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Keynote Speakers

Spectroelectrochemical methods and approaches for radioanalytical chemistry

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Keywords: electrochemistry, spectroscopy, europium, ruthenium

Field and in-process radioanalytical methods are needed for environmental, nuclear medicine, and nuclear safeguards applications where chemical detection of analytes is desired. Many analytes in these applications are redox sensitive, leading to the opportunity to develop electrochemically-based detection techniques. Spectroelectrochemistry uses spectroscopy coupled with electrochemical techniques to identify target analytes of specific oxidation states. This can often provide rapid quantification with sensor designs that are inexpesive, portable, and robust. The analyte of interest must be both redox and spectroscopically active. For analytes and/or complexes of analytes that fluoresce, sensitivity is dramatically increased over approaches that use ultraviolet-visible absorption.

In this presentation, recent advances in spectroelectrochemistry to detect transition metals and f-elements relevant to nuclear medicine and nuclear safegaurds will be described. Specifically, recent results from study of ruthenium spectroelectrochemistry with the complexants of 2,2'-bipyridine and 1,10'-phenanthroline will be discussed [1], along with results from europium redox and luminescence using four different bipyridine-based sensitizing ligands [2]. Approaches to modulate between redox states, leading to control of analyte speciation, and enhancement of spectroscopic sensitivity will be explained.

Acknowledgments

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A survey of the UGent nuclear-analytical contributions to fission-track age determination and to luminescence dating

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Keywords: nuclear-analytical techniques, neutron activation analysis, beta-counting, alpha-counting, gamma-counting, calibration, annual radiation dose, fission-track age determination, luminescence dating

In the mid 1980s, the k_0-NAA group at the Institute for Nuclear Sciences (INW) of the Gent University (UGent) started putting its nuclear-analytical expertise at the service of the Geological Institute so as to untangle the then existing worldwide confusion in the fission track (FT) dating calibration in its absolute mode, which was at that moment in the stage of its last gasp. As brought to light, the scepticism and disbelief in this calibration approach was mainly caused by the inadequate procedures followed in the thermal neutron flux assessment, either directly via metal monitors or indirectly via NBS U-doped pre-irradiated glass SRMs. Our remediation consisted in optimizing, validating and recommending reliable flux determination methods, introducing the Westcott-formalism to account for the non-ideal cross section behaviour of the ^{235}U(n,f) reaction. Additionally we initiated and co-operated in the issuing (1996, 2006) of properly characterized new European (IRMM) U-doped glass reference materials. In this way we were significantly contributing to restoring the confidence in the absolute calibration of FT age determination.

In the early 1990s, the Geological Institute called upon the INW to form a team for jointly setting up and running a luminescence dating laboratory – up until then not existing in Belgium. Next to fully contributing to the logistics (instrumentation, personnel --), the k_0-NAA group focussed on the assessment of the annual (K, Th, U) radiation dose – with mainly the following contributions: 1/ a large-scale comparison and optimization of methods, involving auger-hole NaI(Tl) gamma-ray field measurement and its calibration, low-background NaI(Tl) and extended-range Ge gamma-ray spectrometry, k_0-assisted INAA and ENAA, thick-source ZnS alpha-counting and low-background GM beta-counting; 2/ the study of possible errors in these measurements, namely a) the effect of different sample-calibrant composition in gamma-spectrometry, b) the identification of disequilibria - notably in the ^{238}U decay series -, exploring the possibility of direct gamma-spectrometric measurement of the ^{226}Ra 186.2 keV line for detecting ^{238}U/^{226}Ra disequilibrium, and c) the assessment of ^{222}Rn loss from encapsulated sediments; 3/ the investigation of the significance of the internal dose rate in the optically stimulated luminescence dating of sedimentary quartz; and 4/ the preparation and characterization of loess sediment for use as a reference material in the annual radiation dose determination. This contributed, at the UGent and elsewhere, to the possibilitiy of assessing a more accurate and precise radiation dose rate in luminescence dating.

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The support of the Flemish Research Fund and the Ghent University is highly acknowledged. The author is especially grateful for the indispensable co-operation by people from the Institute for Nuclear Sciences and the Geological Institute of the UGent: Frank Bellemans, Line Vancraeynest, Syed Hossain, Raymond Jonckheere, Peter Van den haute, Johan De Grave, Tony De Wispelaere and especially Dimitri Vandenberghe, and from other Institutes: Chris Ingelbrecht, Michelle Derbyshire (IRMM/Geel) and Jan Kučera (Řež/CZ).

Radioanalysis of ultra-low level radionuclides for environmental studies and decommissioning of nuclear facilities

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Keywords: Radioanalysis, mass spectrometry, environmental tracer, environemntal radioactivity, ^{129}I

Human nuclear activities have produced a large amount of radionuclides, some of them were released to the environment, while most of them are remained in various radioactive waste to be deposited. Some of these radionuclides are important in view of nuclear waste depository, decommissioning of nuclear facilities, radiological emmergency prepardness, environmental radioactivity and tracer studies of environmental processes. Besides the bulk concentration, species of radionuclides, especailly the redox sensitive radionuclides, play a critical role in their behaviors in the environment. Combined the effective chemical separation procedures with sensitive measurement techniques, a series of analytical methods have been developed for determination of these radionuclides in my research teams. With these methods, various radioactive waste from decommissioning and operations of nuclear facilities were characterized, environmental processes and impact were investigated by analysis of these radionuclides and their species. Some works on the radioanalytical methology and their applications are presented in this work.

Methodology of radiochemcial analysis of hard-to-measure radionuclides for characterization of various radiological waste, focusing on rapid and sequental separation with high decontamination and radiometric measurement of each radionuclides, such as ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{63}Ni, ^{93}Mo, ^{99}Tc, ^{129}I, ^{135}Cs and isotopes plutonium, neptunium, americium and curium. Characterisation analysis decommissioning waste of some nuclear facilities using these methods are demostrated.

Radioanalytical methodology for determination of radionuclides and theri species in environmental media, emphasizing on effective separation of target radionuclides from large environmental samples and highly sensitive measurement with advantced ICP-MS and AMS, enable to determine fg or nBq level radionuclides such as ^{129}I, ^{99}Tc, ^{236}U, ^{237}Np, ^{239}Pu and ^{240}Pu. Automated approache using flow inject techniques was developed and applied for rapid analysis in case of radiological emmergency prepardness and analysis of large number of environemntal sampels.

Oceanographic tracer studies for water mass interaction, transport, circulation and marine environment using long-lived ^{129}I, ^{99}Tc and ^{236}U based on their well know source term, high ocean residence time and redox feature of iodine. A large scale investigations by analysis of seawater samples collected from Arctic to Antarctic, as well as some areas such as Chinese Seas and Baltic Seas are demostrated.

Study on emission, dispersion and transport pathway of atmospheric pollutions by speciation analysis of anthropogenic ^{129}I as well as isotopes of plutonium in environmental media. Spatial and temporal variation of radionuclide levels and their species were acquired by analysis of sediment and ice cores, tree rings, time series precipitation, aerosols and seeweeds collected from different locations, enable to explore the source term and transport pathways of pollutions.

Investigation of environmental impact of historic nuclear and industry activities by systematic sampling and radioanalysis of environmental samples (soil, water and vegetation) over large area for important radionuclides, such as ^{239}Pu, ^{240}Pu, ^{241}Am, ^{129}I, ^{137}Cs, ^{90}Sr, maping their distribution, exploring their sources and corresponding contribution and impact.

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Contributions and suports of all my team members and colleagues in DTU Nutech, IEECAS and Lanzhou University, as well as collaborators are highly acknowledged.

The 1,2,4-triazine ligands – from irradiated nuclear fuel reprocessing to chromatography resins

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Keywords: 1,2,4-triazine ligands, nuclear fuel reprocessing, chromatography resins, BTBP, BTPhen

The 1,2,4-triazine ligands have been developed as a perspective tool for one of the hot topics in the back-end of the nuclear fuel cycle - separation of trivalent actinide (An) and lanthanide (Ln) elements. Even though the main field of their application is liquid-liquid extraction, modifications for other prospective applications, specifically for liquid chromatography, recently emerged.

In this contribution, properties and applications of various liquid-liquid extraction systems and hydrophilic masking agents based on the 1,2,4-triazine ligands (BTP, BTBP, BTPhen) will be briefly summarized and the development and properties of extraction chromatography resins and solid extractants with 1,2,4-triazine ligands or functional groups, respectively, described in detail. In the first part, the possibility of residual actinides separation from the DIAMEX/SANEX secondary waste streams using two novel solid extractants – E5–$CyMe_4BTBP$[cyclohexanone] and E5–C_5BTBP[nitrobenzene] will be described. With E5–C_5BTBP[nitrobenzene], very good separation of americium and europium was achieved. In model laboratory experiments, the maximum achievable flow-rate for a negligible Am break-through was ~ 5 BV/hr; 98.6 % of europium could be washed from a loaded column in 8.7 BV of the eluant; the europium fraction contained only 0.3 % of the total amount of americium sorbed on the column. Americium could be efficiently eluted with 0.5M glycolic acid with pH ~ 4 – 99.7 % of americium was recovered in 3.1 BV of the eluant and the americium fraction contained only 1.4 % of the europium originally sorbed on the column.

As the first group of the solid extractants, $CyMe_4$-BTPhen-functionalized silica-coated maghemite (γFe_2O_3) magnetic nanoparticles (MNPs) were prepared and characterised. It has been shown that these MNPs are capable of quantitative separation of Am(III) from Eu(III) from HNO_3 solutions (4 M). These MNPs also show a small but significant selectivity for Am(III) over Cm(III) with a separation factor of around 2 in 4 M HNO_3. The water molecule in the cavity of the BTPhen may also play an important part in the selectivity. Next, influence of coating the MNPs by zirconia (ZrO_2) on their ability to extract Am(III) from Eu(III) and Am(III) from Cm(III) in a range of HNO_3 concentrations (0.001 – 4 M) was investigated. Extraction of Am(III) and Eu(III) was reported, but little or no selectivity could be seen between Am(III) and Cm(III) at concentrations of 4 M HNO_3.

Silica gels were used as supports for the novel BTBP/BTPhen functionalized solid extractants developed to extract minor actinides from lanthanides and other fission products. BTPhen functionalized silica gel was capable of near quantitative removal of Am(III) in the presence of Eu(III) from aqueous HNO_3, while BTBP functionalized silica gel is able to remove problematic corrosion and fission products that are found in PUREX raffinates.

The latest developments in this field have been the materials where the CyMe$_4$-BTPhen actinide selective ligand has been immobilized onto the electro-spun polystyrene fibre support. Its solid extraction properties for selective removal of Am(III) from Eu(III) and Am(III) from Cm(III) were investigated. It was shown that at 4 M HNO_3, the resulting fibrous solid extractant produced separation factors of $SF_{Am/Eu} \sim 57$ and $SF_{Am/Cm} \sim 2.9$.

Based on these studies it can be concluded that the solid extractants with 1,2,4-triazine ligands are becoming mature materials ready for both analytical applications and technology.

Nature resourced radiochemistry

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Keywords: radio-green chemistry, nature resourced radiochemistry

In recent times chemists are more concerned about the synthetic chemicals and their effect on environment and human health. The chemical sciences and the chemical industries are now guided by the green chemistry principles. The radiochemistry being an important branch of chemistry, also started to practice green chemistry mandates in radiochemical experiments – the branch is named as “Radio-green Chemistry”. The other new trend in radiochemistry and related science is to explore the chemicals which are synthesized in nature. In nature thousands of chemicals are being efficiently produced in ambient temperature and pressure. The use of “nature resourced chemicals” in radiochemical experiments can be viewed as an advanced version of green chemistry. In last one decade, we have identified some natural chemicals, e.g., hesperidin, a bioflavonoid, was isolated from orange peel and proposed as radiopharmaceutical-ligand with positron emission tomography (PET) isotopes. Besides, hesperidin works as good separating agent for separation of no-carrier-added ^{89}Zr from bulk yttrium target. The same chemical was also used to remove environmentally hazardous, long lived alpha emitting polonium radionuclides. Another interesting example is piperine, an alkaloid derived from fruits of piper nigrum (commonly known as black pepper), – excellent specific reagent for gold. The experiment was confirmed by radiotracer study using ^{198}Au. Probably the enone group can form a sandwich type of complex with gold which is responsible for its extraction. The developed method may also be useful for recovery of gold from the waste effluent. We have also used various seed proteins, which are usually thrown away, to study radionuclide protein interaction. Baker’s yeast Saccharomyces cerevisiae can selectively and quantitatively accumulate. ^{152,154}Eu radioisotopes, long-lived fission product, from a synthetic mixture of other long-lived radionuclides at neutral pH. The “Nature Resourced Radiochemistry” [1] would pave a new way in radio-green chemistry research in future.

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Advancing the state-of-the-art in nuclear forensics

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Keywords: nuclear forensics, radiochronometry, secondary ion mass spectrometry

The science of nuclear forensics continues to advance through the exploration of new signatures that reveal information about the processing history of materials and how those signatures are used to answer investigative questions. For example, the use of radiochronometry to determine material model ages is being adopted by laboratories around the world to help constrain questions about when a material was last chemically processed. While most laboratories start by developing procedures to measure the U-234 / Th-230 parent / daughter pair for uranium radiochronometry, many are now moving toward more advanced techniques to measure the U-235 / Pa-231 chronometer, and even subsequent uranium and actinium decay series radionuclides like Ra-226 and Ac-227. These measurements are extremely challenging but becoming accessible with advanced mass spectrometry techniques. Equally challenging is building an understanding for how to interpret this data, especially in cases where there is discordance between the different radiochronometers. Another area of relatively new investigation is the use of stable isotope signatures to help understand connections between materials and geography. For example, stable oxygen isotopes, which are well known to vary with latitude, may help constrain where a uranium oxide was produced. Similarly, heavy stable isotopes of Sr, Nd, Sm, and Pb may reveal connections between a uranium material and a particular ore body from which the uranium was extracted. New radiochemistry and multi-collector sector mass spectrometry methods are key to measuring these stable isotopes. Spatially resolved techniques are becoming useful for forensic examination of nuclear material. Secondary ion mass spectrometry, in particular, is capable of determining sample homogeneity, a key parameter for characterizing uranium fuels made by blending different enrichments. All of these methods show promise for extracting relevant information from nuclear forensic samples, and ultimately may improve our ability to provide investigators with key evidence needed for judicial proceedings or material provenance assessments.

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Chemical characterization of the heaviest elements

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Keywords: heaviest elements, atom-at-a-time chemistry, relativistic effects, liquid-phase chemistry, first ionization potentials

Chemical characterization of the heaviest elements at the farthest reach of the Periodic Table is a challenging and fascinating subject not only in nuclear and radiochemistry but also in general chemistry [1, 2]. One of the most important and interesting aspects is to clarify basic chemical properties of these newly synthesized elements, such as ionic radii, redox potentials, and their ability to form chemical compounds as well as to elucidate the influence of relativistic effects on valence electronic structure of the heaviest elements. The heaviest elements with atomic numbers $Z \geq 101$, however, are all man-made elements synthesized at accelerators using nuclear reactions of heavy-ion beams with heavy element target materials. They are only be identified through measurement of their characteristic nuclear decay or that of their known daughter nuclei using sensitive detection techniques. As both half-lives and cross sections of these nuclides rapidly decrease, they are usually available in quantities of only a few atoms or often one atom at a time. Here, recent studies of liquid-phase chemistry and measurement of the first ionization potentials of the heaviest elements at JAEA are presented.

Liquid-phase chemistry of the heaviest elements has been accomplished by partition methods with single atoms, such as liquid-liquid extraction and ion-exchange chromatography. Chemical separation and characterization of the first two transactinide elements, rutherfordium (Rf) and dubnium (Db) in liquid-phases [3] are briefly summarized. The successful redox experiments with nobelium (No) and mendelevium (Md) [4] are also reported. We developed a new experimental approach to investigate single atoms of the heaviest elements with an electrochemical method based on a flow electrolytic cell combined with column chromatography.

The first ionization potential (IP_1) is an atomic/chemical property which most sensitively reflects the outermost electronic configuration. Precise and accurate determination of IP_1 provides significant information on the binding energy of the valence electrons, and thus on increasingly strong relativistic effects. Recently, the IP_1 values of the heaviest actinide elements, fermium (Fm) through lawrencium (Lr) have been measured using a surface ionization technique coupled to a mass separator [5]. We will outline the experimental method and achievements.

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Ultra-sensitive radionuclide analyses: New frontiers in radioanalytics

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Keywords: radiomerics, Ge gamma-spectrometry, underground laboratory, mass spectrometry, AMS, ICPMS, single atom counting

New developments in radiometrics technologies have been associated mainly with underground operations of large volume HPGe detectors thanks to their high detection efficiency, very good resolution and low background, especially when operating underground [1, 2]. Monte Carlo simulations have shown, however, that low radiation environments available in deep underground laboratories have not been fully utilized for an expected background reduction of HPGe spectrometers due to radioactive contamination of their construction parts [3, 4]. The most sensitive technologies for ultra-low-level analyses of long-lived radionuclides in the mass-spectrometry sector have been mainly accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICPMS) [5, 6].

These new developments have had great impact on investigations of rare nuclear processes and applications of radionuclides in environmental, life and space sciences. New scientific investigations have been carried out therefore which have not been possible before either because of lack of sensitivity or required sample size, as it will be documented on investigations of rare nuclear decays (e.g. neutrinoless double beta-decay [7]) and radioactivity studies in the terrestrial and marine environments [8, 9]. Thanks to these new developments we have reached new frontiers in radioanalytics – a single atom counting.

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Recent advances in the production of theranostic radionuclides

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Keywords: theranostic approach; positron emitter; therapeutic radionuclide; production methodology; radiochemical aspects

The concept of combining internal radiotherapy and diagnosis is known as theranostic approach. It involves administering a pair of radionuclides of a particular element in the same chemical form, one a positron emitter for quantitative determination of the dose distribution via a PET measurement and the other a β^-- or α-particle emitter to cause the therapy effect. There are several such "matched-pair" of radionuclides, e.g. ^{44g}Sc/^{47}Sc, ^{64}Cu/^{67}Cu, ^{72}As/^{77}As, ^{86}Y/^{90}Y, ^{124}I/^{131}I, ^{152}Tb/^{161}Tb, etc. [1]. The production methods of the positron emitters ^{44g}Sc, ^{64}Cu, ^{86}Y and ^{124}I at a small-sized cyclotron are now established [1,2], all utilizing the (p,n) reaction on an enriched target isotope. Regarding ^{72}As and ^{152}Tb, however, work is underway to produce them utilizing intermediate energy cyclotrons. Similarly, the production methodologies of the therapeutic radionuclides ^{90}Y, ^{131}I and ^{161}Tb using a nuclear reactor are well established, but the production of ^{47}Sc and ^{67}Cu still needs considerable effort. Besides conventional use of a nuclear reactor and an intermediate energy cyclotron, there is enhancing interest in developing irradiation technologies, providing fast neutrons via the d/Be or d/C breakup process at a cyclotron, and high-energy photons at linear electron accelerators (LINAC). The related new developments will be reviewed, with particular emphasis on radiochemical aspects of the production methods.

Due to rather extensive effort involved in the use of a "matched-pair" of radionuclides, in recent years the tendency has been increasing to treat the therapeutic radionuclide used as the theranostic agent. The dosimetry then relies on γ-ray spectrometry via SPECT which is not quantitative. Based on this approach, the therapeutic radionuclides like ^{47}Sc, ^{67}Cu, ^{177g}Lu and ^{186}Re are considered as theranostic radionuclides because they emit, besides β^--particles, also γ-rays suitable for SPECT. The newer production methods of those radionuclides will be elucidated. The perspectives and availability of theranostic radionuclides will be discussed.

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Actinide separation over lanthanides via aluminium/gallium cathode based electrolysis in LiCl-KCl eutectic

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Keywords: actinides, lanthanides, electrolysis, spent fuel, pyrometallurgy

Pyrometallurgical process is one of the most attractive options for the reprocessing of advanced nuclear fuels and transmutation blankets which are well-known to possess high burn-up and high content of Pu and minor actinides. In a typical traditional pyrometallurgical process, predominant uranium is recovered onto a solid stainless steel cathode, whilst most remaining uranium, plutonium and minor actinides are deposited together at the liquid cadmium cathode. Nevertheless, one of the main drawbacks of this pyrochemical method is that significant amount (~6% wt) of rare earth elements remains in transuranium products. As reported by previous investigations, the deposition potential gap of actinides and lanthanides on a solid Al cathode are much larger than those on other active solid or liquid cathodes, and therefore the separation of actinides from lanthanides by using a solid Al electrode should be a good choice. Keeping this in mind, in this work, attempts of actinide separation over lanthanides by using active solid Al cathode and liquid Ga cathode as well as Al-Ga binary alloy cathode were conducted based on systematic electrochemical behavior investigations and correlated thermodynamic calculations toward representative elements in molten salt.

European monitoring of the atmospheric ruthenium-106 episode in fall 2017

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Keywords: environmental nuclear forensics; Ru-106; environmental monitoring; nuclear accident

In late September 2017, a release of ^{106}Ru happened in the eastern Eurasian border region. The prevailing weather conditions carried the radioactive plume in western direction, over the Black Sea and Ukraine to Central Europe where it was monitored by almost all member states of the European atmospheric monitoring consortion „Ring of Five" (Ro5). The activity concentrations ranged from few μBq·m^{-3} to more than 100 mBq·m^{-3}, depending on the sampling interval and the geographical location of the respective station. In my presentation, I will summarize the efforts and the multi-disciplinary forensic approach of the international community to reveal the circumstances and background of this mysterious environmental release.

Invited Speakers

Actinide analytical chemistry

Use of ^{248}Cm isotope for Cm determination in analysis of ^{242}Cm and ^{244}Cm in environmental samples

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Keywords: curium, tracer, speciation, environmental samples

Curium isotopes are mostly produced by irradiation of uranium and/or plutonium oxides with neutrons in nuclear reactors. Over twenty isotopes of curium are known with mass numbers ranging from 232 to 252, which all are radioactive and primarily α-particle emitters, with ^{242}Cm and ^{244}Cm (respective half-lives of 163 days and 18.1 years) accounting for 90% of those produced in the nuclear fuel cycle. The high specific activities of ^{242}Cm and ^{244}Cm ($\sim 10^{12}$ Bq g^{-1}) has mainly been considered an issue because it significantly contributes to the radiotoxicity of nuclear waste. Curium present in the environment, especially around reprocessing plants such as La Hague (France), must be quantified because it could present a major risk to public health linked to the strong radiotoxicity of these isotopes.

Reliable detection and quantification of curium isotopes in complex environmental matrices require extensive removal of chemical and radiometric interferences for which the procedure yield must be determined using an elemental or isotopic analog. The common yield monitor of curium separation is ^{243}Am, considered as a chemical analog. However, the use of this isotope is also known for its drawbacks. A bias could be observed between the chemical yields of americium and curium. This bias is essentially due to the difference between reduction properties of americium and curium. Additionally, differences between stability constants of curium and americium with inorganic and organic ligands seem negligible but might become significant when combined in a complex radiochemical procedure, involving multiple steps. To understand the behavior of americium and curium during our complex purification procedure and the observed bias, their speciation was investigated by computer simulation. This simulation was executed using the MEDUSA software and the associated HYDRA database, compiled with recently published data.

To avoid the risk of a bias between the chemical yields, and so an incorrect curium activity determination, an alternative approach using ^{248}Cm to enable definitive yield determination was studied when analyzing curium isotopes in environmental samples. A commercial curium solution with ^{248}Cm enrichment of 95.82% (wt) was standardized for its concentration and Cm isotopic composition by alpha spectrometry. Various environmental samples, each spiked with known amount of ^{248}Cm and ^{244}Cm spikes were processed following our radiochemical procedure involving alpha spectrometry counting.

Activities of ^{244}Cm obtained when ^{248}Cm is used as tracer showed excellent agreement with the ^{244}Cm spikes, in contrary to results obtained whith ^{243}Am tracer. Thus, viability of the use of ^{248}Cm for definitive yield determination, when curium isotopes are analyzed, was validated through this new protocol.

Experimental results and method performances characteristics observed from analyzing various types of environmental samples (water, vegetables and sediment) will be presented. A detailed methodology including curium and americium speciation, ^{248}Cm solution qualification, interferences corrections, results and uncertainties calculation will be presented and discussed.

Pyrochemical Pu metal production: Process improvements and considerations for residue processing

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Keywords: analytical chemistry, pyrochemistry, plutonium, uranium

High-purity plutonium (Pu) and uranium (U) metals are essential for manufacturing missions, standards preparation, and other United States (US) Department of Energy (DOE) program needs. Pyrochemical processes are used globally for the production of high-purity Pu and U metals from uranium or plutonium fluoride or oxide. Alkaline earth metals at high temperatures are typically employed in such processes, which include direct oxide reduction, metal chlorination, molten salt extraction, and electrorefining. A variety of starting materials, crucible types, assembly materials, and process conditions can be utilized for successful execution of each process, but the impacts of each process variable on product purity and resultant residues often comes into question. This presentation will discuss chemistry associated with the production and processing of Pu and other metals as used at Los Alamos National Laboratory (LANL) and globally. Through analytical characterization of starting materials, products, and byproducts from Pu pyrochemical processes, potential avenues for process improvement are explored. The development and use of various analytical tools and techniques to study this extremely challenging problem will be discussed. Special consideration of the resultant salt slag is also taken into account from a residue handling perspective.

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A day in the life of a bulk special nuclear material characterization laboratory

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Keywords: analytical chemistry, destructive analysis, americium oxide, ^{238}Pu heat source, plutonium

Multiple studies that demonstrate the breadth of bulk actinide analytical chemistry at Los Alamos National Laboratory (LANL) will be presented here. The analytical laboratory was established during the Manhattan Project and is considered one of the premier analytical laboratories for special nuclear materials characterization. Highlighted here are LANL's unique bulk actinide analytical capabilities that showcase the work of chemists in nuclear facilities to characterize: 1) ^{238}Pu heat source production samples used as Radioisotope Thermoelectric Generators (RTGs) by National Aeronautics and Space Administration (NASA) to support deep space exploration missions; 2) analysis of ^{241}AmO$_2$ to provide to commercial vendors in the production of smoke detectors and neutron generators; and finally 3) plutonium for non-destructive assay (NDA) standards used in various portal monitoring applications. All materials used in these projects are highly radioactive and require a specialized skill set, well-engineered safety controls, and radiological facilities to process and characterize them. These examples were chosen to illustrate the nature of actinide analytical chemists' work, demonstrate global applications, show the diversity of applied analytical tools and challenges, and present the unique chemistry associated with production and subsequent analysis.

Acknowledgments
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Analytical methods and detection techniques

CHNET_TANDEM experiment: muonic atom X-ray spectroscopy for archeological sample non-destructive analysis

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The goal of the CHNET_TANDEM experiment is to implement, develop and optimize non-invasive and non-destructive analysis techniques to be used in the archeometric field for the elementary characterization of cultural heritage samples. In particular, CHNET_TANDEM uses Muonic Atom X-ray Spectroscopy: a technique that has the characteristic of analysing the constituent elements of a sample in a non-destructive and non-invasive manner, revealing X-rays prompt emissions following the formation of Muonic Atoms inside the targets. Muonic spectroscopy is "radiation technique based" that does not make the sample radioactive, and can be used for both superficial and deep elemental analysis, with the possibility of defining the area and depth that can be analysed with great precision.

Due to the muon mass (200 times heavier than electron), the characteristic X-rays, element dependent, are emitted at higher energy, immediately after the muon-atom interaction. The measurement of high energy (from dozens keV to some MeV) X-rays is easier for two main reasons: less auto absorption permits an efficient bulk analysis and the possibility to use high resolution detectors such as High Purity Germanium (HPGe) ones that can distinguish energies of peaks very close to each others.

The utilized facility is at PORT4 of RIKEN-RAL Muon pulsed beam of 20 to120 MeV/c^2,which has an intensity of 10^4 muons per spill at 50 MeV/c^2 and a time structure with two successive 70 ns wide spills (with an inter-peak distance of 320 ns) with a 37,5 Hz repetition rate; a good control of the beam focus z-position, and hence a good spatial resolution along z, is achieved via fine momentum tuning/sensitivity of 1 MeV/c^2. The experimental setup consists of 2 hodoscopes for beam monitoring made by 64 squared scintillating fibers read by SiPM; a high energy resolution spectroscopy system which consists of various types of HPGe detectors: two GEM-S (semi-planar 30X20 mm^2 crystals, with good resolution at low and medium energy), one GLP (small planar 9 X 7 mm^2 crystal, with good resolution at low energy up to 150 keV) and one GMX (N-type coaxial 49X57 mm^2 crystal (for energy up to 3 MeV). The detectors are coupled to ORTEC amplifiers (579 fast-filter shaping time 250 ns and 672 shaping time 500 ns).

A new full digital Data AcQuisition (DAQ) system for an HPGe detectors was also tested for "nuragic" archeological bronze samples and Standard Materials targets analysis in order to test and validate the set-up for quantitative non-destructive bulk elemental analysis of metallic archeological artifacts.

Detection of actinides/lanthanides by Time Resolved Laser Induced Luminescence (TRLIF)/Chemiluminescence (TRLIC) Laser Spectroscopy

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Using short laser pulses for excitation of molecules and ions in liquids and time resolution (TR) for registration of luminescence (TRLIF) and chemiluminescence (TRLIC) produced by actinide and lanthanide ions one can efficiently separate target signals from short-lived background luminescence [1-4]. Selective excitation of detectable molecules and multi-step excitation schemes of luminescence/chemilumunescence can additionally decrease the intensity of background radiation.

Pu, Np, and some U compounds do not produce direct luminescence in solutions, but when excited by laser radiation, they can induce chemiluminescence [1–4] of chemiluminogen (luminol in our experiments). The details of multi-step excitation of luminescence/ chemiluminescence in solutions are considered. It is shown that a multi-step scheme of luminescence/chemiluminescence excitation increase both the sensitivity and selectivity of detection of substances.

Uranyl (or other elements and molecules) has a different circulation period in blood and in urine [4]. By comparison of the concentrations of the uranyl (or other elements and molecules) in blood plasma and in urine one can estimate the time when the uranyl (or other elements and molecules) entered into the organism.

Results of the experiments on Eu, Sm, U, and Pu detection in different solutions are presented.

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Detection of background thermal neutrons in a modified low background germanium gamma ray spectrometer

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Keywords: gamma-rays spectrometer, neutron capture in cadmium, neutron moderation, neutron background, gamma ray background

Since the neutron background at sea level is about 0.015 n/(cm^{2}s) [1], the neutron effects observed in low-background gamma spectrometry are well known features. The general idea of a modification of low background gamma ray spectrometer with germanium detector to enhance signal from background environmental neutrons was proposed by us and initially tested many years ago [2]. The principle of modification is simple: inside low background shield some cadmium and moderator is places. In current version around germanium detector's end-cup a 2 mm thick cadmium plate (30x10 cm) was wrapped around. Moreover, on top of end-cup-another 2 mm thick cadmium plate (10x10 cm) was placed. Detector was in standard lead shield of 10 cm thick bricks with 50x50x50 cm shielded space. The cryostat of detector was made of ultra pure aluminium by Baltic Scientific Instruments (U and Th levels at single ppb range). Inside shield up to 12 plastic 5 L canisters containing water were placed, which played role of moderator. In such configuration background spectra were collected in automatic mode, recording separately each and every hour a day spectrum. Measurements were performed for almost two months. Then spectra were summed together for each hour of day together, reducing number of spectra from 1211 to 24. The aim of this was to check if there is any day cycle of count rates in main background lines of spectrometer. The resulting single spectrum (with acquisition time of 3.8 Ms) from all single hour spectra was summed up as well. After a half of a year experiment was repeated to obtain comparison between summer and winter time. The another set of experiments were conducted with different moderator localized inside shield. Instead of water the graphite was used, namely five graphite cylinders (20 cm diameter, 32 cm height, about 10 L of volume each) with total mass of ~108 kg were placed inside the shield to play the role of moderator. The results and conclusions will be presented on Conference

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Education in radiochemistry

Radioanalytical and nuclear chemistry course at the University of Debrecen

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Keywords: chemist MSc education, radiochemistry specialization, radioanalytical chemistry education, natural radioactive and stable isotopes, tracer methods, radiation- matter interactions

The Chemical Institute of Debrecen University, together with the Institute Nuclear Medicine and Institute of Nuclear Research of the Hungarian Academy of Science, has radiochemical specialization within the chemist MSc education. A course is the lecture and practices of radioanalytical and nuclear chemistry.

The topics of lectures [1]: a short repetition of the formation and production of nuclear, atomic and particle radiation, interaction of nuclear, atomic and particle radiation with matter.

Analytical methods using natural radioactivity: determination of geological and historical ages.

Separation of isotopes. Physical, chemical, geological, and biological information obtained by observing isotope separations.

Basic rules of tracer studies. Selection of tracers. Production of tracer isotopes.

Chemical radioanalytical methods: isotope dilution analysis, radiometric titration, radio gravimetry, radiochemical separation methods.

Radioanalysis in living organisms: *in-vitro* and *in-vivo* methods.

Industrial radioanalysis.

Nuclear and radioanalytical methods based on radiation-matter interactions: classification, characterization on the basis of the irradiation and emitted particles/photons.

Applications of neutrons: activation analytical methods, neutron radiography and tomography, neutrons scattering.

Application of electromagnetic radiation with high energy (gamma, X-ray): X-ray fluorescence analysis, Mössbauer spectroscopy

Application of charged particles: beta backscattering, electron microscopes and microprobes. Rutherford backscattering, particles induced X-ray and gamma spectroscopy.

In practices, the students visit of a nuclear power plant, a nuclear waste disposal site, Energy Science Research Institute and Isotope Institute Ltd. They meet the production of radiopharmaceuticals, they have a prompt gamma activation practice and a ICP-MS analysis of uranium and transuranium elements.

Acknowledgments

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Developing a Massive Open Online Course on Nuclear and Radiochemistry

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Keywords: MOOC, online course, radiochemistry, nuclear chemistry

The idea to propose a Massive Open Online Course (MOOC), one of the most widespread innovative learning tools, on Nuclear and Radiochemistry (NRC) arises from the need to attract more students to this discipline and from the awareness that NRC is still perceived with mistrust by public due to the negative annotation of nuclear energy. To this purpose, a learning path has been designed, able to drive the users (bachelor students with scientific background) to discover the role of R&D activities in NRC for the modern society. Helping to maintain the fading expertise and skills in NRC, the course aims at revealing the numerous applications that rely on NRC skills, other than the more obvious context of nuclear energy production: nuclear medicine, for both diagnostics and therapy, but also dating in archaeology, nuclear forensics, radiation protection, and basic research e.g. on super heavy elements.

The MOOC, under development within the EU-H2020 MEET-CINCH project[1], has been designed according to a specific pedagogical framework that guides the student in discovering that situations of everyday life have connections with radiochemistry. The MOOC has been divided into five "weeks" highlighting the importance of radiochemistry for Environment, Health, Industry, Nuclear Energy and Society. Each week consists of different modules covering all possible applications of radiochemistry in the different areas of the week topic. The module gradually introduces the student to the topic, gives him different examples and applications to understand the theoretical concepts, principles of operation and to acquire a technical terminology. The student can apply and verify the knowledge acquired by means of questions or exercises. Currently, the first week on radiochemistry for the environment has been created along with a prototype video. The week is divided into three modules titled "Natural Radioactivity", "Environmental Monitoring" and "Environmental remediation". The first module introduces the student to natural radioactivity by defining radionuclides, radioactive decay and other basic concepts. In the second module, after another everyday situation, the student becomes aware of artificial radionuclides produced by nuclear fission, as well as TENORMs as consequence of anthropogenic activities. Student can understand the importance of environmental monitoring for making such activities safe for people and environment, as well as the radiochemical methods applied to this purpose. In the last module the student is introduced to application of radiochemistry to support environmental remediation. An attempt to adapt some MOOC introductory videos to enhance nuclear awareness of general public will be evaluated, in particular to highlight the beneficial use of nuclear and radiochemistry for society.

Acknowledgments

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I-131 Production, release, and measurement

Tracking atmospheric iodine-131 by European monitoring networks: the early 2017 release as a showcase

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Keywords: environmental nuclear forensics; I-131; environmental monitoring; radiopharmaceutical factility

In January and February 2017, an unusually long episode of atmospheric iodine-131 ($T_{1/2} = 8$ d) was observed by the European „Ring of Five" (Ro5) network [1]. The episode was marked by a strong temperature inversion that prevented dilution and thus explains the unusually long 8-weeks-duration of the episode. Also, it is suspected that several independent source coincided to form the observed distribution pattern. The strongest source, however, according to atmospheric transport modelling, was located in Western Russia. It is suspected that this source was a radiopharamceutical facility, and that the release was likely an authorized release, which impressively illustrates the capability of the Ro5 network. The current detection limits of the most sensitive Ro5 stations are in the range of 0.1-0.5 µBq/m³, which corresponds to the staggering amount of 1 atom ^{131}I per 10 m³ of air. However, few stations in Europe are equipped with monitors for the detection of gaseous iodine, which should be improved in the future.

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Liquid scintillation and analysis of long-lived radionuclides

Determination of beta-emitting radionuclides in environmental and biological samples by TDCR Cerenkov counting

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Keywords: triple-to-double coincidence ratio, Cerenkov counting, high energy beta-emitting radionuclides

Cerenkov counting technique has been widely used in the analysis of high energy beta-emitting radionuclides in environmental and biological research due to several reasons: (1) the measurement can be conducted on a commercial liquid scintillation counter without any modification of the instrument; (2) the sample is not diluted with any scintillation cocktail and thus remains unchanged for further analysis; this not only allows for counting of a larger sample volume but also helps reduce time and cost on sample preparation and waste disposal; (3) as low energy beta- and alpha-emitting nuclides cannot produce Cerenkov light, they would not intefere with the counting of high energy beta emitters; (4) Cerenkov counting is free of chemical quenching. However, Cerenkov counting efficiency can be strongly affected by color quenching. Even very light color barely visible to the naked eye can produce a significant quench effect with a noticeable reduction in counting efficiency. The color quench for Cerenkov counting is usually corrected by the internal standard method or quench curve method, but these methods are quite time consuming and cancel one of the main advantages of the Cerenkov method of keeping the original unadulterated sample.

Recently, the triple-to-double coincidence ratio (TDCR) method has been sucessfully utilised for quench correction in Cerenkov counting for activity standardization and rapid screening of high energy beta-emitting radionuclides in metrological and environmental applications [1, 2]. The TDCR Cerenkov counting would also be well suited for routine quantitative determination of high energy beta-emitters in low level environmental and biological samples [3]. In this presentation, recent method developments on TDCR Cerenkov counting for rapid determination of high energy beta-emitting radionuclides (e.g., ^{90}Y/^{90}Sr, ^{89}Sr, ^{32}P, ^{106}Rh/^{106}Ru, ^{210}Bi/^{210}Pb, ^{228}Ac/^{228}Ra) in various environmental and biological samples will be overviewed, along with their applications in the fields of environmental radioactivity monitoring, emergency radiobioassay and radio-hazard characterization etc.

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Benin Sculptures dating: contribution of scintillation techniques to the restitution of cultural heritage objects

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Keywords: Plastic Scintillating Resins, ^{210}Pb, Benin Bronze sculptures, restitution.

The Benin kingdom suffered a punitive expedition by the English army in 1897. As consequence of this action, all bronze sculptures of the royal palace were taken and brought to Europe. Nowadays, most of these sculptures are included as part of the collections of European Museums, mainly British and German, but also there are an important number of objects that have been commercialized due to their decorative use. The pressure of the market and the continuous creation of the Benin artists have led to the existence of an important number of original Benin Sculptures, but created after 1897; and fake Benin Sculptures, produced at other locations different from Benin.

Revision of the colonial actions is including the restitution of the original stolen objects. This is the case of Benin, but to consider this restitution is necessary to know which come from the punitive expedition and which not.

A research project has been started by the University of Barcelona with the Collaboration of the Museum of Five Continents of Munich to develop a dating method for discriminating between Benin Sculptures created previous or after 1897.

This method is based on the determination of ^{210}Pb activity of sculptures complemented with the information corresponding to the stable lead isotopes relationship and the elemental composition of the bronzes in major and minor components. According to the remaining ^{210}Pb activity on the sculptures, these could be discriminated as created before and after the punitive expedition.

Plastic Scintillating Resins (PSresins) based on the 18-crown-6-ether extractant were used for the determination of ^{210}Pb activity.

The study was divided in two steps: the analytical feasibility and the application feasibility.

In the analytical feasibility study, the chemical attack of bronze samples was optimized and the characterization of the PSresin in terms of detection efficiency, background, detection limit and selectivity of the resin against the components of the bronze matrix was studied. Next, using these data in the worst scenario of lead content in the sculptures (1% of Pb and 10 dpm/g of ^{210}Pb) an amount of 0.5 g of bronze was established when the measured is performed after 35 days when ^{210}Pb and ^{210}Bi are in secular equilibrium. This amount is compatible with the preservation of the physical integrity of the objects.

In the application feasibility step, a set of Benin sculptures produced before and after 1897 were analyzed. These analyses allow establishing an activity threshold of 8.82 dpm ^{210}Pb/g Pb for the activity of a sculpture produced before 1897 as long as the amount of lead analyzed was enough (6 mg). Stable lead isotopes results discriminate about the origin of the raw materials whereas ^{210}Pb activity indicates the date of creation of the sculpture.

