ratio (TDCR) method could be employed to correct for quenching [2]. On the other hand, luminescence is not an issue since the internal conversion electron peak is far from the luminescence region [2]. By assuming the attainment of secular equilibrium between parent and daughter nuclides, the students are requested to estimate Ba-137m half-life and Cs-137 activity by minimization of the reduced χ^2 value with respect to the theoretical decay curve. Accuracy within 5% are easily obtained with reduced χ^2 values close to one.

Thanks to the proposed exercise, the students get acquainted with the concepts and practices of radiochemistry and radiation measurement, such as radioactive sample manipulation, radiochemical separation, radiometric measurement by LSC, and data analysis. The acquisition of these skills is pivotal to build the knowledge background of future nuclear experts.

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Mass spectrometry

113

Mass spectra analysis of ions produced from Ca and Ni fluoride target materials by caesium sputtering

Filip Babčický[*], *Tomáš Prášek, Mojmír Němec*

Department of Nuclear Chemistry, Czech Technical University, Prague, Czech Republic
[*]E-mail: babcifil@fjfi.cvut.cz

Keywords: DTM radionuclides, AMS, nickel, calcium, fluoride matrices

One of the most important baseline tasks during the operation and decommissioning of nuclear power plants and other nuclear devices is identification of the radionuclides present and quantification of their activities. Very often the activity and the signal measured with radiometric techniques is intensive enough to obtain clear results from analysis mimicking ALARA procedure – short measurement times, small samples, sufficient distance from the source. Unfortunately, there are also radionuclides which cannot be detected easily because of their nuclear and emission properties such as ^{63}Ni, ^{59}Ni, ^{41}Ca, ^{79}Se, ^{107}Pd, globally called difficult to measure (DTM) radionuclides. In these cases, it is a challenge to detect small, e.g. smeared activities of these nuclides. One of the options can be a proper separation followed by mass spectrometric measurement – but in such case isobaric interferences of ions with the same mass-to-charge value must be solved and suppressed. This work focuses on preparation of samples for determination of Ni and Ca isotopes with accelerator mass spectrometry (AMS) and possible advantages of using in fluoride target matrices for measurement, which may allow to utilize differences in chemistry of isobars directly in the ion source of the AMS. Mass spectra of the sputtered fluoride matrices of Ni, Co, Ca, K were thoroughly measured and evaluated, showing performance of these materials during sputtering with caesium negative ion source.

210

Comparison and optimization of the TIMS analysis method for declared information verification of Special Nuclear Material

Jung Youn Choi[*], *Haneol Lee, Hyun Ju Kim*

Korea Institute of Nuclear Non-proliferation and Control (KINAC), Daejeon, Republic of Korea
[*]E-mail: raon@kinac.re.kr

Keywords: Special Nuclear Material, uranium isotope ratio, TIMS, Sequence method, TE method

As a regulatory agency, KINAC verifies the declared information of nuclear facilities of Special Nuclear Material (SNM) collected from nuclear facilities. To verify the reported results, analyze the uranium isotope ratio using TIMS (Thermal Ionization Mass Spectrometry).

The process samples to be analyzed are easy to digest in the form of uranium oxide (pellet and powder), so chemical pre-treatment is relatively simple. In addition, since the presence of minor isotopes (^{234}U, ^{236}U) does not have a decisive influence on the results of uranium enrichment analysis, the process sample is currently being analyzed using the Sequence method and the RSD value is 0.2 % within.

However, The TE method is recommended because it minimizes mass fractionation effects of minor isotopes (^{234}U, ^{236}U) in uranium isotope ratio analysis using TIMS, TE method is the process sample analysis method currently used in the facility, so we will apply the same analysis method to verify the reported value.

In addition, The results may vary depending on how the detailed analysis conditions (filament heating, sample loading, etc.) constituting the TE method are set, so the previously established Sequence method and TE method will be compared through CRM and sample analysis.

This optimized TIMS method will be fully utilized not only to verify SRM declaration information but also in situations where the target of analysis is expanded due to the increase in nuclear facilities in the future.

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277

Sequential separation of iodine species in nitric acid media for speciation analysis of I-129 in a PUREX process of spent nuclear fuel reprocessing

Tianyi Jia[1,2*], *Keliang Shi*[1,2], *Yanyun Wang*[1,2], *Junqiang Yang*[1,2], *and Xiaolin Hou*[1,2]

[1]Frontier Science Center for Rare Isotopes, Lanzhou University, 730000 Lanzhou, P. R. China
[2]School of Nuclear Science and Technology, Lanzhou University,730000 Lanzhou, P. R. China
[*]E-mail: jiaty19@lzu.edu.cn

Iodine-129, a long-lived radionuclide, is one of important volatile fission products in the spent nuclear fuel (SNF) and most critical radionuclides for radiation safety, waste treatment and product quality in the reprocessing of spent nuclear fuel due to its active chemical property and highly mobility in the environment. Although a lot of effort has been devoted, the chemical species of iodine-129, its distribution and behavior in the spent nuclear fuel solution are still not well understood because of lack of reliable speciation method for iodine-129 in high acidic media.

For efficient and accurate speciation analysis of ^{129}I in the nitric acid solution of spent nuclear fuel in its reprocessing process, a sequential procedure for stepwise separation of different iodine species in 3 mol/L HNO_3 was proposed based on the solvent extraction using CCl_4 and mesitylene. Molecular iodine (I_2) was first separated by solvent extraction using CCl_4, and iodide (I^-) remaining in the aqueous phase was oxidized to I_2 by adding $NaNO_2$ and then extracted to mesitylene. Finally, iodate (IO_3^-) was reduced to I_2 using $NH_2OH \cdot HCl$ and extracted to mesitylene. The separation efficiency of 98–99% for tracer amounts of $^{129}I_2$, $^{129}I^-$, and $^{129}IO_3^-$ in 3 mol/L HNO_3 and less than 2% crossover among different iodine species were achieved.

The established sequential separation procedure can be used for separation of different species of ^{129}I in HNO_3 media, providing a practical method for speciation analysis of ^{129}I in the SNF solution.

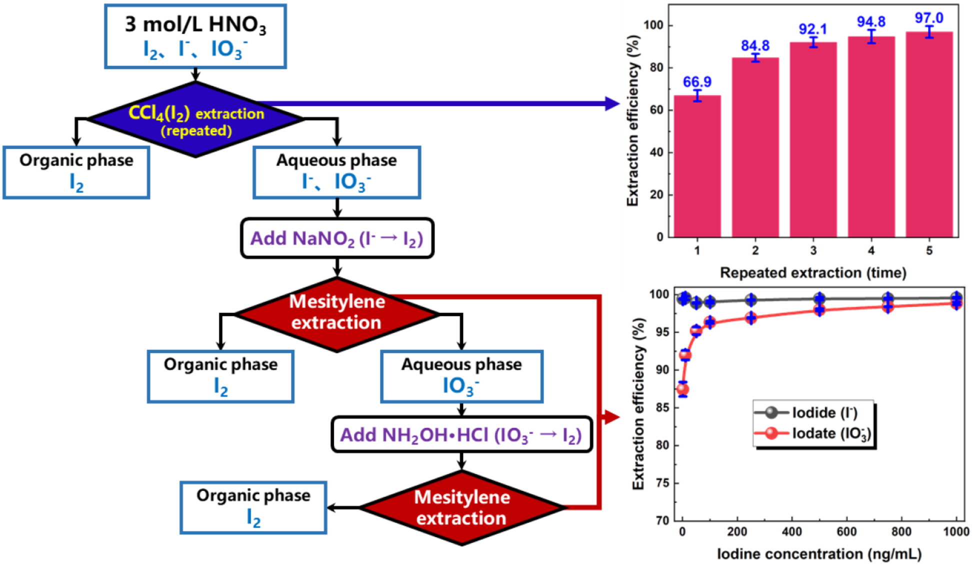

Figure 1. Schematic diagram of the sequential separation procedure of different species of ^{129}I in 3 mol/L HNO_3 media

263

Accelerator studies of tree rings in proximity of the aluminium processing factory in Ladomerská Vieska (Slovakia)

Jakub Kvasniak, Miroslav Ješkovský, Jakub Kaizer[*]*, Jakub Zeman, Ivan Kontuľ,*
Pavel P. Povinec

Faculty of Mathematics, Physics and Informatics, Comenius University, 84248 Bratislava, Slovakia
[*]E-mail: jakub.kaizer@uniba.sk

Keywords: tree rings, PIXE, pollution, metals

Environmental pollution has been recognized as a growing problem. The presence of particulate matter, oxides, metals, and other contaminants in the environment can cause adverse health and psychological problems [1-4]. Although harmful effects on human health are well documented, historical trends of pollution do not exist in most areas. The possibility of using tree rings to obtain information on environmental contamination was introduced in the 1970s [5]. Several studies have explored this option [6]. In principle, trees should be able to some extent record the state of the environment in their yearly rings. There are three pathways for metals to enter the tree: foliar uptake, root uptake, and direct deposition on the stem, with subsequent diffusion through the bark [5]. Ladomerská Vieska (Žiar nad Hronom district) has been known for aluminium processing for a long time, as the history of this sector of industry can be dated back to 1951 [7]. Although the original company is not currently operating, the area is still heavily industrialized [8]. Cores from five trees were collected with increment borer around the industrialized area, divided into individual tree rings, and chemically processed. The prepared samples were analysed with the PIXE technique in the CENTA facility at the Faculty of Mathematics, Physics and Informatics of the Comenius University in Bratislava. Heavy metals have been found in tree ring samples that will be compared with available historical records of emissions. The spatial distribution of contaminants with the wind rose in the studied area has also been studied.

Acknowledgments

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35

Optimization of measurement protocol for U particles in environmental samples by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

Hyun Ju Kim[*], *Haneol Lee, Jung Youn Choi*

Korea Institute of Nuclear Non-proliferation and Control (KINAC), Daejeon, Republic of Korea
[*]E-mail: hyunju1157@kinac.re.kr

Keywords: LA-ICP-MS, nuclear material, uranium, particle analysis

The detection of uranium (U) isotopic analysis is of particular significance in connection with verification of nuclear activities or absence of undeclared nuclear material activities in facilities for a specific safeguards-related application. Environmental samples (swipe sample) were collected by wiping at the inspected area surface using cotton swipes known as widely verification method by International Atomic Energy Agency (IAEA) in subject to nuclear safeguards. [1] The particle analysis in environmental samples has been conducted normally mass spectrometry methods such as SIMS (Secondary Ionization Mass Spectrometry), ICP-MS (Inductively Coupled Plasma-Mass Spectrometry), FT-TIMS (Fission Track-Thermal Ionization Mass Spectrometry) methods. [2-4]

Among the various methods, the ICP-MS has widely used method for precise and accurate to identify multi elements simultaneously. However, ICP-MS requires a sample pre-treatment process to bring them into a solution. The recent trend of particle analysis is developing a method that can be analysed directly without a pre-treatment process. For this reason, Laser Ablation (LA) was coupled with ICP-MS equipment to carry out the direct analysis for particles in environmental samples. LA techniques can be used to directly analyse various solid form samples and a pre-treatment (dissolution) procedure of the samples is not required.

This study aims to determine a reliable analysis method for U isotope at trace and ultra-trace level measurement in environmental samples by LA-ICP-MS.

Currently, particle analysis of U in environmental sample is carried out through LG-SIMS (Large Geometry-Secondary Ionization Mass Spectrometry). We have investigated that U particle analysis protocol in environmental sample by ICP-MS (iCAP RQ, Germany, Thermo Fisher Scientific) coupled with 193 nm LA (RESOlution SE, USA, Applied Spectra, Inc.) in order to obtain a rapid and accurate analysis results. The validity of the particle analysis results for LA-ICP-MS will be verified by comparing the LG-SIMS particle analysis results.

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119

Simultaneous determination of actinide-isotopes by online solid-phase extraction–inductively coupled plasma–mass spectrometry

Makoto Matsueda[1,2*], *Tomohiko Kawakami*[3], *Yuko Teruyama*[3], *Motoki Terashima*[1],
Kazuki Iijima[1], *Makoto Furukawa*[2,4], *Yoshitaka Takagai*[2,5]

[1]Collaborative Laboratories for Advanced Decommissioning Science, Japan Atomic Energy Agency, Fukushima, Japan
[2]Faculty of Symbiotic Systems Science, Cluster of Science and Technology, Fukushima University, Fukushima, Japan
[3]Kaken Inc., Ibaraki, Japan
[4]PerkinElmer Japan Co., Ltd., Kanagawa, Japan
[5]Institute of Environmental Radioactivity, Fukushima University, Fukushima, Japan
[*]E-mail: matsueda.makoto@jaea.go.jp

Keywords: actinide, simultaneous determination, online solid-phase extraction, ICP–MS

Actinides have a significant radiotoxicity risk of internal exposure to human body due to their emission of high energy α-particle. An analysis of the actinides is important for safe management of nuclear power plants and radioactive wastes. A traditional method using α-spectrometry needs a time-consuming and complicated multi-step pretreatment process. Inductively coupled plasma–mass spectrometry (ICP–MS) can potentially realize rapid and simple analytical method by reducing the pretreatment process through combining various automatic chemical separation systems. Such a combination including a hyphenation of chemical instrument and pretreatment system can also be achieved to improve applicability of ICP–MS for simultaneous determination of actinides. Moreover, separation of isobaric interferences (e.g., $^{241}Pu^+$–$^{241}Am^+$, $^{238}UH^+$–$^{239}Pu^+$, $^{192}Pt^{40}Ar^+$–$^{232}Th^+$) has remained as a fundamental problem of ICP-MS. In this study, we developed an automatic analytical system of online solid-phase extraction (SPE)–ICP–MS equipped with multi-separation steps of SPE for simultaneous determination of actinides (Th, U, Pu, and Am).

The online SPE–ICP–MS consisted of ICP-MS (PerkinElmer, NexION 2000) and a customized online preconcentration (Precon) system. The Precon system includes two peristaltic pumps, two 6-port selection valves, a 10-port switching valve, an autosampler, and SPE column. The SPE column was originally prepared by that commercially available chemical separation resin was manually packed into the empty columns. This one-shot analysis system constructed by this online SPE–ICP–MS could simultaneously determine four isotopes of the actinides (Th, U, Pu, and Am).

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152

Variations in beam currents using different carrier metals in small rain samples for ^{10}Be measurements by AMS

Grisel Méndez García[1,2*], *Regina Romero*[3], *Santiago Padilla*[4], *Corina Solís*[2], *Efraín Chávez*[2], *and Arcadio Huerta*[2]

[1]CONACyT - Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico
[2]Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico
[3]Facultad de Ciencias, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico
[4]Centro Nacional de Investigación Humana (CENIEH), Burgos, España
[*]E-mail: griselmendez@fisica.unam.mx

Keywords: radiochemistry, BeO, rainfall, AMS

The low natural concentrations of ^{10}Be have limited the amount of ^{9}Be that can be added in the Accelerator Mass Spectrometry (AMS) measurement. This has made sample handling difficult, due to the small sample size, as well as measurements. The ideal chemical species to measure ^{10}Be is beryllium oxide (BeO). Mixing BeO with a metallic matrix, e.g. iron (Fe), copper (Cu), silver (Ag) or niobium (Nb), has been found to significantly improve ion formation at the source. And that co-precipitation of Be with one of the aforementioned metals maximises the amount of sample and facilitates laboratory work by creating a more homogeneous matrix for AMS measurements. This work analyzes the possibilities offered by carrier metals in the process of Be co-precipitation in small rain samples from an urban area. Preliminary results show that the Fe used as precipitant in the radiochemical procedure employed in our laboratory does not offer the optimal conditions for ^{10}Be analysis by AMS for this type of samples.

231

Sources of metals and plutonium isotopes in sediments of the south-eastern Baltic Sea

Galina Lujanienė[1], *Nijolė Remeikaitė-Nikienė*[2], *Kęstutis Jokšas*[3], *Pavel P. Povinec*[4*],
Hong-Chun Li[5], *Sergej Šemčuk*[1], *Rūta Barisevičiūtė*[1], *Vitaliy Romanenko*[1],
Galina Garnaga-Budrė[6]

[1]SRI Center for Physical Sciences and Technology, Vilnius, Lithuania
[2]Environmental Protection Agency, Klaipėda, Lithuania
[3]SRI Nature Research Centre, Vilnius, Lithuania
[4]Comenius University, Faculty of Mathematics, Physics and Informatics, Bratislava, Slovakia
[5]NTUAMS Laboratory at National Taiwan University, Taipei, Taiwan
[6]Marine Research Institute, Klaipėda University, Klaipėda, Lithuania
*E-mail: pavel.povinec@uniba.sk

Keywords: metals, $\Delta^{14}C_{TOC}$, $\delta^{13}C_{TOC}$, $^{240}Pu/^{239}Pu$ atomic ratio

Anthropogenic activities have led to an accumulation of various toxic pollutants in the sediments of the Baltic Sea. Heavy metals and radionuclides are particularly toxic pollutants that have been released into the environment [1]. They are of general concern because of their negative effects on ecological systems and human health due to their toxicity and carcinogenicity.