These results show the capability of the proposed procedure and the plastic scintillation resins for the discrimination of Benin sculptures. A wider set of sculptures is in process of examination.

Development of radiochemical procedures for the determination of actinides

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Keywords: Actinides, alpha-spectrometry, ICP-MS, UTEVA resin, TRU resin, DGA resin

Accurate determination of actinides from thorium to curium through uranium, neptunium, plutonium and americium has always been a challenge for the analysts. The radionuclides of these elements typically emit difficult-to-measure alpha, low energy beta or gamma radiation, therefore their determination requires careful radiochemical separation from matrix components and interfering radionuclides. There are many methods for the separation of individual elements or groups of actinides followed by measurement of the emitted radiation or the mass of the radioelements.

Our goal was to develop procedures for the simultaneous separation of all actinides most preferably by the use of a single chromatographic column. Extraction chromatographic (EC) materials of high distribution ratios and selectivity for actinides against any other element and selectivity for actinides against each other were looked for. To increase the selectivity of the chromatographic resin for given actinides, on-column oxidation state adjustment was combined with proper selection of the acidity of the eluents, addition of specific complexing agents and changes in environmental conditions (temperature).

Three methods have been developed in course of the years based on commercially available EC resins, i.e. UTEVA[1] containing dipentyl-pentylphosphonate, TRU[1] containing octylphenyl-N,N-diisobutyl-carbamoylmethylphosphine oxide and DGA containing N,N,N',N'-tetraoctyldiglycol-amide[1] sorbed on inert support. Complete procedures have been developed for the separation of Th, U, Np, Pu using UTEVA resin, for the determination of Th, U, Np, Pu, Am-Cm in small samples using TRU resin, and for the same elements from bigger samples using DGA resin.

Samples were destroyed either by dry and wet digestion using mineral acids in open or closed microwave systems, or by fusion. Pre-concentration procedures tailored to the EC separation based on co-precipitation of actinides were used whenever it was necessary. The EC resins proved to retain actinides from acidic load solutions and offered possibilities for the sequential elution. Alpha sources were prepared by micro-coprecipitation. ^{241}Am, ^{244}Cm, ^{239,240}Pu, ^{238}Pu, ^{238}U, ^{235}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Th were determined by alpha spectrometry, ^{237}Np was determined by ICP-MS combined with gamma spectrometry. Basic steps of the procedures with their performance parameters (chemical recovery, decontamination factors, trueness and precision) will be discussed in the presentation.

The methods were originally developed for determination of actinides in radioactive wastes, in certain cases they were extended for the analysis of environmental (soil, sediment and swipe test) and biological (urine) samples. Each method has its proposed fields of application. Examples will be given to show the pros and cons.

[1] Products of TRISKEM-International

Mass spectrometry

Development of a strategy to establish a standard method to determine Tc-99 in radioactive wastes

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Keywords: radioactive waste, radiochemical method, scintillation counting, ICP-MS

With a half-life of 214000 years, Tc-99 is a major contributor to the radioactivity of nuclear waste at long term. Due to its high mobility in the environment as pertechnetate anion, the determination of Tc-99 is a key issue for the management of radwaste. In France, the National Radioactive Waste Management Agency (ANDRA) imposes its declaration from 0.01 Bq/g and limits its activity concentration to 44000 Bq/g for low and intermediate level radwaste [1].

As a beta emitter, Tc-99 has to be isolated from the interfering radionuclides through a radiochemical procedure prior to any measurement, often liquid scintillation counting or ICP-MS. Many literature works deal with the radiochemical characterization of Tc-99 in environmental samples [2]. There is a guide standard for the determination of Tc-99 in soil [3] and a standard project is currently being finalized for water samples [4]. However, no radiochemical standard or common method has been published for the measurement of Tc-99 in radwaste. Since the decommissioning and dismantling of nuclear sites are in growth, it is of prime interest to set up a standard method for its accurate quantification.

The aim of this presentation is to detail the different steps which led to the establishment of a common radiochemical procedure to analyze Tc-99 in radwaste. In the framework of CETAMA commission, a working group dedicated to Tc-99 has been created in 2015 in France. Nine laboratories have shared their in-house protocols and compared them to the literature works. They have finally selected a method based on extraction chromatography (using TEVA® resin) by taking care of the elimination of interfering elements (especially ruthenium and molybdenum for ICP-MS analysis). Finally, an intercomparison exercise was set up to validate the common method. In the future, the developed strategy will be applied for the analysis of Ni-63 and Fe-55 in nuclear wastes.

Acknowledgments
The authors thank the members of the Working Group "radionuclides analysis in waste" (WG14 - CETAMA).

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Carbon isotope mass spectrometry of organic compounds in Baltic Sea sediments: implications for dumped chemical weapons impacts on the marine environment

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Keywords: Baltic Sea sediments, carbon sources, *Pseudomonas putida,* carbon isotopes

The aim of this study was to use radiocarbon and lipid-derived biomarkers to trace toxic organic substances at a CWA dumpsite. Estimation of effect of utilization of chemical compounds with different radiocarbon content on dating of sediments as well as Δ^{14}C analysis of organic fractions such as total lipid extracts and phospholipid-derived biomarkers have been applied.

Distributions of Δ^{14}Cstudied in bottom sediments collected during 2011-2016 in the Curonian Lagoon and in the open Baltic Sea indicated wide variations of $\Delta^{14}C_{TOC}$ (from –446.1‰ to –6.7‰) while $\Delta^{14}C_{TLE}$ values were more depleted with the average value of –536.0‰. The most depleted $\Delta^{14}C_{TOC}$ and $\Delta^{14}C_{TLE}$ values in bottom sediment samples were found at the CWA dumpsite located at the Gotland Deep and were attributed to the different carbon sources. Organic carbon sources in the sediments estimated using an End Member (EM) mixing-model for three sources of OC–continental, marine and fossil– on average were as follows: 26%, 53%, and 21% of the total, respectively, while the content of fossil carbon sources in the Gotland Deep sediments was higher (32%), as compared to the near shore zone with 13%.

The laboratory experiments on differential carbon utilization by *Pseudomonas putida* isolated from bottom sediments showed that microorganisms responsible for the degradation of organic matter may not necessarily use all compounds equally from complex mixtures naturally present in environmental systems. Preferential utilization of glucose (up to 80%) from the mixed media was found for *Pseudomonas putida* bacteria. In the absence of glucose the diesel fuel utilization by *Pseudomonas putida* was found to be at the same level as in the media with glucose. Incorporation of the inorganic carbon was estimated to be rather low (2%–10%). The microorganisms can choose easily assimilable organic carbon from complex mixtures and provide differential involvement of various substances into the carbon cycle. Large ^{14}C depletions observed in sediments collected in the Gotland Deep of the Baltic Sea may indicate a leakage from the dumped chemical weapons.

Acknowledgments

The author would like to thank colleagues from Lithuanian institutions as well as Hong-Chun Li from the National Taiwan University and Pavel Povinec from the Comenius University for long-term collaboration. Financial support provided by the Research Council of Lithuania (contract No. MIP-080/2012) is highly acknowledged.

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Ultrasensitive (<1 mBq), cheap, and fast detection method for ^{7}Be allowing high sample throughput

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Keywords: Be-7, Be-10, accelerator mass spectrometry (AMS), rainwater

Beryllium-7 ($T_{1/2}$ = 53.22 d), mainly measured via γ-spectrometry, is used as a (natural) radiotracer for education and science [1]. For activities < 0.1 Bq and especially for samples also containing so longer-lived ^{10}Be ($T_{1/2}$ = 1.387 Ma), accelerator mass spectrometry (AMS) is the method-of-choice.

We demonstrate that ^{7}Be and ^{10}Be can be quantified at the DREsden AMS (DREAMS) facility [2,3] on the same prepared BeO. Detection limits (^{7}Be) are as low as ~ 0.6 mBq, hence, one-to-two orders of magnitude better than “standard/ordinary” and “sophisticated” decay counting (e.g. in an underground laboratory). Uncertainties for small samples are usually 6-7 % for small samples. The method is validated by γ-counting of two larger rainwater samples showing an excellent agreement with the AMS result [4].

Samples as small as tens of millilitres of rainwater can be chemically processed (after acidification) within a few hours without expensive and time-consuming ion exchange. Isobar (^{7}Li) suppression by chemistry and AMS is sufficient to guarantee an ultrasensitive, cheap, and fast detection method for ^{7}Be allowing high sample throughput.

The DREAMS facility allows external user access free-of-charge via a proposal system. Further information can be found at www.hzdr.de/ibc or www.ionbeamcenters.eu.

Acknowledgments

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Mössbauer spectrometry

Tin analysis: difficulties and some solutions

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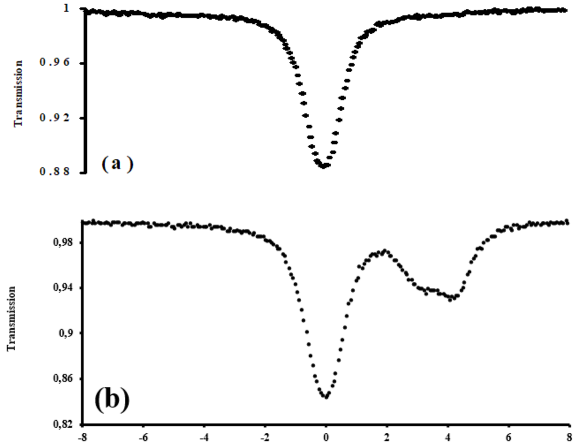
Keywords: tin analysis, Mössbauer spectroscopy, atomic absorption spectroscopy, tin(II) chloride fluorides

Chemical analysis has reached a level of sophistication such that most analytical chemistry research involves detecting and measuring nanomoles, and perhaps picomoles, of compounds in mixtures. This is particularly useful for biomolecules and polluants. However, synthetic chemists have often difficulties establishing the formula of new compounds because no reliable analytical method exists or it does not work properly or it suffers from interferences with other elements present in the compounds to be analyzed. Tin is one of these elements difficult to analyze in many situations. The presenttion will describe the analysis and characterization of tin in novel barium tin(II) chloride fluorides. The use of atomic absorption spectroscopy and sudy of the interferences with the other elements will be presented. However, the presentation will focus more particularly on the use of ^{119}Sn Mössbauer spectroscopy. The influence of temperature on the result of the analysis will be underlined (figure). The presenttion will focus on the use of Mössbauer spectroscopy for the study of the oxidation number of tin and the presence of partial oxidation of tin(II) to tin(IV), for the mode of tin(II) bonding (ionic or covalent) and for the study of the lattice strength.



^{119}Sn Mössbauer spectrum of a mixture of 33.8 mg $SnCl_2 \cdot 2H_2O$ and 21.9 mg SnO_2 (17.8 mg Sn in each) at (a): 298 K and (b): 12 K

In-beam Mössbauer spectra of ^{57}Mn implanted into $LiAlH_4$

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Keywords: in-beam Mössbauer, ^{57}Mn, lithium aluminum hydride, iron hydride

In-beam Mössbauer spectroscopy using a short-lived nucleus, ^{57}Mn, is a useful method to investigate the microscopic natures of solid materials. We have previously demonstrated the in-beam Mössbauer spectra of ^{57}Mn implanted into solid LiH, and the ^{57}Fe arising via the β-decay of ^{57}Mn was found to have substitution positions of both Li^+ and H^- sites [1]. Lithium aluminum hydride ($LiAlH_4$) is commonly known as a reducing agent and a hydrogen source. Iron hydride compounds have attracted attention but few molecular compounds have been found only in extreme environments. In this study, in-beam Mössbauer spectra of ^{57}Mn implanted into $LiAlH_4$ were measured varying temperature between 17 and 300 K to investigate the chemical form of Fe atoms trapped in the $LiAlH_4$ lattice.

Experiments were performed using the heavy ion synchrotron accelerator facility (HIMAC) at the National Institute of Radiological Sciences (NIRS). ^{57}Mn nuclei were produced by projectile fragmentation of the primary beam of ^{58}Fe ions and a nuclear reaction target of ^{9}Be. Disk-shaped $LiAlH_4$ was employed as the Mössbauer sample. A parallel-plate avalanche counter (PPAC) was employed as a detector, and high-quality spectra were obtained by the β-γ anti-coincidence method [2].

The Mössbauer spectrum measured at 17 K showed two sets of doublets. The major doublet **A** ($\delta = -0.22$ mm/s, $\Delta E_Q = 0.65$ mm/s) was assigned to FeH_4^-, in which the Fe has an Al substitutional position. The Mössbauer parameters were in agreements with the results estimated by density functional calculations. The other minor doublet **B** ($\delta = -1.5$ mm/s, $\Delta E_Q = 1.1$ mm/s) was assigned to the Fe atom having a Li^+ substitutional position. With increasing the temperature of the sample, the intensity of the doublet **B** decreased. This result indicated that the Fe atom was preferentially stabilized at the Al substitutional position having the FeH_4^- form. The intensities of Mössbauer emission changed according to the temperature, and the Debye temperature of the Fe atom trapped in $LiAlH_4$ was estimated to be $D = 170$ K.

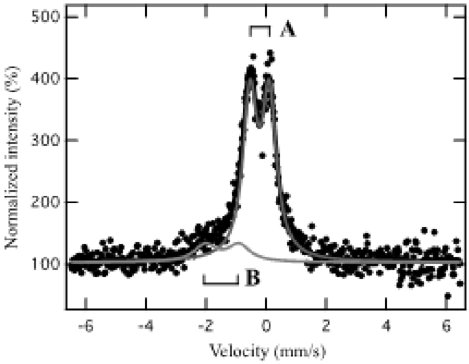

Fig. 1. In-beam Mössbauer spectrum of ^{57}Mn implanted into $LiAlH_4$ measured at 17 K.

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Neutron activation analysis

Studies of protein-bound selenium using pseudo-cyclic neutron activation and temerature-depenedent X-ray absorption spectroscopy

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Keywords: selenium, NAA, XAS, XANES

Selenium has been recognized as an essential trace element in 1957 when it was demonstrated that it could prevent necrotic liver degeneration in rats. It is known to have a biological function as the selenoenzyme glutathione peroxidase and is present in many other enzymes and proteins. Its biological effects are related to vitamin E. Selenium deficiency can result in several diseases while it can be, on the other hand, highly toxic in its many chemical forms. There has been an ever-increasing interest in determination of selenium and its species. The most commonly used methods for selenium determination are inductively coupled plasma mass spectrometry (ICP-MS) and neutron activation analysis (NAA). We have taken advantage of the unique features of NAA, such as its ability to analyze a few milligrams of solid as well as liquid samples non-destructively and independent of chemical species, and to determine low levels of selenium with excellent precision, accuracy, sensitivity, detection limits, and overall expanded measurement uncertainty. The determination of selenium by instrumental NAA (INAA) requires lengthy irradiation, decay and counting schemes if the long-lived nuclide ^{75}Se (118.5 d) is used. Instead we have developed several methods including cyclic INAA (C-INAA) and pseudo-cyclic INAA (PC-INAA) for the detection of the short-lived nuclide ^{77m}Se (17.5 s) using both thermal and epithermal neutrons in conjunction with conventional and anti-coincidence gamma-ray spectrometry. We have used PC-INAA in combination with a number of biochemical techniques, namely dialysis, ammonium sulphate precipitation, gel filtration, ion exchange and hydroxyapatite chromatography, HPLC, chromatofocusing, isoelectrofocusing, isotachophoresis, sedimentation equilibrium and enzymatic assay to separate, purify, and characterize new protein-bound selenium species in the sub-cellular fractions of bovine kidneys. We are also interested in a better understanding of the interaction of metal nanoparticles (NP) and nanoclusters (NC) with proteins. Because of the size, some metal NP and NC can have significant effects on their quantum electronic and chemical properties. We have observed an intriguing bonding behavior of selenolate-protected Au_{25} nanoclusters ($Au_{25}(SeR)_{18}$) using temperature-dependent X-ray absorption spectroscopy (XAS) from both the metal (Au L_3-edge) and ligand (Se K-edge) perspectives. We found that the Au_{13} core of $Au_{25}(SeR)_{18}$ remains relatively unchanged at low temperatures while aurophilic interactions on the surface are significantly longer in distance compared to their thiolate-protected counterpart, $Au_{25}(SR)_{18}$. Temperature-dependent studies showed a significant thermal contraction of the Au−Au framework in $Au_{25}(SeR)_{18}$, which is absent in the $Au_{25}(SR)_{18}$ system. This unusual bonding behavior of $Au_{25}(SeR)_{18}$ is proposed to be induced by the dimeric staple-like motif (-Au-Se-Au-Se-Au-) surface structures, where aurophilic bond distances and Au-Se-Au bond angles are sensitive toward temperature change. Density functional theory and molecular dynamics (DFT-MD) simulations were conducted to confirm this mechanism and provide further insight into the bonding behavior of the $Au_{25}(SeR)_{18}$ nanocluster. Finally, we used near-edge XAS results to demonstrate that the thermal contraction effect induces a change to the electronic properties of both the Au and Se and consistently accounted for using ab initio simulations of the near-edge and valence band structure.

The role of NAA in securing the accuracy of analytical results in the inorganic trace analysis

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Keywords: NAA, accuracy, quality assurance, certified refernce materials (CRM)

Neutron activation analysis (NAA) is still one of the best and most important methods in the field of inorganic trace analysis, despite constant diminishing number of competent laboratories using this technique. NAA, as practically the only method free from blank, has an important role in quality assurance in trace analysis and is frequently being used for checking the accuracy of analytical determinations obtained by other methods.

Some examples of such verification of the accuracy of analytical results obtained by other methods in which NAA played a key role will be quoted.

In this lecture the contribution of NAA to the certification of the candidate reference materials (CRM), which were certified on the basis of world-wide interlaboratory comparisons will be analyzed over the time span of several dozen years. It will be demonstrated that the share of NAA results in this certification process is much greater than it could be expected from the actual share of NAA in global analyses. The cases when the certification had to be based solely on the basis of NAA results will be emphasized.

The importance of definitive methods (i.e. the methods of guaranteed accuracy, primary methods), based on radiochemical version of NAA will be presented and their significance for certification process and generally for analytical quality assurance will be discussed. Such methods which according to VIM 3, should now be called: **ratio primary reference measurement procedures (RPRMPs)** have been elaborated in our Laboratory for several elements: As, Cd, Co, Cr, Cu, Fe, Mo, Ni, Se, U. Several examples will be presented.

State-of-the-art of neutron activation anlysis at Frank Laboratory of Neutron Physics of Joint Institute for Nuclear Research, Dubna, Russia

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Keywords: automation of reactor neutron activation analysis, monitoring of atmospheric deposition of heavy metals and radionuclides, monitoring aquatic ecosystem, bionanotechnology, medicinal plants, extraterrestrial materials, microscopy, radioecology

The history of the development of neutron activation analysis in the Laboratory of Neutron Physics at Joint Institute for Nuclear Research is briefly outlined. Created under initiative of Academician I.M. Frank in the 1960s, a small group now turned into a large international team involved in projects in the framework of programs coordinated and supported by IAEA, the European Union, the Russian Fund for Basic Research (RFBR), as well as grants of Plenipotentiaries of JINR member states. Modernization of the pneumatic system equipped with three automatic sample changers and created NAA database to automate the measurement and processing of gamma spectra of induced radionuclides are described. Experience in the Life Sciences and Materials Science is summarized. Examples are given of projects related to the monitoring of atmospheric deposition of heavy metals and radionuclides carried out in the framework of the United Nations Program on Long-Range Transboundary Air Pollution in Europe (UNECE ICP Vegetation), a project to assess the state of the environment in Egypt, based on the analysis of soil and the sediment basin of the river Nile, as well as project on monitoring trace elements in aquatic ecosystem in the Western Cape, South Africa («Mussel Watch Program»), *etc*. In combination with microscopy, the synthesis of nanoparticles of various metals via biotechnology is studied. Our investigations on applying NAA to solve the problem of industrial wastewater treatment were awarded Gold Medals by the European Union, in 2013 and 2015. New areas of research – study of natural medicinal plants and search for cosmic dust in natural planchettes (Arctic and Antarctic mosses, Siberian peat bog cores, *etc*) – reflect the public and scientific interest in these topics. Future extensions of th sector´s research is connected with the radioecological studies using precision gamma-spectrometry and a low-background laboratory for carrying out measurements of natural and anthropogenic radioactivity. Perspective of creating the Centre of Collective Useage at the planned Dubna Neutron Source of the fourth generation (DNS-4) to be put into operation in 2035-2036 is mentioned.

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Fluorine determination in biological and environmental samples with INAA using fast neutrons from a p(20 MeV)+Be neutron generator

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Keywords: fluorine determination, instrumental neutron activation analysis, fast neutrons

Fluorine is an essential element for mammals, but its elevated levels exhibit toxicity that has a wide spectrum of clinical manifestations grouped under the term fluorosis. The most significant sources of occupational and environmental exposure to fluorine involve aluminium smelting processes and combustion of fossil fuels (especially coal with a high fluorine content), respectively. Therefore, reliable analytical methods are required to monitor fluorine levels in the environment. Several nuclear analytical methods (NAM), such as particle induced gamma-ray emission (PIGE), neutron and photon activation analysis (NAA and PAA, respectively) can be used for this purpose as recently reviewed [1].

Here we present a new activation method based on the $^{19}F(n,2n)^{18}F$ reaction using fast neutrons produced by a p(20 MeV)+Be accelerator-driven fast neutron source installed at our U-120M cyclotron providing continuous neutron spectrum up to 18 MeV with a neutron fluence rate of approximately $8x10^{10}$ cm^{-2} s^{-1} at a 12-µA proton beam current. Measurement of the 511 keV annihilation radiation of ^{18}F, a pure positron emitter with $T_{1/2}$=1.83 h, is interfered by the ^{11}C radionuclide ($T_{1/2}$=20.36 min), another pure positron emitter, produced by the $^{12}C(n,2n)^{11}C$ reaction on activation of polyethylene irradiation capsules and highly abundant carbon in biological and environmental samples. To avoid this interference, selective formation of ^{18}F had to be arranged by activation with neutrons with energy below 20 MeV, which is the threshold of the $^{12}C(n,2n)^{11}C$ reaction (cf. fig. 1). Activation with higher-energy neutrons would require sufficiently long decay time (up to 4 h) to let the ^{11}C interfering activity decay, which would results in deterioration of the fluorine limit of detection (LOD). Results of fluorine determination for several biological and environmental reference materials achieved with the new INAA procedure are presented and compared in terms LOD, accuracy and precision with other methods.

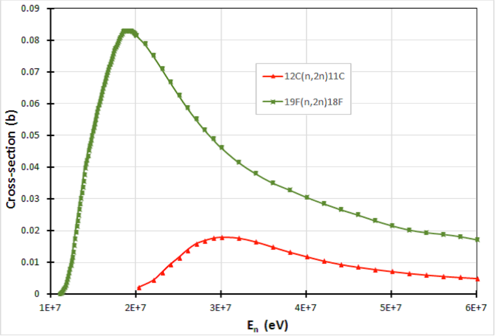

Fig. 1. Excitation functions of the $^{19}F(n,2n)^{18}F$ and $^{12}C(n,2n)^{11}C$ nuclear reactions analytical

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Nuclear forensics

Results from the third Galaxy Serpent web-based table top exercise tilizing the concept of nuclear forensics libraries

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Galaxy Serpent is an ongoing series of virtual, web-based international tabletop exercises designed to mature the concept of National Nuclear Forensics Libraries (NNFLs) and demonstrate their utility in supporting a nuclear forensics investigation involving nuclear and other radioactive (RN) material found out of regulatory control. Teams participating in the third and most recent version of the exercise were provided surrogate uranium ore concentrate (UOC) data, which they used to organize a model NNFL. This served as a comparative instrument in a follow-on hypothetical scenario involving RN material out of regulatory control, allowing teams to successfully determine whether investigated materials were consistent with each other, and with holdings in their model library. The design of the dataset, methodologies utilized and aggregate results of the exercise will be presented, along with an account of how teams handled embedded design challenges, and benefits realized from participant teams.

Comparison of ^{230}Th-^{234}U and ^{231}Pa-^{235}U model ages of uranium reference material CRM-125A using a multi-instrument analysis approach

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Keywords: radiochronometry, certified reference material, uranium, isotope dilution mass spectrometry

The application of multiple radiochronometers, e.g., ^{230}Th-^{234}U and ^{231}Pa-^{235}U, in a nuclear forensic investigation of bulk uranium provides increased confidence for interpreting age-dating results. Analyses of well-characterized U reference materials with known purification ages serve as critical quality control measurements for validating chemical purification and mass spectrometric methods. We have developed a streamlined method for purification of Pa and Th from bulk U, having previously applied this method to U radiochronometry certified reference material CRM-125A [1, 2]. Precise and accurate age-dating results require proper calibration of spike materials (*e.g.*, ^{229}Th and ^{233}Pa) for isotope dilution mass spectrometry (IDMS). Nuclear forensic laboratories around the world have a variety of spike materials and mass spectrometers (both single collector and/or multi-collector instruments) that can be utilized for age-dating. To evaluate U-Th-Pa model age accuracy and precision achievable across a range of instrument designs, we performed ^{230}Th-^{234}U and ^{231}Pa-^{235}U radiochronometry of CRM-125A using three different instruments at LLNL: 1) ThermoScientific iCap quadrupole single collector inductively coupled plasma–mass spectrometer (ICP-MS), 2) ThermoScientific Element XR single collector ICP-MS, and 3) Nu Plasma HR Multi-Collector ICP-MS. Six IDMS aliquots of CRM-125A were dissolved, chemically separated, and purified. All aliquots were prepared using a ^{233}Pa spike, the NFRM ^{229}Th spike [3], and an in-house ultra-high purity ^{233}U spike. The ^{233}Pa and ^{233}U spikes were independently calibrated on each instrument. U, Th, and Pa IDMS aliquots were split and analyzed with the suite of mass spectrometers. Paired ^{231}Pa-^{235}U and ^{230}Th-^{234}U model ages produced by all instruments are concordant. The attainable accuracy and precision of model age results for CRM-125A from each instrument will be presented. Results from this multi-instrument intercomparison can be used to guide discussion with collaborating laboratories on anticipated radiochronometric data quality using both single and multi-collector instruments.

Acknowledgments

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Improved radioanalytical method for the separation of U, Pu and Am for the analysis of safeguards swipe samples in IAEA Environmental Sample Laboratory

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Keywords: Safeguards, americium, multicollector inductively coupled plasma mass spectrometry

Environmental sampling has been applied as a strengthened IAEA safeguards measure that contributes to confirming the absence of undeclared nuclear material or nuclear activities. The collection of environmental samples at or near a nuclear site combined with ultrasensitive analytical techniques to determine mostly their U and Pu isotopic signatures can reveal signatures of past and current activities in locations where nuclear material is handled. Besides U and Pu, the determination of ^{241}Am can also provide additional information which is relevant from safeguards point of view.

The Am analysis of standard radioanalytical procedure of the IAEA Environmental Sample Laboratory applied in the bulk analysis of environmental swipe samples for safeguards purposes was originally developed to determine the ^{241}Am content of the samples by alpha spectrometry. This procedure was improved and optimized to allow the determination of ^{241}Am content by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) also for age determination purposes. The existing radioanalytical procedure was modified to significantly increase the Pu decontamination factor and to minimize the impurity content of the Am aliquot.

Investigative radiochemistry as key element of nuclear forensics

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Keywords: nuclear forensics, nuclear security

The challenges in nuclear safeguards and in nuclear security have significantly changed over the last decades. On the one hand, Safeguards evolved from the pure verification of declared amounts of material to a much more information driven approach. On the other hand, nuclear security threats such as illicit trafficking or nuclear terrorism deserve high attention. While the legal mandates in both areas are significantly different, there are many similarities and synergies at technical level.

The development and application of more investigative (radio-) analytical methodologies is required and more thorough, interpretative and comparative evaluation of results needs to be performed for providing the information requested. The discipline which makes use of these analytical techniques is referred to as nuclear forensic science. It aims at providing investigative leads to law enforcement and at providing clues on the origin and intended use of nuclear or other radioactive material involved in illicit incidents. It benefits from the wealth of information inherent to the material. Specific applications, possibly in combination with only minute amounts of sample call for methods of high sensitivity, low detection limits, high selectivity and high accuracy. The selection of the method or combination of methods is done according to the sample and according to the information required. These new analytical challenges and the response will be illustrated using examples from recent work at JRC.

Nuclear fuel cycle

The economic analysis of biofouling resistant adsorbents for the recovery of uranium from seawater

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Keywords: seawater uranium, neutron activation analysis, nuclear fuel cycle, biofouling mitigation

The oceans naturally contain 1,000 times more uranium than what is estimated to be available via terrestrial extractions. The nearly infinite nature of this resource thus acts to reduce the long term uncertainty associated with nuclear power costs by establishing supply security, as well as a price ceiling on the cost of uranium. Ongoing research of advanced adsorption materials has shown that a major driver in the projected cost of seawater uranium recovery is the capacity of adsorbent. One mechanism of loss of 14 adsorbent uptake performance has been identified as marine biofouling on the material surface. While the recent development of silver nanoparticle polymer composites was shown to be capable of partially restoring adsorbent uptake ability in surrogate materials, obvious economic trade-offs exists. This work thus quantifies the cost of industrial scale uranium recovery using silver nanoparticle doped adsorbents by constructing a predictive model for adsorbent performance as a function of composition and cumulative seawater exposure time. While the silver doped adsorbents are not found to categorically provide an economic advantage as compared to baseline adsorbents suffering a loss in uptake due to biofouling, a break even analysis shows that only a 50% increase in capacity restoration factor would be necessary to offer a benefit. The quantification of uncertainty surrounding the projected cost of uranium recovered using silver doped adsorbents, as determined via Monte Carlo methods, showed that the possibility for cost savings likewise exists via the manipulation of various other and input parameters. Therefore, this work has demonstrated great promise considering the dominant impact uranium uptake was seen to have on final recovery cost, as well as the transformative effects seawater uranium could have on the perceived sustainability of nuclear energy generation.

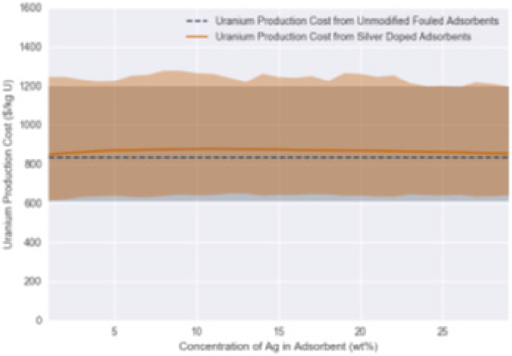

Fig. 1. Projected uranium production cost and associated confidence interval for silver doped (solid orange) and unmodified fouled adsorbents (dotted navy blue).

Zr-93 and Nb-94 analyses on Savannah River Site radioactive waste matrices

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Keywords: Savannah River Site, Zr-93, Nb-94

Over 60 years of plutonium processing and nuclear fuel reprocessing at the US Department of Energy's Savannah River Site (SRS) has resulted in the generation of millions of gallons of high-level radioactive waste stored in 51 waste tanks. While plutonium programs have ceased, nuclear fuel reprocessing continues at the Site. Remediation of the aging waste tanks have led to the development of a number of waste processing facilities designed to ultimately close the legacy tanks as well as provide a waste treatment pathway for any new radiological waste generated from ongoing Site nuclear processes. Decontamination plants using calixarene-based Cs-137 extractions and monosodium titanite treatments have been built to decontaminate high level waste salt solutions. Decontaminated solutions are grouted on Site, high activity sludges and high activity streams from the decontamination plants are vitrified. Emptied waste tanks are grouted and closed. These high activity waste cleanup efforts currently underway at the SRS have created an ongoing need to characterize the inventories of the various feeds and products of the various waste treatment facilities as well as the waste tank heels prior to tank closure. While the products of the salt processing remain chemically consistent, the isotopes requiring characterization as well as the detection limits required for those analyses are continuously evolving. The sludge from the heels of each tank slated for closure often have unique chemical constituents as well as unique radiological distributions compared to previous tank heels characterized. Continuous programmatic evaluations of allowable closed tank radiological inventories result in steadily decreasing detection limit targets for isotopes that are required to be characterized. Numerous target isotopes are often required to be characterized to levels as much as 10 orders of magnitude lower radioactive concentrations than interfering isotopes. The Tank Closure and associated waste treatment programs have required characterization of up to 54 radioisotopes. Dose rates of samples were at levels requiring initial manipulations to be carried out in remote manipulated Shielded Cells facility prior to hands-on radiohood operations. An overview of current radiological processes ongoing at SRS will be discussed. Radioanalytical methodologies for two of the radioisotopes on the waste characterization lists, Zr-93 and Nb-94, will be discussed in detail.

Diamide, dithioamide, and sulfonamide ligands for actinide/lanthanide separation and other nuclear fuel cycle applications

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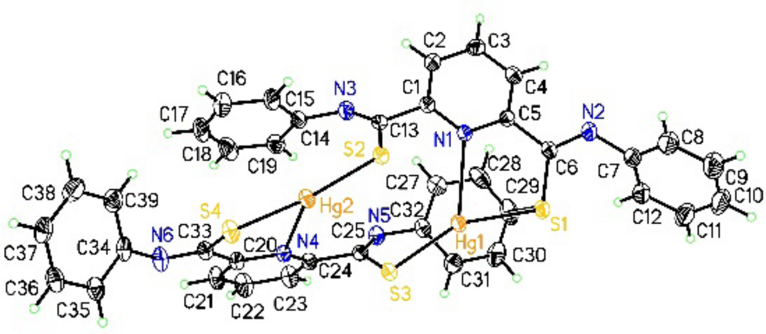
Keywords: extraction, actinide separation, thioamides

Minor actinides in used nuclear fuel are responsible for much of its radiotoxicity and heat generation. Actinide/Lanthanide separation via selective complexation and solvent extraction by soft S- and N-donor ligands can utilize the slight differences in relative hardness of An(III) vs. Ln(III), for selective separations. Furthermore, the presence of organic mercury, and actinides in the alkaline high-level waste at the Savannah River Site (SRS) has sparked interest in synthetic ligands for Actinide, and Hg(II) separation.

As part of our efforts in selective An(III)/Ln(III) separation and Hg(II) coordination and extraction, soft-donor ligands containing thioamide and/or pyridine sites that are derived from o-phenylenediamine or from dipicolinic acid,[1] were studied for complexation of Hg(II) and f-elements. Comparative studies between C=O vs. C=S ligands showed that the O-donor diamide binds Ln(III) in acetonitrile, while the S-donor ligand did not show any Ln(III) binding. Yet the same S-donor ligand extracted Am(III) vs. Eu(III) selectively from acidic solutions.[1] Hg(II) complexation studies by UV-Vis and NMR showed strong binding in solution. The X-ray structure for the Hg(II) complex (Fig. 1) shows a dimeric structure with two S and one pyridine N bound to each Hg. Sulfonamide ligands and analogs showed remarkable differences in Ln(III) complexation, and extraction of Sm(III) from alkaline solutions (as a surrogate for Am).

Figures



ORTEP view of X-ray structure of a dimeric Hg(II) complex (50% probability ellipsoids).

Acknowledgments

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Production of radionuclides

Recent efforts in extension and updating of the IAEA-NDS data base for charges particle reaction cross-sections relevant for medical radionuclide production

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Keywords: cross-sections, charged particles, data-base, IAEA-NDS

Until the initiative of the IAEA in 1995 to undertake and organise a Co-ordinated Research Project (CRP) entitled “Development of Reference Charged Particle Cross-section Database for Medical Radioisotope Production” no systematic effort had been devoted to the standardization of available cross-section data for radionuclide production through light charged-particle nuclear reactions. The focus of this first CRP was on the radionuclides most commonly used for diagnostic purposes and on the related beam monitor reactions. The results were published in 2001 in TECDOC-1211 and made available on-line in the medical portal of the Nuclear Data Section [1]. An additional set of data for therapeutic radionuclides was published as an IAEA Technical Report [2]. Although ten years later the recommended cross sections were still believed to be accurate enough to meet the demands of all current applications, further development of the evaluation methodology and more experiments were needed for determination of the uncertainties and their correlations. Hence a new CRP was launched in 2012 with as aim to update and broaden the cross-section database of [1] by undertaking a full survey of new literature data, earlier experiments and new dedicated experiments. The published datasets had to be corrected for up to date monitor cross sections or nuclear decay characteristics and a selection of sets had to be made allowing a fit with the Padé approach, from which new recommended data with uncertainties had to be produced. The results are made available in 2017-2019 to users in two forms: a set of 4 articles [3, 4, 5, 6] and inclusion in of the IAEA-NDS medical portal.

The presentation will give an overview of methods used and results obtained for the nearly 100 reactions studied for monitoring and for production of SPECT- (γ-emitters), PET- (β+ emitters and generators) and therapeutic radionuclides. Details on the process of gathering and selection input data will be presented, illustrated with tables and figures, stressing that the process is not standardized. Results for Padé fitting, often after several re-selections or addition of late data will be discussed. The output as presented in the articles, including evolution of uncertainties with energy, and in the updated database (same format as used in the 2007 on-line version of TECDOC-1211) for selected reactions will be illustrated.

The collaborators to the 2012-2018 IAEA-CRP are**:** A**.**V. Ignatyuk, R. Capote, B. V. Carlson, J. W. Engle, M. A. Kellett, T. Kibedi, G. Kim, F. G. Kondev, M. Hussain, O. Lebeda, A. Luca, Y. Nagai, H. Naik, A. L. Nichols, F. M. Nortier, S. V. Suryanarayana, S.Takacs, F. T. Tarkanyi, and M.Verpelli.

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Radiochemical methods in radionuclide production at a Cyclotron

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Keywords: radiochemical separation, radionuclide production, ion-chromatography, solvent extraction, precipitation, dry distillation

The research on radionuclide development, be it for measurement of nuclear data or for clinical scale production, often demands the removal of unwanted bulk material and the isolation of the desired radionuclide in a pure no-carrier-added form. Specific radiochemical methods have to be applied to reach this goal, which have to take into account the individual demands on purity and specific activity as well as the subsequent processing of the radionuclide. In the following an overview of typical radiochemical methods shall be given, which have been used in nuclear chemistry research at the Research Centre Jülich in Germany.

A common method for separation and purification is the use of ion-exchange resins of all kinds. In this field significant progress could be observed in the past years, allowing fast isolation of trace amounts of radioactivity in rather small volumes of eluent, e.g. ^{52g}Mn formed via the ^{52}Cr(p,n)-reaction [1] or ^{64}Cu formed via the ^{64}Ni(p,n)-reaction [2]. Alternatively, solvent extraction can be employed as the separation method, which also leads to the phase transfer of the produced radionuclide from an acidic or basic solution into an organic solvent. Often a combination of those methods is used. A limiting factor can be the solubility of the bulk target. Here, electrolytic de-composition may come into play for certain materials. By inverting the electrolytic procedure small amounts of metallic target materials can be transferred into a solution very quickly. This technique can be very advantageous when dealing with enriched target material, e.g. ^{58}Ni to produce ^{55}Co via the ^{58}Ni(p,α)-reaction [3]. In the opposite case, the dissolution of a bulk target may require the use of rather large volumes of solvent, which represents a serious obstacle for the fast and effective separation of trace amounts of a radionuclide. In that case the co-precipitation using a non-isotopic carrier can be put ahead of any further separation methods. A subsequent purification of the precipitated product radionuclide is always necessary when following this route. An example is the purification of ^{86}Y formed via the ^{86}Sr(p,n)-reaction on a $^{86}SrCO_3$ target [4]. A different separation scheme was adopted for ^{193m}Pt formed via the ^{192}Os(α,3n)-reaction [5]. At first the bulk target material was removed by distillation and then the desired radioplatinum was purified by solvent extraction. Finally, the radiochemical separation via dry distillation or thermo-chromatography will be discussed. The essential prerequisite to use this method is a sufficiently large difference of the sublimation temperatures of the produced radioisotope and the target material. A well-known example for the use of this technique is the production of radioiodine (^{120,123,124}I) from highly enriched tellurium targets ([^{120,123,124}Te]TeO_2), leading to the isolation of pure no-carrier-added product in about 1 hour leaving the enriched target material unharmed [4]. Similarly radiobromine is separated from a NiSe target [6] and radiotechnetium is advantageously separated from a MoO_3 target via thermochromatography.

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Prompt gamma activation analysis

Feasibility study of Compton imaging for PGAA

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Keywords: prompt gamma, Compton imaging, spatially resolved PGAA

The current state of the art in spatially resolved PGAA is achieved by collimating either the incident neutron beam or the emitted gamma rays, requiring scanning of the sample or collimator [1]. We are exploring a one-sided tomographic method for imaging prompt gamma rays, without moving the source, sample, or detector. This approach has been developed as a proton beam range finder for proton beam cancer therapy in a clinical setting [2], and has recently been investigated for use in the neutron capture prompt gamma environment [3]. Employing the principle of Compton Telescope (Fig. 1), dual plane pixelated CZT detectors developed from the commercial H3D system [4] with external timing synchronization electronics are used to measure prompt gamma rays that are scattered in the first plane and subsequently absorbed in the second plane. We apply the list-mode ML-EM algorithm [5] to estimate the spatial distribution of the origin of the prompt gamma ray emission. We report preliminary findings of imaging the H 2.2 MeV gamma ray peak in a standard cold neutron beam PGAA setting. Measurements have been performed to assess the feasibility of spatially resolving H features in plastic test samples in the mm scale. Challenges such as limited dynamic range due to high prompt gamma background are addressed. This study will aid detector design and reconstruction software development for PGAA of real samples in the future.

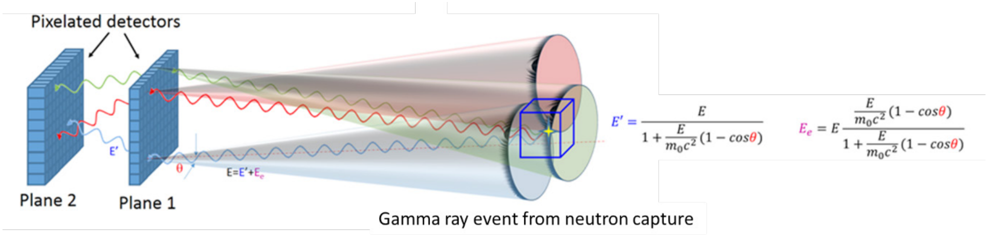

Fig. 1. Principle of Compton imaging employed in PGAA. The spatial information is determined by statistical reconstruction of the scattered events governed by the Compton energy-angle correlation.

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Extension of prompt-gamma activation analysis towards irregular shaped and non-homogeneous samples

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Keywords: prompt-gamma activation imaging, neutron imaging, Monte Carlo simulations, bulky samples

Prompt-gamma activation analysis (PGAA) is originally intended to measure the elemental composition of small, homogeneous and regular-shaped samples. In the analytical practice, however, these criteria are often limiting the applicability of the technique.

Composition measurement of valuable, homogeneous, but bulky objects with irregular geometrical shapes (geological samples, meteorites, ancient stone tools, cast bronze artifacts, industrial items, …) is a typical task at the Budapest PGAA facility. Here, any sampling, powdering is in obvious conflict with the requirement of non-destructivity. So far, approximations had to be made when correcting the neutron self-attenuation and gamma self-absorption.

In order to make the PGAA technique more competitive and fully utilize its most attractive feature, the non-destructivity, even for objects with arbitrary shapes, sizes, and matrices, accurate corrections shall be determined for each individual object.

At first, the case-by-case geometry has to be defined based on data from 3D structured-light optical scanning or segmentation of neutron/X-ray tomography data. The latter is still applicable when non-homogeneous or heterogeneous samples are to be studied. Then these detailed object geometries, including its proper placement, have to be loaded into Monte Carlo simulation frameworks, such as MCNP 6.2 and geant4, where the instrument components (detector, sample chamber, beamline) are already carefully implemented, and computer simulations have to be done to reproduce the experiment. In the recent versions of MC codes, not only regular shapes are available, but specific geometries can be specified, e.g. as an unstructured mesh, or using a voxel-approximation. Mesh is preferred for homogeneous objects for computational reasons, while the voxel-based approach offers more flexibility.

The workflow of the analysis is presented on relevant examples, where this comprehensive approach seems to offer a benefit.

Acknowledgments

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Radioecology and environmental radioactivity

Dry deposition velocity of molecular gaseous iodine

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Keywords: dry deposition, molecular iodine

In case of serious accident on a water pressurized nuclear reactor, iodine (^{131}I, ^{129}I) can be released into the environment in different physicochemical forms: particulate (aerosol particles) and gaseous. A fraction of emitted iodine may deposit on artificial and natural covers including plants. Previous studies have shown that there are from 1 to 3 orders of magnitude discrepancies in dry deposition velocities of gaseous molecular iodine in the environment (N. Karunakara, 2018). The deposition velocity is calculated from the ratio between the deposition rate and the concentration in the atmosphere.

To understand these discrepancies, an experimental method was developed to determine the dry deposition velocity of gaseous stable iodine (^{127}I) on natural cover. Gaseous stable iodine was emitted from a generator. Herbal squares samples (16 cm x 16 cm) were placed 3 m from the emission source and exposed to the atmospheric deposition during 30 minutes. Iodine masses collected by the samples were quantified as well as iodine concentration in the atmosphere above the samples.

The dry deposition velocities varied between 0.05 and 0.5 cm s^{-1}. These results show a relationship between the dry deposition velocities of ^{127}I (cm s^{-1}) and the wind shear velocities (m s^{-1}) ($r^2 = 0.75$).

The dry deposition model of gaseous iodine (^{127}I) will be coupled with the existing pattern of deposition of particulate iodine to establish a global model. This global model will be performed at the La Hague site from gaseous and particulate ^{129}I emitted into the atmosphere by Orano (nuclear fuel reprocessing plant).

Atmospheric ^{129}I particles are collected on filters and ^{129}I gaseous on charcoal every 15 days. At the same time, ^{129}I deposited on square grass samples (1 m x 1 m) located at 2 km from the release are collected every month. These samples are measured by gamma spectrometry.

Reconstruction of long-term dynamics of Chernobyl-derived ^{137}Cs in Upa river based on current vertical distribution in bottom sediments of the Scheckino dam reservoir and its semi-empirical modeling

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Keywords: Chernobyl, ^{137}Cs, Upa river, bottom sediments, semi-empirical modeling

Today, 8 years after the Fukushima accident, when emergency and short-term phases are over, the most relevant issue is long-term dynamics of radiocesium in the environment. Detailed analysis of Chernobyl data covering an extended time period can provide a basis for long-term prediction of changes in environmental radioactive contamination in Fukushima.

Three cores of bottom sediments were collected in 2018 to the depth of about 200 cm in the deep part of Schekinskoe dam reservoir on the Upa river, Russia, severely contaminated by ^{137}Cs after the Chernobyl accident in 1986. The Upa river basin, selected as analogue of Abukuma river (Fukushima Prefecture) in terms of size and ^{137}Cs deposition, has an area of 9,500 km^2 and the mean annual rainfall is 540 mm/year, which is about 3 times lower than in Fukushima Prefecture. The collected bottom sediment cores were sliced in 2-cm layers, dried at 105^{o}C and passed through 2-mm sieve. They were then measured for ^{137}Cs using γ-spectrometry.

Unfortunately, systematic regular monitoring of radioactive contamination of the Upa river was not carried out. The only data available are total ^{137}Cs activity concentrations in water in the first years after the accident (1987-1991). The obtained ^{137}Cs vertical distribution in sediment accumulation zones in the central part of the reservoir suggests that practically no vertical mixing of sediments took place, the ^{137}Cs peak being well-defined, rather than diffused. If sediment accumulation rates after the accident are more or less uniform, layers of bottom sediments can be attributed to certain time of sedimentation. The fact that ^{137}Cs activity concentration in bottom sediments of a specific layer is corresponding to ^{137}Cs concentration on suspended matter at that time allowed us to obtain the dynamics of particulate ^{137}Cs activity concentrations in the Upa from 1986 to 2017. Over the time since the accident the ^{137}Cs concentrations have decreased by more than an order of magnitude, with only minor changes occurring during the last 15 years. Using a typical value of distribution coefficient K_d for the rivers of Chernobyl contamination zone, dissolved ^{137}Cs activity concentrations in the Upa river have been estimated and changes of the radionuclides over 30 years after the accident have been studied. The resulting estimates of dissolved ^{137}Cs concentrations in the Upa river are in good agreement with measurements for 1987-1991. The proposed and tested method allows us to reconstruct the long-term dependence of radionuclide concentrations in rivers and reservoirs based on their vertical distribution in bottom sediments.

Reconstructed time dependencies of particulate and dissolved ^{137}Cs activity concentrations in Upa river are described well by proposed semi-empirical "diffusional" model based on assumption that time dependence of particulate r-Cs in river corresponds to time dependence of its concentration in topsoil layer on the catchment which can be approximated by dispersion-convection equation with physically meaningful parameters.

Acknowledgments

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Structural curiosities of lanthanide (Ln)-modified bentonites analyzed by radioanalytical methods

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Keywords: lanthanide-bentonites, cation exchange, X-ray-fluorescence spectrometry (XRF), X-ray diffraction (XRD), Scanning electron microscopy (SEM)

In this work, the structure of lanthanide-bentonites was analyzed for nuclear waste treatment, and environmental protection purpose by several analytical methods. The main mineral of the bentonite is the montmorillonite, which has a permanent negative charge. The negative charge is neutralized by cations attracted to the interlayer space where cation exchange takes place and sometimes modifies the properties of the bentonite. The natural interlayer cations may be exchanged by Lns. The importance of lanthanide ions is that they are model interactions between soil and transuranium ions, also, lanthanide cations are produced during the fission of ^{235}U in nuclear power plants.

Ln-exchanged bentonites were prepared from Ca-bentonite by ion exchange procedure from Ln-perchlorate solution. To prove the successful modification Scanning Eletron Microscopy, Energy Dispersive X-ray analysis (SEM-EDX) was used showing distribution of Ln's and other components of bentonite. The natural bentonite and the lanthanide exchanged bentonites were characterized by X-ray diffraction (XRD), which revealed the same mineral composition, and the increase of the basal spacing of montmorillonite. The Ca^{2+}, Fe^{3+}, and Ln's^{3+} amount on the bentonite were determined by X-ray-fluorescence spectrometry (XRF). In most Ln-bentonites, the quantity of the exchanged Ln ions was about 80-90% of the cation exchange capacity (CEC) of the bentonite. For some lanthanide bentonite (Y^{3+}, La^{3+}, Ce^{3+}, and Gd^{3+}), however, the sorbed quantity of lanthanide ions was higher that the cation exchange capacity. Moreover, the iron(III) content of lanthanide bentonite was less than that of the original Ca-bentonite.

The observation is that lanthanide ions can somehow supersede iron from the octahedral positions of crystal lattice. We assume that the departure of positively charged iron ions from the lattice increases the negative layer charge and the cation exchange capacity. This can motivate the enhance sorption of lanthanides.

To prove our previous statement, we examined how the pH and the concentration influences the bentonite structure without and with Lns. Ca-H, Ca-Y and Ca-La cation exchange were carried out. The results revealed that the pH has high influence during the Ca-H cation exchange procedure. The more acidic solution the more calcium was exchanged. In this case, iron loss was not observed. In the case of Ca-Y, La cation exchange procedure, the pH has low influence, meanwhile the concentration has higher influence to high amount of iron loss during divalent- trivalent cation exchange. Thus, high amount of trivalent lanthanides cause the structural iron release.

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Identification of radionuclide uptake mechanisms by native flora in the vicinity of uranium mines in arid South Australia

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Keywords: radioecology, gamma-ray spectrometry, flora, concentration ratios, impact assessments

Environmental risk assessments for radiological contamination follow internationally accepted methods including use of the Environmental Risk from Ionising Contaminants: Assessment and Management (ERICA) tool. Concentration ratios are the essential input for these models. However, the available international input data are primarily from temperate Europe and North America, and may not apply in arid conditions. It has previously been shown that Australian native species accumulate higher amounts of radionuclides from their environment when compared to similar species from other climates.[1,2] This research aims to develop a concentration ratio dataset relevant for U and Th series radionuclides in arid and semi-arid conditions. Two uranium mines are the focus of the research. Olympic Dam (BHP, South Australia) is the largest mine in SA, utilising underground mining with the ore being processed on site. Beverley (Heathgate, South Australia) is an in-situ recovery uranium mine. The two mines offer different conditions when considering the natural background radiation and the type of mining operations. Samples of flora and surrounding soil have been collected and concentration ratio data has been developed. Analysis has included gamma-ray spectroscopy, neutron activation analysis, alpha-particle spectroscopy and inductively coupled plasma mass spectrometry. The Diffusive Gradients in Thin-film (DGT) technique has been applied to determine the bioavailability of radionuclides and metals within the soil for uptake within native flora. Alpha track analysis, using a nuclear emulsion gel layer, has been used to identify radionuclide accumulation and spatially-resolve its location within structures of the leaves. Overall this research provides a better understanding of the behavior of radionuclides in an arid environment and provides data on the mechanisms of radionuclide uptake in flora. It augments existing international data for use in models in Australia and other localities with similar arid environments.

Acknowledgments

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Radiolabeled compounds and radiopharmaceuticals

Pretargeted imaging with ^{18}F-labeled tetrazines

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Keywords: pretargeted imaging, tetrazine ligation, fluorine-18, indium-111

Introduction and Objectives

Pretargeted PET imaging between a radiolabeled tetrazine and mAbs modified with trans-cyclooctene (TCO) allows for the use of short-lived radionuclides such as fluorine-18. Compared to direct labeling approaches of mAbs, pretargeted imaging reduces the radiation dose to healthy tissue while maximizing imaging contrast. Our aim with the present study was to explore suitable approaches to $_{18}$F-label a broad variety of reactive tetrazines. Standard approaches are tedious for these kinds of structures. Finally, the newly developed ^{18}F-tetrazines were evaluated in a murine colon carcinoma model using the TAG72-targeting mAb CC49.

Methods and Results

Cu-catalyzed azide-alkyne [3+2] cycloaddition (CuAAC) was identified as a strategy to access a tetrazine library via an indirect labelling approach. Structure such as H-tetrazines, but also bis-pyridyl-tetrazines could easily be labelled. Direct labelling of reactive tetrazines only succeeded applying Cu-mediated ^{18}F-labeling using tin-precursor species. RCY between 5 and 60 % were feasible using this kind of chemistry. Consequent evaluation experiments indicated a clear dependence on polarity and tumor uptake.

Conclusion

We successfully established direct and indirect approaches suitable for ^{18}F-labelling of highly reactive tetrazines. More than 15 labeled tetrazines were evaluated in vivo. Two compounds showed suitable characteristics to be used for pretargeted imaging.

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Impact of emerging radiofluorination methods on preclinical and clinical PET imaging

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Keywords: [^{18}F]Fluoride, ^{18}F-labeling, PET, Cu-mediated, onium precursor

In recent years we developed the so-called "minimalist" approach to ^{18}F-fluorination. The term "minimalist" was coined by us due to the exceptional simplicity of this protocol. This ^{18}F-labeling method requires neither additives nor time-consuming azeotropic drying steps and enables not only the efficient preparation of different prosthetic groups but also clinically relevant tracers [1]. We also adopted this method to Cu-mediated radiofluorination of (aryl)(mesityl)iodonium salts [2]. Thereafter, we focused on the development of simple and efficient protocols for Cu-mediated ^{18}F-fluorination of boronated and stannyl substrates [3]. This efforts ultimately led to the discovery of alcohol-enhanced Cu-mediated radiofluorination [4]. The novel protocols enabled to produce known radiolabeled aromatic amino acids like 6-[^{18}F]fluoro-3,4-dihydroxyphenylalanine (6-[^{18}F]FDOPA), 6-[^{18}F]fluoro-3-hydroxyphenylalanine (6-[^{18}F]FMT) and 2-[^{18}F]fluorophenylalanine (2-[^{18}F]FPhe) with unmatched efficacy. Furthermore, the novel procedures allowed the preparation of the hitherto unknown but clinically highly relevant tracers like [^{18}F]fluorotryptophans ([^{18}F]FTrps), 2-[^{18F}]fluorophenethylamine ([^{18}F]FPEA) or radiolabeled muscarinic acetylcholine receptor ligands. These tracers significantly expand the diagnostic toolbox for the visualization of pathological processes in cancer and neurological disorders.

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Separation, speciation

Radioisotope separation in support of fundamental physics research

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A variety of grand challenges in fundamental physics is being addressed using approaches that rely on radionuclides. Oftentimes, well-separated and also well-characterized samples present in tailor-made form to match requirements of the specific setups are needed to facilitate successful studies.

One example that I will discuss focuses on thorium-229, which is the nucleus with the lowest-lying known isomeric state, located below 10 eV excitation energy above the ground state [1]. This system offers the unique situation of having a nuclear transition placed in the optical 'photon' rather than the keV-MeV 'gamma' energy range access, rendering thorium-229m accessible with laser-based techniques. In the absence of exact knowledge of the excitation energy, recoil-milking of the alpha-decay daughters of uranium-233, which are in the isomeric state in 2% of all cases, currently offers the sole source for thorium-229. This is in the focus of efforts to construct an ultra-precise 'nuclear' clock, or the hunt for physics beyond the standard model including studies of potential temporal variations of fundamental constants. I will describe the preparation of experiment-specific purified uranium-233 as well as thorium-229 samples, along with uranium-234 and thorium-230 [2]. As another example, I will discuss the production, isolation, and characterization of mg quantities of holmium-163 [3] used by the Electron Capture in Holmium (ECHo) collaboration [4] to determine the mass of the electron neutrino.

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Large scale production of ^{134}Ce, a new PET radionuclide

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Keywords: ^{134}Ce production, lanthanide separation

The radionuclides employed in targeted alpha therapy are often actinides (e.g. ^{225}Ac, ^{227}Th) with multiple radioactive daughters. Successful treatment relies on the radiopharmaceutical's ability to "hold-on" to ^{225}Ac (or ^{227}Th) while it is delivered to the target cancer cell. Imaging surrogates of the radiopharmaceutical permit non-invasive pharmacokinetic assays and enable rapid screening of prospective compounds in living subjects. ^{134}La ($t_{1/2}$ = 6.67 m, 2.7 MeV β+) emits positrons, enabling its use in positron emission tomography (PET) imaging in the form of an *in vivo* generator with its parent, ^{134}Ce. Due to similar ionic radius and coordination geometries, the ^{134}Ce/^{134}La pair can be used as a surrogate for ^{225}Ac or ^{227}Th (non-PET isotopes) in the investigation of novel alpha-emitting radiotherapeutics. Furthermore, ^{134}Ce/^{134}La has potential therapeutic use as an Auger electron and positron-emitting generator for radionuclide therapy.[1]

In this contribution the large-scale production and purification of ^{134}Ce from a proton-irradiated lanthanum target will be discussed. The lanthanum (22 g) target was irradiated using a 100 MeV proton beam at the Isotope Production Facility (IPF) at Los Alamos Neutron Science Center (LANSCE). After target dissolution, ^{134}Ce ($t_{1/2}$ = 75.9 h) was separated from the ^{nat}La target (and accompanying impurities) by oxidizing cerium to the +4 oxidation state followed by purification using anion-exchange chromatography. The entire procedure (dissolution, purification and characterization) can be conducted rapidly (3 days) and requires only one separation column. The final product was isolated in high-purity (La decontamination factor >10^5), reasonable yield (78% from dissolution), and high specific activity. The product was distributed to collaboratorss located over 1000 miles away and used to generate the first *in vivo* μPET images conducted to date with ^{134}Ce.

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Spectroscopic analysis on sorption speciation of uranium on solid-water interface

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Keywords: spectroscopic analysis, sorption speciation, uranium, minerals

Hexavalent uranium is a prominent radioactive contaminant in both sediments and aquifers around nuclear activity sites, and poses a potential health and environmental risk to the biosphere. Understanding on the detailed interaction at the solid-liquid interface between uranium and natural media, i.e. oxides and minerals, is crucial for the safety assessment of high level radioactive waste geological repository, as well as prediction of uranium's geochemical fate in the environment. However, the interactions between uranium and minerals are complicated by the ubiquitous ligands in natural media such as phosphate, humic substances et al, thus the detailed insight into U speciation at solid-water interface is critical in governing the subsurface mobility of uranium in disposal environment. Full understand on complicated interaction mechanism between uranium and ligands at the solid-water interface requires full identification of surface speciation with the aid of sensitive spectroscopic analysis.

In this work, the adsorption of uranium on TiO_2 and granite was investigated by a combination of batch measurements and spectroscopic techniques, including second harmonic generation (SHG), cryogenic time-resolved laser induced fluorescence spectroscopy (TRLFS), and extended x-ray absorption fine structure (EXAFS). Results showed bidentate complexes were formed on TiO_2 surface. Phosphate is beneficial for uranium immobilization in granitic terrains, the spectroscopic confirmation revealed that multiple surface species including inner-sphere complexes and surface precipitates were formed on granite surface with their abundances varying as a function of acidity. The EPMA results showed that uranium mainly located on mica mineral. The detailed interaction between uranium and mica showed that uranium sorption on phlogopite mica was strongly dependent on pH while minimally affected by the ionic strength, multiple inner-sphere surface species were formed with their abundance varying as a function of pH. The presence of HA made significant difference on uranium sorption behavior as well as surface species. These findings are helpful for understanding on the geochemical fate of uranium in granitic environment as well as setting a reliable reference for surface complex models.

Oral Presentations

Actinide analytical chemistry

Radiochemical separation of actinides produced in multinucleon transfer reactions as a model for neutron-rich isotopes of heavy elements separation

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Keywords: separation, heavy actinides, multinucleon transfer reactions

Investigation of chemical properties of new elements is one of the most contemporary task for chemists. Currently, superheavy elements (SHE) are being produced by irradiation of actinide target (^{240,242}Pu, ^{241,243}Am, ^{242,244}Cm, ^{249}Bk, ^{249}Cf) with heavy ion beam [1]. Moreover, during this irradiation neutron-rich nuclei of heavy actinides (Es-Lr) are produced in multinucleon transfer reactions, which is a promising way to produce neutron-rich SHE nuclei [2]. However, predictable half-lives of new Es-Lr isotopes are low, so we need to improve our liquid-phase chemistry technique based on cation-exchange chromatography with α-HIB as an eluent. New technique is required to be highly sensitive and effective for actinide separation and to allow making quick separation.

In our work, we suggest optimal parameters of Am, Cm, Cf separation, which are calculated, using plate model of chromatography. We determined concentration eluent levels needed when distribution coefficients of target elements are near zero. Results of previous experiments with these elements and calculated positions of heavy actinides at the chromatogram under our conditions will be discussed.

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Development of a protocol for the determination of Pu, Am and Sr isotopes at trace levels in a single environmental sample

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Keywords: radiochemical separation, plutonium, americium, strontium, environmental contamination

Since the 1990s, the Laboratory of Environmental Radioactivity Metrology (LMRE) of the French Institute of Radioprotection and Nuclear Safety (IRSN) monitors the French territory by analysing samples at very low levels of radioactivity, in all compartments of the environment. Activities and isotopic signatures are also used for transfer studies and dose assessment.

In this context, the quantification of Pu, Am and Sr isotopes is carried out routinely in the laboratory, under ISO 17025 accreditation and using two separate protocols – one for Pu and Am and one for Sr. This allows to reach very low decision thresholds (~0.5 mBq.kg^{-1} for ^{238,} $^{239+240}$Pu and ^{241}Am, and ~0.5 Bq.kg^{-1} for ^{90}Sr) and to emancipate from all interferents during countings by alpha spectrometry and gas proportional counter [1]. However, the radiochemical treatments are time consuming (up to 3 weeks for each protocol), mainly because of the large amount of sample (from 20 to 200 g of ash sample), and the counting times can last up to 2 weeks.

Following the Fukushima accident, an extremely fast, efficient and automated protocol needed to be set up in the laboratory in order to be able to quantify the isotopes of Pu, Np, Th, U, Am, Cm and Sr in a single day [2]. The strategy was to use a small quantity of sample (up to 0.7 g), to dissolve it with alkaline fusion and to separate the elements with three chromatographic columns directly connected to the ICP-MS instrument. For naturally occurring elements and those with a long half-life (U, Th), the decision thresholds of this protocol are low enough for non-contaminated samples. However, for anthropogenic radioisotopes with a shorter radioactive half-life (e.g. ^{239,240}Pu, ^{241}Am and ^{90}Sr) the decision thresholds obtained are suitable for crisis situations but may be too high for environmental monitoring.

Therefore, our purpose is to develop a single protocol allowing Pu, Am and Sr determination while maintaining the excellent performances of our routine protocol for environmental monitoring, but also greatly decreasing the sample turnaround time and the number of steps. After dissolving the sample (up to 50 g of soil), the coprecipitations were optimized (nature of the coprecipitates and pH) to carry the three elements together. Then, Pu, Am and Sr were separated from each others using extraction resins and each fraction was purified from the residual matrix components. The operating conditions of this step were chosen in order to remove all counting interferents and with a prospective automation. The protocol gives very good results for a synthetic matrix and for environmental samples containing a significant amount of natural elements (such as U, Th) and lanthanides. The chemical yields are greater than 80% for the three elements and interferences are negligible during alpha spectrometry and beta counting. In addition, the duration of the protocol has decreased significantly in the environmental monitoring mode; 8 days for the radiochemical treatment of Pu, Am, Sr plus 15 days of counting time for each element.

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The effect of gamma radiation on hexavalent americium autoreduction

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Keywords: hexavalent americium, reduction kinetics, gamma irradiation, americium oxidation

One strategy to accomplish the difficult lanthanide/actinide separation related to used nuclear fuel management is to oxidize americium to the hexavalent state. When americium is oxidized to the highest valent states (V and VI) its geometry is transformed from a spherical cation to a linear dioxo cation via hydrolysis in solution. The hexavalent americium is analogous to U, Pu, Np, in both geometry and charge density allowing them to be co-managed in a group decontamination. Thus simplifying the current suite of separation schemes under consideration. In previous studies by this group, the rate of reduction of hexavalent ^{243}Am due to self-radiolysis was measured across a range of total americium and nitric acid concentrations. These so-called autoreduction rates exhibited zero order kinetics with respect to the concentration of hexavalent americium, and pseudo-first order kinetics with respect to the concentration of total americium. Although hexavalent americium is thermodynamically and radiolytically unstable, these studies have shown it is stable enough for a viable separation. In the current study, the stability of hexavalent americium is further probed by measuring how gamma radiation effects the previously established Am(VI) autoreduction rates. Irradiations were also conducted with hexavalent americium in high nitric acid concentration with redox active metal ions present in solution. The empirical modeling results for the irradiated systems will be compared to the autoreduction rates of hexavalent americium previously determined on the benchtop.

OCTAPA: A study of pre-organization of aminopolycarboxylates for actinide/lanthanide coordination in nitrate media

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Keywords: separations, complexant, coordination, aminopolycarboxylate, nuclear fuel cycle, actinide, lanthanide

Aminopolycarboxylates are used in the nuclear fuel cycle as aqueous complexants for trivalent *f*-element group separations. The enhanced affinity of trivalent actinides over lanthanides by aminopolycaboxylates supports feasability of partition and transmutation strategies paramount to closure of the nuclear fuel cycle. In this study the influence of structural motifs aimed to reduce reorganization energetics and enhance ligand acidity to promote metal complexation in highly acidic meadia were evaluated. The ligand basicity and metal complexation constants of N,N’-bis(6-carboxy-2-pyridylmethyl)ethylenediamine-N,N’-diacetic acid (OCTAPA), a modified aminopolycarboxylate, were assessed. Coordination properties were evaluated by lifetime measurements. The combination of themrodynamic and coordination characterization reveal new insight into the tune ability of aminopolycarboxylate complexants and their role in developing improved *f*-element separations schemes. Liquid-liquid extractions were used to evaluate the utility of OCTAPA for group *f*-element Ln/Am separations in nitrate/nitric acid media using a strong cation exchangingextractant. This contribution evaluates modified aminopolycarboxylates as holdback complexants for overcoming liquid-liquid solvent extraction kinetic/thermodynamic challenges and relates structural modifications to the perturbation of thermodynamic properties for the development of improved separation schemes.

Development of automated separations for actinides analysis

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Keywords: plutonium, uranium, automation, chromatography

This study highlights the adaptation of a commercially available Elemental Scientific Prep-FAST inc. automated chromatography system to radiochemical analysis. We have developed novel methods for automated sample preparation of standards and radiometric geometries, isotope dilution analysis and separation of trace impurities from uranium and plutonium samples.

The methods were optimised for our application and sample to sample times of 15-35 minutes were achieved. These samples were used to analyse 75 trace elements in uranium and plutonium and for the separation of trace actinides (Am, Cm, Np, Pu, U) for quantification. Spiked uranium and plutonium samples were analysed with less than 4-7% relative standard deviation for triplicate measurements for trace elemental analysis. The results were comparable with our current quality assured methods for analysis and offer additional safety and efficiency benefits to the operator. The methods also yielded a 20-fold reduction in sample size and a 4-fold reduction in waste produced compared with our conventional methodologies

Determination of neptunium-237 in plutonium materials

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Keywords: analytical chemistry, neptunium, plutonium

Neptunium-237 is present in most plutonium samples as it is a decay product of plutonium. The isotope is also produced in nuclear reactors via neutron capture. In a plutonium sample, ^{237}Np primarily arises from alpha decay of ^{241}Am, progeny of the short lived ^{241}Pu. There are a several analytical techniques that can be used to measure the ^{237}Np concentration in plutonium samples. The most common techniques are radioanalytical based methods (alpha spectroscopy, gamma spectroscopy, and/or scintillation counting) with mass spectrometry methods becoming increasingly utilized. Los Alamos National Laboratory (LANL) has developed several analytical methods over the years to determine ^{237}Np. A radioanalytical method is the first method that was developed and has been refined over the years. This method requires chemical separation of Np from other alpha-emitting radionuclides to determine ^{237}Np concentration through a combination of alpha and gamma spectroscopy. This is a workhorse method whose performance has been verified and validated over several decades. This method, however, is very time consuming and requires highly trained personnel to reliably execute. This presentation will discuss possible radiometric approaches to shorten the total analysis time required to determine ^{237}Np concentration in Pu materials but maintain needed method performance.

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Tetra- and hexavalent actinide quantification in complex rare earth metal mixtures with potentiometric multisensor system

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Keywords: actinides, lanthanides, chemical sensors, PUREX, on-line control

The development of the analytical methods for on-line monitoring of the chemical composition of PUREX process streams is an urgent and importnat task. The methods currently applied for the chemical control require sampling, pretreatments steps, impose radiation exposure of personnel and are not fast. As a possible way to overcome these limitations there were several studies on application of UV-Vis-NIR and Raman spectrometry combined with multivariate data processing for quantification of key components in technological solutions [1, 2]. These studies show a good promise for the development of on-line monitoring system for PUREX, however, the detection limits of optical methods not always comply with the analyte concentration ranges. In this case electrochemical methods can serve as a reasonable addition to the optical spectrometry. The purpose of this study was to explore the applicability of potentiometric multisensory system composed of 12 cross-sensitive sensors for uranium and thorium quantification in multi-component mixtures simulating PUREX process tailing solutions. Plasticized polymeric sensor membranes contained various ligands with high extraction capacity to lanthanides and actinides suggested in liquid extraction. The sensitivity of the individual potentiometric sensors to tetra- and hexavalent actinides (UO_2^{2+} and Th^{4+}) in aqueous nitric acid solutions with pH = 2 has been studied. It was found that some of the sensors show the pronounced sensitivity to actinides with electrode function slopes above 20 mV/dec for thorium and above 30 mV/dec for uranium. These sensors were combined into the multisensor system that was applied for UO_2^{2+} and Th^{4+} quantitative determination in presence of each other and lanthanides cations (La^{3+}, Pr^{3+}, Sm^{3+}, Gd^{3+}, Yb^{3+}). The nitric acid quantification in the set of mixtures with UO_2^{2+} and La^{3+} was also performed using the same system. Multivariate regression models relating the response of the multisensor system with analyte concentration were calculated using projection on latent structures (PLS) algorithm. The composition of the mixtures is shown in Table 1.

Table 1. *Composition of the model mixtures for multivariate calibration*

Target analyte	**Concentration, 10^{-3}·mol/l**		**Concentration, 10^{-5}·mol/l**				
	UO_2^{2+}	**Th^{4+}**	**La^{3+}**	**Pr^{3+}**	**Sm^{3+}**	**Gd^{3+}**	**Yb^{3+}**
UO_2^{2+} (uranium set)	0.42 – 29	0.10	7.2	9.5	6.6	6.4	5.8
Th^{4+} (thorium set)	9.5	0.01 – 1	7.2	9.5	6.6	6.4	5.8

The results of PLS models validation with independent set of samples show the possibility of simultaneous quantification of both uranium and thorium with mean relative error (MRE) equal to 17% and 14% correspondingly, and HNO3 quantification with MRE = 7%. This accuracy is appropriate for real-time technological control of PUREX process.

Acknowledgments

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Changing the rules of the game: Used fuel studies outside of a remote handling facility

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Keywords: used nuclear fuel, noble metal phase, nuclear materials science

Recent advances in micro-fabrication tools like the FEI Helios NanoLab 660 dual Focused Ion Beam (FIB) and Scanning Electron Microscope (SEM) now make it possible to easily and reliably prepare micron (or smaller) specimens for analyses or further experimentation. Pacific Northwest National Laboratory (PNNL) has exploited this capability at the Category II Nuclear Facility, the Radiochemical Processing Laboratory, to facilitate nuclear materials analysis and experimentation of used nuclear fuel. Micron-scale specimens of un-irradiated UO_2 fuel pellets of various enrichments were prepared at PNNL and shipped to the University of Missouri's Research Reactor (MURR) for irradiation (Figure 1). Prior to shipping, samples were attached to commercially available TEM half-grids via ion deposition, which were then housed in specially designed aluminum sample holders approved for use at the reactor facility. In this manner, materials analysis could be achieved with minimal sample handling following return after irradiation. Additionally, by reducing the size, and therefore dose, the required cooling time after irradiation and prior to analysis was greatly diminished, and handling of these samples could proceed outside of a hot cell facility. Results from these experiments provided insight into the production of noble metal phase particles and high pressure fission gas bubbles in used nuclear fuel as a function of burnup. Experiments were performed at a fraction of the time, effort and expense of similar bulk-scale studies. Conducting nuclear materials analysis at the micron-scale holds the promise of enhancing collaboration and material accessibility to the broader research community, improving accessibility to cutting edge research tools by the nuclear materials science community, lowering the risk to the scientist by reducing radiation dose and exposure, reducing facility and research costs associated with the requirement to conduct nuclear materials science within glovebox or remote handling facilities, and minimizing waste.

Figures

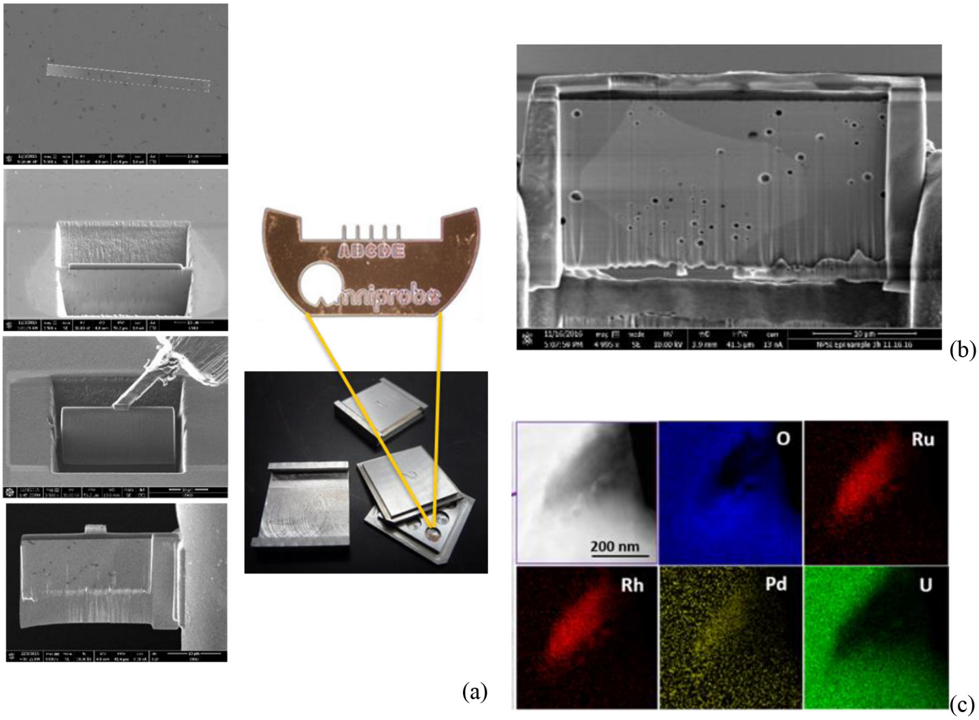

Figure 1. (a) Preparation of UO2 by FIB for micron irradiation studies at MURR. (b) Scanning Electron images of one of the samples after irradiation. (c) Elemental map of an irradiated micron-size sample of UO2 showing the presence of noble metal phase particles.

Complexation studies of Th(IV) with hydroxamic acid ligands by affinity capillary electrophoresis

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Keywords: thorium(IV), hydroxamic acids, siderophore, complexation, affinity capillary electrophoresis

The transfer of metal cations in soils and sediments is not only controlled by geological and physico-chemical parameters (clay and organic matter contents, pH, Eh, etc.) but also by microorganisms. The latter take part in the mobilization/immobilization of trace metals [1]. Therefore, the presence of actinide(IV) (Pu, Th, etc.) contaminants after accidental discharges raises the question of their transfer in the environment and the resulting risk of food chain contamination. Siderophores, as natural iron-specific chelators, have to be considered in this context [2]. These low molecular weight, hydrosoluble compounds are excreted by bacteria and fungi to overcome the limited bioavailability of iron under aerobic conditions (ca. 10^{-18} M at neutral pH) by dissolution of iron oxohydroxides present in the soils.

This work is devoted to the complexation study of Th(IV) by desferrioxamine B (DFB) (Figure 1) and by other hydroxamic acids [3], which are effective ligands in capturing and transporting An(IV) [4]. Affinity capillary electrophoresis (ACE), which requires only a few µL of solutions, was used with UV detection. ACE is based on the change in the electrophoretic mobility of detected species due to the interaction with other species present in the electrolyte. The injected sample contains a fixed amount of ligand. A set of runs is performed using (H,Na)ClO_4 mixtures at constant pH and ionic strength, while the background electrolyte (BGE) contains varying amounts of Th(IV). The change in electrophoretic mobility with the increase of cation concentration in the BGE is used to assess the speciation and equilibrium constants. This method is fruitful for studying metal complex formation equilibria and gives valuable information for further modeling of their behavior under environmental conditions [5].

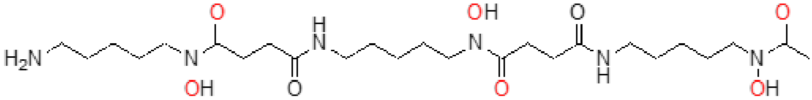

Figure 1. Structural formula of desferrioxamine B (DFB).

Acknowledgments

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Direct speciation of radionuclide uptake into plant parts by DESI MS and TRLFS

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Keywords: DESI MS, speciation, radionuclides, TRLFS

Now, more than 30 yeras after the reactor accident in 1986, ^{241}Am, becamethe dominating α-emitter in the Chernobyl exclusion zone due to buildup from its precursor ^{241}Pu ($T_{1/2}$ = 14.35 a) by beta decay. It is possible that this nuclide enters the human food chain via contaminated soil and plant transfer. In order to understand the uptake mechanisms on a microscopic scale the radionuclide's chemical speciation needs to be investigated, as different compounds will exhibit differences in their bioavailability. Therefore, the ambient Desorption Electrospray Ionization Mass Spectrometry (DESI MS)[1] technique was introduced for the speciation directly in plant parts. First results were obtained for europium as non-radioactive homologue for trivalent actinides.

Plants are grown in liquid Hoagland medium[2] for known and controlled conditions. A method for DESI MS measurements of leaves, stems and roots was developed and samples were analyzed after contamination. Additional results were obtained by TRLFS (Time-Resolved Laser Fluorescence Spectroscopy)[3] and ICP MS.

Eu species were identified directly from different crops with DESI MS after contamination (Fig.1). Marked species are europium hydroxides and/or nitrates with a maximum of two water molecules around the species. We report on the first mass spectrometric proof for europium species in plant parts. Additionally, TRLFS measurements (Fig.2) indicate europium carboxylate and/or phosphate species due to a strongly increased $^7F_2$ - $^7F_1$ emission band intensity ratio. Therefore, more europium species are presented in the obtained DESI MS spectra. ICP-MS results show the highest europium concentration in the root, followed by the leaves and the stems. Due to the results described above, further TRLFS measurements will be performed to identify the missing europium species in the mass spectra. Besides, further crops will be contaminated and analyzed with DESI MS and TRLFS. Concluding, these techniques represent an important step for the direct speciation of radionuclides in plants.

Figures

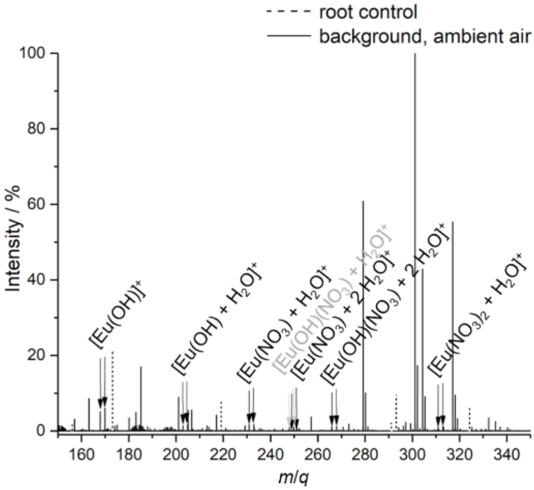

Fig.1: DESI MS spectrum of contaminated root with marked europium species.