The distribution trends of metal concentrations (As, Cd, Co, Cr, Cu, Pb, Hg, Li, Ni, V, Zn, and Al) as well as the activities of ^{241}Am and the Pu isotopes in the southeastern Baltic Sea were studied in the sediments to estimate their contents and sources. In addition, total organic carbon (TOC), $\Delta^{14}C_{TOC}$ and $\delta^{13}C_{TOC}$ were measured in sediment samples (0—5 cm), collected with a Van Veen grab (sampling area of 0.1 m^2) in the Lithuanian zone of the Baltic Sea [2].

The analysis of metal concentrations in the sediments was carried out using ICP-OES (ISO 11885:2007). The activity of ^{241}Am, ^{238}Pu and $^{239,240}Pu$ were measured by alpha spectrometry after radiochemical separation [3]. The atomic ratios $^{240}Pu/^{239}Pu$ were determined by AMS.

The content and isotopic ratios of carbon in the samples were measured at the State Research Institute Center for Physical Sciences and Technology (Vilnius, Lithuania) using a Thermo Scientific Delta V Advantage mass spectrometer coupled to a Flash EA 1112 elemental analyzer. Measurements of $\Delta^{14}C_{TOC}$ in sediments were carried out using a 1.0 MV HVE Tandetron AMS in the Department of Geosciences of the National Taiwan University. To estimate the sources of OC in sediments, an EM (end-member) mixing model was applied for three sources of OC (continental, marine and fossil) [4].

The highest levels of metals and radionuclides were found at the bend of the Neman River and in the Gotland Deep. A strong correlation was found between the elements studied and total organic carbon. Radiocarbon and stable carbon isotopes used to estimate pollution sources and distribution patterns of radionuclides and metals in sediments indicated a continental source of Pu from the Chernobyl accumulator. A clear continental origin with good correlation was also found for Hg.

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80

Developing a chemical sample preparation procedure for accelerator mass spectrometry of ^{231}Pa in environmental samples

Janis Wolf[1,2*], *Astrid Barkleit*[2], *Sebastian Fichter*[1], *Robin Steudtner*[2], *Anton Wallner*[1]

[1]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany
[2]Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany
[*]E-mail: j.wolf@hzdr.de

Keywords: protactinium, accelerator mass spectrometry, ^{233}Pa

Accelerator mass spectrometry (AMS) is an ultra-sensitive method for the detection of low concentrations of trace isotopes. It allows counting of single atoms, which are filtered according to their mass. This is advantageous to decay counting as even low abundance radionuclides with long half-lives can be detected. The measurement of ^{231}Pa ($t_{1/2} = 3.28 \cdot 10^4$ a) by AMS has many applications including nuclear forensics [1], U/Pa dating [2, 3] and radiological risk assessment of the ^{235}U decay chain [4].

Pa is not yet routinely measured by AMS and procedures for the preparation and detection of ^{231}Pa in environmental samples are currently being developed [4,5]. AMS is a relative detection method making it necessary to add a well-known amount of an isotopic spike to samples to determine the concentration of ^{231}Pa. As ^{231}Pa is the only long-lived Pa isotope, the short-lived isotope ^{233}Pa ($t_{1/2} = 26.98$ days) is most commonly used as spike. This enables the measurement of the isotopic ratio ^{231}Pa/^{233}Pa and easy monitoring of the efficiency of the sample preparation as ^{233}Pa can be measured by Gamma spectrometry.

To obtain a ^{233}Pa spike, it is required to separate it from a solution of its long-lived mother nuclide ^{237}Np using an ion-exchange or extraction chromatography resin. Different separation procedures are tested and compared with the aim to find a procedure that can be performed easily, quickly and requires no additional safety precautions to routine AMS sample preparation procedures. The recovery of ^{233}Pa and ^{237}Np from the resins is monitored by Gamma spectrometry.

Additionally, chemical separation procedures of Pa from U are required, as ^{233}Pa decays into the isobar ^{233}U ($t_{1/2} = 1.60 \cdot 10^5$ a), which may compromise the measurement of ^{233}Pa. Thus, the ^{233}Pa spike is added to environmental water samples containing natural U and separation procedures using different extraction chromatography resins (e.g. UTEVA, TK400) are performed. The partitioning of U and Pa in the separation procedure is deduced by ICP-MS measurements and Gamma spectrometry. This finally enables the reliable detection of ^{231}Pa in environmental samples.

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Neutron activation analysis

201

Micelle-mediated extraction for simultaneous preconcentration of cadmium, cobalt, copper, manganese, nickel, and zinc with 1-(2-Pyridylazo)-2-naphthol and their determination by neutron activation analysis

Aurora Pérez-Gramatges[1,2] *and Amares Chatt*[1*]

[1]Trace Analysis Research Centre, Department of Chemistry, Dalhousie University,
6274 Coburg Road, Room 212, PO BOX 15000, Halifax, Nova Scotia, B3H 4R2, Canada
[2]Chemistry Department, Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês
de São Vicente 225, Gávea, Rio de Janeiro, RJ, 22451-900, Brazil
[*]E-mail: a.chatt@dal.ca

Keywords: cloud point extraction, selected transition metals, neutron activation, gamma-ray spectroscopy

Concentrations of many elements in natural waters are generally below the detection limits of most-commonly used instrumental analytical techniques. Therefore, it is necessary to employ preconcentration steps prior to their reliable determinations. The most commonly used preconcentration techniques include liquid and solid phase extractions, various types of chromatography, hydride-generation, and surface adsorption. Surfactant-mediated extraction methods have lately become quite popular. Micelle- mediated extraction, more commonly known as cloud point extraction (CPE), procedures have been reported for the extraction of metal chelates. The CPE technique offers good selectivity when specific ligands and optimum conditions for separation of phases are used. A method for the simultaneous preconcentration of six transition metals, namely cadmium, cobalt, copper, manganese, nickel, and zinc, by CPE followed by their determination using neutron activation analysis (NAA) was developed in this work. The method involved the use of a non-ionic surfactant, namely PONPE-7.5, and the chelating agent 1-(2-pyridylazo)-2-naphthol, commonly known as PAN, for the extraction. Factors such as solution pH and PAN concentrations, which can influence the extraction efficiency of these metals, were investigated. The irradiations were performed at the Dalhousie University SLOWPOKE-2 Reactor (DUSR) facility at a neutron flux of 5 x 10^{11} cm^{-2} s^{-1} followed by high-resolution Ge(Li) gamma-ray spectroscopy. Two different irradiation-decay-counting (t_i, t_d, t_c) schemes were employed: 10 min, 1 min, 10 min for Cd, Co, Cu and Mn, and 3h, 1h, 2h for Ni and Zn. Quantitative recoveries (> 96%) were obtained for all elements in a single extraction step under optimal conditions. A preconcentration factor of 70 was achieved leading to detection limits of the order of nanogram per mL. The method was validated using NIST SRMs. The details of the CPE method will be presented along with results.

228

INAA of concrete

Heather Chen-Mayer[1*], *Maria Vega Martinez*[1], *Aliyah Welker*[2], *Sangho Nam*[2], *Cameron Goodwin*[2], *Richard Livingston*[3], *Mohamad Al-Sheikhly*[3]

[1]Materials Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA
[2]Rhode Island Nuclear Science Center, Narragansett, RI, USA
[3]Department of Materials Science & Engineering, University of Maryland, College Park, MD, USA
[*]E-mail: chen-mayer@nist.gov

Keywords: concrete, chlorides, INAA

Chloride diffusion in concrete plays an important role in the corrosion of metal reinforcement. Chloride concentrations can be considered as a predictor for service life of concrete infrastructure. Ideally such an analysis should be in-situ and nondestructive, because extensive sample preparation can change the composition. Neutron induced prompt gamma analysis is a candidate due to its ability to penetrate bulk concrete and multi-elemental sensitivity. However, obtaining quantitative information from these bulk measurements relies on taking ratios of the signal from chlorine to that from a major element in the matrix, which varies by concrete mix design. Therefore, independent verification of the concrete composition is needed as a direct calibration of the prompt gamma technique. A preliminary Instrumental activation analysis (INAA) study was performed on concrete samples for this purpose.

Disks were cored from concrete slabs (90 cm x 90 cm x 2.54 cm) cast from a mix design of cement, coarse and fine aggregates, and water, with four levels of added calcium chloride plus the 5th slab as blank, resulting in nominally sub-percent levels of chlorine by mass fraction -- around the threshold level for promoting corrosion. Each of the five cored disks was crushed and mixed to obtain adequate particle sizes and homogeneity. Aliquots of 200 mg were taken in triplicate from each powder concrete sample and loaded into high density polyethylene (PE) vials (8 mm dia, x by 5.8 mm height) sealed with snap-cap. Additional vials contain the following: for quality control (QC), five replicates of SRM 1880b (Portland Cement); for calibration, high purity chlorine standard solution (SRM 3182), high purity salts of $CaCO_3$ (SRM 915b) and SiO2 (Alfa Aesar). The chlorine standard solution was dispensed into PE vials filled with high purity powder graphite to have the same geometry as the samples. Blanks were prepared using vials filled with graphite and empty vials. The samples were distributed into 5 rabbits by the nominal Cl level, with each rabbit containing 7 vials (triplicate samples, QC, standards and/or blank). High purity Ni foils (3 mm dia. x 0.03 mm thickness, about 7.5 mg) as neutron-flux monitors were sandwiched between vials. The packaging resulted in 5 rabbits and 35 vials total, plus 40 flux monitors.

Irradiations were carried out at the Rhode Island Nuclear Science Center 2 MW light water reactor (thermal flux 10^{12} n/cm^2-s. fast flux 10^{11} n/cm^2-s). After a 1 min irradiation, the vials were counted and recounted based on the nuclide of interest in a high purity germanium detector, either in contact with the detector, or 2 cm away, with counting times from 1200 s to 3600 s, and some longer counts of 18000 s. The entire experiment took place over a period of 3 months, generating a total of 110 spectra. The detector efficiency was calibrated daily. Spectra were analysed using Genie 2000 with standard nuclear library, generating reports on nuclide identification and activity. A Python script was written to process all the PDF report files and to perform further decay correction to the time of irradiation for the select nuclides. By taking ratio to the standard with known mass, activities were converted into mass fractions. The 5 levels of apparent Cl mass fractions (%) were determined to be 2.1, 1.1, 0.23, 0.076, and 0.001 (no Cl added), respectively, well separated even with 10% uncertainties based on counting statistics. These were in good agreement with results from subsequent manual analyses of the stored spectra. A complete analysis of the data will guide future effort with optimized times for irradiation, waiting, and counting.

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129

Qualifying the raw materials of additive manufacturing for use in Neutron Activation Analysis

Katalin Gméling[1*]*, Zoltán Schneider*[2]*, Zoltán Fehér*[3]*, Gábor Benyács*[1]*, Sándor Janik*[4]

[1]Nuclear Analysis and Radiography Department, Centre for Energy Research, Budapest, Hungary
[2]Kvint-R, 3D Printing Solution, Budapest, Hungary
[3]Varinex, Industrial 3D Printing, Budapest, Hungary
[4]Reactor Department, Centre for Energy Research, Budapest, Hungary
[*]E-mail: katalin.gmeling@ek-cer.hu

Keywords: PEI, PEEK, high-temperature resin, reactor irradiation, NAA

Nuclear research and industry require different kinds of radiation-resistant and radiation-shielding materials. There is a need in the Neutron Activation Analytical (NAA) community for radiation-resistant sample holders, which are easy to prepare, and cost-effective. 3D printing, also known as additive manufacturing, could offer an obvious solution, if providing radiation-resistant raw materials, which are easy to decontaminate, thus they are supposed to be acid-proof and heat-resistant. There are countless 3D printing plastics, and the manufacturers provide extensive information on their physical behaviour, but there is no data on their chemical compositions, trace element contents, radiation resistance, and activation properties.

These polymers are mostly carbon and hydrogen but would be advantageous to have nitrogen-containing material instead of hydrogen, as nitrogen absorbs fewer neutrons. Testing the purity of the material is also important, as even a small amount of contaminating trace elements in the material can increase their residual activities, making them problematic to handle after irradiation.

Material testing started with those of the highest heat resistance, as heat is generated in the material due to neutron irradiation. PEEK, PEKK, PEI, and other ultra-high temperature plastic were proposed by 3D printing companies because they have high strength and stability at high temperatures, and very low coefficient of thermal expansion, which make them ideal for applications where dimensional stability is also important. Next to that, they have good chemical resistance and flame retardance. The NAA measurement on the samples showed that the purest material is Stratasys ULTEM 1010, which is a type of polyetherimide (PEI) resin, and HT250 as well as HI TEMP 300-AMB are ultra-high temperature plastics have adequate chemical compositions for irradiation. PEEK is considered one of the best-performing, semi-crystalline thermoplastics available today, but it has a bit higher Na, K, and Ca contents than PEI. PEKK is developed for space and industrial applications, as Stratasys Antero 800NA characterized by high strength, high heat resistance, low outgassing, and superior chemical resistance, but it has high Cl content.

Further testing of these classes of materials is essential for different irradiation conditions and for the fabrication of customized tools to be used in a radiation environment, to allow their widespread use and thereby advance the use of nuclear analytical techniques.

232

Availability of neutron activation facilities to foreign users at Research Center Řež, Czech Republic

Alena Krechlerová[1*], Michal Košťál[1], Ján Milčák[1], Jan Kučera[2]

[1]Research Center Řež, Hlavni 130, Husinec Řež 250 68, Czech Republic
[2]Nuclear Physics Institute of the Czech Academy of Sciences, Hlavni 130, Husinec Řež 250 68, Czech Republic
[*]E-mail: Alena.Krechlerova@cvrez.cz

Keywords: experimental reactor, reference neutron field, ^{252}Cf source, D-T fast neutron source

Research Centre Řež is a research organization operating various facilities usable in neutron physics and radioanalytical measurements, namely two experimental nuclear reactors – a “zero” power (max. 5 kW) LR-0 reactor and a medium power (max. 10 MW) LVR-15 reactor. The LR-0 is mostly intended for reactor physics issues predominantly focused on reactor dosimetry. In the LR-0, a Benchmark Reference Neutron field has been established, a world unique tool used in development of new neutron dosimetry library IRDFF-II [1]. The LR-0 reference field main attributes include a large, dry central irradiation cavity of about 0.5 L volume with a neutron fluence rate of 2+E8 cm^{-2} s^{-1}. This facility allows for irradiation of large samples and even testing of neutron dosimetry devices.

The LVR-15 is a 10 MW multipurpose research reactor, predominantly used for production of various medical and industrial isotopes. In its core, there are four vertical channels usable in neutron activation analysis (NAA) and other activation studies. Three of them are used for long-time irradiation (several hours up to several days), one is equipped with pneumatic transport facility with transport time of 3.5 s, which allows for short-time irradiation (10 s to 3 min.). Unlike the other vertical channels, the last one is operated by the Nuclear Physics Institute of CAS (NPI). In all these channels, maximal neutron fluence rates of thermal, epithermal, and fast neutrons are 3E+13 cm^{-2} s^{-1}, 9E+12 cm^{-2} s^{-1}, and 6E+12 cm^{-2} s^{-1}, respectively. There is also a possibility to irradiate in pure thermal neutron spectra using a silicon filtered neutron field (fluence rate 2E+8 cm^{2} s^{-1}, Cd-ratio 250) in one of horizontal channels of the LVR-15 reactor. It is essential property suitable for calibration of spectrometers during benchmarking of neutron leakage measurements from various material blocks. Irradiation facilities at the LR-0 and LVR-15 reactors can be offered to foreign users in an open access regime for non-commercial purposes.

Another interesting irradiation facility is a ^{252}Cf source (neutron emission 1.4E+8 s^{-1} as of January 2023) operated by Research Centre Řež. It was used in past for measurement of spectrum averaged cross sections, which support the development of IRDFF-II dosimetry library and is usable for testing of various neutron detection tools or activation in standard field. There is also a D-T generator of IEC type [2] (i.e., inertial electrostatic confinement) available, which is applicable in cross section measurements for high energy neutron activation issues. This source provides 14 MeV neutrons with a maximum neutron emission of 1E+10 s^{-1}.

The irradiation facilities of both reactors and other neutron sources are equipped by a number of gamma-ray (mostly HPGe) and neutron spectrometers both in Research Centre Řež and NPI, which allow to examine most activated materials.