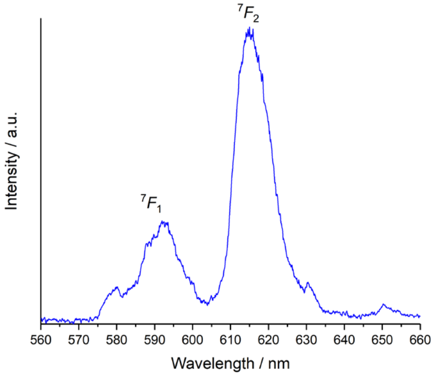

Fig.2: TRLFS spectrum of contaminated root.

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Improvement in flow-sheet of extraction chromatography for trivalent minor actinides recovery

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Keywords: extraction chromatography, minor actinides, CMPO, HDEHP, DTPA

Recovery of trivalent minor actinides (MA(III): Am, Cm) from spent nuclear fuel is one of challenging tasks for reduction in volume and radiotoxicity of final nuclear waste. Japan Atomic Energy Agency have been proposing extraction chromatography as a promising technology for that purpose, and research and development of the technology have been systematically performed [1-4]. Main difficulty of this process is separation of MA(III) and trivalent lanthanide ions (Ln(III)) due to their chemical similarity. We have already achieved excellent MA(III)/Ln(III) separation using di-(2-ethylhexyl)phosphoric acid (HDEHP) impregnated adsorbent with a di-(2-ethylhexyl)phosphoric acid (DTPA) containing eluent [3]. However, the process required much amount of eluent in order to achieve sufficient MA(III) recovery yields, and DTPA was involved in the final MA(III) product solution. DTPA in the product would result in carbon impurities in a product powder obtained by microwave irradiation denitration process [5]. In our previous study, DTPA-free MA(III) recovery flow-sheet with two steps column operation using octylphenyl-N,N-diisobutylcarbomoyl phosphine oxide (CMPO) and HDEHP impregnated adsorbents was proposed and a demonstration test was carried out [4]. Decontamination factors of Ln(III) against MA(III) were larger than our target value (i.e. 10^2), but recovery yields of MA(III) was about 70 % which was poorer than expected. Further modification in the flow-sheet was required to achieve sufficient MA(III) recovery yields and Ln(III) decontamination simultaneously. In this study, optimization in compositions of eluents for two columns were carried out through inactive fundamental experiments and performance of the optimized flow-sheet was demonstrated by hot experiments on MA(III) involved solution. Appropriate acidity of the eluents were determined as a consequence of series of inactive column separation experiments on CMPO or HDEHP impregnated adsorbents with changing acidity of the eluents. The hot experiments under the optimized eluent condition proved that this improvement made the MA(III) recovery yields drastically enhanced. About 93 % of Am and 97 % of Cm was recovered in nitric acid solution without involving DTPA. Decontamination factor of Nd and Eu were more than 10^2 and more than 10^3, respectively. The MA(III) recovery yields can be further improved to be more than 96 % for Am and 98 for Cm if lower decontamination factors of light lanthanides are acceptable. In this case decontamination factor of Nd was 17. Specs of the final product solution and of the waste solution generated by this process should meet requirements from fuel fabrication or irradiation and waste management procedures, respectively. Each requirement is currently under investigation.

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Analytical methods and detection techniques

Optimization study of electrolysis-based tritium continuous monitor

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Keywords: tritium monitor, plastic scintillator, electrolysis, polymer electrolyte membrane, optimization

Tritium is one of concerning radionuclide due to exposure to the deoxyribonucleic acid. For aqueous sample, a liquid scintillation conunter (LSC) which is not suitable for continuous monitoring has been used to detect the beta ray from tritium because the tritium emits extremely low energetic beta ray. Therefore, a continuous monitoring system for tritium in water was developed based on a polymer electrolyte membrane (PEM) electrolysis. In this study, parameterization and optimization of PEM electrolysis was carried out. The representative parameter was the fractionation factor which is defined as ratio of removal during electrolysis between hydrogen and tritium atoms. Soreefan's work showed the fractaionation factor in a single electrolysis condition: temeperature of 40°C and current of 7 A[1]. The transport rate of proton or tritium in PEM can vary greatly with temperature, which is related to the efficiency of electrolysis. The variation of the fractionation factor with temperature was evaluated and the optimal temperature condition was derived. A plastic scintillator-based chamber was used to detect the tritium[2]. The detection efficiency according to the tritiated hydrogen gas pressure inside the detection part was evaluated. Figure of merit which is defined as $(\text{efficiency})^2/(\text{background coutning rate})$ was used to optimize detecting condition.

Figures

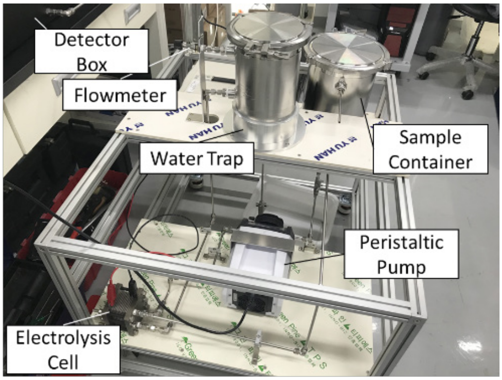

Fig. 1. The electrolysis system and detector box

Acknowledgments

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Analysis of hydrogen isotopes in frozen water using a combination of LIBS and LAMIS with PLSR

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Keywords: hydrogen isotope analysis, laser-induced breakdown spectroscopy, laser ablation molecular isotope spectrometry, partial least square regression

For a direct and rapid analysis of isotopes, optical plasma emission spectroscopy using atomic emission or molecular emission has been extensively studied [1-2]. In this work, laser-induced breakdown spectroscopy (LIBS) and laser ablation molecular isotope spectrometry (LAMIS) are combined with partial least square regression (PLSR) for the quantitative analysis of hydrogen isotopes of protium (H) and deuterium (D). Ice samples prepared with light water (H_2O) and heavy water (D_2O) in varying proportions were analyzed by focusing nano-second pulses of an Nd-YAG laser. After optimizing the detection conditions for the simultaneous measurement of atomic and molecular emission, the Balmer lines of H and D and the vibronic molecular emission spectra of OH and OD were measured, as shown in Fig. 1(a) and (b). The obtained spectral data were applied to the PLSR calibration and the cross validation to determine the isotopic ratio of H to D. Depending upon the spectral ranges selected for the PLSR calibration, the hydrogen isotopic ratio of H to D predicted by PLSR was well coincident with the nominal value, and the relative error of the prediction was less than 1% for the optimized case, as shown in Fig. 1(c).

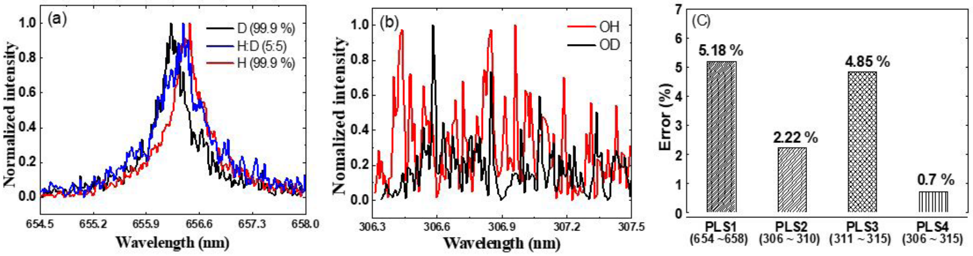

Fig. 1. (a) Isotope shift of H_α/D_α lines, (b) molecular OH/OD emission, and (c) Relative error of PLSR prediction depending on the spectral range for analysis

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MCNP model of L-54 M nuclear research reactor: validation by preliminary i-graphite radiological characterization

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Keywords: decommissioning, AGOT graphite, neutron activation, MCNP, gamma spectrometry, HPGe

Since shut-down in 1979, Politecnico di Milano nuclear research reactor has been kept in safe storage configuration. In this perspective, some actions, such as spent nuclear fuel removal and primary circuit decontamination, were already implemented to ensure safety of workers and public. In view of forthcoming decommissioning activities, preliminary radiological characterizations have been started. Within IAEA collaborative research project on irradiated GRAphite Processing Approaches (GRAPA), an experimental and Monte Carlo integrated approach has been launched for the radiological characterization of activated materials [1]. In particular, nuclear grade graphite (7 m^3) as neutron moderator and reflector is the target of the current investigation. A MCNP model of L-54 M nuclear research reactor has already been developed and its accuracy satisfactorily validated by comparing simulated reactor parameters with the available experimental ones, such as subcritical and supercritical reactivity, control rods worth and calibration [2].

In this work, neutron flux has been calculated at different positions inside the core and the graphite monolith, thus proficiently achieving an ultimate model verification by comparing simulated and experimental data. Furthermore, MCNP computational power has been exploited to obtain the 3D activation map of the main gamma-emitting radionuclides produced in irradiated graphite. To this end, impurity activation precursors in not irradiated graphite were already determined [2]. In this work, the production reactions have been simulated and the reaction rates calculated within the whole graphite stack by multiplying precursors nuclide density, cross-sections of activation reactions and neutron flux. Finally, the radionuclides activity concentrations have been obtained by properly processing MCNP output. With a view to validating the so-obtained results, several samples were collected at different axial and radial positions with respect to the core from the accessible parts of the graphite monolith, in particular from the external surface of the graphite stack and along the length of three extractable graphite rods. The activity concentrations of Easy-to-Measure radionuclides (^{60}Co, ^{133}Ba, ^{137}Cs and ^{152,154}Eu) were determined by HPGe gamma-spectrometry and satisfactorily compared with the simulated equivalents, thus promoting the developed computational approach as valid support to radiological characterization campaigns. Further radiochemical analyses will be performed to determine Hard-to-Measure pure beta-emitting radionuclides (^{3}H, ^{14}C, ^{36}Cl, ^{63}Ni, ^{129}I above all) and complete the model validation.

Thanks to its general principles, this integrated method is successfully applicable to the radiological characterization of any nuclear system undergoing decommissioning, thus entailing efforts and costs restraint.

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Elemental analysis of the geothermic microecology of the Los Azufres (Mexico) volcanic complex by Polarised Energy Dispersive X-ray Fluorescence Spectrometry

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Keywords: PEDXRF, Los Azufres, geothermal, fumarole, hydrothermal

The relatively recent technique of Polarised Energy Dispersive X-ray Fluorescence (PEDXRF) spectrometry employs 3D orthogonal optics between the x-ray tube and the detector such that by double polarization of the primary (tube) radiation, the Bremmstrahlung background is cancelled out. This leads to a notably improved signal/noise ratio, enabling quantitative trace analysis. In the present work we report the analysis of 16 elements spanning the 4th to the 7th periods found in the hot-spring water and sediment (S), the extremophilic primitive plants and their associated rhizospheric soils (RS) and the native volcanic substrate (VS) that together constitute the fumarolic and hydrothermal microcosm of the Los Azufres volcanic complex of central Mexico. The micro-environmental conditions of these fumaroles and hot springs are aggressive. Amongst higher organisms, only extremophilic primitive plants *viz*. mosses and ferns, have the capability to make such niches their habitats. Taking this microcosm as a natural laboratory, we have investigated the distribution of the 16 elements between the aforesaid geological components with the aim of understanding the importance of bio-geochemical weathering as against the purely geochemical one in the Ordovician-Devonian period ~ 460-360 Mya when these plants were the first land colonizers and were ubiquitous. Table 1 shows an excerpt of the results. For all elements except U, the geothermal microcosm showed higher concentrations than the average values for the earth´s crustal rock and the ordinary plant. The RS and plant tissue sequestered high concentrations of the heavy element. This is particularly marked for the case of Th where the biogeochemistry of the plant root zone trapped as much of the Th as the deposition by precipitation by the aggressive chemical action of the hot-spring waters. This suggests that biogeochemical processes were of seminal importance in the primitive geosphere and were key agents of pedogenesis and the earth system recycling of elements. Both were crucial for the subsequent evolution of higher plants, and by extension, animals.

Table 1. Average concentrations in mg/kg of Hg, Bi, Th and U in the RS and in plant (moss & fern) tissue, as well as in the Sediment (S) and Volcanic Substrate (VS), for Bi, Th and U only. Also shown are average concentrations in crustal rock and in ordinary plant tissue.

Element	Average concentrations (mg/Kg)						
	Substrate type			Extremophile Plant		Crustal rock	Ordinary Plant
	VS	RS	S	Moss	Fern		
Hg	–	19.1+0.7	–	2.2+0.	1.5+0.	0.07	0.06
Pb	–	23.4+0.9	–	23.7+0.6	15.8+0.5	10.0	20
Bi	<1.0	<1.0	<1.0	<1.0	~0.9	0.025	0.002-0.008
Th	8.4+0.4	9.9+4.0	9.3+4.0	1.9+0.1	1.0+0.2	6.0	0.03-0.3
U	0.1+0.0	0.6+0.4	0.7+0.8	0.7+0.2	0.7+0.1	1.8	0.07-0.2

Low-background, digital gamma-rays spectrometer with BEGe detector and active shielding

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Keywords: digital gamma-rays spectrometer, BEGe detector, active shield, coincidences

Recent progress in spectroscopic electronics allows using compact, fast, multi-inputs digital analyzers (so called digitizers) which register both energy and time stamps of processed pulses, generated by detectors' preamplifiers, with few nanoseconds precision. It enables to investigate coincidences between freely chosen sub-set from group of detectors and one of possible applications of described device is low-background, high-resolution gamma-rays spectrometer.

Such apparatus has been designed and constructed at the Institute of Nuclear Physics PAN in Krakow and it is equipped with Canberra germanium detector (Broad Energy Germanium - BEGe, BE 5030, relative efficiency ≥ 48%, 0.6 mm Carbon Composite window) and five large area plastic scintillation detectors (type EJ-200 by Scionix) which are mounted to the lead walls surrounding germanium detector and play a role of additional active shielding that consists of rejecting of signal acquired by BEGe detector, while at least one of scintillators detects radiation. The passive shield is a cube with 15 cm thick lead walls (inner 5 cm is made of 2500 years old Pb) with cadmium, electrolytic copper and plastic lining flushed by liquid nitrogen vapours to reduce radon in detector chamber.

Acquisition of the experimental data is performed with 8 inputs digitizer CAEN DT5725 which registers data with time resolution up to 4 ns (250 MSamples/s). As a result of performed measurements, output files, that consist of information about energy and time stamps of incoming pulses for each of detectors separately are generated. During off-line studies of obtained data, number of logic filters may be applied in order to investigate coincidences (in general – any logical relation including delayed processes) between different digitizer's channels. However, primary goal of such analyses is to prepare anticoincidence spectra which allow to notably reduce background of the spectrometer and, in consequence, obtain improved detection limits. Such investigations are performed by means of dedicated software which is currently under development and improvement processes. Moreover, this computer code allows testing time-differences between detectors in order to estimate their mutual delays what is crucial in establishing coincidence windows' length.

Preliminary results of spectrometer tests indicate that about 61% reduction in count rate, (from 1.25 to 0.49 counts per second) in whole spectrum range was achieved. The greatest contributions in count rate reduction have scintillators placed above and below BEGe detector (over 50 %). Additionally, the 511 keV peak's area was diminished almost 3 times. Further tests' results and additional data analyses software's functionalities will be presented at the Conference.

Pu-240 target preparation on thin backing foils for GRETINA experiments using ATLAS

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Keywords: plutonium, targetry, molecular plating

Recent measurements of the octupole strength to the highest spin states in ^{240}Pu were performed using sub-barrier Coulomb excitation in order to unambiguously and convincingly demonstrate the existence of the rotational-aligned phonon condensation in this nucleus. The experiment employed GRETINA in combination with the CHICO2 detector. A ^{208}Pb beam and a ^{136}Xe beam were delivered by the ATLAS accelerator at Argonne National Laboratory (ANL). The ^{240}Pu targets were prepared by the Center for Accelerator Target Science (CATS) using the method of molecular plating onto thin backing foils of C and Al. [1] Similar foils of C and Al were placed in front of the targets for recoil-stopping symmetry and to prevent target material sputtering and contaminating the chamber. For the preparation of these targets, plutonium oxide (10 mg; 99.5% ^{240}Pu enrichment) was obtained from Oak Ridge National Laboratory (ORNL). The plating apparatus, used routinely for actinide targets, was modified for use with the CHICO2 target frame [2]. The plutonium oxide dissolution and plating methodology will be presented.

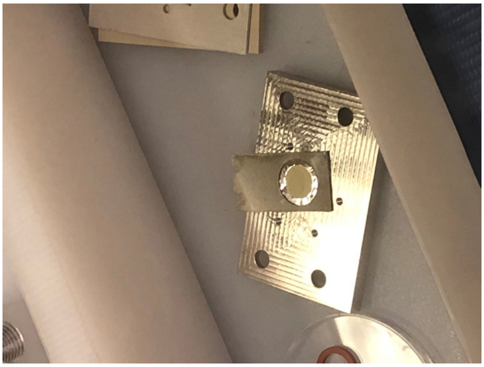

Fig 1. Plutonium plated onto aluminum backing on CHICO2 frame.

Acknowledgments

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Improvement of quality in the evaluation of radium isotopes ^{224,226,228}Ra in oil scale samples

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Keywords: radium isotopes, gamma-ray spectroscopy, interactive peakfitting, gamma-ray self attenuation

It is well known that significantly eleveated concentrations the radium isotopes ^{224,226,228}Ra exist in the scale and produced water in oil exploration (1,2). Currently there are close to 95 million barrels of oil produced each day world-wide resulting in very large quantities of radioactivity. As such it is important to correclty evalaute the concentrations of these radium isotopes not only for their own activity levels but for all thier daughter products. The activity concentration of ^{226}Ra was calculated from 186 keV peak. Thea ctivity concentration of^{228}Ra was calculated from its first daughter product ^{228}Ac using the 911 keV gamma rays since it is a pure beta emitter. Finally the activity concentration of ^{224}Ra was calculated from ^{212}Pb using the 238 keV gamma-ray. The comparative method was used with IAEA 375 (soil) with IAEA 447 (soil moss) and IAEA 448 (oil filed soil) as a quality control. This calibration method was chosen to negate any summing and coincidence effects by using an effciency curve. During our evaluations it became apparent that precautions were needed to take into account the gamma-ray self absoprtion of the oil scales that contained high-Z materials of barium and strontium, interactive peak fitting to separate the overlapping peaks of 238 keV and 241 keV and homogeneity. Furthermore it was realized that there was some inconsistency of the results depending on the reference material used as the comparator. Several kg of scale was collected from an oil field in western Texas and homogenized. A petri dish (6 cm diameter and 1.5 cm height) was used as a sample container for the 20-gram oil scale. All other reference materials were placed in the same geometry. A detailed evaluation of the radioanalytical methods will be presented.

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Background reduction in HPGe-based spectrometers using Pulse Shape Analysis method

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Keywords: gamma-ray spectrometry, HPGe detectors, Pulse Shape Analysis, artificial neural networks

Spectrometers based on High Purity Germanium (HPGe) detectors offer numerous advantages in gamma-ray counting, such as: relatively high detection efficiency, excellent energy resolution and intrinsic radiopurity. Furthermore, by analyzing the shape of the signal observed on the preamplifier's output, it is possible to distinguish between single and multiple interactions of gamma-rays in the detector.

Since events in full energy peaks with energies over 1000 keV consist mostly of multiple interactions, it is possible to reject single Compton scattering events and thus decrease the Compton continuum. In the talk the concept of Pulse Shape Analysis will be described in detail, as well as application of the method based on artificial neural networks to data from HPGe detectors of semi-coaxial and BEGe geometries.

bGamma: new general purposes gamma-ray spectrometry software

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Keywords: gamma-rays, software, spectrometry

Type or The analysis of the energy-distributed spectra obtained from any radioactive sample and measured using a nuclear radiation detection system is still a very critical step in gamma-ray spectrometry due to its complexity. These spectra can include large amount of interference photo-peaks, presence of spectrum artifacts (e.g. sum and escape peaks), complex continuum, specifics of the detector response, among many others. Therefore the correct and precise radionuclide identification and quantification independently of the measurement geometry, sample characteristics and/or detector used; still remains a very demanding and challenging task. BRIGHTSPEC has developed a new advanced software, bGamma™, for gamma-ray spectrum analysis that deals with these complexities and provides a statistically sound spectrum analysis and quantification results.

bGamma software is a general purpose, comprehensive and extensive software package for gamma-ray spectrum analysis, radionuclide identification and quantification. It can analyze any acquired gamma-ray spectrum, independently of the detector used for its measurements and provides all the necessary tools and functionalities for performing the needed detailed and complete analysis.

Some of the main interesting features of the software: connection and control the hardware for correct data acquisition, import spectra from other well-known file-formats (including N42.42, latest revision), perform energy/shape/efficiency calibration of gamma-ray spectra, automatic peak search, ROI automatic/manual marking and its analysis/calculations (singlets, multiplets), includes different methods for peaks/spectrum continuum subtraction, incorporates several peaks' fitting methods (including Bayesian fitting), performs nuclide identification (with separation from possible spectrum artifacts and structures), radionuclide activity calculations, etc. The software incorporates the entire nuclear decay data files (NuDat BNL, USA), making the spectrum analysis easier, faster and without needs of limited nuclear libraries or the use of data library editors. Yet, the user can narrow the nuclide emissions of its interest in a very easy and powerful way. The modern Graphical User Interface (GUI) makes spectrum visualization and analysis very intuitive and provides an important "visual" feedback of the analysis results. Additionally, all the analysis model parameters are at hand for their quick changes and optimization. bGamma software is a multi-document software allowing you to analyze multiple-spectra at the same time and/or acquire data from several connected detectors. The software runs seamlessly on MS Windows®, Linux™ or MacOS®.

Recent advances in the radiochemical separation of polonium and actinides in environmental and bioassay samples

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Keywords: polonium, actinides, separation, alpha spectrometry

Southeastern New Mexico is home to the US Department of Energy's Waste Isolation Pilot Plant (WIPP), the World's only operating deep geologic repository for transuranic waste. Plutonium isotopes ($^{239+240}$Pu), and ^{241}Am are expected to account for more than 99% of the total radioactivity scheduled for disposal in the repository, requiring exhaust air to be monitored for radionuclides during operations. Southeastern New Mexico is also located in the Permian Basin where the recovery of continuous petroleum resources relies heavily on unconventional drilling, resulting in the generation of technologically enhanced natural occurring radioactive materials (TENORM) in drill cuttings, produced/flowback water, sludge, mineral scale, and fall out from natural gas flares. A dominant radionuclide in TENORM is ^{210}Pb, and its progeny ^{210}Po, which although rare at only 0.11 μg/kg of uranium ore, is an emerging contaminant of concern. Concentrations of ^{210}Po can reach 2 Bq/g in sludge, 13 Bq/g in mineral scale, 0.15-4.15 Bq/L in produced water, and has been shown to increase in surface soils due to the ingrowth of radium decay products, all of which can lead to environmental contamination and increased exposures. Understanding the fate and transport of polonium is constrained by its complex analytical chemistry. At temperatures over 100°C, polonium volatilizes, thereby limiting options for environmental and bioassay sample preparations. We discuss recent advances in the rapid radiochemical separation of polonium and actinides (Pu, Am and U) in these samples, including a comparison of TEVA+TRU, and DGA+TRU chromatography columns in the sequential separation of polonium and actinides. The TEVA method involves a rapid co-precipitation step to remove matrix interferences, followed by plutonium oxidation-state adjustment to Pu^{4+}, and an incubation period of ~1 hour, at 50-60 °C, to allow oxidization of the resultant Po^{2+} to Po^{4+}. The polonium and plutonium are then separated on a TEVA column, while separation of americium from uranium is performed on a TRU column. After separation, an alpha-counting source is prepared by micro-precipitation with CuS for polonium and NdF_3 for actinides. Not only is the method simple, and robust, but it can be performed quickly with excellent removal of interferences resulting in high chemical recovery and very good alpha peak resolution. The efficiency and reliability of the procedures were successfully tested by analyzing urine, aerosol filters, and drinking water samples.

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Education in radiochemistry

Active teaching strategies for introducing radionalytical techniques in analytical chemistry master degree

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Keywords: flipped classroom, just in time, case studies, radionalytical techniques, banana

Radioanalytical techniques are a set of singular and attractive spectroscopic techniques that are briefly or not presented in the courses about instrumental analysis of the most part of the chemistry degrees. The program of the master on Analytical Chemistry of the University of Barcelona includes a specific course about this topic for the last 10 years. The course is 2 ECTS and students follow face-to-face activities 2 hours a week for three months. The number of attendances is around 10.

The program of the course includes fundamentals of radioactivity, instrumental analysis, basics of radioprotection and practical aspects. Fundamentals of radioactivity (radioactivity, disintegration law and sources of radioactivity and interaction radiation material) and basics of radioprotection are teaching through the traditional method. For the instrumental techniques and practical aspects, two active teaching strategies were used: flipped classroom and case study.

Flipped classroom, in the just in time strategy, is used to introduce **instrumental techniques**. The procedure followed is to distribute among the students, one week before the class, different published articles. They have to read it and to answer a test before the classroom activity. The questions included in the test are related to different aspects of the analytical procedures as the sample pretreatment, preparation for measurement procedure, matrix influence on the detection, calibration procedure and data treatment. These issues are discussed, one by one, on the classroom activity. Each student points out the information included on his article and their questions about. All participants contribute to the answers and teacher summarizes the most important aspects during and at the end of the session.

Articles are divided in three blocks on base of the type of radioactivity emission studied: beta emitters determination by liquid scintillation and/or proportional counters; alpha emitters determination by semiconductors and/or proportional counters and gamma emitters determination by semiconductor detectors. For the three groups, the articles cover different fields of application as environmental studies, nuclear industry; biomedicine applications... Every two students have a different article.

Case study strategy is applied to a **practical resolution of a problem**. We use for that purpose questions related to the determination of radioactivity on a quite common material: ^{40}K in bananas.

Students have to design and implement the determination proposed. The steps followed include bibliographic research, determination of the bananas amount required as a function of the detection technique to be used (gamma spectrometry and liquid scintillation) introducing concepts as detection limit, calibration procedure, matrix and geometry influence,...; sample pretreatment, sample preparation for measurements, calibration of instruments, total potassium determination by atomic emission technique, data treatment and report delivery.

Students use to develop an emotional implication with the topic and learn a lot about radionalytical techniques. On the opposite side, they also claim sometimes about the large effort required by this course.

Education program for BSc and MSc studies in engineering field, radiochemistry and radioecology specialty of University of Pannonia

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Keywords: radiochemistry, radioecology, environmental engineer, chemical engineer, material engineer

The Faculty of Engineering at the University of Pannonia has a dynamic, innovative teaching and progressive approach, it has been known over decades for its strength in offering a wide variety of graduate and research programs in the fields of engineering and science. The Institute of Radiochemistry and Radioecology at the University of Pannonia has more than 50 years' history. The institute is involved in the teaching of subjects related to radiochemistry, physics, radiation physics and nuclear measurements; and the research programs also focused on these fields. Institute of Radiochemistry and Radioecology takes a roll in several graduate program as a radiochemistry module or a radioecology specialty.

In this study an overall education program is described in case of BSc and MSc programs for environmental engineer, chemical engineer, material engineer students and PhD studies on the prescribed fields. For the featured educational and research work, the institute has excellent technological and infrastructural background. The laboratory complex (including level "B" and level "C" laboratories, environmental lab, radiological lab) was built in 2003 with the most relevant tools e.g. gamma spectrometer with semi-conductor detector, field and laboratory scintillation gamma spectrometer, alpha spectrometer with semi-conductor detector, liquid scintillation alpha spectrometer, gas drift and scintillation total - and -activity measuring tools, continuous and integral radon measuring tools, soil gas radon concentration and soil permeability measuring tools, radon emanation and exhalation measuring tools, water radon measuring tools, environmental dose rates gages, etc.

The aim of the course is to provide advance training in radiochemistry, nuclear measurements and to equip students with the ability to carry out research and development tasks.

Education in Health Physics and dissemination of scientific culture at University of Milano - UNIMI

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Keywords: Health Physics, education, radon measurements, CR-39, alpha particles

At the Physics Department of the University of Milano in the Master Degree is foreseen didactic line in Health Physics. The students are trained in order to apply to Specialization School in Medical Physics; this school allows them to be inserted inside the Hospital System as Medical Physics and to acquire the skills to become Qualified Expert in Radioprotection, according to the new European legislation that must also be implemented by Italy [1]. The object of the Health Physics course is to provide education, including practical training, in radiation science which is relevant to health physics required for medical and biological applications of natural and man-made ionizing radiation. Topics cover: (i) basic knowledge on natural and artificial radioactivity, characteristics of the different types of radiations (photons and charged particles) and mechanisms of their interactions with matter and in particular with the biological sysytem as well as in the knowledge of radiation detection and protection; (ii) an overview of their applications in biomedical and clinical fields as well as in environmental and human health toxicology, including nanotoxicology, reserach. On this basis in the Laboratory classes the students are in-depth trained on: (i) radioactive counting techniques for detecting and measuring different type of radiations with a great deal on computer-based gamma ray spectrometry with high resolution High Purity Germanium (HPGe) detectors; (ii) neutron activation analysis (NAA) by a 37 GBq neutron americium-berylium (Am-Be) source; (iii) the measurement of indoor Rn-222 with different kind of detectors selected as a function of the type of information to be obtained. We will present our laboratories, the instrumentation that the students can use for these types of measures and some of the results that they obtained.

Moreover, in the context of the dissemination of the scientific culture related to nuclear energy, radioactivity and radiation we started up a project devoted to students of Italian High Schools by presenting and discussing good reasons to acquire and conserve expertise and knowledge in the nuclear field as important contribution to society [2,3]. This to try to correct the distorted image of a currently almost demonized nuclear field as consequence of nuclear weapons and some accidents in the nuclear power energy production that occurred in the past, making the “nuclear issue” a taboo, particularly in Italy. The students of High Schools are involved in the experimental measurements of the radon-222 concentration by CR-39 solid state nuclear track dosimeters (SSNTD) inside different places such as their school, home or other indoor sites of their interest. We will outline the main goals of the project, presenting some typical results [4].

Acknowledgments

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High school teaching package to motivate young people into radiochemistry and nuclear chemistry careers

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Keywords: MEET-CINCH, education, radiochemistry, nuclear chemistry, remote controlled, robolabs

A Modular European Education and Training Concept In Nuclear and RadioCHemistry (MEET-CINCH) is an educational and training project funded by H2020-Euratom. The project aims to mitigate the skills gap in nuclear chemistry and radiochemistry, attract new talent to the field and develop a long term sustainable strategy for nuclear chemistry education. National Nuclear Laboratory (NNL) is responsible for the delivery of a "teaching package for high school use", suitable for students aged 16-19 years. The aim of this task is to produce free teaching resources for chemistry teachers that will raise young people's awareness of the available careers in nuclear and radiochemistry and attract them to the field.

NNL is building on existing teaching material from previous phases of the project (CINCH-I and CINCH-II) and adapting it for use in high schools. Earlier CINCH projects developed six remotely operated "Robolab" experiments at the Universities of Oslo (UIO) and Hannover (UH) for teaching undergraduate students. Working in collaboration with UH and UIO, NNL has extensively tested the suitability of the Robolabs for high school students, considering the target group's level of chemistry knowledge and potential IT challenges in schools. As the success of this task is largely dependent on input from school teachers and students, NNL has been engaging with several schools throughout the duration of the project to ensure that end-user requirements are met.

In June 2018, NNL carried out classroom trials with five separate schools and has selected the IonLab experiment (developed by UH) for further development. IonLab allows students to remotely control an extraction chromatography experiment, separating strontium-90 from yttrium-90 [1]. Building on student and teacher feedback, NNL is developing interactive teaching material to enhance the student's learning experience. A „flipped classroom" concept has been adopted in which students are introduced to the learning material before class using an e-learning platform. In addition, UH is converting IonLab into an interactive screen experiment (ISE) which will allow students to work on the experiment individually, as opposed to an entire class controlling one experiment. Other advantages of ISE include reduced maintenance of the physical experiment and software, the ability for multiple users to carry out the experiment and continued access to IonLab following completion of the MEET-CINCH project.

Acknowledgments

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Educational activities in radiochemical analysis at DTU Nutech

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Keywords: education, radiochemical analysis, radioecology, environmental monitoring, nuclear decommissioning, waste characterization, laboratory exercise

The nuclear and radiochemistry community has been challenged by requirements from analysis of radionuclides in different situations including radioecology, environmental monitoring, decommissioning of nuclear facilities and waste management. Especially in recent years, high demands have been set up by the increased nuclear decommissioning activities for waste classification. Analysis of hard-to-measure radionuclides in unusual matrixes (such as metals, steel, graphite, concrete, plastic, soil, sludge water, ion-exchange resin, evaporate concentrate) are difficult tasks.

Research in radioanalytical chemistry has a long history at Center for Nuclear Technologies, Technical University of Denmark (DTU Nutech), and the state-of-the-art methods have been applied successfully for the determination of ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{93}Mo, ^{93}Zr, ^{99}Tc, ^{129}I, ^{210}Po, ^{210}Pb, ^{226}Ra, ^{237}Np, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am, ^{244}Cm as well as different gamma emitters.

To facilitate knowledge sharing and experience exchanging, many educational activities have been organized at DTU Nutech [1]. For example, the CONCERT [2] training course entitled ‘Assessment of long-term radiological risks from environmental releases: modelling and measurement’ in 2017 and 2018, comprised 22 h lectures, 10 h tutorship and 32 h laboratory training.

Laboratory exercises were also organized in connection with a series of NKS (Nordic Nuclear Safety Research) workshops/seminars for radioanalytical chemistry at DTU Nutech, including NKS-B RadWorkshop in 2010, 2013 and 2018, and ICP-User seminar in 2017 [3].

The very recent NKS-B RadWorkshop in 2018 focused on the radioanalytical chemistry in nuclear decommissioning and waste management. The high interest from the participants to join the RadWorkshop 2018 highlights the rapidly increasing demands and challenges in analysis of radionuclides for decommissioning. According to feedback from participants, there is a clear need in the nuclear and radiochemistry filed for such educational activities, where hands-on exercises are included and practical questions from day-to-day experiments can be answered.

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How to educate talented high school students in nuclear chemistry?

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Keywords: education, high school, talented students, nuclear chemistry

The education of high school students is not an easy task. The still common method of pure teaching is not an effective way for students to understand the relatively difficult topic which nuclear chemistry definitively is. In this work different way of education was carried out and "tested" on the group of 15 talented high school students which are interested in chemistry. They are also competitors of Fast and Attractive Chemical Education (FACE - a chemical competition for high school students in the Czech Republic).[1] The education was inspired by Peer Instruction method used by prof. Eric Mazur.[2] Using this approach students were able to understand the behaviour of elementary particles by themselves by solving several tasks. Moreover, students were very excited by this type of education.

The oral presentation will discuss the organizational details of this lecture as well as the tasks solved by the students.

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I-131 Production, release, and measurement

Radioactive iodine in the atmosphere: from source term to dose – Status of IRSN research

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Keywords: iodine, atmosphere, source term , dispersion, monitoring, prophylaxis

In case of an accident release, radioactive iodine isotope dispersion into the environment is a problem of main concern due to possible human health impact. Authorized discharges result sometimes in measurable levels of radioactive iodine releases into the atmosphere also contributing to public concerns and interrogation – even if at trace level. The half life of some radioiodine isotopes (8 days for ^{131}I and 15 millions years for ^{129}I) implies a possible dispersion into all compartments of the environment – from the troposphere to the terrestrial or marine biosphere and finally into the food chain – inducing potential human health effects. The major accidents of Chernobyl and Fukushima or even the recent iodine release events detected in Europe have shown that the knowledge of the radioative iodine distribution between its various chemical forms is still insufficently accurate to satisfactorily adress the public concerns.

Research at IRSN on iodine dispersion in the atmospheric compartment is aimed to adress the major issues of this problematic : 1/ accurate source term evaluation for realistic dose assement, 2/ improved crisis management to better protect the public in case of radioactive iodine release into the atmosphere.

To perform these evaluations, IRSN relies on modelling tools dedicated to the evaluation of the source term (ASTEC, PERSAN, ... codes), and to the prediction of its dispersion into the environment taking into account the health impact (C3X, SYMBIOSE and CONDOR tools). Modelling tools are also completed by radioactive iodine monitoring in the environment (OPERA Air program covering the whole french territory) and mobile in vivo measurement units dedicated to the monitoring of exposed populations. The Software tools allow for an accurate dose assessment.

In order to improve its expertise and knowledge on radio-iodine behaviour in the atmosphere, IRSN is currently sustaining large research efforts over 6 thematics covering all the aspects linked to this issue: source term evaluation, atmospheric dispersion modelling including the terrestrial and marine boundaries, development of more sensitive and accurate monitoring equipement, dosimetry tools (ICARE and MIODOSE) and upgrade of prophylaxis policies (PRIODAC research program).

Improved understanding of radio-iodine dispersion in the atmosphere in terms of speciation and physical forms can be obtained by combining experimental studies and development of new modelling schemes. Model validation will be gained by facing fields measurements in case of routine iodine discharge (^{129}I or ^{131}I to some extent) or accidental/incidental situation. In this view, the development of new field monitoring devices capable of identifying the nature of iodine (gaseous vs particulate material and iodine speciation) is a challenging issue. At least, the dose evaluation operationnal tools and the iodine prophylaxis policy will benefit from the dispersion model improvement.

The ability of the nuclear safety field community to accurately characterize radio-iodine dispersion, dose evaluation and progress in the use of countermeasures is thus of utmost importance. Such high accuracy data will help to better advise authorities and emergency crisis managers to improve the protection of the public if a severe nuclear power plant accident is to occur.

Global observations of iodine-131 by the International Monitoring System of the CTBTO

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Keywords: nuclear explosion monitoring, radioiodine, atmospheric radioactivity

For the purpose of global monitoring for nuclear explosion signatures under the Comprehensive Nuclear-Test-Ban Treaty (CTBT), a unique International Monitoring System (IMS) with 80 radionuclide stations is being established. Each station is equipped with a high-volume sampler and high sensitivity HPGe detector (Schulze et al., 2000). The daily samples are analysed by the International Data Centre that releases immediately to all State Signatories an automated report followed by a quality-reviewed report. These reports focus on 83 CTBT-relevant radionuclides including I-131 but also I-135, I-133 and I-130, being all fission products. In addition, separate systems of noble gas detectors at initially 40 sites analyse the atmospheric air for radioxenon isotopes of interest. I-131 is a CTBT-relevant isotope with high significance. It is a direct precursor of Xe-131m which is most relevant for possible detection of underground nuclear tests.

This paper summarizes the observations made at all IMS stations since their beginning of operation (see Figure 1). It discusses the I-131 trends and global distributions with a special emphasis on the nuclear debris observed as a consequence of the Fukushima accident when several other radioiodine isotopes were observed including I-132 (Stoehlker et al., 2011). The implications of I-131 for CTBT verification are investigated in connection with other radioiodine isotopes, specifically I-135 and I-133 (Kalinowski et al., 2014). This paper also considers the significance of I-131 for interpreting the four CTBT-relevant radioxenon isotopes (Xe-135, Xe-133, Xe-133m, and Xe-131m).

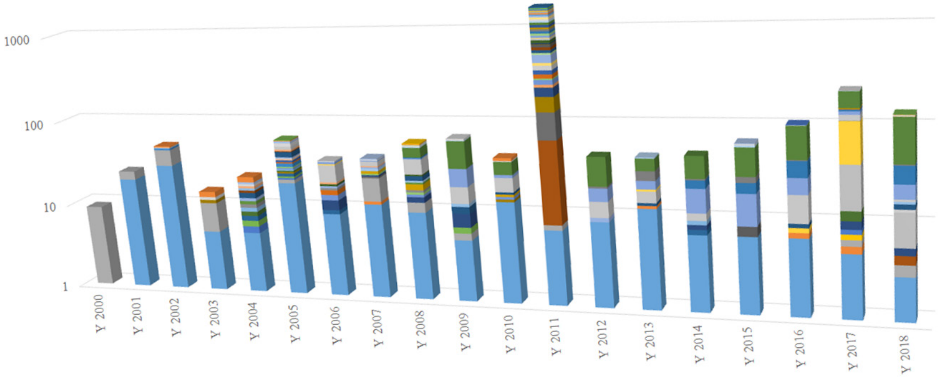

Figure 1: Development over time for annual detections of atmospheric I-131. The slices of the histogram bars show the share of individual stations. Please note the logarithmic scale.

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European-scale detection event of airborne ^{131}I in January/February 2017

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Keywords: ^{131}I, European event, radiopharmaceuticals, apportionement, meteorological conditions, Ro5

Traces of particulate radioactive iodine (^{131}I) were detected in the European atmosphere in January/February 2017. Concentrations of this nuclear fission product were very low, ranging 0.1 to 10 $\mu Bq \cdot m^{-3}$ except at one location in western Russia where they reached up to several $mBq \cdot m^{-3}$. Detections have been reported continuously over an 8-week period by about 30 monitoring stations. We examine possible emission source apportionments and rank them considering their expected contribution in terms of orders of magnitude from typical routine releases: radiopharmaceutical production units > sewage sludge incinerators > nuclear power plants > spontaneous fission of uranium in soil. Inverse modeling simulations indicate that the widespread detections of ^{131}I resulted from the combination of multiple source releases. Among them, those from radiopharmaceutical production units remain the most likely. One of them is located in Western Russia and its estimated source term complies with authorized limits. Other existing sources related to ^{131}I use (medical purposes or sewage sludge incineration) can explain detections on a rather local scale. As an enhancing factor, the prevailing wintertime meteorological situations marked by strong temperature inversions led to poor dispersion conditions that resulted in higher concentrations exceeding usual detection limits in use within the informal Ring of Five (Ro5) monitoring network.