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256

Modernized control of a pneumatic facility for short-time NAA at LVR-15 reactor in Řež, Czech Republic

Zbyněk Horák, Jiří Mizera, Jan Kameník, Marek Fikrle, Jan Kučera[*]

Nuclear Physics Institute of the Czech Academy of Sciences, Husinec-Řež 130, Czech Republic
[*]E-mail: kucera@ujf.cas.cz

Keywords: neutron activation analysis, short-time irradiation, LVR-15 reactor

Neutron activation analysis (NAA) with short-lived radionuclides ($T_{1/2}$ in the range of 10 s to several h) provides the possibility to determine a significant number of elements, namely F, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Mn, Cu, Sr, Ag, In, Te, I, Ba, Dy, and U. For this purpose, experimental nuclear reactors are being equipped with a fast transfer facility to be able to carry out such type of measurement. Formerly, the LVR-15 experimental reactor with a thermal neutron fluence rate of 3×10^{13} cm^{-2} s^{-1} in a vertical irradiation channel at the outskirts of the active core was equipped with a vacuum-driven transfer facility with transport time of 3.5 s. It was operated using an Atmel 89C2051 microprocessor, which controlled just the transport of a polyethylene (PE) irradiation capsule (rabbit) and its irradiation for a preset time. Since the control unit became obsolete, spare parts became unavailable and servicing became problematic, the whole control system has been modernized.

Newly a PC is used to control the transfer system and also a Canberra Genie gamma-spectrometer with two HPGe detectors (one coaxial and one planar) driven by Genie™ 2000 spectrometry software. Hardware is controlled by inexpensive NI (formerly National Instruments) entry-level stand-alone data acquisition (DAQ) devices USB-6001 and USB-6501. Dedicated printed circuit boards are used for adapting inputs and outputs of the above DAQ devices to the pneumatic transfer system hardware (vacuum valves and pumps, transport sensors).

A control program was developed in NI´s LabView graphic programing environment. It communicates with Canberra Genie™ 2000 spectrometric software via ActiveX components. Together with the new control unit, also the laboratory terminal for loading/unloading the rabbit was redesigned and new transport sensors were made and installed.

The modernization of the pneumatic transfer system resulted in simplification of the operator work and improved documentation of the irradiation process from the control PC log with details of the irradiation and acquisition procedures. Manual operations consist of only loading the rabbit with the sample into the terminal prior to irradiation and unloading the rabbit, the sample repacking and transfer to one of the HPGe detectors after irradiation. Compared with the old system, the transfer time of 3.5 s has not changed, as well as the minimal and maximal irradiation times in the range of 5 s to 3 min. The maximal irradiation time is restricted by the limited radiation and temperature resistance of the PE rabbit.

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242

Oxygen determination in the Ti certified reference material ERM-EB090b by instrumental photon activation analysis

Ivana Krausová[1], *Jiří Mizera*[1,2*], *David Chvátil*[1], *Václav Olšanský*[1]

[1]Nuclear Physics Institute, Czech Academy of Sciences, Husinec-Řež, Czech Republic
[2]Institute of Rock Structure and Mechanics, Czech Academy of Sciences, Praha, Czech Republic
[*]E-mail: mizera@ujf.cas.cz

Keywords: IPAA, titanium, oxygen, certification, CRM

The certified reference materials (CRM) ERM-EB090a and ERM-EB090b (Titanium) were released with certified values for trace metal contents in 2018. Beside trace metal impurities, also contents of C, H, N and O are important for mechanical properties of titanium. Therefore, in 2019-2020 a new study was organized as an interlaboratory comparison to get quality data for certifying the mass fractions of these elements. For C assay, combustion combined with IR spectrometry was used exclusively. For N, H and O assays, the inert gas fusion technique was used followed by thermal conductivity detection (N) and IR detection (H and O) by most laboratories. As alternatives, two nuclear analytical methods were employed – prompt gamma activation analysis (PGAA) for H assay, and instrumental photon activation analysis (IPAA) for O assay [1]. Performance of IPAA in O determination in the Ti CRM ERM-EB090b utilizing irradiation with 23 MeV bremsstrahlung photons produced at the MT-25 microtron is presented in our contribution.

In principle, IPAA is capable of determining C, N and O via their short-lived photoactivation products ^{11}C, ^{13}N and ^{15}O, pure positron emitters measurable only via the annihilation gamma line 511 keV. The nonspecific annihilation radiation is interfered by number of other positron emitting radionuclides, but the interferences can be suppressed by optimizing photon energy and irradiation-decay-counting times thanks to large differences in the threshold energies of photonuclear reactions or in half-lives of their products. For the interfering radionuclides which are not pure positron emitters and have also specific gamma lines, contributions to the 511 keV line can be evaluated and subtracted. We successfully applied such approach previously in the assay of N and F [2,3]. For the CRM ERM-EB090b, preliminary calculations and pilot tests indicated that trace amounts of C and N in Ti are below their IPAA detection limits, and only O determination via ^{15}O (half-life 2.04 min) is feasible. An optimized IPAA procedure included 3-min irradiation, 3-min decay, and a sequence of ten 1-min counting runs, evaluated by the 511 keV line decay curve analysis, with correction for interferences from Ti using the 159 keV line of ^{47}Sc produced from ^{48}Ti as an internal standard, and from Mo and Fe evaluated using external standards. The IPAA result for O content in Ti CRM ERM-EB090b (4.07±0.61 g/kg) is within uncertainty limits in agreement with the assigned certified value (3.57±0.19 g/kg). Performance of the IPAA procedure has mainly been limited by the decay time between the end of irradiation and start of counting, excessively long due to the absence of fast pneumatic transport system (out of operation during the interlaboratory comparison).

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165

Characterization of silicone wristbands as passive underwater samplers for radionuclides

<u>Georg Steinhauser</u>[1], Bin Feng[1,2]*

[1]TU Wien, Institute of Applied Synthetic Chemistry & TRIGA Center Atominstitut, 1060 Vienna, Austria
[2]Leibniz Universität Hannover, Institute of Inorganic Chemistry, 30167 Hannover, Germany
[*]E-mail: georg.steinhauser@tuwien.ac.at

Keywords: fission products, sorption, neutron activation analysis, environmental monitoring, argon, environmental radioactivity, nuclear release

Monitoring of airborne radionuclides usually depends on high-volume samplers that filter large amounts of air. However, continuous sampling in aqueous systems is much more challenging. We have tested regular, commercially available silicone wristbands with respect to their ability to sorb radionuclides from aqueous systems. Although quantification is somewhat challenging, we found that many fission products and activation products are adsorbed by the silicone matrix (e.g., when the wristband is positioned in the pool of a TRIGA Mark II research reactor).

Most surprisingly, the silicone matrix proved to be selective for activated argon, i.e. ^{41}Ar, which called for a more systematic investigation of the argon sorption kinetics inside a wristband. This study exemplified the usefulness of neutron activation analysis (NAA) for argon, which is not a typical element in NAA.

208

Self shielding effect in a strong absorber of Gd in neutron activation analysis

Gwang-Min Sun[1*], *Kishore B. Dasari*[1,2], *Jaegi Lee*[1], *B.G. Park*[1], *M.S. Kim*[1]

[1]Neutron Utilization Research Division, Korea Atomic Energy Research Institute, Daejeon, Republic of Korea
[2]Research Institute of Natural Science, Gyeongsang National University, Jinju, Republic of Korea
[*]E-mail: gmsun@kaeri.re.kr

Keywords: self-shielding effect, strong absorber, Gd, effective absorption radius

^{155,157}Gd are non-1/v absorbers and 2200 m/s absorption cross-sections of ^{155}Gd and ^{157}Gd$_{⍰}$is 60,900(1,100) b and 254,300(4,900) b, respectively, which are the highest among the stable natural isotopes. Their effective absorption radii are 1.38 Å and 2.84 Å, respectively. Macro cross-section for ^{157}Gd($S_{\gamma,157}$) is about 970 cm^{-1}, and absorption mean free path(l_γ) is about 10 mm. The neutrons with energy around a resonance at 0.0314 eV, and the lower-energy neutrons undergo the self-shielding effect due to the strong absorption within the target. And the thick target also shows heavy self-shielding effect. To check the change of the neutron spectral density inside the target, we investigated the absorption rate of neutrons at the condition of the parallel neutron beam incident on a purely absorbing planar Gd target of various thicknesses and the diluted Gd samples with thin target approximation. The effect of strong absorption within the target was investigated on the concept of effective absorption radius. Considering the actual experimental environment, it was difficult to make a thin target (⍰$_{⍰}$(v_r) t<<1) because the cross-section of Gd is very large even when t ~ 1 μm. In order to satisfy the condition of ⍰$_{⍰}$(v_r)t ~ 0.1% << 1, the thickness of t ~ 10^{-8} cm must be implemented. Therefore, in the case of an element with a high cross-section such as Gd like this study, target was made as a diluted target by dissolving Gd_2O_3 , $^{155}Gd_2O_3$, and $^{157}Gd_2O_3$ in nitric acid and diluting them respectively. We investigated the non-linearity in the analytical sensitivity of Gd according to the Gd mass and some theoretical evaluation was done and the simulation was compared with the experimental results.

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14

Perspective and progress of neutron activation analysis at CARR

Yonggang Yao[*], *Caijin Xiao*

Department of Nuclear Physics, China Institute of Atomic Energy, No.1 Sanqiang Road,
102413 Beijing, China
[*]E-mail: yaoyonggang1985@126.com

Nuclear activation analysis (NAA) is a widely applied analytical technique which allows qualitative and quantitative elemental analysis of various types of samples by means of nuclear radiation measurements. There are four types of NAA technologies are developing at the 60 MW China Advanced Research Reactor (CARR) of China Institute of Atomic Energy (CIAE) with the thermal neutron fluence rate of 8 x10^{14} cm^{-2} s^{-1}. The main goal is to establish a scientific CARR-based NAA platform including instrumental NAA (INAA), prompt gamma-rays activation analysis (PGAA), neutron depth profiling (NDP), and delay neutron counting (DNC). The platform will be equipped with advanced devices, analysis techniques, optimized parameters and expert system. As a consequence, the NAA platform are potential multifunctional tools. Therefore, the subject of this study represents an important step toward the development of a multi-radiation NAA platform for several applications in materials, geochemistry, environment, biology, archaeology and nuclear science, etc. We look forwards to the adoption of NAA in various fields of research in China thanks to the advanced platform. Besides, a recent research work (i.e., the Chang'E-5 lunar samples analyzed by the instrumental NAA) will simply be introduced.

Nuclear forensics

94

Star segmentation and classification using deep learning in nuclear forensics FTA

Noam Elgad[1*], *Itzhak Halevy*[1], *Mark Last*[2], *Rami Babayew*[1]

[1]Unit of Nuclear Engineering, Ben Gurion University, Beer Sheva, Israel
[2]Department of Software and Information Systems Engineering, Ben Gurion University, Beer Sheva, Israel
[*]E-mail: Noam_elgad@yahoo.com

Introduction:

Fission Track Analysis (FTA) study of nuclear forensics includes a detection of the presence of fissile materials. The research is carried out by collecting radioactive samples from objects in an arena of a nuclear event. After collecting the samples using a dedicated sampling paper, it is placed between two Lexan resin sheets, which are used as a detector, and irradiated with a flux of thermal neutron that creates fission traces. The shapes of the traces detected are various star-like figures (fission roses) that express the tracks of nuclear fission products. Identification of those traces can tell interesting things about the origin of the measured substance. The process of identifying the shapes is carried out under a microscope by collecting 700 images out of 7,000 selected, separating the sample paper and searching for the shapes in each of them. This task can be grueling and depends on the human eye limitations, while finding an elusive star-like shape is much like finding a hole of a needle in a haystack. The star identification process goes a long way from manual naked eye scan to the last automatic image processing tool being developed for this purpose in the recent years.

Methods:

This work proposes a new approach to the detection of star shape in images using the latest technologies of deep learning models for fission track classification and segmentation, using U-Net network based on a network of neurons of the Fully Convolutional Network type with a 5-fold cross validation analysis for small sized stars, i.e. less than 60µm, and under 200 pixels with less than 10 leaves and without black center.

This work included the creation of a new database of image stars, characterization of different star types, model design, architecture and optimization; conducting training for single class and multi class data sets; development of segmentation metrics evaluation; automation of segmentation for batch of multiple images; frequency and epoch optimization tests; targeted research to set thresholds for filtering background noise and to improve identification; development of semi-automated adaptive threshold setting for data labeling and a collaboration with additional research adjusting the model in order to classify several simulated artificial stars.

Results:

The model we created achieved a total area of 0.84 under the ROC curve. In addition, we built a model for bigger and richer stars that achieved a total area of 0.90 under the ROC curve. Also, preliminary models were built which can differentiate between roses of different shapes and sizes at the same time.

Conclusions:

This work offers a novel approach for identification of star shapes in microscopic images using the latest technologies of deep learning for segmentation and classification. New methodology for data tagging using a semi-automation labeling process were introduced. U-Net fully convolutional network (FCN) model were designed to perform segmentation of different patterns of star like shapes both in single class and multi class segmentation.

121

Lead isotopic ratios analysis for uranium ore and U_3O_8 for nuclear forensics purposes

Tebogo Gilbert Kupi[1*], *Arefa Montshioa*[1], *Manny Mathuthu*[1], *Marthie Coetzee*[2], *Danel van Tonder*[2]

[1]Centre for Applied Radiation Science and Technology, North-West University, Mahikeng Campus, Mahikeng, South Africa
[2]Unit for Environmental Sciences and Management, North-West University, Potchefstroom Campus, Potchefstroom, South Africa
[*]E-mail: corresponding.tebogo.kupi@nwu.ac.za

Keywords: lead, isotopic ratios, nuclear forensics, signature

In this work, uranium ore and U_3O_8 samples selected for investigation originate from a South African uranium mine. The aim of this study was to determine the lead isotopic ratios of the samples as a signature for the uranium mine. Measurements were carried out using an inductively coupled plasma mass spectrometer (ICP-MS) PerkinElmer NexION 2000. Both measured results of samples show significant variation and thus provide valuable information about the processing stage, geochemical formation, and origin.

202

Study on uranium age-dating using ^{230}Th/^{234}U radiochronometer with the upgraded chemical separation method

Ranhee Park[1*], *Eunju Choi*[2], *Jungwoon Choi*[1], *Kun Ho Chung*[3], *Sang Ho Lim*[1]

[1]Nuclear Chemistry Technology Division, Korea Atomic Energy Research Institute, Daejeon, Republic of Korea
[2]NORM Safety Center, Korea Institute of Nuclear Safety, Daejeon, Republic of Korea
[3]Environmental Safety Technology Research Division, Korea Atomic Energy Research Institute, Daejeon, Republic of Korea
[*]E-mail: ranhee@kaeri.re.kr

Keywords: uranium age-dating, MC-ICP-MS, ^{230}Th/^{234}U radiochronometer, nuclear forensics

The analysis of nuclear materials for the nuclear forensic provides important information in establishing the origin, processing history, and expected intentions of nuclear material(NM). Radiochronometric age is an important tool to establish a timeline of nuclear material production for nuclear forensic investigations. After the chemical separation of each radionuclide in the NM purification process, their radioactive progenies begin to grow in the nuclear material. Therefore, the date of the last chemical parent-daughter separation can be calculated from determining accurate amounts of parent and daughter isotopes in the sample if a perfect initial purification and no accidental contamination are assumed. Uranium age-dating methods are based on the accurate determination of a daughter-mother radionuclide pair such as ^{230}Th/^{234}U, ^{231}Pa/^{235}U. Any uranium series age-dating method requires isotopic ratios or abundances measurement of each radionuclide: specifically determined by direct atom counting on a mass spectrometer. In this research, we have studied uranium age-dating using ^{230}Th/^{234}U radiochronometer, one of the most straightforward chronometers to determine the date of uranium production. Two different methods (applied by TEVA or UTEVA resins) to chemically separate mother and daughter nuclides were presented and each result was compared in terms of the calculated age of uranium mateials. Detailed uranium and thorium isotopic analyses with MC-ICP-MS (Neptune Plus, Thermo Scientific, Germany), calculation, and data analysis are also presented.

Acknowledgments

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125

Applicability of atomic force microscopy in nuclear forensic examination

Csaba Tóbi[1,2]*, Emese Csipa*[2]*, Nguyen Quoc Khánh*[3]*, Zsolt Kovács*[4]*, Zoltán Homonnay*[5]

[1]Hevesy György PhD School of Chemistry, Eötvös Loránd University, Budapest, Hungary
[2]Nuclear Security Department, Centre for Energy Research, Budapest, Hungary
[3]Institute of Technical Physics and Materials Science, Centre for Energy Research, Budapest, Hungary
[4]Department of Materials Physics, Eötvös Loránd University, Budapest, Hungary
[5]Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary
[*]E-mail: tobi.csaba@ek-cer.hu

Keywords: atomic force microscopy, nuclear fuel pellets, nuclear forensics, scanning electron microscopy

Nuclear forensics is the examination of (1) nuclear or other radioactive material or (2) evidence contaminated with radionuclides in the context of legal proceedings under international or national law related to nuclear security. Nowadays, there are several non-destructive analytical methods which can be used to categorize and characterize nuclear or other radioactive materials for nuclear forensic purposes. These methods also include various microscopic techniques such as optical or scanning electron microscopy. However, these techniques give information mainly on surface morphology. In the case of the surface analysis of nuclear fuel pellets data is provided regarding the crystal structure, which can be unique regarding the production technology of the given fuel pellet. The atomic force microscopy (AFM) can be useful technique for this purpose, too.