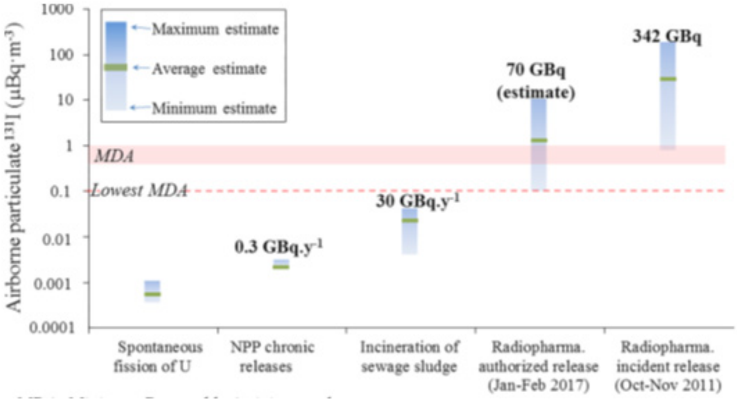

Figure 1: Source apportionment of particulate ^{131}I in the air over Europe in January/February 2017 based on source term estimates of various ^{131}I emissions.

Liquid scintillation and analysis of long-lived radionuclides

Towards potentiometric multisensor system for plutonium quantification in PUREX process streams

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Keywords: plutonium, chemical sensors, PUREX, on-line control

Plutonium is one of the key components to be controlled in technological streams of spent nuclear fuel reprocessing. The analytical methods which are currently in use for that purpose are based on radiometric techniques and inductively coupled plasma atomic emission spectrometry and mass-spectrometry. While providing for very high sensitivity and selectivity the ICP methods are laborious and time consuming. In order to avoid these issues in the recent years there was a strong interest in development of on-line monitoring tools based on fiber optic UV-Vis-NIR and Raman spectrometry with chemometric data processing [1,2]. This approach appeared to be very promissing and effective, however detection limits of optical methods may not be low enough for certain analytes.

In this respect electrochemical methods can be a nice supplement to the optical spectrometry as they allow for reliable quantification of much smaller amounts of analytes. Potentiometric methods are of special interest as the instrumentation and overal experimental layout of the potentiometry is quite simple and with the idea of on-line and at-line measurements. However the literature on the construction of potentiometric sensors for plutonium quantification is scarce and only few reports are available (see e.g. [3]) where the strong influence of pH and uranium on plutonium function was observed.

In this study we have tested several potentiometric sensors with polymeric membranes containing various ligands suggested in liquid extraction for separation of actinides and lanthanides as possible Pu-selective electrodes. It was found however, that all of these sensors are also sensitive to lanthanides and uranium and particular single highly selective plutonium electrode is hardly possible. In these circumstances we have applied multisensor approach and employed the array of these cross-sensitive sensors as a single analytical instrument for plutonium quantification in complex mixtures simulating PUREX technological streams. Potentiometric sensor array made of 17 polymeric plasticized membrane sensors was shown to be applicable for plutonium quantification in the complex mixtures. The root mean squared error of prediction was about 5 mg/L in the range 0-50 mg/L of plutonium in presence of 10-1000 mg/L of uranium in 0.01 M nitric acid. The attained precision seems to be sufficient for technological monitoring purposes and the response time of the sensor array does not exceed 2 minutes.

Acknowledgments

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Novel approach for strontium preconcentration from seawater

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Keywords: strontium, synthetic zeolite, seawater

Determination of ^{90}Sr in the environment is essential within the radiological monitoring programs. Due to strontium similarity to calcium, ^{90}Sr may enter the human body and deposit in bone tissue. There are numerous methods developed to make its determination easier and faster[1,2]. However, the determination of strontium in complex matrices, such as sea water, is still challenging. The methods are mostly time-consuming and tedious. In recent years, methods for ^{90}Sr determination via its progeny ^{90}Y are proposed. In the literature novel methods are described for the determination of both ^{89,90}Sr in case of emergency situation, using combination of Sr resin and DGA resin[3,4] or by using Empore Rad Disks[5]. However, all approaches include preconcentration step by precipitation of strontium with phosphates, carbonates or oxalates[6]. Within this study, a different approach is proposed by using a synthetic zeolite, Z4A. Small amount of this inexpensive material may be mixed with predetermined quantity of seawater at a sampling site and filtrated. The preliminary results have shown that within 5 minutes, 10 g of zeolite can pick up more than 90 % of strontium from 1 L of seawater. Therefore, the sample size may be reduced which may simplify further sample handling.

Acknowledgments

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Fast method for the determination of radiostrontium and plutonium isotopes in food samples

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Keywords: strontium, plutonium, extraction chromatography, DGA-resin, Sr-resin, food

Rapid radioanalytical methods are important in the case of a radiological emergency and for the defence against nuclear hazards, especially for pure alpha and beta emitters like $^{239/240}$Pu and ^{90}Sr. A quick evaluation of the radiological situation is crucial for taking effective countermeasures. Depending on their activities, ^{90}Sr and its daughter ^{90}Y might be highly radiotoxic isotopes with high affinity to bone tissue and a significant risk of bone cancer. Plutonium isotopes represent a high risk if elevated activities are ingested because of their mutagenic and carcinogenic effects. In order to quickly determine the activity levels of these radionuclides in food, it is necessary to develop fast radiochemical procedures [1].

A combined fast method was developed for the determination of radiostrontium and plutonium isotopes in food samples with different fat/sugar/protein content. First, it employs microwave digestion. The purification step uses two extraction chromatography cartridges containing DGA-resin and Sr-resin, respectively. The experiments were carried out with tracer solutions. The radionuclides were measured using alpha spectrometry and subsequent liquid scintillation counting (LSC) for plutonium isotopes and via LSC for radiostrontium.

The preliminary results of the key steps of the combined fast method will be presented.

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Application of multiple quench parameters for confirmation of radionuclide identity in radioanalytical quality control

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Keywords: radioactive waste, radionucide identification, LSC measurement

Radioactive waste sentencing in support of nuclear decommissioning relies on robust characterisation of waste streams. Quantification of difficult-to-measure radionuclides typically relies on chemical separation prior to radiometric analysis to ensure that the target analyte is effectively separated from any radiometric interferences. Spectral deconvolution can be applied to correct for interferences that have co-extracted with the analyte. However, for beta emitting radionuclides, spectral deconvolution is not usually effective, particularly if the identity of the co-extracted species is not known. Robust measurement therefore relies on efficient chemical separation alone. Confirmation of the effectiveness of the separation is usually achieved through visual inspection of spectra.

This paper presents an alternative, less subjective, approach for the evaluation of liquid scintillation spectra in order to confirm the absence of radiometric interferences. The technique is based on an approach originally developed for identification of radioactive contaminants in emergency screening of drinking waters [1] and uses multiple quench parameters to determine the mean energy of a beta emitting radionuclide irrespective of the sample quench level. The application of the technique to routine analysis is demonstrated using reference standard and operationally-derived spectra from radioactive waste samples.

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Radiochemical characterisation of spent IER by combination of separation, LSC measurement, and pyrolysis at NRG

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Keywords: LSC, Separation, Characterisation, Nuclear waste, Sampling, Ion exchange resins

The High Flux Reactor in Petten, Netherlands, is used for isotope production for medical purposes as well as material research reactor. During its exploitation several type of operating radioactive waste are produced and accumulated. Although treatment and characterization of IER is already practiced by several operating reactors, the approach taken by NRG offers a combination of characterization techniques and a methodology, integrating some of the complex issues encountered in waste management business such as: Representative sampling/Homogeneity; Nuclides analysis selection; Homogeneity guarantee; Analysis method (including separation, LSC and pyrolysis work); Reproducibility. Despite its apparent homogeneity, the presence of hot spots inside an IER container is always a risk; to reduce it recommendations mentioned in IAEA-tecdoc 1537 are applied: "[…]a simple and stable waste stream could be declared homogeneous if NDA measurements of Cs-137 and/or Co-60 made at different locations are within a 30% relative interval."

A number of sampling campaigns have been carried out on batches of used IER from various years. (N.B: IER are changed on average every two years and are stored by years and types: anionic or cationic).

The required validation of the homogeneity has been carried via gamma spectrometry and relative spread of Co60 and/or Cs-137 content measurement.

1. Non-Destructive:
   - Gamma spectrometry (specifically for Co-60 and Cs-137)
   - Total alpha/total beta via Liquid Scintillation Counter (screening)
1. Destructive:
   - Alpha spectrometry
   - Specific beta-emitting nuclide analysis
     - H-3
     - C-14
     - Cl-36 (under advanced development)
     - Fe-55
     - Ni-63
     - Sr-90
     - Tc-99(under advanced development)

Destructive analysis, elaborated by the Consultancy and Services group, consists as a first step on a complete digestion of the resin to maximize the recovery of radionuclides. From the aliquot, selective separations and extractions are operated to isolate the desired radionuclides. The thus isolated radionuclides are later measured using a liquid scintillation counter (LSC).

The key step of the selective separation has been developed at NRG with good recovery rates (in the order of magnitude of 75% for most of the radionuclides) achieving limited losses of activity and better accuracy in the measurement. This selectivity has been checked and validated following ISO -17025 standards.

Low concentration of certain radionuclides are allowed thanks to the very low counting activity LSC in use at NRG and the controlled radiochemical process. The radiochemical methods developed are foreseen to be extensively applied to other decommissioned or to be decommissioned components of nuclear power plants as well as for various complex waste streams.

Results (to be updated with latest results at the time of the presentation) show an excellent recovery level for the most significant nuclides. More importantly, based on the multiple samples per batch analysed so far homogeneity can be assumed within a batch of ion exchange resins.

The results provided so far are fitting the profile of required characterization for both transport and incineration. It also constitutes a “radionuclide identification card”, and, as such can contribute to the standardization of the treatment and characterization of such waste streams.

Pine needle and milk powder reference materials preparation and its uncertainty evaluation on strontium 90 analysis

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Keywords: ^{90}Sr, intercomparison, food, CRM

Food and drinking water safety monitoring are more and more concerned by public and government. Based on the organizing of nationwide monitoring and assessment of radioactivity in food and drinking water following the Fukushima Dai-ichi nuclear accident. We prepare the reference material (RM) for the routine tasks of the radioanalytical laboratories intercomparison and measured results quality control.

The sample of pine needles and milk powder were selected separately in Beijing and Hohhot China. The stontium 90 solution were two steps spiked in the dried powder samples, milk powder was spiked with cesium 137 solution as well. Mixed by V-shaped blender for homogeneity, then freeze-dried, filled bottles and Gamma ray irradiation sterilized with a total dose of 25kGy using a cobalt 60 source. A unit of the sample consists of approximately 30 gram of pine needles powder and 100 gram of skim milk powde respectively.

The batch experiments for the stability and uniformity performed by the Di-(2-ethylhexyl) phosphate (HDEHP) extraction chromatography separation, yttrium-90 precipitated and counting. Composed the method using Sr-spec crown ether (also lab prepared crown ether on teflon powder) separation with liquid scintillation counter for the ^{90}Sr defination value during the labs interccomparison. The ^{90}Sr measurement procedure uncertainty components, standard uncertainty and expanded uncertainty were respectively calculated and its mainly originated from counting, detection efficiencyof equipment, chemical recovery of the method. The RM uncertainty is mainly from stability testing, homogenization testing and labs defining testing results. The relative uncertainty of the recommended value is 3.1% of 32.3 Bq/kg ^{90}Sr in pine needle powder, the certificate RM number is GBW 04329. A description of the material preparation, uncertainty analysis and the results of the interlaboratory comparison will be presented and discussed.

Acknowledgments

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Simple measurement of actinides in urine using solid-state scintillation

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Rapid methods of determination of internal contamination play the key role during emergency situations in particular for incident response teams and affected populations. Such determination represent the first and the most important step in the protection of health resulting in decision about the further operability of the first responders, or their treatment. For this reason, these methods and their particular techniques must be fast, reliable, robust, simple and cost-efficient, as well as providing high quality throughput. On the other hand, they are characterized by lower precision and they are often biased. The presented method is based on direct measurement of urine using powder scintillator YAP:Ce together with an alkaline medium as a replacement for traditional liquid scintillation cocktail. The work was focused on optimizing work procedures, alkaline media and the influence of various ions and organic compounds with respect to the model radionuclides. The overall efficiencies for trivalent actinides (Am-241 and Cm-244) were greater than 85 % and 94 %; therefore, this method could be suitable for rapid determination of gross activity of trivalent actinides.

Importance of the background uncertainty for assay sensitivity and improvement by Hidex Digital Pb Shield (DigPb) method

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Keywords: uncertainy, background, Digital Pb shield, assay sensitivity, Figure of Merit

The background evaluation is a key point in the analysis of environmental samples due to extremely low amount of radioactivity usually present. Blank samples are prepared and measured at same time or e.g. monthly under the same measurement conditions as the unknown samples. Manufacturers of the counters are often comparing the sensitivity of the counters using Figure of Merit (FOM) by assuming the background counts rate (B) follows Poisson distribution (FOM = E^2/B). This is, however, misleading if B is not following Poisson distribution, which can be caused e.g. by system malfunctioning, luminescence or mathematical manipulation of the data. The same problem arises if B of a single measurement is used in the detection limit calculations. As consequence, background counts distribution should be checked routinely to identify possible problems. Both mean value and the uncertainty are expressed according to a Poisson distribution. Guidance for uncertainty calculation is given as an example in ISO Guide (ISO, 1995) and in European documents EA 1999 and EURACHEM 2000. Some publications (e.g. Forte et. al., Appl. Rad. Isotopes, 2015) state that square root of blank counts is not used as uncertainty since Poisson distribution cannot be assumed for blank counts since they are few and they are not only due to nuclear decay. As consequence, the background and it's uncertainty should be measured using repeat counting.

Hidex Digital Lead Shield (DigPb) is a statistical method to improve uncertainty of the results, yielding this in improved assay sensitivity and lower detection limit. The statistical principoles of method has been originally published by Wallac Ltd – Turku, Finland with titles Digital overlay and 3/2 techniques. After that it's been described as Spectra Fitting Method by two Takiue & Matsui and described in Annuziata's handbook of radioactivity. Hidex has improved this method by adding a sensitivity analysis quantifying the improvement of the uncertainty – i.e. how much the assay sensitivity is improving. The improvement of uncertainty can be expressed as a factor F:

$$\boxed{F = \frac{1}{\frac{a_1^2}{b_1} + \frac{a_2^2}{b_2} + \cdots + \frac{a_n^2}{b_n}}},$$

where $a_1 ... a_n$ and $b_{1...}b_n$ is the distribution of the counts of an active sample and background sample in the region of interest. The method yields in new effective background B_{eff}, which is lower than the measaured background B considering $a_i \neq b_i$.

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The detection of tritium generated by proton exchange membrane electolyte

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Keywords: tritium, scintillator, electrolyte, photomultiplier

Tritium, pure beta nuclide, has a short range. So, there is no danger of external exposure. However, when tritium is absorbed into human body via respiration, and ingestion, it can cause the ionization damage of cell deoxyribonucleic acid (DNA). Tritium exists HTO in liquid state and HT in gaseous state. In the nuclear power plant decommissioning site, the detection of underwater tritium is important problem. Existing the detection method takes a long time. Sampling from detection site, pretreatment, and the detection by liquid scintillation counter (LSC) need a much efforts during 4~5 days. So, the technologies that can detect tritium of decommissing site in real time are needed to developed. In this study, the electrolyte by proton exchange membrane (PEM) cell is used as the method can generate HT gas from water containing HTO [1]. HT gas is moved to detection system, reacts with plastic scintillator, and is detected by the photomultiplier. Because the photomultiplier can only count HT gas, the radioactivity concentrations of liquid and gaseous tritium are measured by LSC and Beta-ionix gaseous tritium monitor. Efficiency of tritium can be calculated by the counts per second and the radioactivity concentration of tritium gas.

Table

Table. The radioactivity concentration of liquid and gaseous tritium

Sample	Tritiated water(LSC, Bq/L)	Gaseous tritium(Beta-ionix, kBq/m^3)
BKG 1	25016 ± 312	126.33 ± 6.03
Tritium 1	183542 ± 644	811 ± 16
BKG 2	7688 ± 84	12.78 ± 0.79
Tritium 2	189563 ± 682	835.5 ± 10.7

Acknowledgments

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Evaluation of the characteristics of ^{14}C behavior at reacter coolant in Korean PWRs

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Keywords: PWR, radioactive carbon dioxide, ^{14}C chemical form, reactor coolant, process sampler

This study focused on evaluating the characteristics of the chemical composition of ^{14}C in terms of organic and inorganic ^{14}C inventory of reactor coolants in three korean PWR reactors of different designs. The purpose was to analyze the characteristics of ^{14}C based on the reliable estimation of the ^{14}C release to the environment at domestic PWR sites. ^{14}C is the most important nuclide in the inventory, because it will affect the environment as one of the main dose contributors in future release scenarios from disposal sites, due to its high mobility in the environment, high biological availability and very long half-life(5730 years). Recent studies have shown that the organic compounds produced in coolant in reducing circumstances and formaldehyde, formic acid, and acetic acid are also produced. However, in oxidation circumstances, ^{14}C is changed to oxidized carbon form and is finally changed to $^{14}CO_2$ and $H_2{}^{14}CO_3$ form.

The measurements of organic and inorganic ^{14}C in various water systems were also performed.

The ^{14}C inventory in the reactor water was found to be about 3.1 GBq/kg in PWR type reactor, less than 10% of which consisted of inorganic form. The measurement of ^{14}C was performed in the gas and water phases. Even though organic ^{14}C compound shows the dominant species during the reactor operation, during the release of ^{14}C from the plant stack, the chemical form of ^{14}C shows different chemical compositions due to operation conditions such as temperature, pH, volume control tank venting, and shut down chemistry.

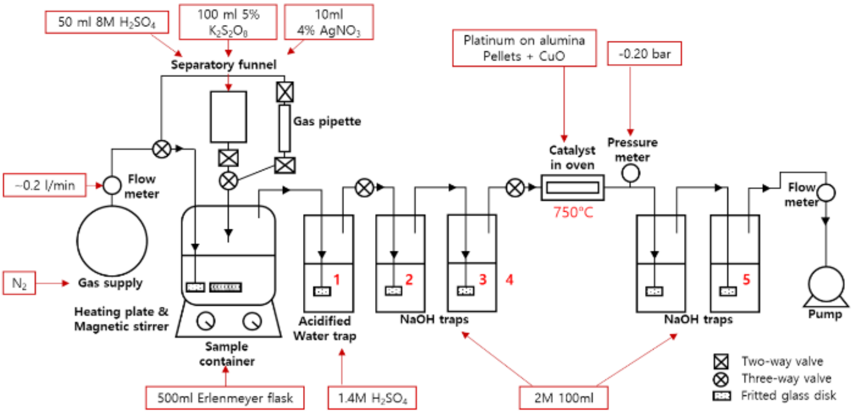

Fig. 1. Schematic diagram of 14C process sampler formeasuring chemical form of ^{14}C.

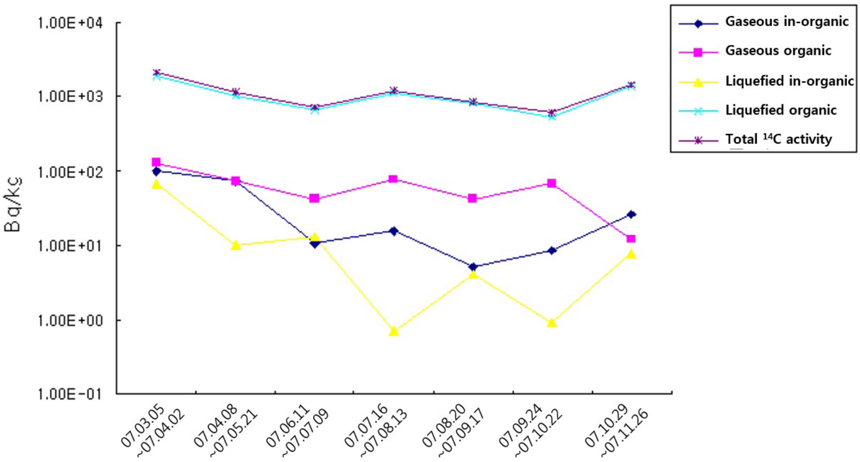

Fig. 2. Trend curves of RCS ^{14}C during normal operation(Kori Unit3)

Acknowledgments

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea(No.20181520302310) Trend curves of RCS 14C during normal operation(Kori Unit3)

Comparison of performances of various scintillation cocktails and vials for ^{3}H activity determination by liquid scintillation counting

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Keywords: LSC, tritium, scintillation cocktail, vials

Determination of low-level tritium (^{3}H) activity concentration in environmental water samples by liquid scintillation counting requires use of a scintillation cocktail mixed with a sample in an appropriate vial. Many of the scintillation cocktails currently in use contain chemical components harmful for biota. Currently, there are several scintillation cocktails that do not contain harmful substances available and it is expected that more will be on the market very soon. From the point of the measurement quality, it is required that the new scintillation cocktails have at least the same performance characteristics as the currently best cocktails used.

We performed several performance tests of different scintillation cocktails for ^{3}H activity concentration measurements by liquid scintillation counter LSC Quantulus 1220: Ultima Gold LLT, ProSafe LT+ (from Al container and from glass bottle) and GoldStar LT2 by Meridian Biotechnologies. Samples of ^{3}H activity concentration in the range 0 to 600 Bq/L were prepared and counted by a standard laboratory procedures (sample:cocktail ratio 8:12 in HDPE vials, tritium window 25-253 channel) by each of the studied cocktail. The following parameters were compared: background count rate, counting efficiency, quenching parameter (SQP), detection limit (DL) and Figure of Merit (FOM). The performances of the UGLLT and GS cocktails were similar (efficiency 23%, SQP 777, DL 1.6 Bq/L, FOM ≈6300) and the best among the studied cocktails.

In addition, several types of vials produced by 3 different producers were also tested by applying similar procedures as above. No significant differences were obtained among the tested vials.

Acknowledgments
We thank Meridian Technologies for providing samples of different scintillation cocktails and some vials.

Studies on the migration of $^{35}SO_4^{2-}$ ions through LSC-TDCR technique in Na_2SO_4/PEG based aqueous biphasic system

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Keywords: aqueous-biphasic, liquid scintillation counting, green chemistry

Aqueous biphasic system (ABS), offers clean and environment friendly extraction and separation methodology compared to classical liquid liquid extraction (LLX) system. For constructing of ABS, solutions of two water soluble polymers or a salt and a polymer/surfactant are mixed together above a critical concentration. Polyethylene glycol solution versus sodium sulphate solution is one of the most popularly used ABS. One of the disadvantages of ABS is that the salt solution and the polymer solution mutually dissolve in each other to some extent and therefore they are called salt-rich/polymer-rich phases. A phase diagram of concentration of PEG versus concentration of Na_2SO_4 solution indicates the working range of the ABS. Several reports on obtaining such phase diagrams are available, which are based on turbidometric titration, cloud point determination and node determination methods [1,2]. However, the phase diagram tells only about the mutual immiscibility of two phases. To get more insight in ABS system, in this paper, attempt has been made to probe the migration of SO_4^{2-} in polymer rich phase in Na_2SO_4/PEG based ABS system. For monitoring the distribution of SO_4^{2} ions, Na_2SO_4 was spiked with $Na_2{}^{35}SO_4^{2-}$ ions, and ^{35}S was monitored by Liquid Scintillation Counter-Triple to Double Coincidence Ratio (LSC-TDCR) (HIDEX 300 SL).

Different strengths of labeled $Na_2{}^{35}SO_4$ were mixed with different strengths PEG-4000, which was shaken for 10 mins. After settling the samples for 10 mins, 0.5 mL of the salt-rich phase was taken in 20 mL glass scintillation vial, mixed thoroughly with 12 mL aqualite cocktail (made HIDEX) and was counted for 500 s in the respective window of ^{35}S ($T_{1/2}$ = 87.37 d; β_{max} = 167.33 keV). Reference samples (without mixing with PEG-4000) were prepared separately corresponding to every experimental sample. The loss of $^{35}SO_4^{2-}$ from the salt rich phase was therefore calculated by comparing the activity of experimental samples and reference sample.

The studies on effect of migration of $^{35}SO_4^{2-}$ ions in extraction/separation of different metal ions is under progress.

Acknowledgments

One of the authors, NN is grateful to University of Calcutta, as well as University Grants Commission.

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Rapid methods for radioestrontium determination in aerosol filters and vegetation in emergency situations using PS resin

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Keywords: plastic scintillation resins, emergency situation, radioestrontium, aerosol filters, vegetation

In emergency situations, such as those caused by nuclear and radiological accidents, terrorist attacks using radiological dispersal devices (RDDs) or "dirty bombs", and improvised nuclear devices (INDs), numerous short- and long-lived radionuclides will be present, requiring rapid identification and quantification. In these situations, ^{89}Sr ($T_{1/2}$=50.56 days) and ^{90}Sr ($T_{1/2}$=28.79 years) or radiostrontium, are one of the most important radionuclides to determine in environmental matrices. In particular, population and animals can inhale radiostrontium in aerosols. In addition animals can incorporate it by ingestion of the vegetation and it can migrate through the food-chain representing also an important risk.

Pure beta emitters, such as ^{89}Sr and ^{90}Sr, require a radiochemical separation prior to measurement. In most cases, extraction chromatographic columns are employed. However, the use of PS resin for strontium, based on plastic scintillator microspheres coated by a selective extractant (DtBuCH18C6), unifies chemical separation and sample measurement preparation in a single step [1]. The main advantages are the reduction in time, effort and reagents required for analysis. Moreover, unlike Liquid Scintillation (LS), no mixed waste is generated. The suitability of the PS resin for emergency situations was also demonstrated with the rapid method developed for radiostrontium determination in milk samples [2].

Following the previous work, this study describes new and rapid methods for radiostrontium determination in aerosol filters and vegetation based on the use of PS resin for strontium separation. The pre-treatment of the samples is performed by a rapid calcination for the elimination of organic matter, and acid dissolution (HNO_3/HCl/H_2O_2/HF) by microwave digestion. After dissolution, alkaline-earth elements are separated by oxalates precipitation, and the isolation of strontium isotopes from other alkaline-earth elements is achieved using PS resin for strontium separation in a 2mL cartridge. After interferents elimination with different elution steps, the cartridge is directly measured in a LS plastic vial by Quantulus 1220.

Different types of aerosol filters (cellulose and glass fiber filters) and vegetation, such as terrestrial vegetation (grass), bushes (rosemary) and aerial vegetation (pine needles) have been analyzed during the study. Good separation yields were obtained (>90%), with limits of detection of 0.03 Bq/filter and 3 Bq/kg for 10 g of fresh vegetation analyzed. The time of analysis is around 8 h and 12 h for aerosol filters and vegetation samples, respectively.

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A rapid method for determination of ^{99}Tc at ultratrace levels in urine samples

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Keywords: Technetium-99, urine sample, rapid determination

Technetium-99 (^{99}Tc) is a challenging radionuclide from presents many problems related to safe disposal. The measurement of ^{99}Tc is of particular interest due to its high mobility, and the fact that it is a beta-emitter with a long half-life ($t_{1/2}$=2.13×10^5 years) with long-term radiological effects[1].

As an isotopes of ^{99}Tc, ^{99m}Tc has been widely applied for medical diagnosis and medical research. It is reported that the ^{99m}Tc has been used in 80% of diagnostic nuclear medicine procedures and almost 30 million examinations are conducted worldwide using this isotope. Because ^{99m}Tc has a short half-life of 6 h and decays to ^{99}Tc, monitoring and safe disposal of ^{99}Tc from human urine is very important, and concern is increasing every day as global use of ^{99m}Tc has increased by more than 4.5×10^{14} Bq per week and is increasing continuously[2]. However, the current methods for the detection of this radionuclide in such mdium are time consuming and can not satisfy for the low level urine sample analysis.

In this work, a method for rapid determination of ^{99}Tc in urine samples was developed. The sample was firstly pre-treated with $K_2S_2O_8$ to decompose the organic matters combined with ^{99}Tc in 0.5 mol/L HNO_3 medium at 100 °C. Then the sample solution was loaded to a TEVA column (2 mL) for ^{99}Tc separation and furification. The target element was finally measured by high resolution inductively coupled plasma mass spectrometry (HR-ICPMS). The developed analytical method was proved to be reliable and can be used to rapid determine low-level ^{99}Tc in urine samples.

Acknowledgments

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Biogenic fraction analyses of liquid fuels by C-14 AMS and LSC at HEKAL

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Keywords: biogenic fraction, liquid fuel, AMS, LSC, radiocarbon

The biocomponent ratio in liquid fuels as well as the usage of renewable resources need to be increased in the fuel consumption of transport sector, as a result of EU directive 2003/30/EC. Based on radiocarbon measurements, it could be relatively simple and fast to measure the weight percentage of the fossil and biological sources by accelerator mass spectrometry (AMS) as recommended in the ASTM D 6866-12 and EN 16640 standards. In this study, a relatively easy and fast sample preparation and measurement method based on AMS measurement was developed at HEKAL using reference samples from the Hungarian MOL Nyrt. oil company and compared with Liquid Scintillation Counting (LSC) technique. Regarding the recent EU regulation for mixing rates of liquid fuels in the transport sector (0,7-2 % biofuel content) and the projected higher rates (2-10 % biofuel content), the method is applicable to determine Fatty Acid Methyl Ester (FAME) and/or Hydrotreated Vegetable Oil (HVO) derived proportions of fuel blends with a 1σ uncertainty better than ±0.3% m/m.

Acknowledgments

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Direct analysis of Pb-210 in water by liquid scintillation counting using a new sulfate precipitation method

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Keywords: lead-210, sulfate precipitation, X-ray fluorescence, triple-to-double coincidence ratio

Lead-210 is one of the most important naturally-occurring radionuclides due to its substantial contribution to skeletal dose in human radiation exposure and its extensive applications (as a chronometer) in the studies of environmental processes. However, the activity concentration of ^{210}Pb in environmental samples is often very low and accurate determination of ^{210}Pb has been quite challenging. The methods by directly measuring the characteristic gamma rays of ^{210}Pb using gamma spectrometry are unfavorable for the poor detection limit and the long counting time (usually >24 hours for each sample). The methods by indirectly determining ^{210}Pb through its progenies (^{210}Bi and ^{210}Po) are also suboptimal because it may take a long time to reach the equilibrium between ^{210}Pb and ^{210}Bi/^{210}Po (~20 days for ^{210}Bi and >1 year for ^{210}Po). In comparison to these methods, direct analysis of ^{210}Pb by liquid scintillation counting (LSC) is preferable since a competent analytical sensitivity for ^{210}Pb could be achievable with low cost in time. In this work, a rapid and sensitive method was developed for the determination of ^{210}Pb in water samples by LSC, which could potentially be modified and used in the analysis of ^{210}Pb in other sample matrices (such as soil, sediment and aerosol, etc.).

To obtain a reliable measurement of ^{210}Pb by LSC, a robust radiochemical procedure with good decontamination of interferences would be required. Sulfate precipitation is a simple and effective method to separate Pb from other elements. In this study, a new sulfate precipitation method to isolate ^{210}Pb was established. Lead along with Sr and Ra (Ba) was first gathered by sulfate precipitation, and the interferences of non-alkaline earth elements (^{210}Bi and ^{210}Po, etc.) were eliminated. The Pb in the sulfate precipitate was then dissolved in strong alkaline solution, while Sr and Ra (Ba) were separated as the sulfate/carbonate precipitate. In addition, X-ray fluorescence (XRF) was applied for rapid determination of the chemical recovery of stable Pb tracer, and triple-to-double coincidence ratio (TDCR) quench correction ultilized for determining the counting efficiency of ^{210}Pb by LSC. The method was validated using 5 litres of tap water samples, and minimum detectable activity (MDA) of ~0.080 Bq was achieved with a counting time of 1 hour. More details about the present method will be presented and discussed.

Determination of ^{135}Cs in environmental samples using chemical separation and ICP-MS/MS

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Keywords: ^{135}Cs/^{137}Cs, AMP-PAN, NH_4Cl, AG 50W×8

Radiocesium is important radioisotopes in the environment, which are mainly originated from the atmospheric nuclear weapons tests, nuclear accidents, discharges from nuclear fuel reprocessing plants and nuclear power plants and other nuclear facilities. Among radiocesium isotopes, ^{134}Cs,^{135}Cs and ^{137}Cs with half-lives of 2.1 years, 2.3×10^6 years and 30.2 years respectively, are more important ones considering the radiation impact and source identification. The ^{135}Cs/ ^{137}Cs isotopic ratio from different sources are significant different because of the different radiation history and condition, therefore can be applied as an unique fingerprint for source identification, nuclear safeguards, forensics and environmental trace studies.

Some methods on the determination of ^{135}Cs and ^{137}Cs in environmental and waste samples have been reported using chemical separation with AMP-PAN, anion and cation exchange and Sr resin columns. However, no method was available for the determination of ultra-low level ^{135}Cs in the large volume seawater and achieved AMP powder samples. In this work, a novel method was developed for separation of cesium from the achieved environmental samples, focusing on the effective recovery of cesium and removal of matrix elements and barium interferences. It was found that cesium strongly adsorbed in AMP can be effectively extracted using NH_4Cl without dissolution of AMP matrix, consequently removed large amount of molybdenum from cesium. After evaporated the NH_4Cl eluate to dryness, the huge amount of ammonium in the sample was removed by heating to 350°C based on the low sublimation temperature (337.6 °C) of NH_4Cl and easily to be decomposed at high temperature. It was found that addition of H_3PO_4 can significantly reduce the loss of cesium in this step. After a further purification of cesium against mainly barium using cation exchange chromatography, ^{135}Cs in the separated samples was measured by ICP-MS/MS with N_2O as reaction gas. Meanwhile ^{137}Cs in the sample was also measured by ICP-MS. Compared with the ^{137}Cs in the original samples measured by gamma spectrometry before chemical separation, the chemical yield of cesium can be calculated. The schematic diagram of the separation procedure is shown in Fig 1, which is much simple and rapid compared to the reported methods. The measured decontamination factors of this procedure for barium and molybdenum are more than 10^4 and 10^6 respectively and the total recovery of cesium is 60%-70%. A detection limit of 10 fg/ml for ^{135}Cs (estimated based on the 3 times of the procedure blanks) was achieved by the developed method. The developed method was validated using IAEA standard reference material IAEA-372.

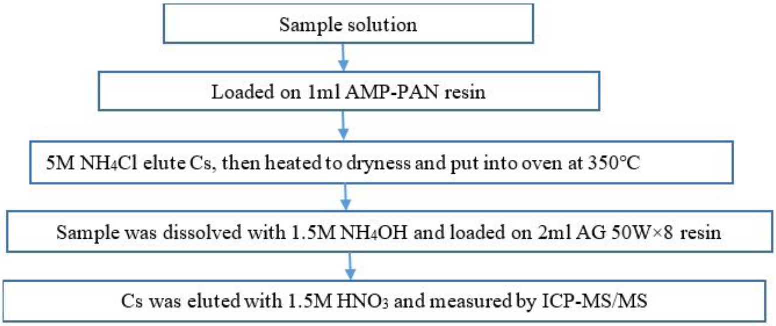

Figure 1. Schematic diagram of analytical procedure for chemical separation of cesium

Mass spectrometry

Radiopurity measurements of selected materials at ultra-low levels for underground experiments using ICPMS

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Keywords: thorium, uranium, copper, aluminum, selenium, TRU Resin, ICPMS

Assessment of construction materials from the radiopurity point of view plays an important role for deep underground physics experiments searching for rare processes and decays, such as SuperNEMO, GERDA, LEGEND, MAJORANA, etc. [1]. Various radionuclides present in the components of the experiment can contribute to the background, natural thorium (^{232}Th) and uranium (^{238}U) being one of the more prolific sources. Determination of thorium and uranium can be conducted by non-destructive or destructive analytical techniques, generally differing in limit of detection, sample size, measurement time, sample pre-treatment steps, and other parameters. Inductively coupled plasma mass spectrometry (ICPMS) is a very sensitive and robust technique which offers relatively quick and inexpensive analysis down to 10^{-15} g per sample of a small size (<0.5 g) [2]. However, due to possible unwanted matrix and isobaric (monoatomic and polyatomic) interferences it usually requires separation of radionuclides of interest from the original sample matrix (which also enables their pre-concentration), resulting in further improvement of detection limits. These steps are especially crucial for radiopurity measurements at the ultra-trace levels. On the other hand, simple digestion and consequent dilution of sample might be sufficient if the concentration of the determined radionuclide is high enough [3].

We shall present results of ICPMS determination of thorium and uranium in selected selenium, aluminum and copper materials. Pure selenium powders of different quality were directly digested and measured after dilution, or ^{232}Th and ^{238}U were first separated and preconcentrated by extraction chromatography using Eichrom TRU Resin. The second approach was also exploited for aluminum powder, solid pellets and target holders used for accelerator mass spectrometry (AMS), as well as for copper samples which comprise high-purity wire, AMS target holders and electrolytic copper in the form of scobs. All measurements were performed by quadrupole or sector field ICPMS in low-resolution mode. Semi-quantitative analysis was also conducted in the case of some selenium and aluminum samples.

Acknowledgments
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Very selective separation and preconcentration technique of ^{210}Pb in drinking water for mass spectrometric determination using crown ether

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Keywords: ICP-MS/MS, lead-210, cloud point extraction, drinking water analysis

Isotopes originating from ^{238}U decay series, such as ^{226}Ra, ^{210}Pb and ^{210}Po, if present in our environment, can contribute significantly to radiation exposure. The potential radiotoxicity of ^{210}Pb results from its short half-life ($t_{1/2}$ = 22,3y), the high energy associated with the ionising particles generated by its progeny, such as ^{210}Po,[1] and chemical similarity to alkaline earth elements. This last feature makes him difficult to isolate in complex environmental matrices. The maximum acceptable concentration for ^{210}Pb in drinking water[2] is 0.2 Bq.L^{-1}, the lowest amongst the naturally occurring radionuclides, which pose a challenge for its rapid and precise determination by radiometric and mass spectrometric approaches. Therefore, the biggest challenge for ^{210}Pb determination is to find an effective approach to selectively extract and preconcentrate this radionuclide. Several selective preconcentration techniques such as co-precipitation and extraction chromatography exist. Recently, cloud point extraction (CPE) has been used for the isolation and enrichment of radionuclides in a variety of matrices. The concept of CPE consists in the aggregation of surfactants containing the analyte of interest based on changes in experimental conditions (e.g. temperature).[3] The efficiency and selectivity of the CPE systems are greatly dependent on the choice of the extracting agent. This presentation will highlights to analytical developments of a CPE methodology using a crown ether[4] for the detection of ultra-traces of ^{210}Pb in environmental matrices by tandem mass spectrometry.[5,6]

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A prototype thermal ionisation cavity (TIC) source with an order of magnitude enhancement in overall efficiency compared to TIMS

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Keywords: thermal ionization mass spectrometry, thermal ionization cavity source, ionization efficiency

We present the design of a prototype thermal ionization cavity (TIC) source mounted on a MAT262 mass analyser together with the first analysis results of micrometre-sized U_3O_8 particles. An order of magnitude enhancement in overall efficiency (ions detected per atoms loaded) compared to conventional thermal ionization mass spectrometry (TIMS) is demonstrated.

In conventional TIMS samples are loaded onto a filament that is subsequently heated during analysis such that the sample evaporates and a fraction of it thermally ionises. As predicted by the Saha-Langmuir equation, this ionization process is increasingly inefficient the higher the ionization energy of the sample element is. For uranium, ionization efficiencies are typically less than 1% unless other ionization enhancing techniques like porous ion emitters are used. Due to the open geometry of the filament, evaporating neutral sample atoms are unredeemably lost to the vacuum chamber of the ion source.

In contrast, in a TIC source the sample is loaded into a cavity that is open towards the extraction lens stack only through a small orifice. The entire cavity is heated and sample evaporation and thermal ionization occurs within it. Thus, evaporating neutral sample atoms on average have several surface contacts with the inner cavity walls – each of which providing a probability for ionization - before escaping the cavity and being lost. Next to other physical processes within the hot cavity this is the predominant effect enhancing the ionization efficiency compared to conventional TIMS.

By studying the physical processes within a hot cavity [1] we have built a prototype TIC source and installed it on a MAT262 TIMS instrument [2]. First analyses of micrometre-size U_3O_8 particles containing 3.7 – 120 pg of uranium in the new TIC source indicate overall efficiencies of 3–19%, limited by the knowledge of the actual uranium amounts in the samples. A direct comparison of the prototype TIC source to conventional TIMS (a TRITON instrument) by analysing ~150 pg of U adsorbed to individual ion-exchange resin beads yielded average overall efficiencies of up to 5% for the TIC source and a factor of 4 – 15 enhancement in overall efficiency compared to the conventional TIMS instrument (depending on the sample loading technique used). Uranium isotope ratios have been measured on these samples as well, yielding results consistent with other measurement techniques.