The AFM is used in many fields of material analysis and connected scientific research activities by scanning the nanostructure of materials and examining thin layers. Thus, also a useful tool for the examination of uranium-containing materials, such as uranium oxide nanolayer. There is just a limited number of research papers in the literature focusing on nuclear forensic analysis by AFM technique.

In our research 5 nuclear fuel pellets, with different origin and morphology, were analysed by AFM to examine the nuclear forensic applicability of the instrument, i.e. to identify the origin and history of the material. Furthermore, the practical applicability of the measurement results provided by the AFM were compared with the results of the scanning electron microscopic technique.

182

Age dating measurements by laser ablation multi-collector ICP-MS in uranium materials

Zsolt Varga[*], *Adrian Nicholl, Maria Wallenius, Klaus Mayer*

European Commission, Joint Research Centre (JRC), Karlsruhe, Germany
[*]E-mail: zsolt.varga@ec.europa.eu

Keywords: age dating, production date, LA-MC-ICP-MS, uranium

To evade the malicious use of the nuclear materials, international safeguards system lead by the International Atomic Energy Agency (IAEA) has been established to verify the correctness and completeness of states' declarations about the nuclear-related undertakings and nuclear material accountancy. However, if such nuclear materials out of regulatory control are found or intercepted, a detailed investigation is required to identify the possible origin, intended use and potential risk related to the material. Such studies involve comprehensive physical, chemical and isotopic characterization (e.g., physical dimensions, crystal structure, chemical impurities) as well as the interpretation of the measured data [1, 2].

Besides these parameters, the elapsed time since the last chemical purification of the nuclear material (commonly referred to as the *age* of the material) can also be measured. This unique possibility is based on exploiting the presence and decay of radioactive nuclides: during production, the radioactive material is chemically purified from their impurities including also the radioactive decay products. Thus, after this process, the radioactive progenies start to grow-in into the material. By the measurement of the daughter-to-parent ratio in the sample (often referred to as *chronometer*), the elapsed time since the last separation (i.e., the age) can be calculated according to the decay equations. This age and the respective production date can help either to identify the origin of the questioned illicit sample or to verify the source of the feed (starting) nuclear material. However, the accurate and precise measurement of the trace-level decay products (generally the ^{230}Th daughter nuclide from the minor ^{234}U parent nuclide is used) is often tedious, time consuming and labour-intensive.

In this work, we used a laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) technique to measure directly the production date (age) of uranium samples using the ^{230}Th/^{234}U chronometer. As for this technique virtually no manipulation or chemical separation is needed, we can avoid the problems deriving from tedious sample preparation and standardization issues. Moreover, the analysis could be performed in a few hours. We analysed several uranium materials having different ^{235}U enrichments: these samples were dated earlier with the traditional method [3]. Using low mass resolution and no separation beforehand, the method is prone to the impurities in the sample, however, it can be applied for low-enriched and highly enriched U materials. The achieved age dating precision for highly-enriched U was a few months, thus highly useful in nuclear forensics to easily differentiate the samples of different origin.

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213

^{90}Sr source age dating by LSC and ICP-MS analysis

O. Zhukov[1*], *M. Hryhorenko*[1], *I. Maliuk*[1], *M. Strilchuk*[1], *V. Tryshyn*[1], *H. Vasylyeva*[2], *K. Mayer*[3], *L. Dallas*[4]

[1]Institute of Nuclear Research of the National Academy of Sciences of Ukraine, Kyiv, Ukraine
[2]Uzhgorod National University, Uzhgorod, Ukraine
[3]Joint Research Centre, European Commission
[4]NSDD DOE, US
[*]E-mail: zhukow@ukr.net

Keywords: age dating, ^{90}Sr, ^{90}Y, ^{90}Zr, LSC, ICP-MS

When ^{90}Sr radioisotope source is found out of regulatory control, the age of the source is a key nuclear forensic signature. Age dating of a radioactive source refers to the determination of the source material production date or date of the last chemical separation. ^{90}Sr decays via the short-lived ^{90}Y ($T_{1/2}$=64 h) to stable ^{90}Zr, so ^{90}Zr/^{90}Sr mass ratio serves as a radio chronometer. The goal of this work is to check proposed method of determination model age of the ^{90}Sr-^{90}Y radioactive sources by measuring ^{90}Sr activity via LSC and ^{90}Zr concentration using ICP-MS by processing of common peak with mass 90.

To test the applicability of this method the liquid ^{90}Sr source with well-defined date 23.04.91 of the source production was used. Its specific activity was measured using a low-background liquid scintillation spectrometer-radiometer Quantulus-1220. Each of the measured subsamples was diluted with an organic scintillator Optiphase "HISAFE 3" up to a volume of 20 ml, and the respective spectra were processed. The obtained specific activity of the sample 3.5 ± 0.1 kBq/g corresponds to the concentration of ^{90}Sr 0.69 ± 0.02 ng/g. Then ICP-MS analysis of the same ^{90}Sr-^{90}Y solution was performed. The detection efficiency of the ICP-MS was determined by measuring a mixture of single high-purity standards of stable Sr, Y and Zr. The concentration of ^{90}Zr was calculated as the difference between the total peak with mass of 90 and the amount of ^{90}Sr. For the accurate quantification of ^{90}Zr, a correction for molecular interference (^{89}Y^{1}H) and contribution Zr_{nat} at mass position 90 was applied. The calculated concentration of ^{90}Zr was 0.79 ± 0.04 ng/g (Fig. 1).

According to the formula $T = \frac{1}{\lambda} \ln\left(1 + \frac{N_{^{90}Zr}}{N_{^{90}Sr}}\right)$

the age of the radioactive source was determined equal T = 31.7 ± 1.2 years. Considered the certificate of the investigated source, its age is more than 30.2 years.

Figures

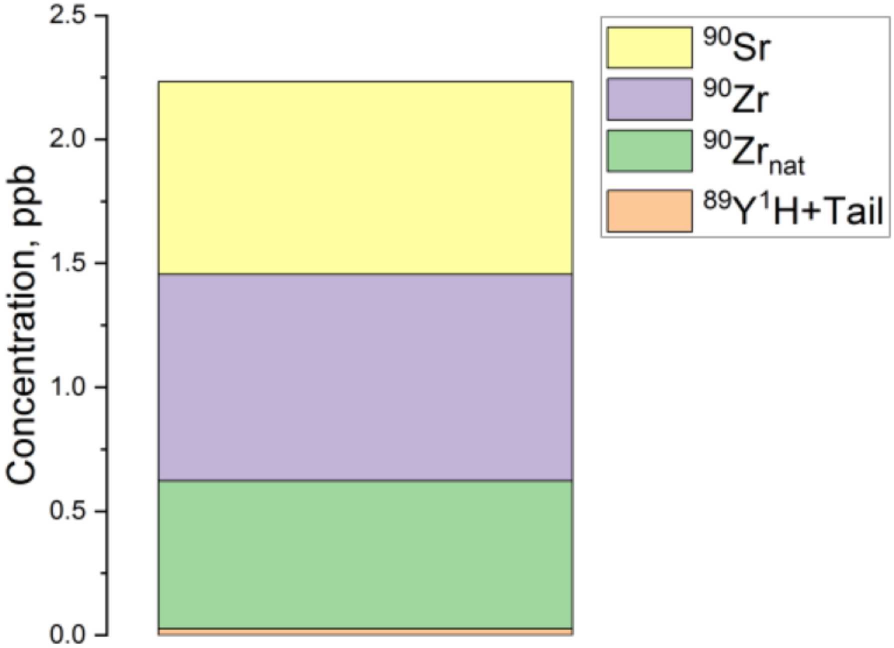

Fig. 1. The concentration of ^{90}Sr, ^{90}Zr, ^{90}Zr$_{nat}$ and tailoring effects in ICP-MS peak with mass 90 amu.

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Production of radionuclides

206

Alpha-conversion electron coincidence in alpha spectra

M. Hryhorenko[1*], *I. Maliuk*[1], *O. Odintsov*[2], *M. Strilchuk*[1], *V. Tryshyn*[1], *M. Zayats*[1], *O. Zhukov*[1]

[1]Institute of Nuclear Research of the National Academy of Sciences of Ukraine, Kyiv, Ukraine
[2]Institute of NPP Safety Problems of the National Academy of Sciences of Ukraine, Chornobyl, Ukraine
[*]E-mail: marina_grigorenko@ukr.net

Keywords: alpha spectra, conversion electron, coincidence

When measuring alpha spectra on a silicon detector with ion implantation the conversion electrons accompanying the alpha decay are also registered by the detector. The alpha spectrum is distorted by true coincidences between alpha particles and electrons. A possible solution to this problem would be measurements at a long distance from the detector, but in the case of low activity of the source or when measuring long-lived nuclides, in order to achieve the required statistical accuracy, measurements are carried out relatively close to the detector [1].

In the alpha spectrum of ^{238}Pu, below the alpha line corresponding to the decay of ^{238}Pu into the ground state of the daughter nucleus ^{234}U, there are two more peaks of alpha particles with energies of 5357 and 5456 keV, respectively, from the decay into excited states of ^{234}U. These excited states are instantaneously deexcited by the emission of conversion electrons due to low-energy gamma transitions. As a result, there is simultaneous emission of an alpha particle and a conversion electron, which can be simultaneously registered by a silicon detector. Therefore, in the experimental alpha spectrum, we will observe the summation of alpha lines with the spectrum of conversion electrons. This effect significantly complicates the processing of alpha spectra, especially in cases where alpha spectra from different nuclides overlap, as in the measurement of ^{239,240}Pu.

Several technical ways of combating this effect are proposed – applying a positive potential to the sample, and using a magnetic field that blocks electrons from entering the detector. In this work, we propose another way of taking into account the summation of alpha and conversion electrons – by modelling the processes of nuclear decay and registration spectra using Geant4 [2]. This makes it possible to obtain energy model spectra that take into account the summation of the energies of alpha particles with atomic electrons accompanying the internal conversion process.

For the least-squares fitting, we used the theoretical spectrum in the form of a convolution of model spectra with a function that describes the shape of the monoenergetic alpha line [3]. The proposed method of taking into account the effect of the summation of the energies of alpha particles and conversion electrons allows you to correctly describe the shape of the spectrum both at a distance of 49 mm and 1 mm from the detector.

Acknowledgments

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43

Response function evaluation of the beta radiation for semiconductor detector using Monte Carlo simulation

Mee Jang[*], *Hyemi Cha, Hyun Cheol Kim, Jong Myoung Lim*

Environmental Radioactivity Assessment Team, Korea Atomic Energy Research Institute, Daejeon, South Korea
[*]E-mail: mjang@kaeri.re.kr

Keywords: Monte Carlo simulation, Strontium, Yttrium, Semiconductor detector

In this research, we evaluated the feasibility of detecting the beta radionuclide such as strontium 90 and yttrium 90 using semiconductor detector instead of Liquid scintillation counter. Usually, the analysis of ^{90}Sr and ^{90}Y requires the chemical separation and liquid scintillation counter (LSC). In liquid scintillation counter, the beta radionuclides can be detected using the sample mixed with scintillation cocktail and photomultiplier tube. In Korea, the Quantulus 1220 is the best-selling LSC, but its production was stopped. The 300SL can be used instead of Quantulus 1220, however, the minimum detectable activity of 300SL is higher than Quantulus 1220. Therefore, it is necessary to develop the new detector with similar performance compared Quantulus1220. There are several possible options of semiconductor for beta radionuclides detection [1-3]. In this research, we simulated the response function of the semiconductor detector such as silicon and CdTe detector using Monte Carlo code. We evaluated the response function according to the thickness and area of the detector, and we designed the system using the results.

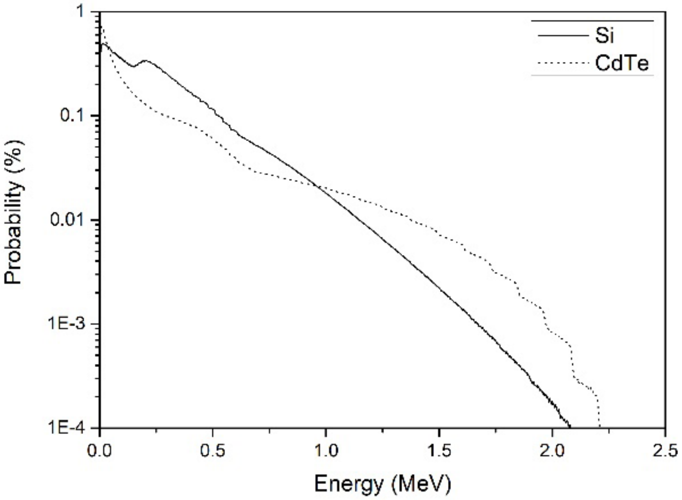

Figure 1. Example of the response function semiconductor detector for ^{90}Sr and ^{90}Y source using MCNPX

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This work was supported by the Nuclear Safety Research Program through the Korea Foundation of Nuclear Safety (KoFONS) using the financial resource granted by the Nuclear Safety and Security Commission (NSSC) of the Republic of Korea.

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132

Low-level Sr-90 measurements within the new concept of radiation monitoring of surface waters in the Czech Republic

Jan Kujan[*], *Ondřej Pařízek, Michal Fejgl*

National Radiation Protection Institute, Prague, Czech Republic
[*]E-mail: jan.kujan@suro.cz

Keywords: surface water contamination, Sr-90, radiation monitoring

Within the project TK02010064 of the Technology Agency of the Czech Republic, a new concept of radiation monitoring of surface waters was proposed.

As the core of the newly created monitoring system, mainly devices of innovative design with the ability of continuous determination of gamma activity concentration were designed. In addition to these systems, advances have been made in the determination of beta activity, including procedures using advanced detection technologies such as fixed scintillators or hybrid pixel detectors.

This paper will present the characteristics of the Timepix detector for the sensitive determination of Sr-90 activity concentration.

This relatively new technology is used in many areas of radiation protection with the advantage of the ability to determine particle trajectories, but in well shielded environments it can also provide low cost portable sensitive measurements of beta activity due to the low background contribution.

This paper will discuss the practical aspect of using this instrument for the purpose of Sr-90 activity concentration determination with emphasis on the chemistry, shielding properties and filtering of the electronic output signal.

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89

Case study: Background fluctuations of gamma detectors in laboratories with a modern ventilation system

Katarzyna Szarłowicz[*]*, Filip Jędrzejek, Marcin Stobiński*

AGH University of Science and Technology, Faculty of Energy and Fuels, Kraków, Poland
[*]E-mail: szarlowi@agh.edu.pl

Keywords: gamma spectrometry, particulate matter, natural isotopes in air, background radiation

This work discusses the issue of background radiation instability, based on a case study from the operation of an HPGe gamma detector located in the building with a modern ventilation system.

In newly constructed commercial buildings, it is increasingly common practice to use special energy-efficient ventilation and air conditioning systems. These are an economic excellent solution, as they have coupled air recovery systems, which are a source of savings related to heating and air conditioning. However, from the perspective of low-level measurements of natural radioactive isotopes, these systems can cause deterioration in the quality of the analytical results. This is caused mainly by the instability of the radioactive background caused by the increased rate of air flow from outside the building, and the specification of such installations. The air circulation is forced by pumps and the amount of air exchanged is several times greater than in gravity ventilation systems. In addition, air is pumped from air intakes located on the roofs of buildings, where higher concentrations of particulate matter periodically occur. The air intakes are equipped with only simple filters that retain relatively large particulate matter when radioisotopes are accumulated on the fine fraction. This has been proven experimentally, in particular for the isotope ^{210}Pb.

To improve the background parameters of the spectrometer, a special system was implemented to ventilate the detector chamber, where the air stream is first cleaned on an H13-class HEPA filter. It is then combined with the stream of nitrogen evaporating from the Dewar vessel and delivered to the sealed detector chamber. The overpressure in the chamber, blocks the flow of air by any other route than through the filter system and the chamber is filled with purified air. To test the functionality of the developed filtration system, an automatic measurement system was built that allowed cyclic measurements. The system allowed for alternating the recording of the spectrum from the purified air and directly from the ambient air, in 4 h cycles. Parallel with the spectrometric measurements, the concentration of particulate matter was measured in the same system as the spectrum. This allowed us to relate the concentration of PMs to the number of counts for specific isotopes in the gamma spectrum.