While there are still some technical challenges that need to be surmounted before routine operation of the new TIC source can be considered, these results demonstrate that the TIC source is competitive when compared to other techniques of analysing uranium oxide particles, such as SIMS, ICP-MS, or LA-ICP-MS.

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Meteoric cosmogenic isotopes production in Atmospheric Aerosols

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Keywords: mass spectrometry, PM10, Mexico City, radiochemistry

The National Laboratory of Mass Spectrometry (LEMA for its acronym in Spanish) is an AMS facility inaugurated in Mexico in 2013 and it is based on a 1 MV High Voltage Europe Engineering isotope separator. Since its foundation, LEMA has made a good number of precise determinations of low concentrations of radioactive isotopes (^{14}C, ^{10}Be, ^{26}Al).

Cosmogenic isotopes as ^{10}Be and ^{26}Al are long lived radionuclides, they are produced in the atmosphere by spallation reactions. Both are produced and deposited in a similar way in aerosols. The study of ^{10}Be and ^{26}Al in atmospheric aerosols has shown to be a potential tool in applications in atmospheric and climate change.

The main objective of this work is the determination of meteoric ^{10}Be and ^{26}Al in small natural samples to be applied in environmental studies.

PM_{10} aerosols sampling was carried out in Mexico City from November 21st to December 3rd in 2012 on quartz filter for 48 hours. There have been significant developments recently due to the establishment of new methods for sample preparation and accurate measurement to detect cosmogenic isotopes in environmental samples. The accelerator mass spectrometry (AMS) is a technique that allows measuring levels of detection around of femtograms (10^{-15}g). The AMS determinations include the chemical isolation of cosmogenic isotopes of ^{10}Be and ^{26}Al from the matrix, the separation involved the use of two different ion exchange resins. The radiochemical procedure to extract, separate and purify ^{10}Be and ^{26}Al has been modified and adapted in our laboratory.

The first results on small samples of particulate matter show that the radiochemical procedure was successfully adapted to ^{10}Be in our laboratory, meanwhile, the concentrations of ^{26}Al were below the limit of detection of the AMS system (10^{-14} on the target). However, the mean value of the production of ^{10}Be in the atmosphere is in accordance with that reported in zones of latitude like Mexico City, around 7.8×10^{8} atoms of ^{10}Be per gram of sample.

A new potential fluoride target matrix for ^{236}U determination in environmental media with accelerator mass spectrometry

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Keywords: ^{236}U, AMS, fluoride matrix

Radionuclide ^{236}U is an alpha emitter with half life $2.342 \cdot 10^7$ years. It originates predominately from neutron capture on nucleus ^{235}U as described by reaction ^{235}U(n, γ)^{236}U, which makes it an ideal tracer for monitoring human nuclear activities, aimed mostly on nuclear safeguards. As concentrations of ^{236}U in environmental media are usually at trace levels, highly sensitive methods of ICP-MS or AMS have to be employed in related analyses, where the latter enables reaching significantly better detection limits. Current techniques of ^{236}U measurement with AMS are based on oxidic target matrices. Nevertheless, fluoride matrices have been studied recently as a suitable alternative, providing higher ion currents and significantly reducing occurring isobaric interferences. Although promising performance in the caesium sputtering source of AMS has been reported, particularly for uranium tetrafluoride [1], application of fluoride matrices in routine analyses still faces several problems regarding the purity of obtained target materials and continuity of the preparation steps with preceding natural sample treatment. For these reasons, a new fluoride target matrix preparation procedure has been developed, more suitable for determination of ^{236}U in natural samples. Applicability of the matrix was demonstrated on series of target samples, which were analysed at AMS laboratory VERA, University of Vienna.

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Americium isotope analysis by Thermal Ionization Mass Spectrometry using the total evaporation method: investigation of method accuracy using a new CETAMA/EC-JRC certified reference material

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Keywords: americium, TIMS, isotope ratio, total evaporation method, isotope dilution

In spent nuclear fuel, americium is one of the major contributors to waste long-term radiotoxicity, once plutonium has been removed. Its isotope and concentration analysis with low uncertainty is of prime interest for nuclear wastes management, environmental monitoring and on-site surveillance of the historical radioactive fallout. ^{241}Am isotope analysis is also important for nuclear forensics since it acts as a clock for plutonium separation: ^{241}Am being a descendant of ^{241}Pu.

Thermal Ionization Mass Spectrometry (TIMS) is a reference technique for actinide isotope measurement with high accuracy (measurement trueness and precision). The total evaporation method (TE method) is the reference technique for isotopic analysis. It consists in evaporating, ionizing and collecting the whole sample deposited onto the TIMS filament. This method overcomes the isotope fractionation which is one of the main uncertainty sources of TIMS measurements, helps decreasing the quantity of analyte and increases the measurement accuracy compared to the traditional method.

However, americium metrological isotope analyses are scarce, due to the lack of Certified Reference Material (CRM). The CRM scarcity has limited the americium measurement uncertainty to about 0.5% and renders the method evaluation with TIMS difficult. Considering the lack of americium CRM and ID-MS spike solution, the Analysis method establishment committee (CETAMA) of the French Atomic Energy Commission (CEA) and the Joint Research Centre of the European Commission (EC-JRC) produced an americium CRM with a high ^{243}Am isotope abundance. An interlaboratory comparison (ILC) was organized by the CETAMA in order to verify the certified values and evaluate the laboratories' performances for americium isotope ratio and concentration measurements.

The goal of this study is to use the ILC assigned values in order to investigate the accuracy of americium isotope measurement using the TE method by TIMS [1].

Different measurements were performed on this CRM in order to determine the isotope ratios and the concentration. 100 ng of Am was deposited onto a filament and analyzed with the TE method. The ^{241}Am, ^{242m}Am and ^{243}Am isotopes were collected with Faraday cup coupled to 10^{12} Ω current amplifier (FC12), Secondary Electron Multiplier (SEM) and Faraday cup coupled to 10^{11} Ω current amplifier (FC11), respectively. The detectors SEM and FC12 increase the sensitivity compared to FC11 for the isotope detection of the lower abundance. Compared to the assigned value, a bias below 0.0001% was observed for the ^{241}Am/^{243}Am isotope ratio. The uncertainty was estimated at 0.11% (k=2). The americium concentration was determined by isotope dilution. The bias was below 0.02% and a concentration uncertainty of 0.81% (k=2) was estimated. This study demonstrated the TIMS performance in order to perform americium concentration and isotope analysis with high accuracy.

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Precise measurement of Te isotopes in environmental samples using Multicollector-Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS)

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Keywords: tellurium isotopes, MC-ICP-MS, soil samples

Tellurium (Te) is an intriguing element in geosciences. It has eight naturally occuring stable isotopes. ^{120}Te is produced by p-process, ^{122}Te, ^{123}Te and ^{124}Te by s-process, ^{128}Teand ^{130}Te by r-process whereas ^{125}Te and ^{126}Te both produced by s and r-processes. All of these isotopes are important from the viewpoint of nucleosynthesis[1,2]. In case of Chernobyl and Fukushima nuclear accidents, a huge amount of radioactive Te (^{127m}Te, ^{129m}Te and ^{132}Te) were released along with other radionuclides such as ^{110m}Ag, ^{125}Sb, ^{131}I, ^{133}I, ^{133}Xe, Cs, etc. into atmosphere[3]. Among the released radioactive Te isotopes, ^{127m}Te, a beta emitter may cause a potential risk to the environment, because it is reported that the contribution of radioactive tellurium to internal radiation dose may not be negligible for radioactive cesium[4]. Precise isotope ratio measurement of Te is a challenging task, beacuse of its very high first ionization potential (9.009eV). MC-ICP-MS is one of the most suitable technique for precise isotope ratio measurement other than thermal ionization mass spectrometry (TIMS)[1,2].

In this present study, a new method has been developed for the measurement of Te isotopes using MC-ICP-MS (Nu Instrument Plasma-3D) using Faraday cups with variable resistor (10^{11} and 10^{12} ohm). ^{120}Te (0.09%) isotope is measured with a 10^{12} ohm resistor whereas rest of Te isotopes were measured using normal Faraday cup collectors. Various concentration of 100, 200, 300, 400 and 500 ng mL^{-1} of Te standards were measured to find the reproducibility of Te isotope ratio. Te concentration of 200 ng mL^{-1} is selected for the isotope analysis based on its reproducibility and 2σ error. The isotope ratio for terrestrial Te standard are 0.002903(7), 0.079645(21), 0.027837(14), 0.222013(19), 0.592252(30), and 1.076154(70) for ^{120}Te/^{128}Te, ^{122}Te/^{128}Te, ^{123}Te/^{128}Te, ^{125}Te/^{128}Te, ^{126}Te/^{128}Te and ^{130}Te/^{128}Te respectively. The isotope ratios were corrected for the mass fractionation by normalizing with ^{124}Te/^{128}Te ratio (0.14853) using the exponential law. The precision of ^{120}Te/^{128}Te, ^{122}Te/^{128}Te, ^{123}Te/^{128}Te, ^{125}Te/^{128}Te, ^{126}Te/^{128}Te and ^{130}Te/^{128}Te isotope ratios were 0.166%, 0.012%, 0.07%, 0.004%, 0.003%, and 0.004% relative standard deviation, respectively. These results were compared with other researchers data using MC-ICP-MS and negative-TIMS. The analytical precision of Te isotope ratios measured by MC-ICP-MS was better than earlier studies[1,2]. The method has been applied to measure Te isotope ratios in certified reference materials (JGB-1, JB-1) supplied by geological survey of Japan (GSJ) and soil.

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An in-situ approach to direct quantification of ^{238}Pu by triple quadrupole Inductively Coupled Plasma-Mass Spectrometry (ICP-QQQ-MS)

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Keywords: triple quadrupole Inductively Coupled-Mass Spectrometry, plutonium, uranium, isobaric interferences, nuclear forensics, isotope dilution mass spectrometry

The triple quadrupole ICP-MS has been an emerging technique for analysis of radio-isotopes due to its capability of discriminating interferences with the use of a reactive gas and additional mass filter (Q2), enhancing selectivity of ions passing through the mass filter. Determination of plutonium and its isotopic composition have been of significant interest in the field of nuclear forensics. Traditional radiometric techniques such as alpha spectrometry and gamma spectrometry have been the common approach for determination of Pu-containing materials and rapid determination of the grade of Pu materials respectively. However, techniques such as alpha spectrometry involves extensive sample preparation, leading to delay in reporting.

The use of mass spectrometric technique faces serious isobaric interferences which is the main bottle neck for most analysis with mass spectrometry. Ubiquitous natural uranium has been the main problem for complete analysis of Pu using ICP-MS and therefore the use of both radiometric and non-radiometric techniques are often required.

Herein, an in-situ determination of ^{238}Pu is reported with the use of mass spectrometric technique, ICP-MS.

In this work, we aim to overcome isobaric issues with the use of a reactive gas, CO_2. However, unlike NH_3, which requires special safety precautions, CO_2 shows poorer selectivity in its reaction with both U and Pu. To overcome this problem, we adopted an 'in-situ' approach with the use of an internal standard ^{242}Pu. Due to the same chemical properties of the isotopes, we are able to optimise the CO_2 flow rate, removing all uranium at m/z 238 and correct for the ^{238}Pu that is present based on conversion % of ^{242}Pu. This work is validated with the use of reference materials with certified amount of ^{238}Pu and ^{242}Pu. Uncertainties involved in this work are calculated based on the guidelines for General Uncertainty Measurement (GUM) workbench.

A new rapid protocol for ^{226}Ra separation and pre-concentration in natural samples for ICP-MS analysis

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Keywords: radium, separation, AnaLig® Ra-01, recognition technology, ICP-MS

Radium-226 (^{226}Ra) is the most abundant radium isotope present in the uranium-238 decay chain. In the last few decades, Ra activities significantly increase in comparison with geochemical background level. Due to its chemical properties favoring its accumulation in human bones increasing the internal radiation dose, ^{226}Ra is considered to be one of the most radiotoxic naturally occurring isotopes. For this reason, it is important to understand the geochemical behavior of Ra. This requires being able to achieve high precision ^{226}Ra measurements in environmental samples.

Before Ra analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), a new rapid protocol for ^{226}Ra separation and preconcentration in natural water samples was developed with a commercially available radium specific resin AnaLig® Ra-01. The distribution coefficients of Ra and other elements were firstly determined over a wide range of acid (HCl and HNO_3) concentrations before defining optimum chromatographic conditions to selectively preconcentrate Ra in natural water sample. Due to this high selectivity, the new developed protocol uses only 50 mg of dry resin and its performance was evaluated using 100 mL of three natural waters with different ionic strengths, spiked with a known quantity of ^{226}Ra. Radium recoveries were obtained around 85 % for drinking water and 70% for seawater so radium was successfully separated and preconcentrated using a single resin. In parallel, a ^{226}Ra sensitivity comparison between different ICP-MS instruments and configurations was performed.

Previous studies use multiple resins while this method use single resin, produces less waste, less operator time, less reagents <25 mL per sample. Despite these encouraging results we believe that the use of 228Ra as an internal tracer to correct for chemistry yield could improve the performances of this new protocol opening up a wide field of applications especially in environmental sciences.

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Determination of ultra-low level ^{236}U in environment samples by ICP-MS/MS with collision/reaction cell technology

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Keywords: ^{236}U, ICP-MS, CO_2 as collision gas, environmental radioanalysis, environmental radioactivity

^{236}U, as a long-lived radionuclide, is mainly originated from anthropogenic nuclear activities in the environment. Based on the unique properties of uranium, it can be used as an ideal tracer for investigation of oceanographic and environmental processes. This requires sensitive determination of ^{236}U in various environmental samples. However, due to the ultra-low concentration of ^{236}U, it is difficult to be determined in the environment, and therefore not well applied in the past decades. In the recent years, high sensitive accelerator mass spectrometry (AMS) has been developed in a few laboratories with a theoretical detection limit down to 10^{-13} for $^{236}U/^{238}U$ atomic ratio and successfully used for the determination of ^{236}U in environmental samples. However, because only a few AMS facilities are available for this work and high cost, it was not widely used. ICP-MS has been widely used for measurement of long-lived radionuclides with advantages of good accessibility, fast measurement, easy operation and low cost. However, it was not well used for determination of ^{236}U in the environmental samples, because of the high challenge to remove the interference of the high tailing from natural occurred ^{235}U and ^{238}U and the hydride $^{235}U^1H$ interferences.

In this work, we present a sensitive measurement method for determination of ultra low level ^{236}U in the environmental samples using ICP-MS with the collision/reaction cell technology. Triple quadrupole ICP-MS (Agilent 8800) was applied to eliminate the tailing interference of ^{235}U and ^{238}Pu. For measurement of ^{236}U, m/z =236 was selected in the first quadrupole, after the reaction cell, target ion (m/z) was selected in the second quadrupole, and then measured in the detector. With this technique, the contribution of tailing of ^{235}U and ^{238}U for ^{236}U measurement can be significantly reduced by a factor of 10^6, down to $<10^{-12}$. Different collision/reaction gases and their mixtures were investigation for eliminating the interference of $^{235}U^1H$ interference. It was observed that helium gas as the collision gas could not break the $^{235}U^1H^+$ molecular ion and not significantly reduce the interference of $^{235}U^1H^+$ ions. However, it was observed that injection of helium gas into the Collison cell, the signal sensitivity of U^+ ion was significantly increased with the flow rate of helium and reach to the highest value at 9.0 ml/min., this might be attributed to the space charge effect. Both O_2 and CO_2 as reaction gas can decompose UH^+ ion, but the reaction of O_2 with UH^+ mainly forms UO_2^+ even at low flow rate, the $^{236}UO_2^+$ ion with a high m/z of 268 is not detectable. While CO_2 reacts with UH^+ in a more gentle way to form U^+ and UO^+, make it easy to be measured. With this approached, the measured UH^+/U^+ ratio can be reduced to less than 1×10^{-7}. With a mixed collision/reaction gas of CO_2/He, the signal sensitivity of UO^+ reaches to 900 Mcps/ppm. With this method, $^{236}U/^{238}U$ ratio down to 10^{-9} can be measured. In combination with chemical separation using extraction chromatography, a detection limit of 3×10^{-14} g or 0.8 nBq for ^{236}U in environmental samples was achieved. This method has been verified by analysis of a certified reference material of soil (IAEA-385), and successfully applied for the determination of $^{236}U/^{238}U$ ratios and ^{236}U concentrations in soil samples collected in north China and Kazakhstan.

Developing and validating a HPIC-SF-ICP-MS method for measuring isotope ratios of Pu, U and lanthanides to characterize spent nuclear fuel and environmental samples

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Keywords: HPIC, SF-ICP-MS, plutonium, uranium, lanthanides, separation, validation, isotope ratios, spent nuclear fuel, burnup, environmental samples

Elemental and isotopic characterization of spent nuclear fuel is of crucial importance in nuclear facilities for various purposes, including the management of spent nuclear fuel [1,2]. The determination of the fuel burnup is essential for the characterization of spent nuclear fuel samples and requires highly sensitive and precise mass spectrometric techniques, such as thermal ionization mass spectrometry (TIMS) or sector-field inductively coupled plasma-mass spectrometry (SF-ICP-MS) to accurately measure the isotopic compositions of plutonium (Pu), uranium (U) and neodymium (Nd). A major issue in mass spectrometry, spectral overlap of isobaric nuclides, can be overcome by separating the analyte elements from one another in advance. Unlike TIMS, SF-ICP-MS can be hyphenated with online separation methods [2], e.g. high performance ion chromatography (HPIC), substantially simplifying the analytical protocol and enhancing the sample throughput. An overview of the whole setup will be presented: a Dionex ICS 5000+ dual quaternary gradient pump HPIC instrument, equipped with Dionex CS5A mixed bed ion exchange chromatography column, and CG5A guard column, was connected to both a UV-Vis detector and an Element 2 sector-field ICP-MS instrument, partly installed inside an alpha glove-box. Separation of Pu, U and lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd & Lu) from the concomitant matrix constituents and from one another was achieved when 1 M nitric acid and 0.1 – 0.3 M oxalic acid were used in gradient elution programs. The resulting chromatograms, as well as the analytical challenges involved in optimizing the HPIC-SF-ICP-MS method and calibration curves for the analytes of interests, will be presented. Additionally, the SF-ICP-MS data acquisition parameters (including the dwell time, mass window, integration window, etc.) and the calculation method selection (between Slope Linear Regression, Peak Area Integration and Point by Point) to achieve isotope ratio measurements with the best obtainable accuracy and precision will be described. The method validation using various environmental samples, certified reference materials and Gd enriched spent nuclear fuel will be discussed. In conclusion, HPIC hyphenated to a SF-ICP-MS unit in an alpha glove-box for the separation and isotope ratio measurements of Pu, U and lanthanide elements will be presented. Isotope ratio measurement uncertainties to be determined at a later stage, will allow evaluation of the performance of the HPIC-SF-ICP-MS method and comparison against that of TIMS.

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Development of methods for determination of uranium and thorium in detector construction materials by accelerator mass spectrometry

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Keywords: AMS, underground experiments, background, ^{238}U, ^{232}Th

One of the biggest challenges for the physics in recent years is to explain fundamental problems such as mass of neutrino, origin and substance of dark matter, etc. To better understand these phenomena, several experiments have been built mostly in underground laboratories to suppress background and to achieve a better sensitivity. In deep underground experiments, contributions from cosmic muons to the detector background is negligible, however other background sources dominates, e.g. radon, and radioactive contamination of shielding and detector materials. The experiments searching for rare processes and decays are very sensitive to background radiation, because it can mimic the studied processes, and therefore activity of shielding and detector materials should be kept usually < 1 μBq kg^{-1} [1].

Dominant sources of radionuclides in construction materials are primordial radionuclides (^{40}K, ^{232}Th and ^{238}U). Uranium and thorium form decay chains and the produced daughters contribute to the background as well. Concentrations of these radionuclides in materials close to active volume of the detector are crucial, and therefore screening of the used materials is necessary before detector constructions.

In recent years, mass spectrometry techniques proved to be superior in analysis of long-lived radionuclides, including ^{232}Th and ^{238}U, when compared to radiometric techniques [1]. Inductively coupled plasma mass spectrometry (ICPMS) and accelerator mass spectrometry (AMS) have been used for determination of uranium and thorium content in various materials. We shall present results on preparation of uranium and thorium targets from different samples in different forms suitable for ion sources used during AMS measurements.

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Mössbauer spectrometry

Mössbauer study of high iron bearing kaolinite

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Keywords: ^{57}Fe-Mössbauer spectroscopy, catalysis, kaolinite

Kaolinite is one of the favourite clay minerals used in industry for various purposes. While the iron content of some kaolinites is detrimental for many applications, in the catalysis of decomposition of organic pollutants in water it is found advantageous. The role of iron in these processes can be connected with its well-known redox catalytic property that may be combined with photoactivity. Nevertheless, catalysis always depends on the local atomic environment of a catalytic center, in this case an iron atom, the chemical environment of which can be readily studied by Mössbauer Spectroscopy.

Kaolinite ($Al_2Si_2O_5(OH)_4$) is an 1:1 type layered structured silicate mineral composed of alternating Al-O and Si-O layers with octahedral (O) and tetrahedral (T) coordinations, respectively. On the basis of ionic size considerations, iron can substitute for Al. Pairs of these TO layers are separated by an interlamellar space of width 7.2 Å that makes this structure capable for intercalation.

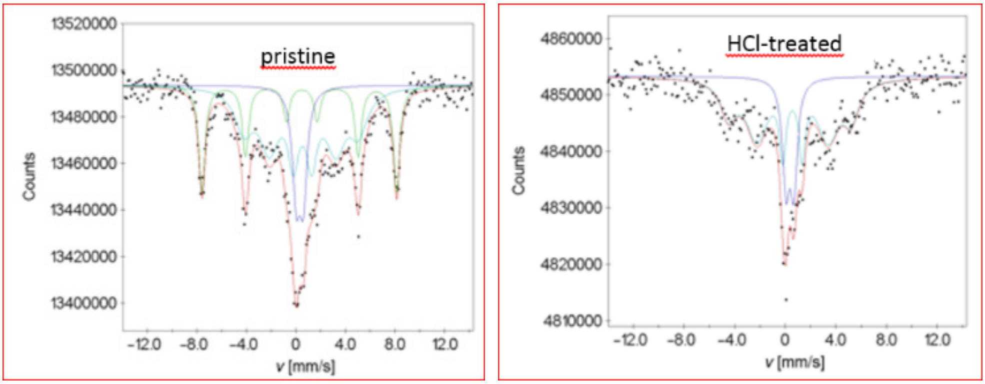

Figure 1. Mössbauer spectra of pristine and HCl-treated kaolinite.

In natural kaolinite, iron is usually found in more than one environment (i.e., substituted at the octahedral site). It may be explained by possible accompanying iron minerals (hematite, goethite, smectite, illite, etc.), but the assignment of all Mössbauer signals to a corresponding chemical environment is often not straightforward.

We have investigated high iron bearing (5 w/w %) natural kaolinite in its pristine form and after treatment with 5M HCl. The purpose of the acidic treatment is to improve the catalytic activity. In the pristine form, three different iron environments could be identified on the basis of the Mössbauer spectra: a paramagnetic doublet could be assigned to iron substituting at the octahedral Al sites, a sextet that unambiguously indicated hematite, and a third magnetically split component that has Mössbauer parameters resembling those of goethite. However, the 5M HCl treatment that dissolved completely hematite, left the third component untouched, indicating its more intimate relation with the kaolinite lattice (Fig. 1). In this work, we discuss the interpretation of the third component based on various models and our experimental findings. The Mössbauer results were complemented with FTIR, Raman, XRD and thermoanalytical data.

^{155}Gd Mössbauer spectroscopic evaluation for imidazole-based Gd(III) coordination compounds

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Keywords: hyperfine interactions, ^{155}Gd Mossbauer spectroscopy, isomer shift

Investigations on the ^{155}Gd Mössbauer isomer shift have been carried out on various Gd(III) metal complexes having a different coordination number (C.N.) and different ratios coordinating oxygen to nitrogen[1-3]. Now We have obtained ^{155}Gd Mössbauer spectra of Gd(III) complexes with tripodal and dipodal imidazole ligands. ^{155}Gd Mössbauer spectra were measured at 12 K using an ^{155}Eu/^{154}SmPd$_3$ source (about 231 MBq) prepared by a neutron irradiation of ^{154}Sm/SmPd$_3$ on a Wissel 1200 Mössbauer system. The values of isomer shift (δ) are referred to the ^{155}Eu/^{154}SmPd$_3$ source at 12 K. The three imidazole-based complexes, [Gd(Me$_3$L)(H$_2$O)$_2$](NO$_3$)$_3$•3H$_2$O (**1**), [Gd(H$_3$L)(NO$_3$)]-(NO$_3$)$_2$•MeOH (**2**) and [Gd(H$_2$L)(NO$_3$)$_2$(MeOH)]NO$_3$•MeOH (**3**), have been investigated by^{155}Gd Mössbauer spectroscopy. Figure 1 shows the three Mossbauer spectra of (**1**), (**2**) and (**3**).

A important tendency for the isomer shift value to decrease with an increase in the C.N, and the number of the nitrogen atom coordinating to Gd(III) has been found for these imidazole Gd(III) coordination compounds. Reduction in isomeric shift due to an increase in nitrogen atoms has been observed from the ^{155}Gd Mössbauer spectra, which has shown that covalency exists in Gd-O and Gd-N bonds. As for the symmetry around the central metal in the complex, the results obtained from optical data have been in good agreement with the results obtained with ^{155}Gd Mössbauer spectroscopy.

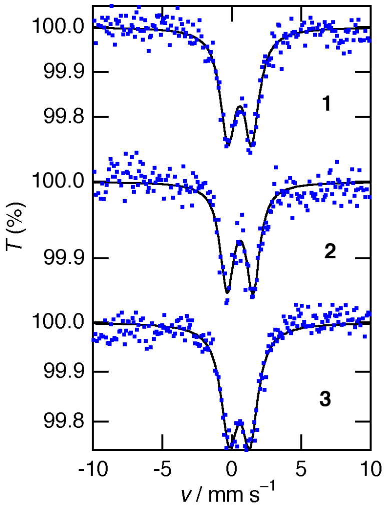

Figure 1. ^{155}Gd Mössbauer spectra at 12 K of **1**–**3**

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Effects of tin doping on the structural, optical and photocatalytic properties of iron oxide nanoparticles

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Keywords: iron oxide nanoparticles, goethite, hematite, Mössbauer spectroscopy, photocatalysts

Due to their low cost, high corrosion resistance, relatively low toxicity and favourable magnetic, optical, catalytic, photocatalytic and adsorption properties, iron oxides are promising materials for different applications [1]. In recent years, a number of papers reported preparation of various iron oxide nanoparticles and nanostructures and their testing as photocatalysts (decomposition of organic pollutants in water) or photoelectrodes (light-induced water splitting). It was shown that performance of iron oxide nanoparticles in these applications considerably depends on their size, shape, crystallinity and doping with different metal cations. Among the various cations considered, tin doping in hematite nanostructures has been shown to be especially efficient in enhancing photoactivity of hematite photoanodes. However, the influence of tin doping on the structural and optical properties of iron oxide nanoparticles and their photocatalytic activity was not sufficiently investigated.

In the present work the influence of tin doping on different properties (unit cell size, crystallite size, particle size and shape, hyperfine magnetic field, thermal properties, optical properties in UV-Vis-NIR spectral range and estimated optical band gap values) of elongated goethite (α-FeOOH) and hematite (α-Fe_2O_3) nanoparticles was investigated. Incorporation of Sn^{4+} cations in the crystal structure of goethite and hematite was confirmed by determination of increased unit cell size by XRPD and reduced hyperfine magnetic field (HMF) by Mössbauer spectroscopy. Also, a strong effect of tin doping on the nanoparticle size and shape was observed by FE-SEM. Diffuse reflectance UV-Vis-NIR spectroscopy showed a significant influence of tin doping on the absorption properties of goethite and hematite nanoparticles in this spectral range. Optical band gaps in prepared samples were estimated using Tauc plots. A significant reduction of direct and indirect optical band gaps in goethite and hematite nanoparticles by tin doping was determined. Photocatalytic performances were examined by decomposition of rhodamine B dye in the presence of iron oxide and H_2O_2 under visible light (420 nm $< \lambda <$ 600 nm) illumination (heterogeneous photo-Fenton reaction) [4,5]. A significant improvement in photocatalytic activity of goethite and hematite nanoparticles by tin doping was observed.

Acknowledgements:

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Mössbauer study of iron-containing alumino silicate glass exhibiting visible-light activated catalytic ability

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Keywords: ^{57}Fe-Mössbauer spectroscopy, visible-light activated catalyst, iron silicate

In order to evaluate the visible-light activated photocatalytic ability of iron-containing aluminosilicate glass, a relationship between visible-light activated catalytic effects and local structure of simulated domestic waste slag with different iron concentrations, abbreviated as R-SNF*x* (*x* = 10, 30 and 50 mass% of Fe_2O_3 in the Na_2O-CaO-SiO_2-Al_2O_3-Fe_2O_3 system) was investigated by ^{57}Fe-Mössbauer spectroscopy, X-ray diffractometry and ultraviolet-visible light absorption spectroscopy. The 80K Mössbauer spectrum of R-SNF30 after heat treatment at 900 °C for 100 min, abbreviated as R-SNF30 HT 900, is tentatively composed of two magnetic sextets with isomer shift and internal magnetic field of 0.51 mm s^{-1} and 45.5 T due to α-Fe_2O_3 nanoparticles; 0.37 mm s^{-1} and 41.5 T due to $CaFe_2O_4$, in addition to a sextet due to regular α-Fe_2O_3 (Fig. 1 middle). As shown in Figure 2, the largest pseudo first-order rate constant (*k*) of $9.75 \bullet 10^{-3}$ min^{-1} was estimated for 20 μmol L^{-1} methylene blue (MB) decomposition test using R-SNF30 HT 900 under the visible-light irradiation. In our previous study, iron-containing aluminosilicate prepared from domestic waste combustion plant in Tokyo showed the smaller *k* of $2.65 \bullet 10^{-3}$ min^{-1} due to the presence of α-Fe_2O_3 NPs [1]. These results indicate that the increase in photo catalytic ability can be expected when minor impurity elements precipitated in separate phases from practical slag. It is concluded that the magnetic components in silica are essential for exhibiting visible-light activated catalytic effect.

Figures

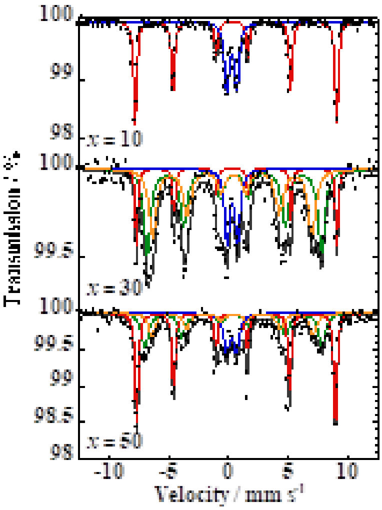

Figure 1. 80K Mössbauer spectra of R-SNF*x* after heat treatment at 900 °C for 100 min.

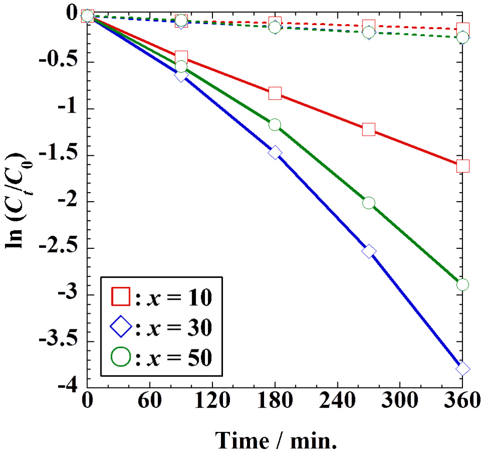

Figure 2. Methylene Blue decomposition test carried out in light (solid lines) and in the dark (dotted lines) using R-SNF*x* heat treated at 900 °C for 100 min.

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Electric explosion of Fe-Co alloy ribbons in water

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Keywords: Fe-Co alloys, HITPERM, Mössbauer spectroscopy

Equiatomic Fe-Co alloys exhibit excellent soft magnetic properties, e.g. high Curie temperature and minimal crystalline anisotropy. Their performance can further be improved by embedding the crystalline grains into an amorphous host forming thereby HITPERM alloys. Nanocrystalline alloys can be formed by fast cooling, e.g. by melt spinning. Addition of Zr and B to the alloy in small amount (< 10 %) promotes the formation of amorphous phase. The optimal crystalline/amorphous structure can be achieved by partial recrystallization of amorphous phase with a controlled heat treatment [1].

Electric explosion of wires (EEW) is a method for melting, vaporization and subsequent fast condensation of the formed nanosized metallic globuli. Typically thin wires are evaporated with a pulse of a high intensity electric current in a quenching liquid [2].

A reasonable question is whether nanoparticles with HITPERM structure can be formed. EEW of thin FeCo ribbons seems as suitable method for the accomplishment. In order to confirm the feasibility of this presumption EEW experiments were performed on $Fe_{45}Co_{45}Zr_7B_3$ amorphous and on $Fe_{50}Co_{50}$ crystalline ribbons in water. The products were characterized by Mössbauer spectroscopy, X-ray diffraction and electron microscopy. Preliminary results confirm the validity of the presumption, coexistence of crystalline and amorphous phases is proved in the formed nanoparticles. For illustration Mössbauer spectra of the amorphous $Fe_{45}Co_{45}Zr_7B_3$ ribbon before the EEW and the formed nanoparticles after the process are shown in Fig. 1.

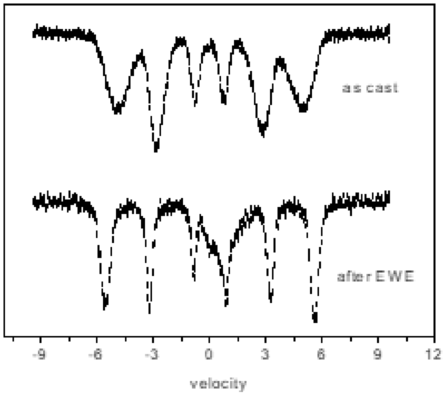

Figure 1. Mössbauer spectra of $Fe_{45}Co_{45}Zr_7B_3$ ribbon before EEW (top) and of the formed nanoparticles after the process (bottom)

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Effects of cutting on surface structure of stainless steels studied by Mössbauer spectrometry

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Keywords: Mössbauer spectrometry, microstructure, steels, hyperfine interactions

Examination of surface microstructure of corrosion resistant steels, which could be used in nuclear industry, is presented employing Mössbauer spectrometry as a principal investigation method. We concentrate on structural and magnetic modifications that are caused by cutting the original material into smaller pieces. Three samples of Fe-Cr-Ni-based steels were investigated: They differ in the contents of minor alloying elements, one of them having increased amount of boron to ensure better resistance against irradiation with neutrons.

After the wire electric discharge cutting, surfaces of the samples were exposed to mechanical grinding, polishing, and eventually to chemical treatment (electrochemical etching) with the aim to remove the disturbed surface layers. We have used transmission Mössbauer spectrometry and Conversion Electron Mössbauer Spectrometry (CEMS) which provide information from the bulk and surface regions of the samples, respectively. Scanning Electron Microscopy was adopted for visualization of surface differences and checking the samples' composition. CEMS spectra show significant differences in the surface properties of the studied steels.

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Cation distribution of $Y_3Fe_{5-x}M_xO_{12}$ (M= Al and Cr, x= 0.25 and 1.0) using Mössbauer spectroscopy

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Keywords: Al- and Cr doped YIG, Cation distribution, and Mössbauer spectroscopy

$Al^{3+}$and Cr^{3+}-substituted garnet $Y_3Fe_{5-x}M_xO_{12}$ (M= Al and Cr, x= 0.5 and 1.0) was fabricated by a sol–gel method. Mössbauer spectra of $Y_3Fe_{5-x}M_xO_{12}$ were taken at various absorber temperatures ranging from 12 to 700 K. As the temperature increased toward T_N a line broadening effect in the Mössbauer spectra was observed. Al ions prefer to occupy tetrahedral-sites. The octahedral coordinated Fe^{3+} ions are linked to six tetrahedral sites containing a statistical distribution of Fe^{3+} and Al^{3+} ions. In this way, seven nonequivalent octahedral sites are expected, corresponding to the following configurations of neighboring tetrahedral ($6Fe^{3+}$, $5Fe^{3+}+1Al^{3+}$,$4Fe^{3+}+2Al^{3+}$, $3Fe^{3+}+3Al^{3+}$, $2Fe^{3+}+4Al^{3+}$, $1Fe^{3+}+5Al^{3+}$ and $6Al^{3+}$). The probability for a Fe^{3+} ion with n nearest-neighbor sites occupied by Fe ions becomes $P(n,y)= {}_6C_n y^n(1-y)^{6-n}$, where y is the iron concentration in tetrahedral site. On the contrary, Cr ions prefer to occupy tetrahedral-sites. So, five nonequivalent tetrahedral sites are expected, corresponding to the following configurations of neighboring octahedral ($4Fe^{3+}$, $3F^{3+}+Cr^{3+}$, $2Fe^{3+}+2Cr^{3+}$, $1Fe^{3+}+ 3Cr^{3+}$, and $4Cr^{3+}$). It results from the distribution (${}_4C_n$) of Fe^{3+} and Cr^{3+} at octahedral site.

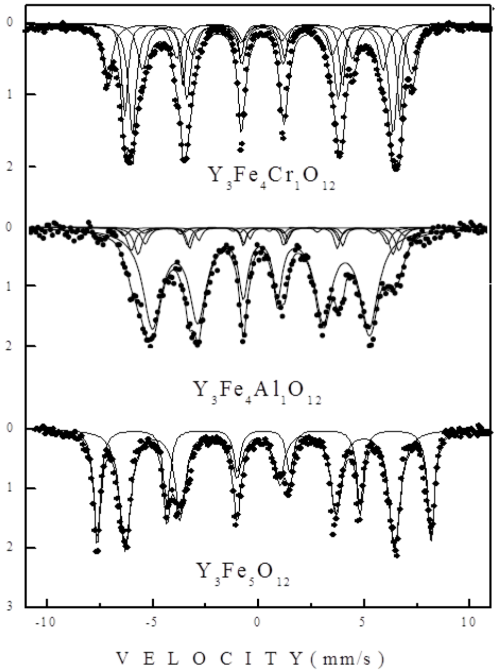

Figure 1. Mössbauer spectra for $Y_3Fe_5M_1O_{12}$ measured at 295 K (M=Al, and Cr)

Acknowledgments
This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korea government (MSIT) (NRF-2018M2A2B3A01071573).

Neutron activation analysis

Application of neutron activation analysis technique on soil samples from farmlands of Yebrage Hawariat, East Gojjam, Ethiopia

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Keywords: NAA, Yebrage, Chemoga, macro/micronutrients

Farmers may not be conscious for their farmland's nutrients, soil organic matter, water and air because they simply concerned only for their labor availability and soil fertility losses. The composition and proportion of these components greatly influence soil physical properties, including texture, structure, and porosity, the fraction of pore space in a soil. The soil of this farmland must be able to supply adequate amount of plant nutrients, in forms which can be absorbed by the crop, within its lifespan. Deficiencies or imbalances in the supply of any of the essential elements can compromise growth, affecting root development, cell division, crop quality, crop yield and resistance to disease and drought. This study was conducted to fill this knowledge gap in order to develop economically vital and environmentally accepted nutrient management strategies for the use of soils in agricultural lands. The objective of this study is to assess the elemental contents and concentration of soil samples collected from farmlands of 'Yebrage' using Neutron Activation Analysis (NAA) techniques regardless of oxidation state, chemical form or physical locations. NAA is used to determine the elemental composition and concentrations present in a soil. The macro/micronutrient and organic matter deficiencies have been verified in agricultural soils through increased use of soil testing and plant analysis. The challenge for agriculture over the coming decades will meet the world's increasing demands for food in a sustainable way. Current issues and future challenges point out that as long as agriculture remains a soil-based industry, major decreases in productivity likely to be attained ensuring that plants do not have adequate and balanced supply of nutrients.

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Health risk assessment to elements and radionuclides in dust samples - Kingdom of Saudi Arabia

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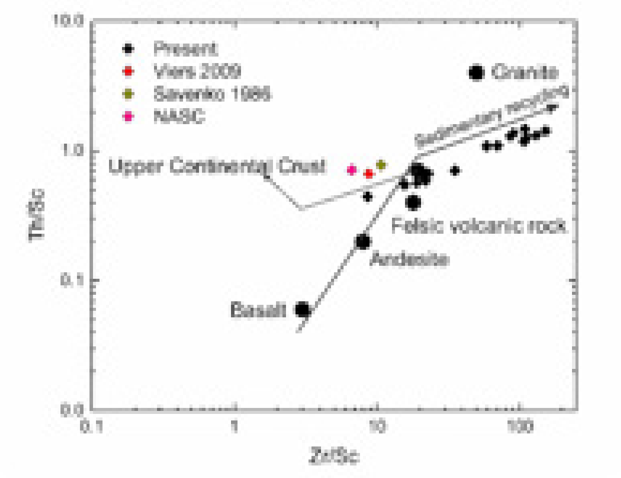
Keywords: major and trace elements, INAA and ICP-MS, equidosimetric evaluation, health risk, dust samples

A total of 15 dust samples were collected from 15 locations in Al Qassim Region – KSA and analysed by means of instrumental neutron activation INAA and inductively coupled plasma mass spectrometer ICP-MS analytical techniques. The concentrations of 42 elements and 11 oxides were measured, the obtained results were compared to those reported by Ganor, Foner, Brenner, Neeman and Lavi [1], , and Rahn, Borys, Shaw and Schutz [2] to a good matching. Enrichment factors were calculated for the obtained elements. The concentrations of the elements were lower than those compared, with an exception for Br, Zr, Hf, As, and Sb. Principal component analysis was carried out for enriched elements to extract three factors; the main contribution was provided by Br and the most enriched elements were As, Br, Zr, Sb, and Hf. The Th/Sc vs Zr/Sc biplot illustrating an increased degree of Zr enrichment, proving a high sedimentary recycling, a characteristic for majority of samples as data confirm by Viers, Dupre and Gaillardet [3], Gromet, Haskin, Korotev and Dymek [4] and . The obtained results show that most probably the source material of these elements is a mixture of UCC and felsic rocks with significant tendency is attributed to granite. For a better understanding, the equidosimetric evaluation, the chemical daily intake of selected elements namely, Cr, Co, Ni, Cu, Zn, and Pb and the associated carcinogenic hazard risk CR and hazard quotient HQ via inhalation were calculated. Further, the annual committed effective dose ACED and related excess lifetime cancer risk ELCR were calculated. The results of risk calculations revealed that there is no significant hazards due to the inhalation of dust from the point of view of toxicity of the selected elements. Contrariwise, considerable values of risk calculations from the inhaled contaminated dust with Th and U were found. Accordingly, the contaminated dust poses an extent health hazard from the radiological point of view and reaffirms a growing conclusion that there is an inverse relationship between the grain size of dust and the radioactivity concentration.



Th/Sc vs Zr/Sc biplot illustrating an increased degree of Zr enrichment

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Standardization of comparator INAA at KRISS for CRM certification and result comparison with k_0-based single comparator INAA and ID-MS methods

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Keywords: neutron activation analysis, CRM, standard-comparator, k_0-standarization

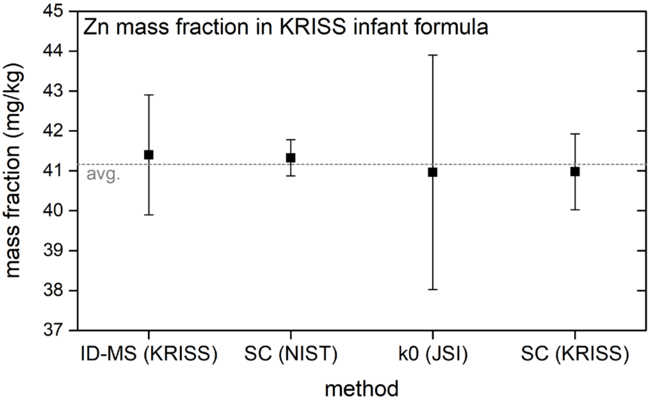
Our research team at Korea Research Institute of Standards and Science (KRISS) has established isotope dilution–mass spectrometry (ID–MS) for the certification of reference materials. This technique is recognized as a primary ratio method for trace elemental analysis and can ensure international equivalence through international comparison. However, the samples might be contaminated during solvation for ID-MS. Chemical pretreatment may sometimes be difficult depending on the substrate and cannot be applied to single isotope nuclides. Instrumental Neutron Activation Analysis (INAA) is a complementary primary ratio (especially for standard-comparator (SC) based) to ID–MS. Developing INAA and establishing standardized procedures are essential to secure measurement capability for National Metrology Institutes.

National Institute of Standards and Technology (NIST), USA and Jožef Stefan Institute (JSI), Slovenia have their own nuclear reactors. These institutions conduct fundamental research related to NAA, steadily utilize NAA for CRM certification, and are currently acquiring the best technology in this field. NIST uses the SC method, whereas JSI uses the k_0-standardization method. The latter does not require standard preparation and is useful in measuring various elements with a specific substrate, such as high-purity materials.

KRISS extends the collaboration with Korea Atomic Energy Research Institute in certifying reference materials using HANARO research reactor facility. HANARO reactor has been recently restarted after a long shutdown. As a part of INAA methodology development, KRISS infant formula CRM (108-02-004) is utilized to analyze the facilities in NIST, JSI, and KRISS by using HANARO reactor and applied comparator method. In this work, most of the elements coincide within the uncertainty as shown in the example of Zn below. Uncertainty in the k_0 method is larger than that in SC method because many parameters (Q_0, f, α, counting geometry, and true-coincidence effects) should be considered.

The technologies and results acquired in this collaboration could be applied to validate INAA in the future, establish the certification process, and improve the certification method at KRISS.

Figure



Comparison of Zn mass fraction in KRISS infant formula CRM

Multielement content of selected Japanese food samples by instrumental neutron activation analysis

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Keywords: multiement analysis, Japanese food samples, instrumental neutron activation analysis

An instrumental neutron activation analysis (INAA) method was applied for the determination of some major, minor and trace elements to 47 different Japanese food samples, namely, 11 fishes, 21 vegetables, 4 sprouts, 3 tofu, 7 mushrooms, and 1 spice. One portion of the sample was irradiated for 1 min at a neutron flux of 4 x 10^{11} cm^{-2} s^{-1} in the Kyoto University Reactor (KUR), Japan. Gamma-ray spectra of the irradiated samples were recorded after 1.5 min decay for 5 min using a Compton suppression Ge detector system. Levels of Br, Ca, Cl, Cu, K, Mg, Mn, Na, Ti, and V were measured using their short-lived nuclides. Then, another portion of the samples was irradiated for 1 h at a neutron flux of 2 x 10^{13} cm^{-2} s^{-1} in KUR. Gamma-ray spectra of these samples were recorded after one-month decay for 30 min using a conventional Ge detector system. Levels of Ag, Ba, Co, Cr, Cs, Fe, Rb, Sb, Sc, Se, and Zn were obtained using their long-lived nuclides. This INAA method was validated using NIST 1566b Oyster Tissue, NIST 1570a Spinach Leaves, NIST 1575 Pine Needles, NIST 1577b Bovine Liver, and NIES No. 27 Typical Japanese Diet certified reference materials. Gamma spectra obtained by Comton suppression Ge detector system and conventional Ge detector system after short irradiation of fish sample are shown in Figure below. It is evident that background levels were considerably reduced using Compton suppression. As for trace elements, Se, Br, Cs, Fe, and Zn were found in fish samples; and Se, Ag, Fe, Zn, and Co were found in oyster samples. Details will be presented.

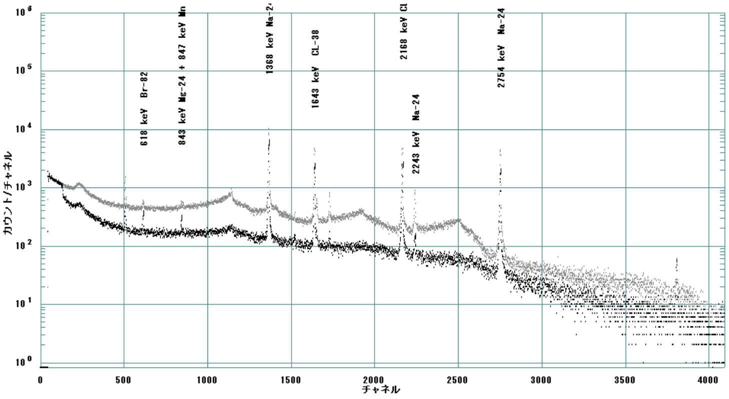

Figure. Gamma spectra of fish sample irradiated for 1 min, cooled for 1.5 min and measured 5 min.
(a: conventional, b: Compton suppression)

Neutron activation analysis of ancient Italian tile samples

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Keywords: Neutron activation analysis, NAA, TRIGA reactor, archaeological provenance

The archaeological examination of ancient artifacts has at its roots the desire to determine an object's provenance, or its place of origin, as well as its location in the chronology of human endeavors, in order to learn more about previous human civilizations. In this work, we used comparative neutron activation analysis (CNAA) to examine Italian roof tile samples dating from the 7th and 6th centuries B.C.E. that were found at archaeological sites near the cities of Tarquinia and Veii. These roof tiles are of interest to Roman archaeologists because they were produced during a time of tile manufacturing development.

A selection of 15 tile samples were provided by Colgate University. NIST SRM 98b Plastic Clay served as the comparator standard and NIST SRM 679 Brick Clay served as the quality control standard. An irradiation fixture was designed to accomodate all of the unknown, comparator, and quality control samples (Fig. 1, left) and was characterized for neutron flux variation. Samples were initially irradiated with a neutron fluence of $6.1\text{x}10^{14}$ neutrons/cm^2 and measured within three hours to determine short lived isotopes. To determine intermediate- and long-lived isotopes the samples were irradiated again with a neutron fluence of $5.8\text{x}10^{17}$ neutrons/cm^2 and measured after eight days and 22 days of decay time.

Elements of interest to our archaeological collaborators include Na, K, Sc, Cr, Mn, Fe, Zn, Rb, Sr, Zr, Sb, Ba, Eu, and Hf. Experimental results show that for these samples, the CNAA technique is capable of the simultaneous measurement of elemental concentrations across more than four orders of magnitude. Typical measurement errors were in the 10-15% range, with a few elements (e.g. Sr and Zr) with error values of 15-25%. Measured elemental concentrations from quality control samples of NIST SRM 679 Brick Clay were evaluated using z-scores; the majority of these samples had $z < 2$, indicating that the measured results are acceptable when compared to the reported reference value and a high degree of accuracy for the measurement.

Scatter plots and statistical methodologies were used to evaluate the measured data. As an example, Fig. 1 (right) shows the relationship between the measured europium and chromium concentrations in the 15 tiles samples. From the plot, it is clear that samples 139-148 form a distinct grouping that excludes samples 149-153; several other scatter plots (e.g. Hf and Rb) show similar groupings, as do results from statistical methodologies. These results demonstrate that clay used to manufacture these tiles originates in at least two distinct locations. Experimental NAA and quality control results will be presented, and insights from the statistical analyses will be discussed.

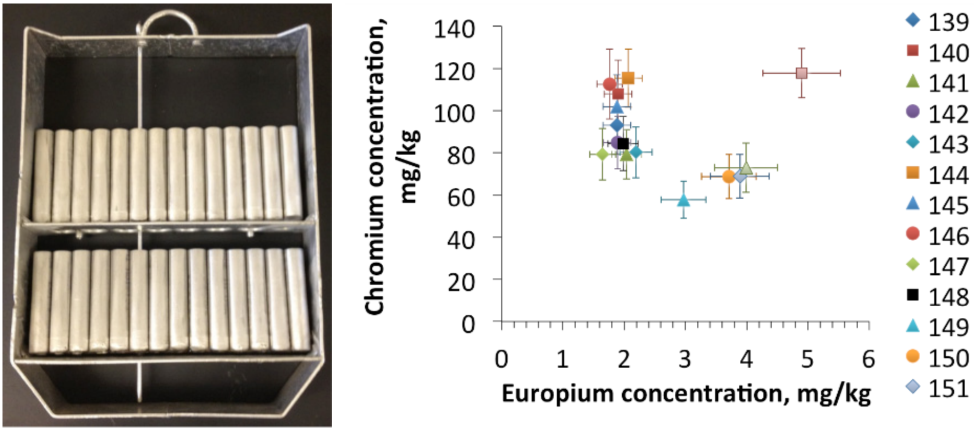

Figure 1. Irradiation fixture for large sample populations (left) and a bivariate scatter plot of measured Cr and Eu in all 15 tiles (right

Homogeneity of carbon nanomaterials studied by INAA

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Keywords: homogeneity, INAA, carbon nanomaterials

The carbon-based nanomaterials (nanocarbons) are attractive in various fields of science and technology due to their exceptional mechanical, electrical, thermal, and optical properties. They may contain usually unintentional admixtures of various elements at variable quantities, which could significantly influence electrochemical response and other properties of the nanomaterials. The key role of metallic impurities in graphene-based electrocatalysts has been recently demonstrated together with the proof that ultrapure graphene is a poor electrocatalyst [1]. Thus, it appears evident that elemental characterization of nanocarbons is of considerable importance. High chemical resistance of nanocarbons, however, often makes elemental characterization a challenging task especially if total sample decomposition is required. Nanocarbons are often expensive and available in limited quantities. Therefore, researchers tend to use small test portion masses for development and validation of analytical methods. This is an appropriate approach only if the elements of interest are homogeneously distributed in the test portion masses.

The aplicability of instrumental neutron activation analysis (INAA) for determination of elemental admixtures in nanocarbons was recently demonstrated [2]. Therefore, INAA was selected for testing of homogeneity distribution of elemental admixtures in four materials. These were carbon black, expandable graphite, single walled carbon nanotubes, and research sample of alkali lignin. The test portion masses were 10 mg and 30 mg, which were analyzed usually in five replicates of each mass. The quality control of analysis was performed by assay of various reference materials, which included NIST SRM 2483, NIST SRM 1547, NIST SRM 1633b, and NRC CRM SWCNT-1 together with the tested nanocarbons.

Altogether 25 elements were determined in all tested replicates of at least one of the nanocarbons studied. Homogeneity of the materials tested was assessed from a comparison of the combined uncertainty of a single determination with the standard deviation calculated typically from five replicate analyses.

Acknowledgments

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Detection methodology of position-dependent neutron energy using a threshhold detector array

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Keywords: activation foil, threshold detector, neutron flux, neutron energy, spatial distribution

This study aimed to verify whether neutron energy and flux could be simultaneously measured by a new technique that used array-type threshold detectors. Neutrons generated by HANARO research reactor were measured using array-type threshold detectors fabricated by superimposing four array-type activation foils composed of Au, Ag, In, and Cu. The measurement results were compared to the simulation results obtained using MCNPX and FISPACT codes. The study results showed that the position-dependent neutron energy in irradiation rabbit.

Analysis of Aristolochia Longa L. medicinal plant from Algeria

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Keywords: Aristolochia Longa, INAA, compounds, public health, Algeria

The rhizomes of Aristolochia Longa (berztam), traditional Algerian medicinal plant collected from Taourirt Aden Kabylia village situated in Northern Algeria were analyzed by instrumental neutron activation analysis. The mass fractions of Cr (15.22 ± 3.5 µg/g) **,** Na **(**269.98 ± 25.01 µg/g), La (0.478 ± 0.041 µg/g), K **(**1.33 ± 0.23 µg/g), Br (1.2 ± 0.19 µg/g) , As (0.697 ± 0.038) and Sb (66.09 ± 11.24 µg/g), were determined. The essential elements found in Aristolochia Longa may confer some of their beneficial properties, but the potential toxicity due to the Aristolochia Acids content may require investigation by CG/MS.

Table I. Quality Control assessment results (µg/g) for the AIEA - certified reference material Samples

Element	**IAEA-V10**		**IAEA-SL**	
	Measured	**Reported**	**Measured**	**Reported**
K*	24.65 ± 2.96	21 ± 2		
Cr	6.42 ± 0.798	6.5 ± 0.75	94.92 ± 8.54	104 ± 9
Na*	0.692 ± 0.064	0.5 ± 0.3		
Br	10.82 ± 1.73	8 ± 2	6.82 ± 1.73	9.79 ± 1.58
Sb			1.31 ± 0.12	1.4 ± 0.23

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Bulk analysis of meteorites using INAA at FRM II

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Keywords: INAA, k0-method, meteorite, micrometeorite

In March 2017, the 49th German meteorite was found lying on top of a rock pile on the side of a potato field, near the city of Cloppenburg, Lower Saxony, Germany [1,2]. With two other meteorites (Oldenburg (fall in 1930), Benthullen (find in 1948 or 1951)) from the same region and meteorites from other countries, we started a program to analyze extraterrestrial samples in 2017. We have analyzed in total three chondrites, three achondrites of the HED group (Howardite-Eucrite-Diogenite) (Dhofar 1675, NWA 2690, NWA 2698), a lunar and a Martian meteorite (NWA 7986, NWA 4925), two iron meteorites (Gibeon, yet unnamed new find from Libya/Chad in 2019) and six potential micrometeorites. The bigger samples (10-20 mg) were normally irradiated twice: for 3-5 min and for a long time up to 1 h in the rabbit position. The much smaller micrometeorites (9-38 µg) were irradiated for 24 h in the high-flux capsule irradiation position (Φ_{th}>1E14 $cm^{-2}s^{-1}$). We used the k0-method for the analysis [3].

With the high and pure thermal neutron flux at the FRM II, up to 45 elements could be determined in most samples [3]. According to the element compositions, the meteorites could be classified or earler classifications could be confirmed. Although, the sample weights of the micrometeorites are very small and manipulating them was challenging, we could determine up to 16 elements. All of them show a rather high Fe concentration, i.e. 55-70 weight-%. However, for Ni and Ir, we can only give a detection limit of about 0.4% and 2 ng/g, respectively. Their potential origin are under discussion.

Acknowledgments

We thank A. Muszynski and M. Szyszko (Poznan, PL), A. Bischoff (Uni. Münster), D. Heinlein, J. Feige (TU Berlin) and A. Gärtner (Senckenberg Dresden) for providing and preparation of samples and the TUM-Kolleg program for financial supports.

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The High-Brilliance Neutron Source (HBS) Project - Perspectives for Neutron Activation Analysis

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Prompt and Delayed Gamma Neutron Activation Analysis (PGNAA, NAA) is a powerful non-destructive analytical technique to determine the elemental or isotopic composition of samples of various origins (geological, environmental, archaeological, cosmological, biological and industrial). The use of this method is hampered by the availability of powerful neutron sources. The Juelich Centre for Neutron Science is developing a compact accelerator driven pulsed neutron source to offer access to science and industry to neutrons as medium-flux, but high-brilliance neutron facility. The High-Brilliance Neutron Source (HBS) will consist of a high-current proton accelerator, a compact neutron production and moderation unit, optimized systems for transport of thermal and cold neutrons and fast neutrons collimation. The project will allow the construction of a scalable pulsed neutron sources ranging from a university-based neutron laboratory to a full user facility with open access and service. We will describe the current status of the project and the perspectives for neutron activation analysis at universities and research institutes.

Measurement of neutron spectrum parameters for NAA irradiation holes in the Jordan Research and Training Reactor

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Keywords: JRTR, Neutron activation analysis, Thermal neutron flux, α and *f* parameters

The Jordan Research and Training Reactor(JRTR) was designed, constructed, and commissioned by Korea Atomic Energy Research Institute and DAEWOO consortium. There are three irradiation holes, named as NAA #1, #2 and #3, for neutron activation analysis interfaced with pneumatic transfer system. In order to perform instrumental neutron activation analysis with an absolute method or with k_0 method, neutron spectrum parameters such as thermal neutron flux, α and *f* for the irradiation holes should be measured. Cd-ratio method was applied for the determination of the aforementioned parameters. 0.1%

Au-Al wires and Zr foils were irradiated with and without Cd-cover for 2 minutes at NAA #1 and for 5 minutes at NAA#2 and NAA#3. The irradiated monitors were measured and the Cd ratios were determined for Au-198, Zr-95, and Zr-97 nuclides. Then, the parameters were calculated at NAA#1, #2 and #3 irradiation holes. The results are summarized in Table 1.

Table 1. Neutron spectrum parameters determined at NAA #1, #2, and #3 in JRTR

Irradiation Hole	**Thermal neutron flux ($cm^{-2} \cdot s^{-1}$)**	**α**	***f***
NAA #1	3.05E+13	0.13	67
NAA #2	7.59E+12	0.18	770
NAA #3	7.46E+12	0.16	917

Active biomonitoring of atmospheric pollution in the Western Cape Province (South Africa) using INAA and ICP-MS

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Keywords: active biomonitoring, trace elements, mosses, lichens, instrumental neutron activation analysis, inductively coupled plasma mass-spectrometry

In this study, active biomonitoring was used to assess elemental content of atmospheric pollution due to urbanisation, industrialisation and vehicle emissions, in selected areas of the Western Cape, South Africa using the moss- and lichen-bags. Two moss species (*Pterogonium gracile* and *Leptodon smithii*) as well as two lichen species (*Usnea subfloridana* and *Parmotrema perlatum*) were exposed for 3-months at three sites. A total of 47 elements were identified and their concentrations were determined by epithermal instrumental neutron activation analysis (INAA) and Inductively Coupled Plasma Mass-Spectrometry (ICP-MS). Our results show that some of the identified elements are indicative of their expected pollution sources. For example Fe, Al, Hg, As, Cd, Fe, Pb, Ba and Na are fingerprints from a combination of emission sources like oil rig facility, steel plant, heavy mineral plant, galvanising plant and the oil storage facility as well as sea-salt emissions. Relative accumulation factor (RAF) values were calculated for all the identified elements. In some cases, leaching of elements from the moss and/or lichen tissue during the exposure time was observed, leading to negative RAF values. This highlights the ability of these biomonitors to reveal their saturation effect for some of the identified elements.

Activation analyses at MLZ, Garching, Germany

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Keywords: prompt gamma activation analysis, neutron activation analysis, high-flux neutron beam

The research reactor in Garching, operated by the Technical University Munich, Research Neutron Source Heinz Maier-Leibnitz (FRM II), offers unique possibilities for nuclear analytical chemistry to the users of the Heinz Maier Leibnitz Zentrum (MLZ). Prompt Gamma Activation Analysis (PGAA) is performed in the strongest cold-neutron beam of the world ($6 \cdot 10^{10}$ cm^{-2} s^{-1}). The high flux makes possible the analysis of samples with masses of less than a milligram, or even activation in beam. This combination of PGAA with in-beam Neutron Activation Analysis (NAA) adds a long series of heavy elements which can be determined as trace elements, while PGAA in its classical form is most suitable for the determination of light elements. The method, in-beam activation analysis has been offered and successfully used by national and international researchers in the frame of the proposal system of MLZ.

NAA performed using the irradiation facilities of the FRM II reactor has been used for routine analytical applications. Recently, NAA as a highly sensitive method has been added to the analytical arsenal of the PGAA group and will shortly be introduced in the proposal system thus making it available to the scientific community, too. The irradiation channels of FRM II are highly thermalized enabling the analysis of elements with significant resonance integrals more reliable and accurate. The NAA facilities make possible the high-accuracy determination of k_0 values with very little contribution from epithermal or fast neutron activation.

The talk presents the characteristics of the two facilities, the typical applications of the methods as performed at MLZ, and also the future plans.

Upgrade of a TRIGA carousel neutron irradiation facility

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Keywords: TRIGA, irradiation facilities, neutron activation analysis, automation, pneumatic transfer system

The Jožef Stefan Institute's (JSI) TRIGA Mark II reactor has three irradiation devices available for neutron irradiations: the fast pneumatic transfer system (FPTS), the TRIGA standard pneumatic transfer system (PTS) and the pneumatic transfer system of carousel irradiation facility (CIS). The PTS was upgraded and automated for operation three years ago [1]. FPTS and PTS irradiation locations are in-core, among the fuel elements, while CIS is placed within the graphite reflector that surrounds the core. Consequently, the neutron flux there is much more thermalized and therefore the CIS is preferred as an irradiation location for neutron activation analysis (NAA) in the reactor. The CIS is presently equipped only with a simple pneumatic transfer system for extracting irradiated samples. The system is sufficient for long irradiations, but for short irradiations it is not user-friendly, as the procedures have to be done manually by the reactor staff, with applying a stopwatch from the reactor platform.

Therefore, it was decided to bring the old system up to date. The main goal of upgrading is to improve overall quality of irradiations with the CIS and the focus is on making the new system more user-friendly, with increased safety, improved timing precision, logged traceability of system events and automated data processing. The CIS is now connected with the recently renewed PTS, thus allowing inserting samples also directly from the remotely located NAA laboratory, irradiating them in the carrousel position and returning them back to the NAA laboratory. The newly added sensors help improve timing precision, prevent operator mistakes and allow for digital records of all the samples irradiated in CIS. By introducing remote operation, also radiation dose on the personnel is reduced. An important feature of the new assembly is the fact that most of the existing tubing remains intact. Therefore, the upgraded assembly is generally applicable to any TRIGA-type pneumatic transfer system. Further details of the upgraded CIS are given and discussed throughout the presentation.

Acknowledgments

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Neutron activation analysis of mercury in compact fluorescent lamps

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Keywords: analytical protocol, INAA, European legislation, sample preparation, analytical bias, quality control

Neutron activation analysis (NAA) is a powerful tool for the analysis of the elemental composition of a sample, especially under difficult circumstances. This is especially relevant for sample materials that require special or laborious sample preparation. In the present study [1], we attempted the loss-free analysis of mercury in compact fluorescent lamps (CFL) by instrumental neutron activation analysis. By applying instrumental neutron absorption analysis (INAAA) [2], we revealed the presence of neutron absorbing boron in the lamp's glass matrix. By radiochemical NAA (RNAA), we quantified the losses of mercury via the gas phase to check for the accuracy of the EU analytical protocol that is in force to check for compliance with the upper limit of the mercury content of the CFL. We found that about 2% of the mercury are present in the gas phase at 20 °C and that the European anlytical protocol introduces an avoidable analytical bias.

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Maker culture in the NAA lab

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Keywords: neutron activation analysis, 3D printing, automation, open-source, maker

The Elemental Analysis Laboratory at Texas A&M University is a self-supporting service center that has been performing NAA since the 1950s. The automated systems that we use for performing FNAA and INAA, which are more than twenty-five years old, contain aging hardware and software components. Looming lifecycle limits and the financial risks associated with system failures and extended downtime are real and prominent concerns. Significant replacement costs for critical technology are an obstacle for a budget-conscious laboratory.

However, the rapid growth of "maker culture" – the social movement that applies a DIY ethos to creating new technologies or modifying existing technologies – has made it possible to fabricate customized laboratory tools (hardware and software) at a fraction of the traditional cost. Maker culture encourages open-source information, skill sharing and a collaborative approach to problem solving, which are all made possible through the web. Inexpensive single-board computers, digital fabrication techniques, and cloud computing are common features. As a result, we have begun modernizing our legacy NAA systems using maker-inspired ideas and low-cost materials and tools that the growth of maker culture has made readily available. Specifically, our lab is working to implement cloud-based solutions for migration to a digital workflow, 3D printing of irradiation capsules, and open-source embedded computers for data acquisition and process automation.

Acknowledgments

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Characterization of soil, sediment, and wastewater samples from hydraulic fracturing processes using the CNAA method

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Keywords: NAA, CNAA, hydraulic fracturing samples, RSEC

Regulatory monitoring of oil and gas (O&G) development requires the accurate multi-elemental analysis of soil, sediment, and wastewater samples on a regular basis. Typically, the qualitative and quantitative characterization of wellbore samples is managed through conventional methods using inductively coupled plasma optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS). The main objective of this study was to apply a non-conventional, neutron activation analysis (NAA), method for the multi-elemental analysis of solid and liquid hydraulic fracturing samples with an accuracy of ppm (mg/g or mg/l). To evaluate the suitability of the NAA method for this application by comparing its results with the other conventional methodology results.

For this research, fifteen solid (soil and sediment) and seven liquid (wastewater) fracking samples, collected from the Pennsylvanian wells, were provided by Civil and Environmental Engineering Department at the Pennsylvania State University. The samples were analyzed at the Radiation Science and Engineering Center (RSEC) using the comparative neutron analysis (CNAA) method. Due to the similarity in elemental content, the National Institute of Standards and Technology (NIST)-certified Montana II Soil and Buffalo River Sediment certified standard reference materials (SRMs) were used as the comparators. The fracking samples and SRMs were properly encapsulated, irradiated in the Dry Tube 1 of the Penn State Breazeale Reactor (PSBR), and counted using at the RSEC Radionuclear Applications Laboratory with an HPGe detector. Then, all collected gamma spectra were analyzed for the concentration of short-, intermediate-, and long-lived isotopes of Cl, Mn, Eu, K, Na, As, La, Ca, Ba, Rb, Pa (thorium activation product), Cr, Fe, Hg, Sr, Sc, Se, Zn, and Cs elements. To check and verify the experimentally obtained trace element concentration values, a quality control analysis was performed using both SRM certificates, issued by the NIST. As a result, the magnitude of the error in each element was determined, except for cesium and chromium; therefore, their concentrations values were declared as non-certified.

Another accuracy check on the elemental concentrations of three oil and gas wastewater samples conducted by comparison of the CNAA measured values with the most probable values (MPV) determined via an inter-laboratory study, which involved 15 different laboratories from the US, Canada, and Germany. The MPVs determined through the nonparametric statistical analysis on the all collected concentration values, which were determined using different equipment and techniques. The difference in CNAA and MPV results is indicated in percentages, which vary between 0.1% and 56.6%. The relatively large error for some elements can be caused by multiple factors, such as a high concentration of hydride even after dehydration and possible fractionation during the dehydration process.

NAA results for soil and liquid samples from hydraulic fracturing processes will be presented and comparative accuracy of some of the elemental concentrations will be discussed.

Nuclear forensics

Gamma spectrometric determination of plutonium age using intrinsic efficiency calibration

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Keywords: plutonium, age-dating, gamma spectrometry, nuclear forensics

A method for plutonium age-dating is presented in this paper. It relies on measuring the ^{241}Am/^{241}Pu activity ratio by high resolution gamma spectrometry using intrinsic efficiency calibration and it is similar to the methods implemented in the MGA [1] and PC/FRAM [2] software. This method was applied to determine the age of six plutonium samples of various isotopic compositions and various origins. The samples consisted of reference materials as well as “unknown” historical materials available in Romania and Ukraine. The results were compared to those obtained by using MGA and PC/FRAM, as well as to the certificate data (where available). It was shown that the new method was also suitable for determining the age of a sample which was mainly composed of ^{241}Pu. For this specific case, MGA was not applicable. The described method was also implemented as a user-defined parameter set within PC/FRAM. Therefore, it was possible to apply PC/FRAM and succesfully calculate the age of the sample enriched in ^{241}Pu.

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Preparation and calibration of a Pa-231 reference material

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Keywords: isotope dilution mass spectrometry, nuclear forensics, ^{231}Pa, ^{233}Pa, radiochronometry, reference material

A ^{231}Pa reference material has been prepared and characterized for the amount of ^{231}Pa (Fig. 1). This reference material is primarily intended for calibration of ^{233}Pa tracers produced for ^{231}Pa - ^{235}U model age measurements associated with nuclear forensic and nuclear safeguards. Primary measurements for characterization were made by isotope dilution mass spectrometry of a ^{231}Pa stock solution using a ^{233}Pa spike. The spike was calibrated by allowing multiple aliquots of the ^{233}Pa spike solution to decay to ^{233}U and then measuring the ingrown ^{233}U by isotope dilution mass spectrometry using a certified U assay and isotopic standard as a spike (CRM 112-A). The molality of the ^{233}Pa spike and the ^{231}Pa master solution were independently verified by massic activity measurements performed at multiple National Metrology Institutes. A total of 112 units of the reference material were prepared with each unit being comprised of a 30 mL FEP Teflon bottle containing a known amount of ^{231}Pa (~1.46 10^{-10} mol) in an acid solution of 2 mol L^{-1} HNO$_3$ and 0.1 mol L^{-1} HF. This new reference material will simplify calibration of the ^{233}Pa isotope dilution spikes, provide metrological traceability, and potentially reduce the overall measurement uncertainty of ^{231}Pa – ^{235}U model ages determined for uranium bearing materials.

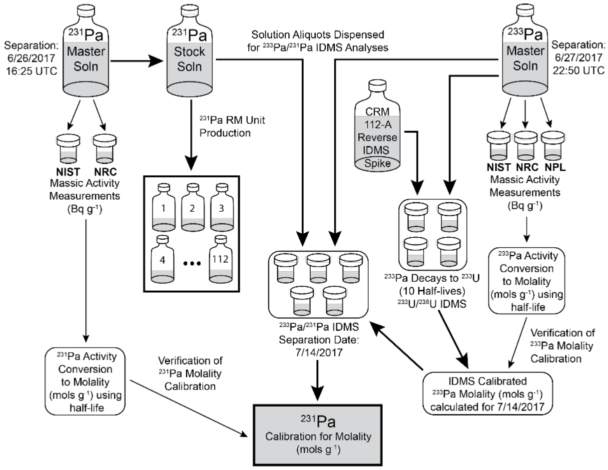

Fig. 1. Schematic of the ^{231}Pa reference material production and characterization process. The heavier arrows indicate material transfer and analyses performed for the primary calibration of the ^{231}Pa material. Lighter arrows indicate material transfer and analyses for verification measurements.

Implementation of high precision isotope ratio measurement of uranium ore concentrate at Canadian nuclear laboratories

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Keywords: nuclear forensics, uranium ore concentrate, high precision isotopes, TIMS

One of the many technical practices of Nuclear forensics (NF) involves the characterization of nuclear and other radioactive materials using a variety of analytical techniques to assist the overall process towards determining the origin and history of material in the context of investigations related to nuclear security events involving radioactive and nuclear materials. Mass spectrometry is commonly used in NF for isotope ratio measurements as a potentially distinguishing property. A National Nuclear Forensics Library (NNFL) is a tool that catalogues and integrates various types of information, including chemical and physical material signatures, about known materials that can then be referenced to support provenance assessment activities during an investigation of unknown material(s) under investigation. Canadian Nuclear Laboratories implemented a procedure [1] for high precision U, Pb and Sr isotope ratio measurements of uranium ore concentrate (UOC) at the request of the Canadian Nuclear Safety Commission, in support of Canada's NNFL Development Program and under the Nuclear Material Signature and Provenance Assessment Capability Development Project. The work involved modifications to an accredited thermal ionization mass spectrometry (TIMS) procedure for U isotope ratio measurement to enable integration of the sample preparation for all three elements. The impact of changing the digestion acids and separation technique will be discussed in this presentation, along with the required modifications to the TIMS operating parameters. Particular attention to detector calibration and other sources of uncertainty will be explored. Data will be presented for ^{235}U/^{238}U and ^{234}U/^{238}U ratios measured in a variety of UOC materials and how careful control of uncertainties may generate characterization data that could be distinguishing.

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Non-destructive analysis of pure-beta emitters: Applications in nuclear forensics

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Keywords: pure-beta emitters, non-destructive technique, nuclear forensics

This paper describes the development of a non-destructive method for the characterization of pure beta minus radioactive sources. The main challenge in analyzing pure-beta emitters consists in the fact that they do not emit any characteristic gamma lines (Fig. 1), having a continuous spectrum. Moreover, beta spectrometric methods which exist nowadays, require radiochemical sample preparation which is a destructive approach. This might be challenging in the case of very strong radioactive sources found outside the regulatory control.

The method described in this paper consists in calibrating the experimental set-up which is based on thick plastic scintillator and photomultiplier tube, by using reference sample, and afterwards performing the same measurements on the unknown pure-beta minus emitter samples.

The lesson-learned during the successful analysis (within criminal investigation) of a real pure-beta emitter sample found outside the regulatory control in Romania will be presented as an example of an application of the developed method.

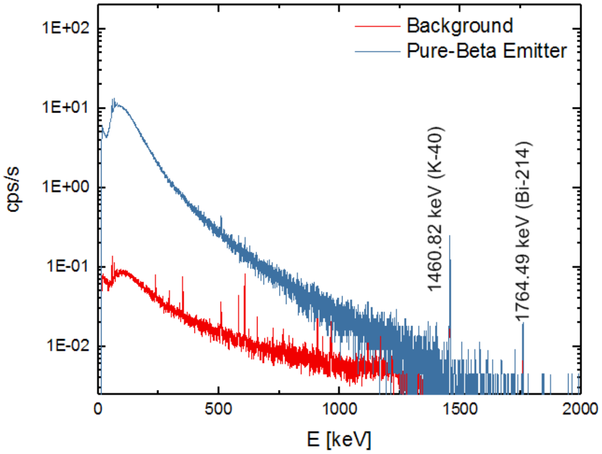

Fig. 1. Gamma spectrum of a pure-beta emitter (blue -where the two noticeable gamma lines are from the natural background) and the background (red) acquired using a HPGe (High-Purity Germanium) detector

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Development of a plutonium age dating capability for nuclear forensics

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The Actinides Analysis group at AWE specialises in the bulk chemical analysis of actinide materials, with a particular emphasis on plutonium and uranium metals. We have developed a bulk Pu age dating capability using validated analytical techniques (TIMS, HRGS, Potentiometric Assay) typically used for the quality assured analysis of plutonium metal. This work presents the application of this capability to a variety of plutonium samples from various processing routes (reprocessing/pyro-processing) to research the utility of the signature for forensics. We study the ^{241}Pu-^{241}Am-^{237}Np and Pu-U chronometers in detail and use concordant and non-concordant chronometers to predict processing histories.

Age dating uranium materials using $^{231}Pa/^{235}U$ radiochronometry: A review of $^{231}Pa/^{235}U$ advancements and observations

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Keywords: radiochronometry, nuclear forensics, protactinium, age dating, uranium

Radiochronometry, or the science of age dating nuclear material, is a technique often employed during nuclear forensic investigations and exercises to provide information about the timing of the last chemical purification of an unknown material that is often associated with the material production date. Over the last decade, significant international research and development efforts have taken place to expand the use of the $^{231}Pa/^{235}U$ (daughter/parent) radiochronometer to measure model ages of uranium materials. The $^{231}Pa/^{235}U$ radiochronometer is generally used in tandem with the $^{230}Th/^{234}U$ radiochronometer when dating uranium samples to increase confidence in the interpretation of model age results. This review focuses on advancements in radiochemistry[1,2,3], tracer preparation[2,4], and certified reference material production[5,6] that have occurred in the field of $^{231}Pa/^{235}U$ radiochronometry. We will discuss how these advancements have contributed to establishing baseline $^{231}Pa/^{235}U$ capabilities at laboratories, and how they have promoted the measurement of $^{231}Pa/^{235}U$ ‘consensus’ ages of uranium certified reference materials[1,2,4,7,8]. A bilateral US-China collaboration applying $^{231}Pa/^{235}U$ radiochronometry to certified reference materials NBL CRM U850, NBL CRM U010, and IRMM 1000b will be provided as an example of ‘consensus’ age determination. We will also statistically evaluate published[2,4] and measured $^{231}Pa/^{235}U$ model ages of the IRMM 1000b certified reference material made since the production and certification of IRMM 1000b in 2012[5]. In addition to reviewing recent $^{231}Pa/^{235}U$ research contributions, we will show $^{231}Pa/^{235}U$ model age results of uranium metals produced in the United States. These results demonstrate that real-world materials may not support the radiochronometry model age assumption that ^{231}Pa is efficiently separated from uranium during uranium production and highlight the need for future radiochronometry research.

Acknowledgments

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IAEA residential assignment program to nuclear forensics in Hungary

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Hungarian Academy of Sciences Centre for Energy Research (MTA EK) was nominated to a Collaborating Centre for Nuclear Forensics of the International Atomic Energy Agency (IAEA) in 2016. Close co-operation between IAEA and MTA EK (predecessor Institute of Isotopes) in the field of nuclear forensics started about 20 years ago.

The main tasks of the IAEA Collaboration Centre is to participate in scientific programs in the field of nuclear forensics (e.g. Coordinated Research Programs of the IAEA) to provide technical assistant for other Member States and mainly to host different IAEA training programs, like the one week long Practical Introduction Training Course or 2.5 month long Residential Assignment Program on nuclear forensics.

The IAEA Residential Assignment Program is the most advanced training of the IAEA in the field of nuclear forensics. It was piloted in Hungary in 2014 as test version and since that it has been introduced in other, more advances laboratories, as well.

The objective of the Program in Hungary is to provide a scientist in-residence with a comprehensive overview and understanding of the scope and application of nuclear forensic examination. It includes practical learning objectives associated with the commencement of a nuclear forensics examination, training in the techniques and methods used within the nuclear forensics laboratory as well as in evidence handling techniques. A model case exercise is used as part of the laboratory study to emphasize the key learning objectives. Main aim of the program is to follow a nuclear forensics examination in the real time-frame (2 months) considering the international guidelines and standards from the IAEA and Nuclear Forensics International Technical Working Group (ITWG).

The program based on a team exercise includes hypothetical scenarios to motivate the participants to work together, share the experiences and follow the investigation in a scientific team. During the program participants should plan the analysis based on the questions of the investigator and international guidelines. The program follows a nuclear forensics examination from crime scene investigation and radiological evidence collection, through material characterization at the laboratories until data interpretation, origin assessment using the Hungarian National Nuclear Forensics Library system.

Participants have the possibility to investigate real nuclear samples and get specific training on analytical techniques as physical characterisation in glove-box, mass spectrometry, scanning electron microscopy, gamma-spectrometry, X-Ray Diffraction, etc.

The program is also extended with topics of specific scientific interest of the participants and relevant visits e.g. at the Hungarian Traditional Forensics Institute of the National Police and Hungarian Atomic Energy Authority.

MTA EK's mission is to extend and develop capabilities in nuclear forensics with sharing knowledge and experiences regionally and internationally and to build close co-operations with Member States.