The filtration system has accomplished its purpose. Improvements in background counts were observed, especially for the ^{210}Pb isotope. These results validate the existing theory; it is predicted that the lead isotope in the atmosphere is absorbed by dust particles, and the relatively long half-life leads to increased concentrations in airborne aerosols [1,2]. Improvements in spectrum quality were also observed for isotopes such as ^{40}K, ^{214}Pb, and ^{214}Bi.

Acknowledgments

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87

Laboratory incinerator for solid tritium waste

Catalin Stelian Tuta[1*], *Cristian Postolache*[1], *George Bubueanu*[1], *Catalina Mihaela Barna*[1], *Irene Popovici*[2]

[1]"Horia Hulubei" National Institute for Physics and Nuclear Engineering, Magurele, Romania
[2]Romanian National Commission for Nuclear Activities Control, Bucharest, Romania
[*]E-mail: catalin.tuta@nipne.ro

Keywords: tritium, radioactive wastes, incinerator

In both CANDU (from Cernavoda, Romania Nuclear Power Plant) and ITER (International Thermonuclear Experimental Reactor) type reactors, a wide range of wastes containing tritium radioisotope is generated [1]. The pure low energy beta radiation and physico-chemical properties (permeation in most materials, diffusivity, spontaneous isotope exchange, etc.) of tritium require a specific approach [2]. Also, the solid waste accurate radiological characterization is difficult due to the uneven distribution of tritium in different materials. This fact, as well as and previous leaching tests do not recommend the final storage of tritiated waste using classic methodologies [3]. The conversion of tritium from radioactive waste to tritiated water, followed by radionuclide concentration and quantitative recovery is the optimal solution [4].

In this paper, a mini-incinerator dedicated to tritium containing conditioning waste is presented.

The main technical characteristics of the new equipment are:

- Active incinerator volume made 316 L stainless steel with 40 L capacity;
- Two stages Incineration/Calcination system (thermal degradation in air flow and catalytic oxidation of partial combustion products);
- Combustion gases cooling system;
- Tritiated water vapor retention system.

Using a Total Combustion/Calcination facility [2], the optimal thermal regimes for each type of radioactive waste were identified and the amounts of non-radioactive residues resulting from the incineration/calcination stages were estimated.

The new facility was tested on a representative range of tritium waste. The residual tritium in resulted residues was determined using Total Combustion/Calcination coupled with Liquid Scintillation Counting method [2].

The maximum processing capacity of non-combustible solid waste is up to 20 kg/batch. In the case of combustible waste, the processing capacity is smaller by an order of magnitude.

The new equipment can be used in tritium laboratories for preconditioning of tritium waste.

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Prompt gamma activation analysis

82

Developing a PGNAA setup for heavy metal detection in solid samples

Tariq Al-Abdullah

Physics Dept, King Fahd University for Petroleum and Minerals
E-mail: tariq.alabdullah@kfupm.edu.sa

A valuable method for figuring out the concentrations of various elements in natural materials, either online or in situ, without changing their chemical forms in matter, is prompt gamma-ray neutron activation analysis (PGNAA). The current study sought to increase the yield of a portable PGNAA (Genie 16) system that records gamma rays from neutron inelastic scatterings utilizing a $CeBr_3$ detector and a dc 2.5 MeV neutron beam. It is difficult to prevent the superimposition of gamma rays from the element of the detector and those from heavy metals. Testing was done to increase the signal-to-background ratio, nevertheless. The efficacy of the new optimization was verified by analyzing the minimum detectable concentrations (MDC) of chrome, titanium, and zinc in soil samples. The MDC values have improved, according to the study. The improvement in the detection limit has also been adopted for detecting the same elements using thermal neutron reactions.

176

Applications of PGAA to investigate cultural heritage items from the Marche Region, Italy

Massimo Rogante[1*], *László Rosta*[2], *Zsolt Kasztovszky*[2], *Zoltán Kis*[2], *László Szentmiklósi*[2], *Boglárka Maróti*[2], *Veronika Szilágyi*[2] *and Katalin Bajnok*[2]

[1]Rogante Engineering Office, Contrada San Michele, 61. 62012 Civitanova Marche, Italy
[2]Budapest Neutron Centre, Centre for Energy Research, 1121 Budapest, Hungary
[*]E-mail: main@roganteengineering.it

Keywords: PGAA, Picenan metalwork, Roman metalwork, pottery

A review is presented concerning PGAA carried out at the BNC to study archaeological finds from the territory of the Marche Region, Italy. In particular, the experiments involved:

– bronze artefacts from the Picenan Civilization, from the necropolis of the Matelica site, province of Macerata, dating back to the 7th century B.C. Several fragments were analysed, together with a piece from the Fabriano archaeological area, province of Ancona, added for comparison
– metal finds dating back to the 9th-4th centuries B.C., also presumably found in the Marche region, belonging to the collection of the *Academia Georgica Treiensis* (AGT) of Treia, province of Macerata; a main purpose has been to compare the acquired data related to the binding elements Cu, Sn and Pb with those obtained by PGAA on the Picenan bronzes from the Matelica necropolis
– votive statuettes made of pottery, belonging to the AGT collection.

These investigations have been performed through a multistage process by combining complementary non-destructive and non-invasive large-scale techniques.

The main objective has been to facilitate the correct description of the considered objects from a technological and a material point of view, also in the perspective of comparison with finds from other sites in the region.

A feasibility study is finally presented, related to the analysis of metal finds from the *Tifernum Mataurense* area in Sant'Angelo in Vado, province of Pesaro-Urbino, archaeologically datable between the early and late empire.

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Radioanalytical methods of long-lived radionuclides

186

Determination of ^{135}Cs activities in spiked radioactive solids by ICP-MS and NAA

Feng-Chih Chang[1*], *Cheng-Yuan Chuang*[2], *Shu-Jen Yeh*[1], *Jiunn-Hsing Chao*[3]

[1]Chemistry Division, Institute of Nuclear Energy Research (INER), 32546 Taoyuan, Taiwan
[2]Radiation Laboratory, Taiwan Power Company, 25399 New Taipei, Taiwan
[3]Nuclear Science and Technology Development Center, National Tsing Hua University, 30013 Hsinchu, Taiwan
[*]E-mail: fcchang@iner.gov.tw

Keywords: ^{135}Cs, radioactive solids, inductively coupled plasma mass spectrometry, neutron activation analysis

Determination of ^{135}Cs/ ^{137}Cs isotopic ratios in environmental samples is a robust tool to investigate the radio pollution source and its migration. However, few information of ^{135}Cs was reported referred to instrument limitations and inter-laboratory comparison activities. In this study, mass concentrations of ^{135}Cs in spiked solid samples were measured by three certified radiochemistry laboratories. The cesium isotopes in spiked radioactive solid samples were extracted by chemical separation methods, ammonium phosphomolybdate (AMP) adsorption and ion-exchange chromatography. Then, ^{135}Cs/ ^{137}Cs isotopic ratios were measured by inductively coupled plasma mass spectrometry (ICP-MS), single and tandem quadrupole MS applied in two different laboratories, neutron activation analysis (NAA) cooperated with high purity germanium (HPGe) detector by the third laboratory. Instrument limitations and isobaric interference during determining ^{135}Cs/ ^{137}Cs isotopic ratios were discussed in this inter-laboratory comparison activity.

Figures

Figure 1. ^{135}Cs adsorbed in resin by shaker

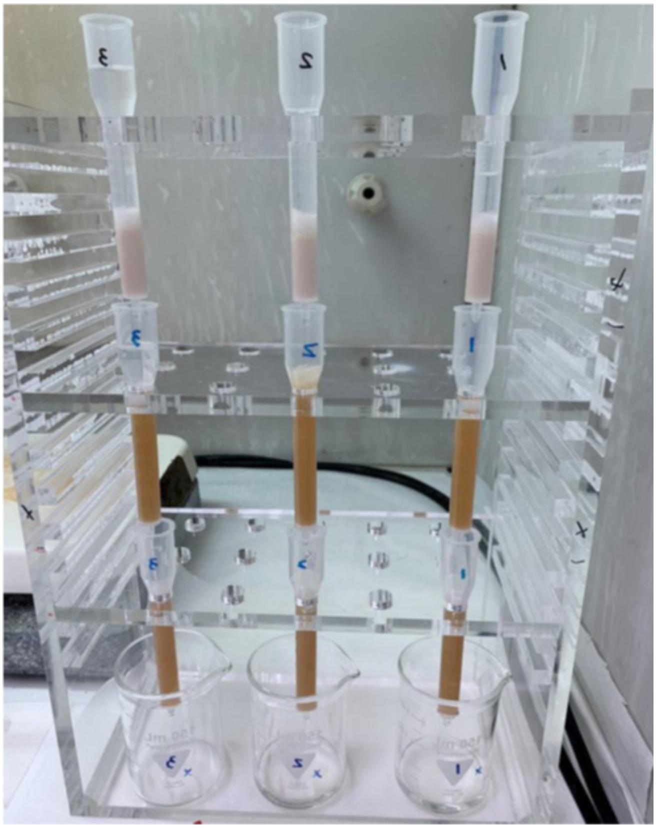

Figure 2. Ion-exchange chromatography before ^{135}Cs measurement

21

Development of a method to quantify Pd-107 in radioactive wastes

Marina Faure[1*], *Céline Gautier*[1], *Isabelle Billard*[2], *Pascal Fichet*[3], *Christelle Colin*[1], *Elodie Laporte*[1]

[1]Université Paris-Saclay, CEA, Service de Physico-Chimie, F-91191, Gif-sur-Yvette Cedex, France
[2]Université Grenoble Alpes, Université Savoie Mont Blanc, CNRS, INP, LEPMI, F-38000, Grenoble, France
[3]CEA, DES/DDSD/DFDE/SGOF, Building 611, F-91191, Gif-sur-Yvette Cedex, France
[*]E-mail: marina.faure@cea.fr

Keywords: radioactive waste, palladium, precipitation, ICP-AES

With a half-life of 6.500.000 years, Pd-107 has the longest period among the radioactive isotopes of palladium. This radionuclide results from the fission of U-235 and needs to be taken into account for the management of radioactive waste in France, especially regarding its contribution to radioactivity for a safe long-term storage. The French National Radioactive Waste Management Agency (ANDRA) requests its declaration above 10^{-4} Bq/g and waste containing more than $3x10^{5}$ Bq/g cannot be handled as “low and intermediate level radwaste” anymore [1]. Considering the increase of decommissioning and dismantling activities of nuclear sites, Pd-107 quantification with good accuracy is a significant challenge. Besides, as Pd is a rare and expensive metal also used in organic chemistry and in automotive industry [2], an efficient extraction method could bring additional information to improve its recycling in other fields. Therefore, developing an accurate method to extract and quantify Pd-107 in nuclear waste is of high interest [3].

As a beta emitter, Pd-107 has to be isolated from interfering radionuclides through a radiochemical procedure prior to any measurement by liquid scintillation counting or ICP-MS. Few methods for Pd-107 quantification in radwaste already exist [4]. However, they often use chemical reagents affected by REACH restrictions or non-commercial extracting agents, which needs to be synthetized by organic chemistry. Moreover, these methods use liquid-liquid extractions, which expose the operator to radiations and potential contaminations. Besides, most studies performed to separate Pd from the other platinum group elements are conducted without taking into account common analytes encountered in radioactive waste such as ^{137}Cs, ^{60}Co, ^{55}Fe, ^{63}Ni or mass-interfering elements like Ag or Zr.

The aim of this presentation is to investigate the selectivity of common precipitation steps in order to isolate Pd-107 in radwaste containing interfering elements. Precipitations with ammonia or with sodium hydroxide of a solution containing 29 elements including Pd are performed. The resulting samples, in particular the supernatants, are analysed by ICP-AES. This first investigation provides information on Pd behaviour in these different conditions, on the efficiency of each precipitation method and will highlight the elements recovered with Pd. The optimization of the radiochemical method also includes separations on Ni-resin® to fully purify Pd.

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127

Measurement of actinides and ^{90}Sr in faecal and urinary samples for PROCORAD 2022

Guosheng Yang[1*], *Eunjoo Kim*[1], *Jian Zheng*[1], *Hatsuho Seno*[1], *Hirofumi Tazoe*[2], *Munehiko Kowatari*[1], *Osamu Kurihara*[1]

[1]National Institutes for Quantum Science and Technology, Chiba, Japan
[2]Institute of Radiation Emergency Medicine, Hirosaki University, 036-8564, Aomori, Japan
[*]E-mail: yang.guosheng@qst.go.jp

Keywords: actinides, ^{90}Sr, bioassay, PROCORAD

To provide timely information for prompt decision-making in emergency radiation therapy, it is critical to maintain the accuracy and precision of bioassay techniques. For this purpose, we participated in the Intercomparison Campaign Plan organized by the Association for the PROmotion of Quality Control in RADiotoxicological Analysis in 2022 (PROCORAD 2022). In PROCORAD 2022, we participated in five item comparisons: 1) Uranium in urine, 2) Actinides in urine, 3) Actinides in faecal matter ashes, 4) Urine DTPA-actinides, and 5) Strontium in urine. Generally, for each item, one blank, one low-level sample, and one high-level sample were included. To measure ^{239}Pu and ^{240}Pu in 20-mL urinary samples by sector field - inductively coupled plasma mass spectrometry (SF-ICP-MS), organic matter decomposition, LaF_3/CaF_2 coprecipitation, and chromatographic purification using 2 mL of AG MP-1M anion exchange resin column were performed [1]. To measure U isotopes in a 2-mL urinary sample by ICP-MS, organic matter decomposition and chromatographic purification using 2 mL DGA extraction resin cartridge were performed. To measure Pu, U, and Am/Cm isotopes in a 300-mL urinary sample and a faecal matter ash by alpha spectrometry, organic matter decomposition, iron hydroxide coprecipitation, and chromatographic purification using 2 mL of TEVA and 2 mL of DGA resin cartridges were performed [2]. For the measurement of ^{90}Sr by beta counting analysis, organic matter decomposition, chromatographic purification using 1 mL of DGA resin cartridge, and iron hydroxide coprecipitation were performed. For the measurement of ^{90}Sr by ICP-MS/MS analysis, organic matter decomposition and chromatographic purification using 2 mL of DGA and 2 mL Sr resin cartridges were performed.

The results in PROCORAD 2022 were all comparable with the assigned values. Especially, the |Z-score| of the results that we submitted for the measurement of Urine DTPA-actinides were below 0.5, and then, our lab was qualified as TOP LABO for this item comparison.

Acknowledgments

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Radioecology and environmental radioactivity

7

Low-level tritium measurements in freshwater and seawater samples

Małgorzata Dymecka[*], *Grzegorz Szaciłowski, Katarzyna Rzemek, Grażyna Kaczyńska, Adam Dudziński, Jakub Ośko*

Radiation Protection Measurements Laboratory, National Centre for Nuclear Research, 7 A. Sołtana Str, 05-400 Otwock., Poland
[*]E-mail: malgorzata.dymecka@ncbj.gov.pl

Keywords: tritium measurement, water, electrolytic enrichment, liquid scintillation counting

Tritium (^{3}H), the radioactive isotope of hydrogen, is formed naturally through the nuclear reactions induced by cosmic rays in the upper layers of the atmosphere. Small amounts of tritium are also formed in the lithosphere. Artificial tritium is released to the environment by nulear weapons testing, spent nuclear fuel reprocesing, nuclear reactors. A large quantity of tritium was released into the atmosphere from thermonuclear weapons tests performed in the 1950s and 1960s.

Tritium is a valuable tracer in hydrological studies, for example for understanding the groundwater cycling [1].

Radiation Protection Measurements Laboratory of the National Centre for Nuclear Research performs environmental radiation monitoring on the premises and in the vicinity of Nuclear Centre at Otwock.

Recently new regulations laying down detailed requirements for the environmental monitoring programme, which should be implemented by the operators of nuclear facilities, have been introduced to Polish legislation (Regulation of the Coucil of Minsiters of August 9, 2022). Due to the fact that new regulations define a number of water matrices such as: groundwater, drainage water, surface water, rainwater for which tritum determination is mandatory, the use of a sensitive method becomes crucial for the ability to monitor variability in tritium concentrations.

The aim of this study was to test and compare two potential tritium determination methods allowing to obtain a lower minimum detectable activity concentration (MDC) than the standard method used in our laboratory. The standard method is based on sample decolourisation with activated carbon, filtration and distillation. Sample pre-treatment is followed by the measurement in liquid scintillation counter.

First tested method was a modified standard method with extended measurement time and optimized cocktail:sample ratio. Second experimental procedure was using electrolytic enrichment step. Both tested methods involved the use of Perkin Elmer Tri-Carb 3180 TR/SL liquid scintillation counter equipped with the BGO detector guard and a cooling system.

Calibration measurements were carried out using certified tritium standard solutions and on the basis of obtained results counting efficiency for both methods and basic parameters: enrichment factor Z, retention factor K and separation factor β describing electrolysis proces were determined.

The analytical procedure was applied to saline and non-saline surface water samples taken from the Baltic Sea and from rivers in various regions of Poland.

Conducted studies have shown that electrolytic enrichment followed by liquid scintillation couting, although more laborous, will be the more preferred method for tritium analyses in natural waters, since it provides over five times lower minimum detectable activity concetration of 0.2 Bq·dm^{-3} and therefore more accurate and reliable results can be obtained.

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85

Temperature effect on U-232 and Am-241 absorption by PN6 in environmental waters

Ioannis Ioannidis[1*], *Ioannis Anastopoulos*[2], *Ioannis Pashalidis*[1]

[1]Department of Chemistry, University of Cyprus, P.O. Box 20537, Cy-1678 Nicosia, Cyprus
[2]Department of Agriculture, University of Ioannina, UoI Kostakii Campus, 47040 Arta, Greece
[*]E-mail: iioann03@ucy.ac.cy

Keywords: uranium, americium, radionuclides, absorption, microplastics, PN6, temperature effect

The adsorption of U-232 and Am-241 at ultra-trace levels by PN6 has been investigated in different natural aqueous media (seawater and waste water) under different temperatures. The results show a significant effect of temperature in sorption efficiency (K_d) of radionuclides by PN6 below the given concentration levels (picomole range). Increasing temperature increases adsorption, indicating that adsorption is an endothermic process. Moreover, evaluation of sorption data reveals that partition coefficient values (K_d) differ significantly between laboratory and environmental waters. In environmental waters, K_d values decrease dramatically due to the presence of various cations (e.g., Ca^{2+}, Fe^{2+}) that effectively compete with U-232 and Am-241 sorption by PN6 and due to increased ionic strength (salinity). However, even under environmental waters, the adsorption affinity of PN6 for both U-232 and Am-241 is significantly higher than those suggested for seawater sediments, indicating the primary role of microplastics as carriers of radionuclides in aquatic environments.

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170

XRF elemental analysis and $^{236/238}$U ratios of samples from the Almyros' river outflow in Crete

Petros Leivadaros[1,2*], *Jan John*[1], *Mojmír Němec*[1], *Nikolaos Kallithrakas-Kontos*[2]

[1]Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Czech Republic
[2]School of Mineral Resources Engineering, Technical University of Crete, Chania, Greece
[*]E-mail: leivapet@fjfi.cvut.cz

Keywords: uranium, ratios, environmental radioactivity, isotopic research

A variety of nuclear and isotopic techniques have been used for marine pollution monitoring[1]. Several specific radiological researches have occurred also in the island of Crete in southern Greece, e.g. a study of ^{238}U, ^{234}U, ^{210}Pb, and ^{210}Po concentrations. Wide range of activities was carried out, and radionuclides determined, in groundwaters and water masses that stratificate in the north deep basin of Crete and the surrounding area of the island[2,3].

The bays of Souda and Almyros represent an area of particular ecological and radiological interest. There, the southern arm of the estuary of the river Almyros, flows to the south of Kalyvaki beach, while its northern arm represents a second section of the same river complex and forms a very clear stratification of fresh, semi-sweet & salt waters which are separated by their densities due to their large difference in salinity and temperature differentiation, especially in spring when the sampling took place (May 2022). The overall area includes one of the biggest NATO bases in Europe and, at the same time, there is an output of a water flow possibly carrying a load of remains of old mining activity in the central area of Crete.

Six water samples and two soil samples were collected from the study area – two sweet water samples from each of the southern and northern outflows of the river, two salt water samples from the central coast zone, one soil sample from the seashore at the northern river outflow and another from the beach area. The water samples were pre-treated with Na_2SO_3 sodium sulphite and TBOT - tetrabutylorthotitanate (titanium butoxide) for iodine and uranium pre-treatment, respectively. Parts of all the samples were subjected to X-ray fluorescence (XRF) analysis. The $^{236/238}$U ratios, that can contribute to the identification of both the source of contamination and the difference between the sediment depositions and water masses' load are under examination on the new MILEA (IonPlus, Switzerland) AMS in Řež near Prague. The combination of these two methods should give a first look on the radiological state of the study area, filling up the literature gaps and pointing out whether there is any need for further research. Sampling methodology and lab treatment, alongside with the elemental analysis, will be described in the presentation.

Acknowledgments

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51

First attempts to assess the radiological risk due to the presence of natural radionuclides in construction and building materials used in Uruguay

*Ana Noguera**, *Rodolfo Reboulaz, Heinkel Bentos Pereira, Laura Fornaro*

Departamento de Desarrollo Tecnológico, Centro Universitario Regional del Este,
Universidad de la República, Ruta 9 y Ruta 15, 27000, Rocha, Uruguay
*E-mail: anoguera@cure.edu.uy

Keywords: natural radionuclides, hazard indexes, construction materials, environmental radioactivity

^{40}K and the radionuclides of the ^{238}U and ^{232}Th series are present in the earth's crust, and therefore are components of the construction materials that are made from it. Radioactivity from building materials together with radioactivity from the ground are the major sources of exposure of the population to ionizing radiation. In this work we report, for the first time, the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in different construction materials marketed in Uruguay. Portland cement, prepared cement mixtures, gypsum, bricks, blocks (concrete and clay), fibre cement, sand and tiles were purchased in the market, quartered, ground and stored for four weeks in containers with Marinelli geometry, in order to reach secular equilibrium between ^{226}Ra and its decay products. The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K was quantified by gamma spectrometry using a gamma spectrometry system with a high purity germanium detector (HPGe) ORTEC-AMETEK, GMX35P4-76-RB. The activity concentration ranges for the three natural radionuclides are shown in Table 1. To evaluate the excess of gamma radiation due to the use of construction materials, the activity concentration index (I) was used according to European regulations, since there are no national regulations.

Table 1: Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K and activity concentration index (I) for different materials available in the Uruguayan market. LD = limit of detection.

Material	^{226}Ra (Bq.kg^{-1})	^{232}Th (Bq.kg^{-1})	^{40}K (Bq.kg^{-1})	I
Cements and mixtures	< LD – 38.8	< LD – 15.0	148–384	< LD – 0.32
Structural elements (bricks and blocks)	8.8–45.7	23.5 – 49.5	210–518	0.32–0.57
Gypsum and fibre cement	3.5–13.6	4.6–12.1	43.7–296	0.024–0.37
Tiles (ceramic and porcelain)	34.6–69.2	50.3–93.0	700–800	0.64-0–96

A value that exceeds the recommended value (I < 1) implies that the reference level of equivalent effective annual dose of 1 mSv.yr^{-1} has been exceeded, and that it is not recommended to use this material for housing construction, although it may be used for other purposes. Although materials whose activity concentration index exceeds the recommended value have not been evaluated up to now, further studies are necessary to guarantee the radiologically safe use of building materials in Uruguay, and to establish the pertinent standards.

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195

Influence of Ba^{2+} concentration on Ra and ^{210}Pb extraction from aqueous samples using EMPORE® radium RAD disk

Gabriele Wallner

Institute of Inorganic Chemistry, University of Vienna, Vienna, Austria
*E-mail: gabriele.wallner@univie.ac.at

Keywords: radium RAD disk, Ra and ^{210}Pb recovery, Ba content of water samples

The determination of radium isotopes in aqueous samples has become very convenient since EMPORE® radium RAD disks are available: the acidified sample is sucked through a membrane (impregnated with a crown ether) and the Ra isotopes (as well as ^{210}Pb, a radionuclide also important in the view of radiation protection when investigating drinking water) are held back on the membrane. The 0.25M EDTA solution used to eluate these radionuclides is then mixed with a scintillation cocktail and subsequently measured by liquid scintillation counting (see e.g. (1)).

Already 1996 Scarpitta and Miller (2) found out, that with 0.25 M basic EDTA solution not only Ra and Pb, but also Sr and Ba could be eluted from the membrane. When investigating waters with high ionic load such as brines or flowback wastewaters, Nelson et al. (3) compared different methods of Ra determinations, among them also the Ra RAD disk method, which proved false due to high Ba concentrations.

For drinking waters (tap water or mineral waters) in the EU the maximum Ba concentration is 1.0 mg/L (Commission Directive 2003/40/EC). There are, however, mineral waters which clearly exceed this limit (4). So we found it worthwhile to re-investigate the Ra recovery in dependence of the Ba concentration of the water sample. As our ^{226}Ra-solution was purchased already in the 1990s a certain amount of ^{210}Pb has since then grown in, making us able to present not only Ra, but also ^{210}Pb recoveries.

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Radiolabeled compounds and radiopharmaceuticals

260

Development of a separation method for the medical radionuclide 47Sc from bulk amounts of Ti

Xiuyun Chai[1], *Mohamed F. Nawar*[1], *Ronald Zingg*[1], *Matthias Lüthi*[2], *and Andreas Türler*[1*]

[1]Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern,
3012 Bern, Switzerland
[2]Federal Institute of Metrology, METAS, 3003 Bern-Wabern, Switzerland
*E-mail: andreas.tuerler@unibe.ch

Theranostic radionuclides have gained growing interest in nuclear medicine applications because various isotopes of an element have virtually comparable kinetics and chemical reactivity, if the vector is tagged with a therapeutic radionuclide of the same element as the diagnostic one, the biological behaviour may be anticipated to be essentially equivalent. Radionuclides of scandium, namely 43Sc and 44Sc as positron emitters and 47Sc as beta emitter are gaining attention. The 44Sc/47Sc and 43Sc/47Sc pairs are considered real theranostic pairs. 47Sc is a special one among many metallic radionuclides due to the proper half-life (3.35 days) and gamma-ray energy (159.4 keV), which makes it a good candidate for theranostics. In this case, we developed a gas-solid phase separation method for the medical radionuclide 47Sc from bulk amount of titanium. The release ratio of 47Sc from 25 μm thickness titanium foil depends on the temperature of the tube furnace (1 hour heating time). Release of up to 99.90% of Sc at 1100 °C was observed. Development of separation 47Sc from a significant amount of Ti has been achieved when encountered with 0.05 mm thickness Ti foil. Consequently, our findings have a promising use for separating the Sc-47 from the solid Ti by the gas-solid phase separation.

Radionuclide separation

155

Fast on-line KCl-aerosol dissolution for liquid-phase chemistry with homologues of superheavy elements

Pavel Bartl[1*], *Mojmír Němec*[1], *Václav Zach*[2], *Alice Bulíková*[1], *Lucie Šifnerová*[1],
Jan Štursa[2], *Jon Petter Omtvedt*[3], *Jan John*[1]

[1]Department of Nuclear Chemistry, Czech Technical University in Prague, Prague, Czech Republic
[2]Nuclear Physics Institute, Czech Academy of Sciences, Řež, Czech Republic
[3]Department of Chemistry, University of Oslo, Oslo, Norway
[*]E-mail: pavel.bartl@fjfi.cvut.cz

Keywords: gas-jet transport, particle into liquid sampler, solid aerosol dissolution, chemistry of superheavy elements

In recent couple of years, a research oriented towards aqueous phase chemistry of the homologues of the superheavy elements (SHEs) has been carried out at the Czech Technical University (CTU) in Prague. In this work we describe a pilot test of one module of an on-line versatile aqueous chemistry apparatus that is being developed within this research—specifically, a coupling of the Particle Into Liquid Sampler (PILS), originally developed as an aerosol sampling system for ion chromatography, with the Gas-Jet Transport (GJT) system, which delivers cyclotron-produced radionuclides from a Recoil-Transfer Chamber (RTC). The radionuclides are delivered in the laboratory attached to the surface of solid KCl aerosols (adsorption takes place in the RTC) and such mixed phase must be promptly and efficiently transferred into a stream of a liquid phase in order to account for extreme instability and scarcity of a superheavy element.

The idea of linking the PILS and GJT systems is an original one and it has not been realized before in the field of chemistry of superheavy elements and their homologues. When compared with the systems that have been employed for this purpose in the past, the PILS-GJT experimental layout turned out to be very promising as its pilot test provided sufficient activity yields (40 - 57 %) and very high gas-to-liquid mixing ratio (up to 5800). These parameters also make the system suitable for the future coupling with various microfluidic chemistry systems. The approach has a good prospect for enabling aqueous chemistry studies with short-lived superheavy elements and their homologues. The operation of this system also generates very small volume of the liquid waste over the time with contributes to minimizing mixed waste production.

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169

Microfluidic liquid-liquid extraction of Mo and W in sub-minute contact times

Alice Bulíková[1*], *Pavel Bartl*[1], *Mojmír Němec*[1], *Václav Zach*[2], *Jan Štursa*[2], *Jon Petter Omtvedt*[3], *Jan John*[1]

[1]Department of Nuclear Chemistry, Czech Technical University in Prague, Prague, Czech Republic
[2]Nuclear Physics Institute, Czech Academy of Sciences, Řež, Czech Republic
[3]Department of Chemistry, University of Oslo, Oslo, Norway
[*]E-mail: bulikali@fjfi.cvut.cz

Keywords: liquid-liquid extraction, microfluidics, extraction kinetics, superheavy elements

In recent couple of years, a research devoted to the aqueous chemistry of superheavy elements and their homologues has been carried out at the Department of Nuclear Chemistry, Czech Technical University (CTU) in Prague. The superheavy elements, characteristically short-lived and difficult to produce, call for rapid techniques in small volumes when it comes to their chemical separation. These criteria are the main advantages of microfluidics making it a logical liquid-liquid extraction (LLE) technique in advancement towards a fully automated on-line set-up for production, transport, chemistry, and detection of produced elements. As part of the research, a rapid on-line microfluidic liquid-liquid extractor is being developed.

The apparatus has been implemented in a tracer-scale LLE of Mo and W, which serve as chemical homologues of Sg, from nitric acid solutions into a kerosene phase utilizing commercial organophosphorus acids as extracting agents. The apparatus allows for exploration of sub-minute kinetics not achievable in manual batch experiments. The flow rate can be adjusted using various precise pumping devices resulting in a fine range of contact times of the two phases. Emphasis is put on fast extraction rates with the primary goal of confirming sufficient yields within shorter contact times. In the latest experiments, the apparatus has been upgraded by incorporating a new phase separator capable of passive compensation of pressure fluctuations.

Acknowledgments

This work was supported by the Centre for advanced applied science (CAAS), Project Number CZ.02.1.01/0.0/0.0/16_019/0000778, provided by the Ministry of Education, Youth and Sports of the Czech Republic and the CTU Grant 'Development of separation systems for analytical, decontamination, and speciation methods', Project Number SGS21/169/OHK4/3T/14. Measurements were carried out at the CANAM infrastructure of the Nuclear Physics Institute of the Academy of Sciences of the Czech Republic Rez. The authors thank the operators of the U-120M cyclotron.

109

Method validation of radiochemical analysis for the bioshield concrete samples from decommissioning process of research reactor

Da-Young Gam[*], *Ji-Young Park, Heewon Kim, Hyunchel Kim, Jong-Myoung Lim*

Korea Atomic Energy Research Institute, Daejeon, Republic of Korea
[*]E-mail: gdy@kaeri.re.kr

Keywords: radiochemical analysis, bioshield concrete, diisobutyl ketone(DIBK), iron 55

For the disposal of decommissioned concrete from research reactors, under regulations for low- and intermediate-level radioactive waste in Korea, the radiological characteristics of wastes (e.g., activity concentration of gamma nuclides, gross alpha, H-3, C-14, Fe-55, Ni-59, Ni-63, Sr-90, Tc-99, and I-129) are essential. Some of bioshield concrete samples, which is the nuclear reactor dismantling waste from KRR2 research reactor of KAERI, highly contained about 5~30% concentration of iron for the purpose of radiation shielding. It was a significant amount of iron contents compared to other concrete samples and excess iron roles as an interference to reduces the efficiency of chemical separation using extraction chromatography and counting system. The precipitation method using hydroxide, which is commonly used for iron separation, is not suitable when the sample has excess iron because the iron precipitation process drags down the rest of the nuclide together. Therefore, in this study, a pretreatment method was developed and optimized to preferentially separate high contents of Fe from solution using diisobuthyl ketone (DIBK) for the purification of the target nuclides (e.g., Fe-55, Sr-90, Ni-63, and Tc-99) in the sample solution. Based on the validation results of the optimized pre-treatment process, we can conclude that the methods using DIBK solution can be used for rapidly and fully recovering the specific target nuclides from the sample solution with a high degree of accuracy and precision. The Fe separation using DIBK from the sample solution completed within 1 hr, and also simultaneously processed the multiple samples. The chemical recoveries of the target nuclides were over than 80% for the bioshield concrete samples which contained about 30% of Fe. Since the optimized method can be used to separate Fe from other nuclides easily and quickly, it is expected to contribute to shortening the analysis time for continuous nuclide separation of the bioshield concrete containing the high concentration of iron.

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57

Use of inorganic sorbents in the treatment of liquid radioactive waste

Jan Gut[1*], *Pavel Kus*[1], *Vojtech Galek*[1], *Martin Skala*[2]

[1]Research Centre Rez, Husinec-Rez, Czech Republic
[2]Metoil s.r.o., Husinec-Rez, Czech Republic
[*]E-mail: jan.gut@cvrez.cz

Keywords: radioactive waste, gamma spectrometry, caesium, ion-selective sorption, sorption, isotopic composition of radioactive waste

Liquid radioactive waste generated during decommissioning of nuclear power plants and during their maintenance is a major environmental and economic burden. Currently, there are 3 main technologies for processing of that waste: Cementation, evaporation, and ion-selective sorption. From an environmental and economic point of view, the ion-selective sorption is the most suitable method, since the volume of the radioactive waste after treatment and economic costs are 100- to 200-times reduced.

This study aims to develop a technology for the processing of liquid radiactive waste, which enables for the safe and efficient transfer of radioactive isotopes from the liquid to the solid phase, which significantly reduces the volume of the final radioactive waste. The technology is based on a sorption using inorganic sorbents. Before starting to process a given amount of liquid radioactive waste and an optimal mixture of sorbents for processing of such waste are selected based on the analysis of the radionuclides present and the chemical composition of the solution.

Several inorganic sorbents were tested and the kinetics of the reaction, i.e. the rate of sorption in the given time periods, were monitored. The source of the radioactive waste was the diluted concentrate from the Dukovany nuclear power plant. Measurements were performed on a gamma spectrometer with an HPGe detector Canberra B16031 and Genie 2000 software. The differences in the concentrations of monitored radionuclides were significant, especially in the case of Cs-134 and Cs-137 during longer sorption.

108

Separation of molybdenum-93 in waste from the decommissioning of nuclear power plants and determination of separation efficiency by cuvette tests

Katerina Horova, Milena Svobodova, Radek Posvar, Radim Janovsky, Vlastimil Miler

UJV Rez, a.s., Hlavni 130, 250 68 Husinec – Rez, Czech Republic
*E-mail: katerina.horova@ujv.cz

Keywords: molybdenum-93, extraction, cuvette test

Molybdenum-93 is produced by exposure of molybdenum-rich material by thermal neutron radiation (for example in steels of the reactor core area), primarily by neutron capture of molybdenum-92. The half-life of molybdenum-93 is $4.0 \cdot 10^3$ years, making it an important radionuclide for nuclear waste disposal and decommissioning.

The main purpose of this work was to develop a method for the determination of molybdenum-93 in nuclear waste from nuclear power plants and its surrounding and decommissioning waste. During the development of this procedure, several matrices based on real samples were tried. These matrices included primar circuit, concrete and steel leachates, enriched with radiochemical contaminants from liquid radioactive waste (concentrate) with a high content of carbon-14, iron-55, cobalt-60, nickel-63, strontium-90, cesium-134 and cesium-137.

In this work, the method for determining molybdenum-93 is based on the liquid-liquid extraction of molybdenum from the aqueous phase into the organic phase. In the first step, molybdenum is precipitated in the aqueous phase using alpha-benzoinoxime and subsequently extracted with an organic solvent into the organic phase. During this process, significant components of the matrix are removed. After backextraction into the aqueous phase, the molybdenum is precipitated by using lead acetate on the filter and measured by low-energy gamma-spectrometry. Molybdenum-93 has two emission lines at energies of 16.5 and 18.6 keV.

The LCK330 cuvette test was used to determine the separation efficiency of this method. The sample is always measured for the input amount of molybdenum at the beginning of the separation and the resulting amount of molybdenum just before the final precipitation. This is how the efficiency of the separation process is calculated. The cuvette test is based on the reaction of molybdate ions with thioglycolic acid forming a yellow complex. The resulting colored compound is determined colorimetrically.

81

Liquid-liquid extraction of strontium from acidic solutions into ionic liquids using crown ethers

Jan Houzar[*], *Kateřina Čubová, Miroslava Semelová, Mojmír Němec*

Czech Technical University in Prague, FNSPE, Department of Nuclear Chemistry, Prague,
Czech Republic
[*]E-mail: houzajan@fjfi.cvut.cz

Keywords: strontium, ionic liquids, liquid-liquid extraction

Sr-90 is one of the most monitored fission products. With its half-life, high fission yield and high-energy β^- particles emitted by its decay product, Y-90, it is one of the most hazardous radionuclides in the radioactive waste management process. New efficient methods and solvents are therefore sought for strontium separation. Over the past 20 years, solutions of crown ethers in ionic liquids have been studied because of their ability to efficiently extract strontium in wide condition ranges. In this study, the influence of various extraction parameters was determined. Extraction efficiency of strontium is highly dependent on the hydrophobicity of the ionic liquid used, with higher distribution ratios obtainable for more hydrophobic ionic liquids. At lower acidities, however, even for the most hydrophilic ionic liquids used in this study, the distribution ratios obtained were much higher than those for commonly used organic solvents ($CHCl_3$ and benzene). Apart from acidity, the extraction of strontium is also affected by other parameters of the aqueous feed solution, such as the presence of interfering cations. At lower acidities, the addition of alkali metal cations (Na^+, K^+) lowers the distribution ratios of strontium significantly but the effect diminishes with increasing acid concentration. The overall results of this study are compared with possible extraction mechanisms.

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6

The study of distribution coefficient of polonium between toluene or cyclohexane solutions of tri-octylphosphine oxide (TOPO) and tri-butylphosphate (TBP) and selected inorganic acids

Grażyna Kaczyńska[*], *Grzegorz Szaciłowski*

Radiation Protection Measurements Laboratory, National Centre for Nuclear Research, 7 A. Soltana Str, 05-400 Otwock – Świerk, Poland
[*]E-mail: grazyna.kaczynska@ncbj.gov.pl

Keywords:

Determination of activity concentration of radionuclides in naturally occurring radioactive materials (NORM) has recently become an important topic in environmental research. Polonium-210 is a natural alpha emitting radionuclides in uranium-238 series. High toxicity and radiotoxicity made it one of the most often studied NORM element. Polonium-210 along with parent isotope (lead-210) can accumulate during industrial processing of NORM bearing materials [1,2] creating a demand for reliable process of extracting polonium from chemically similar metals. The most common method of polonium determination consists of plating of polonium on Ni, Cu or Ag discs and alpha spectrometric measurement. However, in case of industrial materials this process is not always possible as matrix metals often tend to deposit on prepared sources diminishing the resolution of alpha spectrum. Alternative way is to determine polonium by means of liquid scintillation counting (LSC), which also requires sample purification in order to reduce quenching of samples.

In this study a liquid-liquid extraction process, as a part of sample purification for polonium determination was investigated. The distribution coefficients (D) of polonium between *tri*-octylphosphine oxide (TOPO) and *tri*-butylphosphate (TBP) in an organic extractants, namely toluene and cyclohexane and an inorganic solvents: hydrochloric acid, nitric acid, orthophosphoric acid and sulphuric acid have been studied. The studied acidities ranged from 0.1 up to 10 mol dm^{-3}. The obtained results varied from near to 0 for TOPO/toluene and diluted HNO_3 system to almost 1 for TOPO/toluene and concentrated HCl.

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278

The determination of a nuclide vector in concrete and soil samples: Verification of a method

Rainer Kadan[*], *Paul Riegler, Krystle Elbers, Viktoria Damberger, Claudia Landstetter*

Austrian Agency for Health and Food Safety (AGES), Vienna, Austria
[*]E-Mail: rainer.kadan@ages.at

Within the scope of a project, the Austrian Agency for Health and Food Safety (AGES) was assigned to conduct a radiological characterization of concrete and soil samples. Besides the measurement of gamma emitting radionuclides via gamma spectrometry, the laboratory analysed alpha and beta emitting radionuclides as well. Therefore, the samples were radiochemically separated. The laboratory analysed the following radionuclides: Sr-90, Pu-238, Pu-239/240, Pu-241 and Am-241. Based on the resulting activity concentrations, nuclide vectors for the samples were calculated. However, a closer look revealed some inconsistencies.

In order to determine the inconsistencies' cause, the AGES conducted a method verification of the used method. It was of major interest to exclude methodical causes for the inconsistencies. Thus, several aspects required attention like the digestion technique, the chemical separation and the measurement of some radionuclides. Furthermore, some other factors like inhomogeneity, hot spots and reproducibility were also taken into account. Step by step, the AGES-laboratory conducted various experiments to exclude possible causes and to verify the method. For these experiments, the laboratory selected particular soil and concrete samples. The used method based on the consecutive separation of the analytes using extraction chromatographic resins. After a first precipitation, the element fractions were gained by the use of Sr-, DGA and TEVA® Resins by Triskem®.

In the first experiment, the reproducibility of the method was examined by analysing several aliquots of an already digested sample. Next the homogeneity and the representativity of the selected sample were the focus of examinations. For this, several aliquots of the raw sample material (before digestion) were analysed. Then the digestion's influence on the results were subject of this study. The laboratory compared microwave-assisted digestions using concentrated HNO_3 with H_2O_2, half-concentrated HNO_3 and reverse aqua regia with HF with one another. Each sample was compared to an internal reference as well.

The used method, the conducted experiments and the consequential results will be presented as a poster at the conference.

267

Separation of long-lived ^{108m}Ag from ^{152}Eu and ^{60}Co using environmentally benign PEG based ABS

Sayantani Mitra[1], *Nabanita Naskar*[2], *Susanta Lahiri*[2,3*]

[1]University of Calcutta, 35, Ballygunge Circular Road, Kolkata, India
[2]Diamond Harbour Women's University, Sarisha, South 24 Parganas, India
[3]Sidho Kanho Birsha University, Purulia, India
[*]E-mail: susanta.lahiri@skbu.ac.in

Environmental contamination from liquid radioactive waste (LRW) generated from nuclear power plants, decommissioning of a nuclear reactor are of great concern. One of the main constituents of radioactive waste is ^{110m}Ag (activation product of ^{109}Ag), but the relatively long half-life of ^{108m}Ag (activation product of ^{107}Ag) makes it important when storage of radioactive waste is concerned. Majority of the isotopes of europium-^{152,154,155}Eu are fission products. ^{60}Co mainly arises out as activation product in liquid radioactive waste. Therefore, separation of this long -lived radioactive isotopes are of eminent importance before these wastes are released in the environment. The study aims to develop an environmentally benign technique of separation of these isotopes using polyethylene glycol based aqueous biphasic systems (ABS). Here, an ABS of polymer/salt system is developed using PEG 4000 (molecular weight 4000) as the PEG rich phase and nine different inorganic salts and three different organic salts as the salt rich phases. Equal volume of 50% PEG solution was mixed with 2M salt solutions, allowed for phase formation followed by addition of radioactive stock. The system was mechanically shaken and allowed for gravity settling. After complete phase separation, both the phases were separately subjected to gamma spectrometry using HPGe detector.

Out of all the twelve salts taken, best separation of ^{108m}Ag from ^{152}Eu and ^{60}Co was observed in K_3PO_4 followed by Na_2SO_4. In both the cases, Ag was observed to get extracted in the PEG rich phase. In general, ions that have smaller ionic radius tends to get more solvated and prefers to stay in salt rich phase where they attain more favourable energy. The ionic radius of Eu and Co are 94.7 pm and 65 pm respectively which are comparatively lower than Ag (115 pm), thus Ag gets extracted in the PEG rich phase. In case of 2M K_3PO_4: PEG 4000, separation factors achieved were $S_{Ag/Co} = 1.7 \times 10^3$ and $S_{Ag/Eu}= 2.67 \times 10^2$. In case of 2M Na_2SO_4: PEG 4000, separation factors achieved were $S_{Ag/Co} =2.42 \times 10^2$ and and $S_{Ag/Eu} = 1.78 \times 10^2$. The separation factors achieved are quite high and are comparable with the traditional LLX techniques using organic solvents. Thus, polyethylene glycol based ABS are alternative green separation techniques that has huge potential to be used in separation of radioisotopes from LRW.

95

CERN-MEDICIS: An offline mass separation facility dedicated to nuclear medicine

Laura Lambert[1], Elodie Aubert[1], Vincent Barozier[1], Cyril Bernerd[1,2], Philippe Bertreix[1], Aurore Bosched[3], Richard Catherall[1], Eric Chevallay[1], Bernard Crepieux[1], Matthieu Deschamps[3], Alexandre Dorsival[1], Charlotte Duchemin[1], Valentin Fedosseev[1], Pascal Fernier[1], Simone Gilardoni[1], Reinhard Heinke[1], Umair Khalid[4], Moazam Khan[4], Qaiser Khan[4], Edgars Mamis[5], Bruce Marsh[1], Stefano Marzari[1], Nabil Menaa[1], Maxime Munos[1], Fabio Pozzi[1], Francesco Riccardi[1], Jean-Yves Rinchet[1], Sebastian Rothe[1], Thierry Stora[1], Julien Thiboud[1], Joachim Vollaire[1] and the CERN-MEDICIS collaboration*

[1]CERN, Meyrin, Switzerland
[2]KU Leuven, Institute for Nuclear and Radiation Physics, Heverlee, Belgium
[3]CERAP, Meyrin, Switzerland
[4]Pakistan Atomic Energy Commission, Islamabad, Pakistan
[5]Institute of Chemical Physics of the University of Latvia, Riga, Latvia
[*]E-mail: laura.lambert@cern.ch

Keywords: nuclear, medicine, radionuclides

The CERN-MEDICIS (MEDical Isotopes Collected from Isolde) facility is dedicated to the research and development of radionuclides for nuclear medicine (1,2). This unique facility is capable of producing medically relevant isotopes via two different methods. CERN-MEDICIS can irradiate its targets using a parasitic approach by placing them as a secondary target behind an ISOLDE (Isotopes OnLine Device) target, and thereby using the remaining fraction of the 1.4 GeV proton beam that would otherwise be lost into the beam dump. Since the facility resides in a specialised nuclear laboratory capable of handling high activity unsealed sources, there is the opportunity to receive external radioactive sources from collaborator institutes which are then loaded into a target container and later placed on the CERN-MEDICIS front end to proceed further to the mass-separation. This latter approach puts MEDICIS in a unique position, allowing the facility to operate during CERN's regular long shutdown periods while the majority of other facilities at CERN are not able to.

CERN-MEDICIS is a facility that also operates a standalone ("offline") isotope mass separator to produce a radioactive ion beam. After irradiation, the target is heated to very high temperatures (>2000°C) and uses an extraction energy of typically 60 kV (3). The isotopes are vaporised alike a distillation process, followed by ionisation resulting in a radioactive ion beam. From here, the radioactive ion beam is optimised using specific beam optics and passes through a dipole magnet acting as mass separator, for implantation and collection in a small metallic foil. Therefore, the CERN-MEDICIS facility has the exceptional capability of selecting its produced ion beam to one or two parallel masses of choice. This can be further purified if the isotope of interest is laser ionizable which allows an additional elemental selection.

With the focus in the production of novel medical isotopes, this puts a large focus in the field of theranostics driven by cancer imaging, diagnostics, and radiation therapy. The laboratory primarily handles radiometals and radiolanthanides including but not limited to Sc-44,47, Tb-149,152,155 (4), Ba/Cs-128, Sm-153 (5,6), Tm-165, Er-169 (7), Yb-175, Pt-191 and Ac-225. Capitalising on decades of experience from the ISOLDE facility, and since 2017 of several years of experience at MEDICIS itself, there have been a few notable successes in the recent years including first in-vitro and preclinical results in targeted radionuclide therapy, obtained from high molar activity Er-169 (7) and Sm-153 (5,6) batches.

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116

Production and mass-separation of $^{44\text{-}47}$Sc radionuclides at the CERN-MEDICIS facility

Edgars Mamis[1,2*], *Mia Au*[1,3], *Elodie Aubert*[1], *Cyril Bernerd*[1,5], *Eric Chevallay*[1], *Bernard Crepieux*[1], *Matthieu Deschamps*[6], *Alexandre Dorsival*[1], *Charlotte Duchemin*[1], *Patricija Kalnina*[2], *Qaiser Khan*[7], *Alexandros Koliatos*[1], *Laura Lambert*[1], *Maxime Munos*[1], *Elina Pajuste*[1,2], *Maija Radzina*[4], *Edgar Reis*[1], *Francesco Riccardi*[1], *Jean-Yves Rinchet*[1], *Ralf Rossel*[1], *Sebastian Rothe*[1], *Simon Stegemann*[1], *Thierry Stora*[1], *Julien Thiboud*[1]

[1]CERN, Geneva, Switzerland
[2]Institute of Chemical Physics of the University of Latvia, Riga, Latvia
[3]Johannes Gutenberg-Universität Mainz, Mainz, Germany
[4]Medical Faculty of the University of Latvia, Riga, Latvia
[5]KU Leuven, Institute for Nuclear and Radiation Physics, Heverlee, Belgium
[6]CERAP, Geneva, Switzerland
[7]Pakistan Atomic Energy Commission, Islamabad, Pakistan
[*]E-mail: edgars.mamis@cern.ch; edgars.mamis@lu.lv

Keywords: radionuclides, scandium, mass-separation, radioactive ion beams, theranostics

The MEDICIS facility at CERN specializes in extraction and purification by mass-separation of a wide range of novel medical radionuclides, produced in nuclear reactions resulting from 1.4 GeV protons from the CERN Proton Synchroton Booster (PSB) impinging on thick targets, or produced via externally irradiated samples from nuclear reactors and cyclotrons [1]. The mass-separated radionuclides are most often delivered in the form of singly charged atomic ions, but with development of target materials and more versatile and selective ion sources, more refractory or exotic radionuclides and molecular species could be successfully extracted [2].

Molecules have been studied as a method to efficiently deliver beams of release-limited elements such as Y, Zr, Mo, W, Ti, V as well as medical ^{43,44m,44g,47}Sc radionuclides which are promising in “matched theranostic pair” radiopharmaceutical development for cancer treatment [2-4]. The development of molecular beams is motivated by the significantly higher volatility resulting in improved extraction efficiencies, as well as higher radionuclide purity. For instance, extracting radionuclides on a molecular sideband shifts the mass of interest, and can therefore be used as a technique to improve radioactive ion beam purity by choosing to collect on a mass with minimal isobar contamination [4;5].

To produce $^{43\text{-}48}$Sc, natural titanium and vanadium targets were irradiated at MEDICIS with 1.4 GeV protons. The presence of contaminant isotopes such as ^{46}Sc ($t_{1/2}$=83,8 d) in the final product for radiolabelling with radiopharmaceuticals is not acceptable, therefore the Sc radionuclide mass-separation step is mandatory.

Extraction of $^{43\text{-}47}$Sc as fluoride molecular beams was studied with a Versatile Arc Discharge Ion Source (VADIS). Even though mass-separation is crucial part and effective to obtain high specific activity medical Sc radionuclides, chemical purification step must be added to remove isobaric contaminants. Ion exchange chromatography with DGA resin was studied to chemically purify the collected Sc radionuclides.

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148

Enhancing radionuclide extraction by using ionic liquids

Miroslava Semelová[*], *Kateřina Čubová, Mojmír Němec, Jan Houzar, Michal Ficel*

Department of Nuclear Chemistry, Czech Technical University in Prague, Prague, Czech Republic
[*]E-mail: miroslava.semelova@fjfi.cvut.cz

Keywords: ionic liquids, liquid-liquid extraction, 8-hydroxyquinoline

Liquid-liquid extraction is one of possible ways for processing of low-level radioactive waste originating for example from decontamination processes. Worldwide efforts are focused on the development of new, advanced methods for removal of radionuclides and recycling the solutions. The replacement of traditional volatile organic solvent by ionic liquids seems to be promising way for enhancing the extraction with the potential for their recycling and reuse.

Ionic liquids as compounds that can be widely used in many applications, are the object of many studies. Their properties can be adjusted for the specific usage. Many of them seems to be promising in the field of separation processes including solvent extraction. Ionic liquids can be designed as extractant or can be also used as the alternative to traditional volatile organic solvents.

The effect of solvent (chloroform, imidazolium or ammonium based ionic liquid) on radionuclide extraction was studied in wide range of pH values. Besides extraction into pure solvent, 8-hydroxyquinoline was used as the extractant. Extraction efficiency varies depending on extracted radionuclide and its chemical properties. Representatives of activation products (Co, Fe), fission products (Sr, Mo, Tc) and superheavy homologues (Tl) were tested in this work.

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183

Electrochemical adjustment of the oxidation state of short-lived nihonium homologues

Jakub Sochor[1*], *Mojmír Němec*[1], *Pavel Bartl*[1], *Václav Zach*[2], *Jan Štursa*[2],
Jon Petter Omtvedt[3], *Jan John*[1]

[1]Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Prague, Czech Republic
[2]Nuclear Physics Institute, Czech Academy of Sciences, Řež, Czech Republic
[3]Department of Chemistry, University of Oslo, Oslo, Norway
[*]E-mail: jakub.sochor@fjfi.cvut.cz

Keywords: electrochemistry, cyclic voltammetry, oxidation state control, thallium, nihonium homologue

Transactinide research has recently focused not only on issues of their synthesis and identification but also increasingly on the analysis of their chemical characteristics. Among the main ones are the oxidation states; the knowledge of their in/stability allow to predict the existence of chemically stable compounds, and the chemical behaviour of the element itself—following trends given by the Periodic Law has been one of the elemental questions in the research in the chemistry of transactinides.

The work [1], described in this abstract, is devoted to the cyclic voltammetry (CV) of thallium (and indium) using Gamry Reference 600 potentiostat. The results (oxidation and reduction potentials in a given background electrolyte) are subsequently used for setting process conditions for altering the oxidation state of selected homologues of transactinides; specifically, indium and thallium, i.e. nihonium homologues, in small volumes (order of units of millilitres) and concentrations (10^{-3} to 10^{-15} M) were employed in this work.

In addition to non-radioactive experiments with indium and thallium chloride, other experiments were carried out with short-lived cyclotron-produced radioisotopes of thallium using the ^{197}Au (^{3}He, xn) reaction and also with commercially available ^{201}Tl. It was shown that setting the conditions that lead to the oxidation of the analyte is achieved much more easily than in the case of its reduction. However, a very promising result is the fact that the described methodology is suitable for adjustment of the oxidation state of thallium in trace amounts in the entire analysed volume at minimal currents.

All the results of these experimental campaigns will serve as the basis for the preparation and design of flow electrochemical setup for the analysis and adjustment of the oxidation state of short-lived homologues of superheavy elements, while it will be connected to the liquid output from the GJT (Gas Jet Transport) coupled to PILS (Particle Into Liquid Sampler) [1] and will be the source for the microfluidic extraction apparatus also developed at CTU.

Acknowledgments

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218

Lanthanide separation using ion exchange chromatography and high precision neodymium isotopic analysis by MC-ICPMS

Daniel Stubbs[*], *Timothy Gregory, and Simon Woodbury*

National Nuclear Laboratory Ltd., Central Laboratory, Sellafield, UK
[*]E-mail: daniel.stubbs@uknnl.com

Keywords: neodymium, isotope analysis, lanthanides, ion exchange, mass spectrometry, MC-ICPMS

Neodymium isotopic analysis is an important tool with a multitude of uses across the nuclear industry. For example, isotopic abundances of fission-derived neodymium in spent fuel yields information on the extent of burnup and the irradiation characteristics within nuclear reactors [1]. They can also be used in nuclear forensics given the distinct neodymium isotopic fingerprint of uranium ores and their concentrates [2].

Neodymium isotopic abundances can be determined to high-precision using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). As this technique separates isotopes by their mass-to-charge ratios, it cannot discriminate between isotopes of different elements with the same mass (*e.g.*, ^{142}Ce and ^{142}Nd, and ^{148}Sm and ^{148}Nd). Therefore, separation of neodymium from other elements – namely, the lanthanides – is an essential prerequisite to measurement.

Traditionally, chemical purification of lanthanides was achieved by ion exchange chromatography using Dowex and so-called lanthanide-spec “Ln-spec” resins [3, 4]. Given the chemical similarity amongst the lanthanides, these separations often require the use of tall yet narrow glass columns, which drip slowly and preclude the use of hydrofluoric acid during separation. More recently, separation has been achieved using newly developed diglycolamide (DGA) based extractants [5].

We have successfully established an ion exchange procedure using DGA-N resin that yields high purity neodymium fractions with > 95 % recovery. Separation of neodymium from adjacent interfering lanthanides is achieved by passing progressively dilute hydrochloric acid through the column. We calibrated this with commercially available pre-packed TrisKem columns that offer two main advantages: they drip much faster than tall-thin glass columns, allowing the entire separation procedure to be performed in ~5 hours without pressurisation; and they are made of plastic, allowing the addition of hydrofluoric acid into the sample load solution for enhanced matrix separation.

In addition, we have successfully established a technique for high-precision neodymium isotope ratio measurement using a NuPlasma II MC-ICPMS. We have shown by repeat measurement of a purified neodymium solution that all neodymium isotopic ratios (when expressed relative to ^{146}Nd) can be determined to ± 0.03 % uncertainty (2SD; $n = 19$ repeat measurements) in solutions containing only 5 ng mL^{-1} neodymium. Moreover, we found that neodymium isotopic compositions remained accurate to ± 0.1 % (2SD; $n = 19$) in solution containing just 1 ng mL^{-1} neodymium. In our technique that equates to a total neodymium mass required for analysis of ~ 5 ng.

Given the mineral acids used in this procedure can be bought in high purity, combined with our high precision for just minor quantities of neodymium, this method is applicable to analysis of trace quantities of neodymium, and is ideally placed for use in isotope dilution mass spectrometry (ID-MS) technique.

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280

Development of procesess for the solidification of high level radioactive wastes after NPP sever accident and evaluation of their disposal in radioactive waste repository

Lórant Szatmáry[1], Martin Straka[1], Jan Hrbek[2], Dušan Kobylka[3], Květoslav Růžička[4], Petr Gallus[5], Petr Fabián[6]*

[1]ÚJV Řež, a.s., Hlavní 130, Řež, 250 68, Czech Republic
[2]CVŘ Řež, Hlavní 130, Řež, 250 68, Czech Republic
[3]Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering, V Holešovičkách 474/2, Praha 8, 180 00, Czech Republic
[4]The University of Chemistry and Technology, Prague, Department of Physical Chemistry, Technická 5, Praha 6, 166 28, Czech Republic
[5]UJP PRAHA a.s., Nad Kamínkou 1345, Praha – Zbraslav, 156 10, Czech Republic
[6]CHEMCOMEX, a.s., Brněnská 327, Třebíč – Nové Město, 674 01, Czech Republic
[*]E-mail: lorant.szatmary@ujv.cz

Keywords: severe accident; radiaoactive waste; solidification; vitrification; safety assessment

The goal of the project is to assess the concept and selection of a suitable method for stabilizing high-level waste (HLW), originating from a nuclear power plant (NPP) severe accident. Furthermore, to evaluate potential chains of radioactive waste management and disposal. The results of the project will represent a part of the conceptual basis for transposing the treatment of liquid radioactive waste into actual recent practice in the Czech Republic, according to the National Action Plan No. 68. At the same time, the results will represent an insight into how these wastes can be disposed while ensuring the long-term safety of people and the environment, and how their potential volume will be reflected in the planning of disposal capacities.

On March 11, 2011, the Fukushima NPP accident occurred. The Fukushima NPP wastewater removal and decontamination process is the largest known process of its kind. Many decontamination and pre-treatment processes, often the best available technologies, have been tested and used successively during the removal process. Many valuable and previously unverifiable lessons can be learned from the progress of decontamination in the Fukushima NPP area during such a large decontamination process.

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41

Ultrafast and selective separation of ^{99m}Tc from molybdenum matrix using DBDGA deliberately tailored macrocyclic crown-ethers

Junqiang Yang[1,2], *Wenya Tai*[2], *Fei Wu*[1], *Keliang Shi*[1,2*], *Xiaolin Hou*[1,2]

[1]Frontier Science Center for Rare Isotopes, Lanzhou University, 730000, Lanzhou, P. R. China
[2]School of Nuclear Science and Technology, Lanzhou University, 730000, Lanzhou, P. R. China
[*]E-mail: shikl@lzu.edu.cn

Keywords: TcO_4^-, ReO_4^-, molybdenum, solvent extraction, BisDBDGA-DB18C6

Technetium-99m (^{99m}Tc) is an important medical radionuclide. Due to the crisis in supply of molybdenum-99 (^{99}Mo), production of ^{99m}Tc directly via the ^{100}Mo (*p, 2n*) reaction by cyclotron was proposed. In this process, the most critical challenge is to rapidly and efficiently separate ^{99m}Tc from high concentration of molybdenum [1-3]. In this work, a novel ligand, bis(*N,N*-dibutyldiglycolamide)dibenzo-18-crown-6 (BisDBDGA-DB18C6) was successfully synthesized and used for extraction of TcO_4^- /ReO_4^- from molybdenum. The results demonstrated that BisDBDGA-DB18C6 expressed excellent selectivity for TcO_4^- with a high separation factor of 1.6×10^5 against Mo, a fast extraction kinetic (within 45 s), and a high extraction capacity of 211 mmol ReO_4^- ($^{99}TcO_4^-$)/per mole of extractant. The extraction mechanism was proposed as a co-interaction of macrocyclic crown ether and *N,N*-dibutyldiglycolamide group through slope analysis, FT-IR, ESI-MS, ^{1}H NMR titration and theory calculations. Importantly, ^{99}Tc in the organic phase can be quantitatively (> 99%) and easily back-extracted using deionized water, which can be directly used for medical applications.

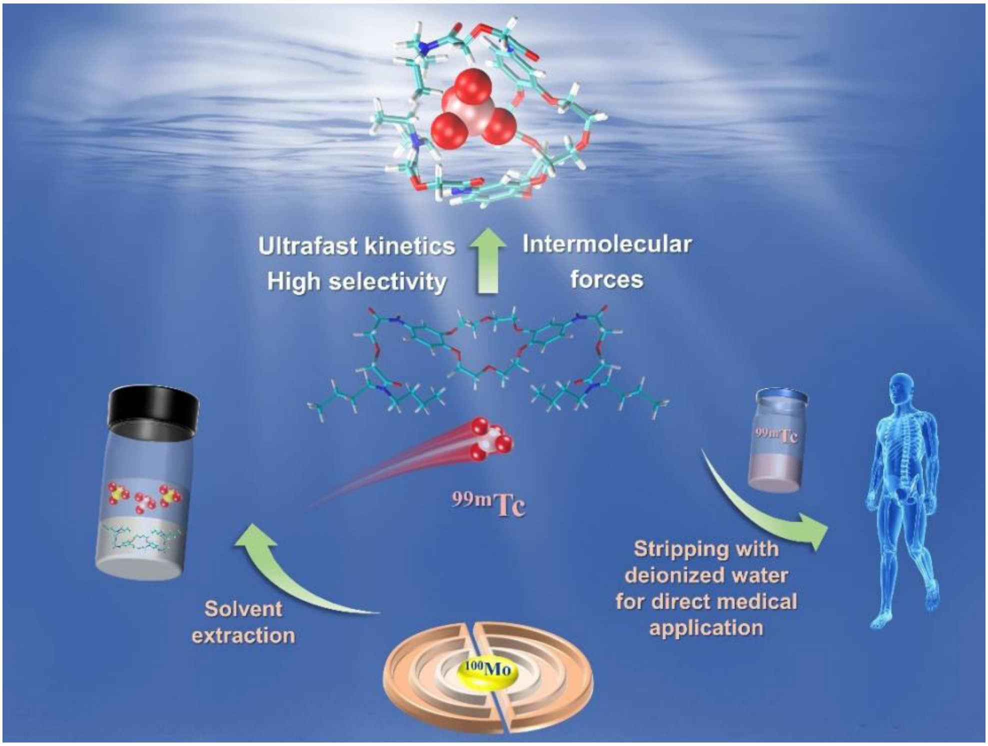

Figure 1 Schematic diagram of efficient extraction and separation of ^{99m}Tc using BisDBDGA-DB18C6

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Sponsor’s Presentation

HIDEX INTRODUCES NEW ULTRA LOW LEVEL LIQUID SCINTILLATION COUNTER

Risto Juvonen

Hidex Oy, Finland
E-mail: risto.juvonen@hidex.com

Since the discontinuation of PerkinElmer Quantulus 1220 in 2014, there has not been a true ultra-low level LS counter available in the global market. The need for a high-performance liquid scintillation counter is obvious for example in hydrogeological applications for measurement of sub-surface concentrations of H-3 in water, detection of C-14 in biofuels or solids, and direct counting of environmental concentrations of alpha and beta isotopes. The PerkinElmer Quantulus GCT or Hidex 300 SLL super low level models can be used up to a certain extent, but do not meet the most demanding user requirements. Hidex is proud to introduce a true ultra-low level LS counter designed to meet such demanding specifications. From a technical perspective the figure of merit (FOM) for H-3 in water for Hidex ULLA is 2 to 3-fold higher than that of Quantulus GCT and Hidex 300 SLL. The high performance of the instrument is accredited to latest innovations, such as, enlarged passive Pb shield and a geometrically optimized active guard. The counter also brings the design of LS counters to a new era with modern electronics and new user interface software, customised to meet modern usability needs. Similar to all Hidex automatic counters, the new ultra-low level counter employs triple-coincidence TDCR detector and high-resolution alpha beta separation with graphical 3D calibration and result validation mechanism.