Identification and classification of uranium powders using colour, image texture and spectroscopy signatures

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Keywords: nuclear forensics, uranium ore concentrate, colour analysis, image texture analysis, hyperspectral imaging, multivariate data analysis

ABSTRACT: the IDENTICLASS project contributes to the Exploratory Research (ER) Programme of the European Commission, Joint research Centre (JRC). This ER project focuses on developing a new approach for the characterization of uranium containing powders, primarily Uranium Ore Concentrate (UOC), to combat illicit trafficking. It combines different analytical techniques (figure 1): colour analysis (via spectrophotometric/colorimetric measurements), image texture analysis applying different algorithms (angle measure technique, AMT; grey level co-occurrence matrix, GLCM; grey level run matrix, GLRM; locally binary pattern, LBP; etc.), hyperspectral imaging that provides information on the molecular structure (obtained by NIR spectroscopy). The expected result of this exploratory research is the development of a new methodology which makes use of a dedicated mathematical model based on data fusion, hence combining colour, image texture features (the results are strongly related to the sample´s morphology) and NIR spectroscopy data (the results are related with the sample´s chemical composition). This new methodology will be developed and tested using a suite of almost 80 UOC samples that are available in the JRC laboratories. An overview of the project and first results on the colour based classification model and a preliminary image texture classification will be presented here.

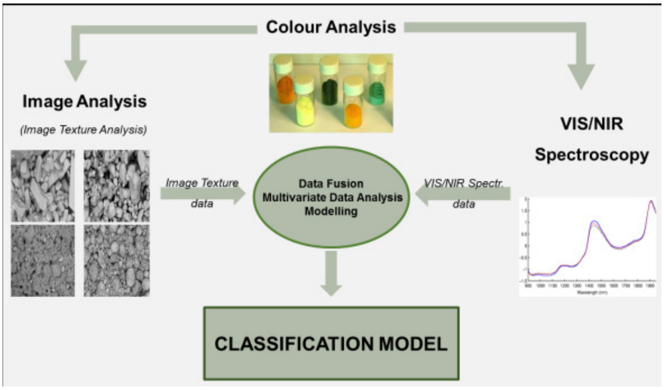

Figure 1. Combination of different analytical techniques for UOCs powders identification and classification

Acknowledgments

The authors would like to thanks Dr Bulgheroni Antonio for his precious contribution in the images acquisition developing procedure.

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Application of ICP-MS isotopic ratio technique in resolving nuclear forensic signatures in cobalt processing

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Keywords: isotopic ratio, cobalt mining and processing, nuclear forensics signatures, gamma spectroscopy

Acts of nuclear terrorism has raised serious concerns on the security and safety of radioactive materials whether in storage facilities or out of regulatory control. One such source of concern is the dispersal of radioactive cobalt (Co-60) around a large public gathering. To counter this challenge, Member States of the International Atomic Energy Agency are urged to develop their own national nuclear forensics libraries from national ore deposits of Uranium and Cobalt. The aim of this work was to apply ICP-MS Isotopic ratio technique to resolve nuclear forensic signatures for cobalt mining and processing in South Africa. We targeted the Cobalt "group of metals, Co, Ni, and Cu", and their correlation with uranium deposits. The results show that variation of Co (in ppm) vs lead isotopic ratios are scattered around 1.95 – 2.01 for $^{208}Pb/^{206}Pb$, 0.80 – 0.83 for $^{207}Pb/^{206}Pb$ and 0.052 – 0.056 for $^{204}Pb/^{206}Pb$). Copper has an average concentration of 0.463 ± 0.024 ppm; Nickel has an average value of 1.393 ± 0.075 ppm and Co has an average value of 0.674 ± 0.036, indicating that in the uranium mine deposits of the Carletonville area, Ni>Co>Cu. The work also investigated the Rare Earth Elemental (REE) pertains as indicative signatures for Co deposits. The results show that the Cobalt hosted uranium deposits are of urananite ores among others, and the patterns are shown in Figure 1 below.

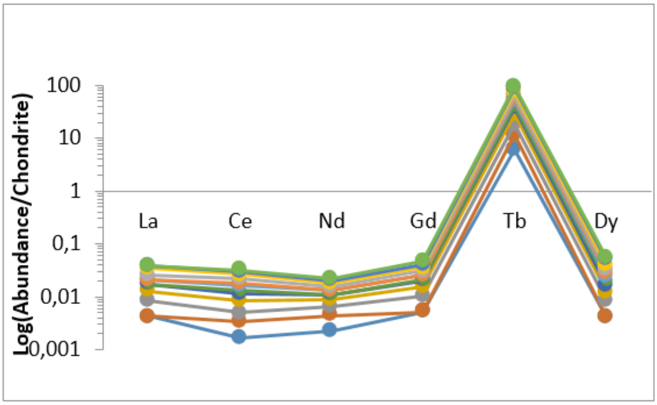

Figure 1: REE patterns normalized with Chondrites for Tailing dam 3.

Joint validation of the “in-situ Uranium Age Dating Method”

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Keywords: nuclear forensics, radiochronometry, isotope dilution, in-situ isotopes, TIMS, ICP-MS

The age of uranium material is one of the important signatures for a nuclear forensics investigation. The ^{230}Th/^{234}U ratio is the most widely used radio-chronometer for uranium age dating. Isotope dilution mass spectrometry (ID-MS) is recognized as the most reliable method to determine the ^{230}Th/^{234}U ratio from which a model age of the material is inferred. To this end, e.g. ^{233}U and ^{229}Th are used as spike isotopes for quantification of the respective amounts of parent and daughter nuclide.

Recently, a new method for uranium age-dating, using in-situ uranium and thorium isotope ratios, was developed. In this method, using the isotope ratio in secular equilibrium between ^{238}U and ^{234}Th (^{234}Th/^{238}U = 1.47×10^{-11}), ^{230}Th/^{234}U ratio is calculated from measured isotope ratios of U (^{234}U/^{238}U) and Th (^{230}Th/^{234}Th). Under the collaboration between EC-JRC and JAEA, the in-situ age dating method was subject to joint validation. Six different uranium materials (samples distributed by the ITWG - Nuclear Forensics International Technical Working Group during the Collaborative Materials Exercises) of CMX-4, CMX-5 and Certified Reference Material U125-A were used for this purpose.

The age dating result by in-situ isotope method was consistent with known production dates of the respective samples. Comparing the results between ID-MS method and in-situ isotope method, the uncertainty of the latter proved to be higher. The uncertainty evaluation according to GUM for the in-situ isotope method indicates that the measured ^{234}Th/^{230}Th ratio provides the highest contribution. The accuracy of in-situ isotope method can be improved by higher precision in ^{234}Th/^{230}Th measurement.

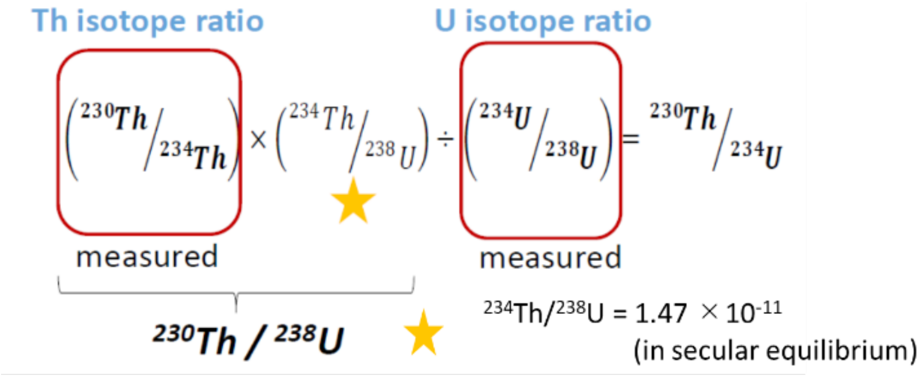

Fig. 1. Equation for in-situ Uranium Age Dating Method. Using the measured isotopic ratios of ^{230}Th/^{234}Th and ^{234}U/^{238}U and this equation, the ^{230}Th/^{234}U isotopic ratio for age determination can be calculated.

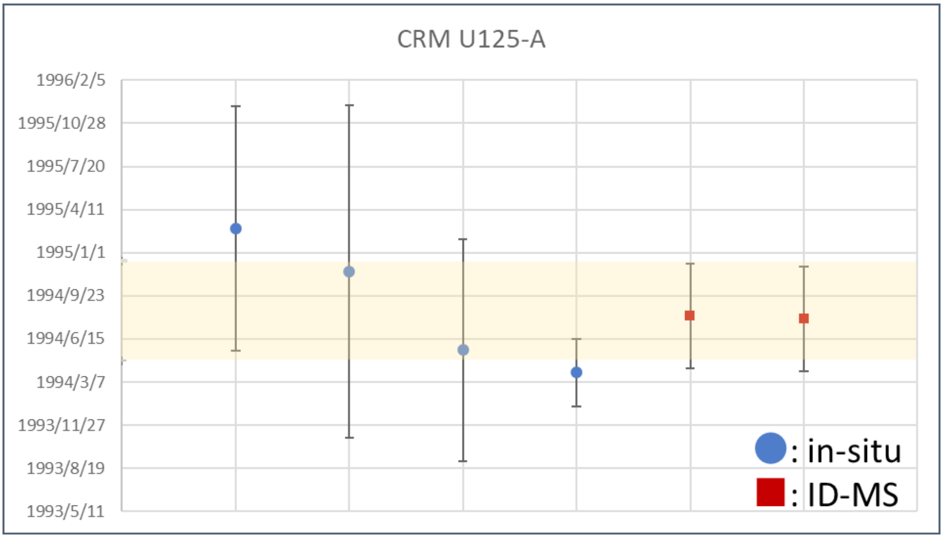

Fig. 2. Age dating results for the uranium certified reference material (U125-A). The colored band indicates the certified model date

Acknowledgments

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Isotopic characterization of uranium ore concentrates by thermal ionization mass spectrometry

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Keywords: uranium ore concentrates, TIMS

The ability to accurately and precisely characterize the isotopic signatures of uranium ore concentrates (UOC) remains a crucial component of current efforts to expand the effectiveness of nuclear forensic libraries used in provenance assessment. However, before a robust library can be built and utilized reference materials for the isotopic compositions of UOC need to be identified, characterized, and used as a quality control to assess isotopic data being collected on UOC. The Nuclear and Radiochemistry group at Los Alamos National Laboratory is currently developing the capability to characterize the isotopic compositions of UOC using thermal ionization mass spectrometry to measure U, Sr, Sm, and Nd isotopes with high precision and accuracy. Analysis of multiple reference materials, including Cup-2, permits a comparison to be made between our techniques and previous measurements of UOC made by inductively coupled plasma mass spectrpometry (ICPMS), and illustrates the ability of TIMS to more preciscely characterize the isotopic homogeneity (or heterogeneity) of UOC from a single ore body. Here we demonstrate the capability to make repeated ^{143}Nd/^{144}Nd measurement of a reference material with external precision on the order of 10 – 15 ppm. These high precision measurements can provide important information for determining the suitability of a material as a new UOC standard reference and for determining standard isotopic ratios for new UOC reference materials .

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Radiochronometric insights by Monte Carlo methods: From spike calibration to model age evaluation

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Keywords: radiochronometry, isotope dilution mass spectrometry, Monte Carlo methods, uncertainty propagation, open-source programming, data visualization

Application of the ^{234}U–^{230}Th and ^{235}U–^{231}Pa radiochronometers in tandem provides enhanced confidence for interpreting a material's production history in a nuclear forensic examination [1]. While paired model ages are typically treated as statistically independent quantities, U-Th-Pa isotopic data used in model age calculations can incorporate common parameters during data reduction and uncertainty propagation (*e.g.*, corrections for instrumental mass fractionation and Faraday/ion counter gain). Paired model ages can thus be variably correlated, the magnitude of which depends on the contribution of independent/random versus shared/systematic uncertainties to the total uncertainty budget of each age. We explore these correlation effects for U-series radiochronometry by multicollector–inductively coupled plasma–mass spectrometry via Monte Carlo (MC) computational methods, applied to both empirical and synthetic datasets [2]. MC methods are a powerful complement to partial derivative-based uncertainty propagation equations [*e.g.*, 3], as they can be used to explore and account for uncertainty correlations with relative ease. For example, due to its short half-life (~27 days), ^{233}Pa spikes must be routinely prepared and calibrated to maintain an active ^{235}U–^{231}Pa radiochronometric capability [4]. An MC algorithm is presented that propagates random and systematic uncertainties to derive a maximally precise, statistically robust ^{233}Pa spike concentration from multiple ^{231}Pa–^{233}Pa calibration solution analyses [5]. This approach is extended to an MC data reduction algorithm in which raw isotope ratio data are converted into reportable U-Th-Pa model ages. These MC results are then projected onto a multi-chronometer concordia diagram [*e.g.*, 6], allowing analysts to visualize graphically covariance of the ^{234}U–^{230}Th and ^{235}U–^{231}Pa systems; assess model age concordance; and compare reproducibility of replicate analyses to one another and/or to independently-constrained production dates. We observe that as the contributions of random uncertainties decrease relative to systematic ones (*e.g.*, raw U isotope ratio measurements and ^{233}U spike calibration, respectively), paired model ages are indeed increasingly correlated. Notably, scenarios can arise in which apparently concordant model ages are discordant when uncertainty correlations are explicitly accounted for. These findings have important implications for the interpretation of radiochronometric data in forensic contexts, and serve to highlight the synergistic roles of partial derivative-based and MC approaches to model age uncertainty determination and mass spectrometric data analysis.

Acknowledgments

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Characterization of depleted uranium based industrial shielding materials for nuclear forensics pusposes

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Keywords: nuclear forensics, NDA, gamma spectrometry, XRF

The aim of this study was to determine the key nuclear forensics signatures of depleted uranium (DU) cylinders contained in industrial devices for shielding purposes. These included isotopic composition analysis of DU by high resolution Gamma Spectrometry and the analysis of major elements present in the casing material, by using X-Ray Fluorescence (XRF). The observed traditional forensics signatures which could be useful for the investigation are also described. These include: text dimensions and spacing of markings present on the container, their colour, etc.

The results obtained in this study were added to the National Nuclear Forensics Library. Nuclear and traditional forensics signatures identified within this study were used by the national judicial authorities and scientific experts in the context of a legal investigation of DU gamma-defectoscope material found outside regulatory control. This case study will be presented as well.

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Advances in environmental safeguards bulk sample analysis at Los Alamos National Laboratory

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Keywords: environmental safeguards, bulk analysis, radiochronometry

The International Atomic Energy Agency (IAEA) collects swipe samples from facilities around the world as one method for verifying compliance with the Nuclear Nonproliferation Treaty and consistency with declared operations. These swipe samples are sent to the Network of Analytical Laboratories (NWAL) for characterization, and as a member of the NWAL, Los Alamos National Laboratory (LANL) is tasked with the bulk measurement of radionuclides in swipes, primarily total U, Pu, and the isotopic composition of U and Pu. Recent work at LANL is improving the accuracy, precision, and sensitivity of our measurements. One of the more challenging aspects of NWAL swipe analysis is adequately purifying uranium for determination by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Many swipes contain high concentrations of heavy elements, e.g. Pb and W, that from isobaric iterferences with U isotopes. We have optimized radiochemistry methods to remove interfering species, and developed MC-ICP-MS analysis protocols to detect the presence of interferring species and process the samples through additional radiochemistry as needed to ensure isotopic measurements are accurate. We are also investigating transitioning Pu analysis from MC-ICP-MS to multi-collector thermal ionization mass spectrometry (MC-TIMS). Experiments to investigate the use of total evaporation MC-TIMS for the determination of Pu isotopes show a significant improvement in sensitivity over MC-ICP-MS methods, and should both decrease our detection limit for Pu and produce higher precision isotope ratio measurements. We will present the results of our radiochemistry and mass spectrometry research, and the quantititative improvements to our analysis of NWAL swipe samples.

Measurement of production date (age) of nanogram amount of uranium

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Keywords: production date, uranium, nuclear forensics, ICP-MS

A highly enriched uranium sample was seized in Moldova in 2011. JRC-Karlsruhe obtained a swipe sample from the confiscated material for nuclear forensic analysis in 2017. As the sample amount was very small (i.e. some particles), only limited number of analysis could be performed. It was chosen to look into the isotopic composition of uranium and the age of the material. In addition to the particle analysis by large-geometry SIMS, multi-collector ICP-MS measurements were performed.

Production date (age dating) measurements typically require milligram amount of material and tedious separation [1]. Using low sample amount can result in poor uncertainties due to the little ingrowth of the decay products and lower measurement precision, e.g. higher contribution from the background. Age dating of U particles by SIMS would require large particles and old material in order to be possible. And this was not the case for this sample. Thus, a new method needed to be developed for the measurement of production date of nanogram amount of uranium samples, i.e. swipes, by MC-ICP-MS.

The particles on the swipe sample were collected on a pyrolytic graphite planchet using the cascade impactor method in a clean laboratory as done for SIMS analysis routinely. The U particles were then leached and dissolved in HNO_3 using a special procedure to minimise the background and consumption of chemicals. The resulted U background was approximately 17 pg. The sample was subsequently split in two fractions in order to measure the production date and the "bulk" (i.e. the average of the particles) U isotopic composition by MC-ICP-MS. The production date of the obtained U solution was measured from the ^{230}Th/^{234}U amount ratio and the age was calculated using the CRM U630 (63% nominal enriched ^{235}U) radiochronometric standard for correcting the difference in U and Th ionisation efficiencies. For quality control purpose 70% highly enriched uranium was used, which has been analysed and validated by several expert laboratories [2].

The MC-ICP-MS showed that the "bulk" U isotopic composition agreed well with the SIMS result, thus indicating that no cross-contamination had taken place during the sample preparation. The measured production date, besides the U isotopic composition, could link the material to other HEU cases of illicit trafficking seen earlier in Europe.

Acknowledgments

The secondary ionization mass spectrometry laboratory of JRC-Karlsruhe is highly acknowledged for their valuable support.

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Nuclear forensics on the 135Cs/137Cs ratio by ICP-QQQ-MS

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Keywords: nuclear forensics, cesium ratio, ICP-QQQ-MS, 135-Cs

The atmospheric fallout and the Chernobyl disaster have released a lot of radioactive material, which has contaminated Germany. The most famous element is the cesium with his directly produced radioactive fission isotope ^{137}Cs ($T_{1/2} = 30$ a). Just with the ^{137}Cs it is not possible to say something about the origin. The remedy is the ratio ^{135}Cs/^{137}Cs with the long-living isotope ^{135}Cs ($T_{1/2} = 2.3$ Ma). Additionally, the formation of the daughter ^{135}Cs from the mother ^{135}Xe depends on the currently occurring neutron flux. The analyse is done by a Triple-Quadrupole-Mass spectrometer (ICP-QQQ-MS). This allows a further suppression of isobaric interference by the use of a reaction gas after a previous element-specific separation. In the case of cesium the nitrous oxide N_2O reacts with the isobaric barium (Ba) to barium oxide (BaO^+).

The radioecological question of the origin analyse of radioactive, amorphous glass beads out of the destroyed reactors in Fukushima, with should be achieved with a spatially resolved laser ablation unit coupled to the mass spectrometer, is in the focus of the research. Another point is the wild boar paradox with the not decreasing amounts of radiocesium and the general analyse of environmental and food samples.

Nuclear fuel cycle

Development of process monitoring tools for the uranium-plutonium separation and purification from spent nuclear fuel by solvent extraction

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Keywords: uranium, plutonium, liquid-liquid extraction, monitoring systems

In the back-end of nuclear fuel cycle, liquid-liquid extraction processes basically used TBP (tri-n-butyl-phosphate) for UOX (uranium oxide fuels) spent fuel reprocessing and recycling. In the PUREX process, uranium and plutonium separation is achieved by reduction of Pu(IV) to Pu(III) with the use of redox reagents. In the framework of the future development of generation IV reactors, higher quantities of plutonium are going to be treated. Recycling higher quantities of plutonium will induce a massive use of redox reagents which could become a significant economic, environmental and/or technical constraint.

For these reasons, the French Alternative Energies and Atomic Energy Commission (CEA) develops new extracting systems which allow to perform the U/Pu partitioning without redox reactions. In these new processes, branched alkyl-monoamides extractants are used and allow uranium/plutonium separation by a decrease of nitric acid concentration. Recently, the scientific feasibility of a new process devoted to the extraction of uranium and plutonium and their purification towards the fission products in one cycle without redox reactions was demonstrated [1] in the shielded process line called CBP in the ATALANTE facility (Marcoule-France).

For these new processes, monitoring technologies have to be adapted and improved in order to finely pilot the liquid-liquid extraction flowsheet. In the first part of this work, analytical tools (and particularly on-line and *in situ* UV-visible spectrophotometric measurements) which have been developed and used to monitor and control the process during the hot test will be described. In a second part, technological developments for an “automatic” piloting system will be presented through an example from a specific liquid-liquid extraction experiment.

Acknowledgments

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A new strategy for selective separation of lanthanides from spent nuclear fuel

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Keywords: lanthanides, spent nuclear fuel reprocessing, ionic liquid, actinides

Reprocessing of spent nuclear fuel became the key issues for the environmentally friendly and sustainable development of nuclear energy. A successful approach involved in recycle of spent nuclear fuel is needed to maximize energy utilization of the fuel by recovering actinide (An) species present while also minimizing the waste destined for geologic storage. This requires a technology to recover not only the U and Pu, but also the MAs (Np, Am and Cm). For those volatiles and semi-volatile fission products would be easily removed by using a dry-processing technique processes. Lanthanides must be separated from minor actinides before next transmutation step because the high neutron capture cross sections of some lanthanides, named as neutron poisons, inhibit efficient transmutation. However, mutual separation of MA and Ln is very different due to their similar chemical properties. Hence, new separation strategies combining green chemistry with low cost and high efficiency for separation lanthanides remain highly desirable.

In the present work, an novel strategy for removing of fission products from spent nuclear fuel by the selective dissolution using carboxyl-functionalized ionic liquid [Hbet][Tf_2N] has been proposed. This innovative method allows the selective dissolution of neutron poisons, lanthanides oxide as well as some fission products with high yield, leaving most of UO_2 matrix and minor actinides behind in the spent nuclear fuel and accomplishing the actinides AnO_2 recovery as a group. Water-statured [Hbet][Tf_2N] can dissolve lanthanides oxide from simulated spent nuclear fuel with a dissolution ratio of 100% at 40°C. However, the dissolution of uranium is almost neglect (<1%) under the same conditions. Less volume of high level radioactive liquid waste (HLW) was generated during this process and there was no need for dissolving spent nuclear fuel since only some fission products was dissolved selectively and separated. The dissolved Nd and U were recovered efficiently from the loaded ionic liquid phase by back-extraction with 1M HCl solution. The ionic liquid phase can be reused again for the dissolution of Nd_2O_3 after washing off the residual acid with water. The high Ln_2O_3 dissolution capability is also elucidated by thermodynamical analysis on the microprocess of the solubilizing and the U/x value related to the lattice energy U for M_xO_y lattice disruption. In additional, the effect of gamma radiation on this ionic liquid [Hbet][Tf_2N] was performed. The selective dissolution of lanthanides oxide from simulated spent nuclear fuel by irradiated [Hbet][Tf_2N] was investigated. This work represents the first case for efficient fission products removal by selective dissolution, avoiding the complete dissolution of spent nuclear fuel, the producing of the large high-level radioactive waste and reducing environmental hazards.

Transient heating measurement in testing analysis: A novel thermal probe

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Proper and accurate methods of irradiation testing on nuclear fuel specimen are very applicable in licensing, research and development. Therefore having a correct measurement of heating value with a quantified uncertainty is vital. This type of measurement is utilized at Idaho National Laboratory (INL) for Advanced Test Reactor (ATR) and Transient Reactor Test (TREAT). Here we report some of our recent advances in analysis and design an innovative nuclear heating sensor/measurement technology which directly measures the parameters of interest using spatially-resolved real-time thermometry of fissionable instrument materials which demonstrate the instruments' use in TREAT. Nuclear and thermal modeling and simulation (M&S) assessments were performed to evaluate the characterization and design of the nuclear-heated thermometer. Also, our effort was focused on the quantification of probable uncertainties in the response of the detector to measured time-dependent nuclear heating. To peruse our investigation, a point kinetics model for the TREAT reactor was developed to predict the energy deposition in the designed thermal probe. The emphasis was placed on modeling the heat transfer environment of the probe and its surrounding sheath in the core of TREAT. The electrically heated test was modeled with the point kinetics/heat transfer code with moderate success and it seems that the heat transfer analysis is reasonably close to predicting the measured data. Also, a finite element thermal analysis was performed and validated against the experimental data. Performing verification and validation (V&V) based on the available experimental data is a core part of this research to quantify the numerical uncertainty and also the mismatch of the simulation results and the experimental data. V&V includes: verifying the correctness and numerical stability of the sub-models; comparing the numerous sub-models that describe separate effects of the fuel behavior with experimental data and comparing the results of the integral fuel performance code with experimental data. By the V&V assessment, we are able to obtain the fidelity and reliability of simulation and design. In this analysis, the V&V assessment was performed based on the ASME and ANS codes and standards.

Effect of cover gas composition on polonium evaporation from liquid lead-bismuth nuclear coolant

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Keywords: polonium, MYRRHA, lead-bismuth eutectic, LBE

Recently, the Belgian government gave the green light to the Belgian Nuclear Research Centre to start the constuction of MYRRHA, the first accelerator driven research reactor in the world. MYRRHA, the first demonstrator of the transmutation of spent nuclear fuel, uses lead-bismuth eutectic (LBE) as coolant material [Abderrahim, 2009].

During operation of MYRRHA, various hazardous radionuclides are produced in the LBE by nuclear reactions. Preventing its release into the environment is a primary objective in the design and safety of MYRRHA. The quantity and chemical nature of the released material is called the “source term”. In MYRRHA the expected dominant contributor to this source term and its radiological consequences is polonium. Therefore, during the development phase of MYRRHA this source term, and consequently the release behavior of polonium from LBE, must be known as accurately as possible.

To this aim we investigated the release behavior of Po from LBE under normal and accidental conditions as well as methods to capture it. The observed quantity of Po released from LBE strongly depended on the composition of the cover gas. In humid atmosphere, for example, an enhanced release of polonium was observed. The polonium gas molecules formed in humid conditions did not adsorb strongly on quartz surfaces. On the other hand, these volatile polonium species were found to be effectively captured by stainless steel surfaces [Maugeri, 2017]. In this contribution we summarize the results of the studies conducted to investigate the influence of the carrier gas composition on the release of Po from LBE. In particular, the effect of the concentration of water vapor and oxygen gas on Po release from LBE is addressed. In addition, the influence of the concentration of dissolved oxygen in LBE on Po release is discussed [Gonzalez, 2016].

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Characterizations of high activity solid deposit samples from fission products tanks

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Keywords: high level analysis, characterization, fission products, dissolution, actinides, decommissioning

For the dismantling of reprocessing facilities in Marcoule, deposit solid samples coming from fission products tanks have been characterized in the laboratories and hot cells of the ATALANTE facility. These experiments consisted in physicochemical measurements on high activity solid samples, specific dissolutions developments and extensive characterizations of dissolution solutions and solid residues.

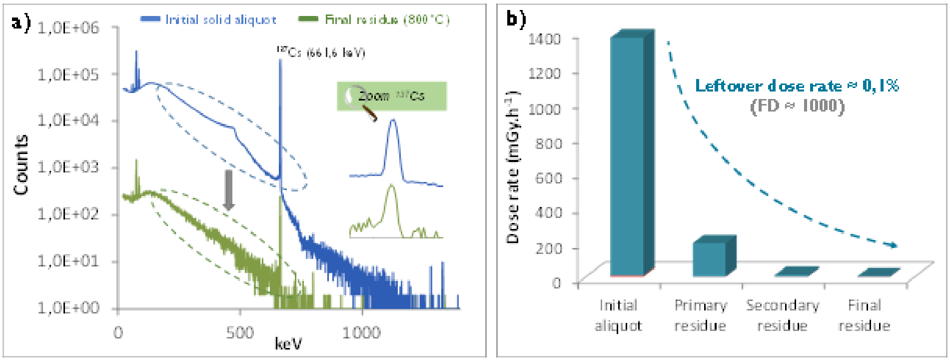
This work required R&D developments in both the chemical and analytical fields: dissolution conditions optimization, Cs, Zr and Sr specific decontaminations, qualitative analyses on solid residues... Many analytical techniques have been implemented in hot cells and glove box laboratories for these characterizations:γ and α spectrometry, isotope dilution by TIMS, L-line X-ray fluorescence, ICP/AES, ICP/MS, ion exchange chromatography, Cherenkov counting… The dissolution process optimizations allowed to retain a dissolving protocol presenting the best dissolution yield:

- of small actinide amounts initially present in deposit solid samples (such as Pu, from 0.7 to 1.4 $mg.g^{-1}$ of dry solid aliquot involved),
- of ^{137}Cs wich concentrates almost all of the initial γ activity (> 99%, up to 1.10^{10} $Bq.g^{-1}$ of dry solid aliquot involved).

These developments have resulted in obtaining final dissolution residues whose dose rate does not exceed 0.1% of the initial solid aliquot dose rate (initially 1.4 $Gy.h^{-1}$ for 400 mg). These characterizations allow determining the composition and nature of the fission products raffinates present in such reprocessing equipment. These data are essential for the definition of recovery scenarios and waste management.

Some of the very specific analytical developments performed for these characterizations in hot cells, such as selective Cs decontamination by extraction chromatography and direct analysis of solid residues by L-line X-ray fluorescence dedicated to actinide analysis are presented.

Figures



Example of dissolution performance: a) comparison of qualitative gamma analyzes on solid, b) decontamination factor

Availability of routine and customized proficiency testing materials for the nuclear fuel cycle

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

Laboratories and processing facilities depend on a flexible supply of proficiency test (PT) materials/samples consistent with the work they currently do and to remain accredited. While government institute supplied PT's may be suitable for a subset of a facility's work, this presentation will outline the availability of traceable PT materials/samples that cover a broader range of matrices and isotopes. These are available to both individual laboratories/facilities and in collaboration with governmental laboratories for their own distribution and administration.

Eckert and Ziegler Analytics (EZA), Atlanta, GA, USA, as an accredited Proficiency Testing Provider, routinely supports nuclear power plants with a variety of effluent and environmental PT's delivered quarterly to comply with regulations. Samples have also been used in the qualification of field monitoring equipment for decommissioning a uranium gaseous diffusion facility among other project focused applications.

EZA has recently upgraded its gas handling system, expanding options for traceable Xenon and Krypton isotopes in a variety of cyliners and containers, complementing its current traceable line up of 33 mL spheres and 0.5 L lecture bottles.

EZA was contracted to support the 2016 Northern Lights exercise. The exercise scenario was a nuclear power plant accident with a significant radionuclide release. The major focus was post-accident emergency phase leading to recovery phase beginning at t = +21 days post release. 14 US federal and state agencies received freshly irradiated mixed fission products from EZA on day 21 post irradiation. Activity ranged from 500 Bq to 3700 Bq per sample. Water, soil, air filters and vegetation samples were provided to the labs. Most labs performed gamma analysis, but a few did radiochemistry for Sr-89/90. The exercise was unique in that it tested both the analysis of real samples combined with logistics and data reporting communication across the US.

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.

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Radiolytic degradation of hydrophilic PyTri ligands for minor actinide recycling

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Keywords: FT-Raman; HPLC, *i*-SANEX, PyTri ligands, radiolysis

The 2,6-bis[1H-1,2,3-triazol-4-yl]-pyridine (PyTri) chelating unit has already showed promising properties for the application to advanced hydrometallurgical processes aimed at recovering minor actinides from highly active raffinates [1-2]. In particular, the water-soluble PyTri-Diol proved to be an exceptional candidate as it exhibited unprecedented radiolytic stability [3]. This is an undeniable key requirement for chemicals involved in the partitioning of highly radioactive solutions, since radiolysis can have a huge impact on system safety and performances.

In this work, the radiolytic degradation of two hydrophilic complexing agents, PyTri-Diol and PyTri-Tetraol, has been investigated by means of different analytical techniques. The radiation damage received at process conditions was simulated by irradiating the stripping solvents up to 200 kGy with ^{60}Co sources (0.14 and 2.5 kGy/h dose rates). HPLC, ESI-MS (coupled with HPLC) and FT-Raman analyses were performed on irradiated PyTri-Diol and PyTri-Tetraol solutions. Linear ligand consumption with the absorbed dose was measured by HPLC. At the lower and higher dose rates, PyTri-Diol G_0-values were found to be around 0.10 ± 0.03 and 0.04 ± 0.01 $\mu mol \cdot J^{-1}$, respectively. The ligand degradation mechanism and the main degradation by-products were hypothesized and preliminary confirmations were gathered from mass tandem ESI-MS. In particular, the ligand degradation was supposed to be caused by indirect radiolysis and to occur on the lateral chains rather than on the chelating unit, coherently with radiation chemistry and preliminary investigations [3]. Further confirmations of aromatic core stability towards radiolysis were achieved by FT-Raman spectroscopy.

Unprecedented PyTri ligands radiolytic stability was proved, thus further recommending their implementation in future processes. In fact, the stripping solvent performances should be unaltered, since the by-products are expected to maintain the selectivity for minor actinides.

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Closed nuclear fuel cycle based on the accelerator driven system

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Keywords: spent nuclear fuel reprocessing, high temperature oxidation/reduction, selective dissolution separation, ceramic UC microspheres

With the development of nuclear power, more and more spent nuclear fuel will be produced and accumulated. Reprocessing of these spent nuclear fuel became the key issues for the environmentally friendly and sustainable development of nuclear energy. Nowadays, the concept of a closed nuclear fuel cycle is highly discussed as a possible, which will make an optimized use of natural resource and minimize the amount of nuclear wastes. Closing the fuel cycle can be achieved through partitioning of uranium and minor actinides and transmuting of long-lived radioactive nuclides in fast nuclear reactors or an accelerator with high energy neutrons.

For the future development of nuclear energy requirements, the concept of an accelerator-driven advanced nuclear energy system (ADANES) has been proposed in China. ADANES consists of a burner system and a fuel recycle system. The waste transmutation, breeding, and power production are implemented in the burner driven by the neutron source outside the accelerator. With the help of the external neutron source, the rest spent nuclear fuel after removing the part fission products will be refabricated to new nuclear fuel and burned. This reprocessing procedure will avoid separating magnanimous uranium and plutonium from spent fuel in contrast with the PUREX reprocess.

Here, the investigation about the separation of some fission products and fabrication of ceramic nuclear fuel microspheres in our laboratory were reported. 1) The studies of the pulverization about UO_2 pellet to U_3O_8 powder and the subsequent reduction through high temperature oxidation/reduction were carried out. For those volatiles and semi-volatile fission products (^3H, ^{14}C, Kr, I, Xe, Mo, Tc, Ru,Te and so on) would be easily removed through this high temperature oxidation processes. 2) The selective dissolution separation for lanthanide oxides from simulated spent nuclear fuel using carboxyl-functionalized ionic liquid [Hbet][Tf_2N] was studied. Water-statured [Hbet][Tf_2N] can dissolve lanthanides oxide from simulated spent nuclear fuel with a dissolution ratio of 100% at 40°C. However, the dissolution of uranium is almost neglect (<1%) under the same conditions. This novel process displays an outstanding performance to separate neutron poisons Ln_2O_3 efficiently and allows the recovery of actinides AnO_2 as a group in solid form. 3) The preparation of homogeneous ceramic nuclear microspheres and UC powder were performed using an improved microwave-assisted rapid internal gelation process and Pechini-type in situ polymerizable complex method, respectively. This improved microwave-assisted internal gelation process greatly simplifies the conventional sol-gel process and avoids secondary organic radioactive waste. It can provide an important guidance for the preparation of Pu and MAs carbides microspheres, especially (U+Pu)C, (U+Am)C, for nuclear reactors in the future.

Investigation of uranium/plutonium separation by using organic reagent in Purex process

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Several organic reducing reagents were investigated in the step of Pu from 30%TBP/OK loaded with U, such as U(IV)/hydrazine, Hydroxylamine, DMHAN/MMH, and HSC. Bench scale experiments of separation Pu from organic phase were carried out, the results were summarized and compared . At the same time the influence of Tc on reduction striping , and Np reduction were also discussed.

The development status of PUREX process for nuclear fuel reprocessing: an insight from patents

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Keywords: PUREX, nuclear fuel, reprocess, development, patents

Spent nuclear fuel reprocessing stands as a major challenge for the nuclear industry[1]. The PUREX process has been one of the successful methods to reprocess spent nuclear fuel for several decades[2], and further enhancements are being carried out in the worldwide. Patents combine extensive technological and commercial information, which reflect the direction of the technology development[3]. Therefore, the global published patents about the PUREX technology are investigated in this work. The key word was selected as PUREX in the title and the abstract in order to search the patents. The results show that there have been 115 related patents by December 20th 2018. The major applicants include China Institute of Atomic Energy, the French Alternative Energies and Atomic Energy Commission (CEA), and British Nuclear Fuels PLC (BNFL). The technology forecasting and the development strategy of PUREX process was provided from the view of patents, based on the nations, the technology field, the trend in the number of patents applications and the inventors. This work will contribute to understanding the advanced developments of the PUREX related technology by a new perspective.

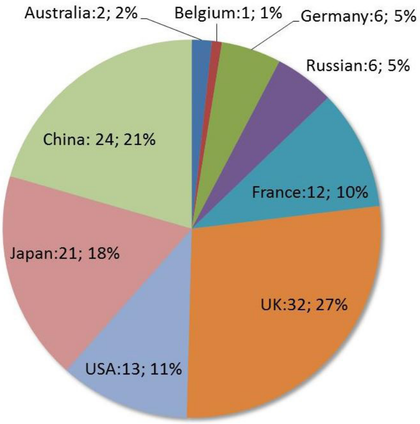

Fig. 1. The national distribution of the patent applicants.

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Production of radionuclides

Probing reactions for medical isotope production using novel rhenium and iridium targets

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Keywords: auger emitters, cross section, isotope production, targetry

Auger-emitting radionuclide emit a large number of low-energy electrons that create damaging ionizations over a range less than the size of single cell. Recently, iridium and gold anticancer drugs have been demonstrated as selectively cytotoxic to cancer cells [1-4]. Incorporation of the Auger-emitting radionuclides [^{186}Ir ($t_{1/2}$ = 16.64 h); ^{194}Au ($t_{1/2}$ = 38.02 h)] could lead to a synergistic killing effect improving the overall treatment by reducing the required dose of the chemotherapeutic agent. Additionally, both radionuclides have gamma emissions suitable for SPECT imaging and could have an immense impact on determining dose and clearance characteristics. We proposed to produce high specific activity radio-iridium and -gold via the ^{185}Re(a, 2n)^{186}Ir and ^{193}Ir(a, 3n)^{194}Au reactions.

Thin (~ 0.6 mg/cm^2) refractory metal targets were produced by a novel “pressure filtration method”. The metal is embedded in a graphene matrix and contain 1:1 metal: carbon by weight [5]. Targets were successfully irradiated at the ATLAS superconducting accelerator via the target stack method interlaced with copper monitor foils for 5 hours with 5 pnA alpha beam at energies between 32-38 MeV. The target activities were counted at Gammasphere, a precision gamma spectroscopy array at Argonne. A calibrated standard source was included in Gammasphere to quantify the absolute gamma-ray detection efficiencies. Production cross sections and impurity formation were derived from the observed spectra. The resulting cross sections, impurity production rates, and potential thick target production yields will be discussed.

Acknowledgments
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Radionucledes for theranostic applications

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Keywords: radionuclides production, theranostic application, cyclotron, deuterons

High Specific Activity Radionuclides HSARNs, obtained by either proton, deuteron or alpha cyclotron irradiation, followed by selective radiochemical separation from the irradiated target in No Carrier Added (NCA) form represent a powerful analytical tool in pure and applied sciences and technologicies. The main applications of HSARNs concern medical radiodiagnostics and metabolic radiotherapy in addition to toxicological, environmental and industrial studies. Nowadays in the contest of the age-long dream of personalized medicine, one of the most advanced fields of the HSARNs application is the new challenge in Nuclear Medicine related to the relatively novel theranostic paradigm that involves specific individual 'dual-purpose' radionuclides or radionuclide pairs with emissions that are suitable for both imaging, therapy and monitor the response to therapy [1]. In this context, a subchapter is an integrated multifunctional nanoplatform, an emerging highlight in nanomedicine, in which a suitable radionuclide is encapsulated in nanocarriers, that are novel products of a multidisciplinary approach [2].

Many of the "neutron-rich" radionuclides suitable for metabolic radiotherapy are produced by nuclear reactor with a very low Specific Activity (SA). In selected cases, they can be produced by bombardment of targets by charged particle beams in NCA form with very high SA. However, if the irradiations are made with deuteron beams some more advantages are obtained [3].

At the Radiochemistry Laboratory of LASA, a wide range of accelerator-produced HSARNs in NCA form have been produced since the 70-ties. At present, nuclear activations of metal-based targets are carried out at the cyclotron IBA K=70 of ARRONAX Center in Nantes France and the gamma and X-ray spectra are measured at Physics Measurements Laboratory in LASA with several HPGe detectors.

We present some examples of radionuclides production that include the optimization by deuteron beams irradiation through the experimental determination of the excitation functions compared with the data present in literature, the curves of theoretical calculations with EMPIRE-3.2.2 and TENDL-2015 codes, the Thick Target Yields and the optimal conditions of the beam energy and energy loss in the targets.

Acknowledgments

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Development of a new generation of ^{99}Mo/^{99m}Tc radioisotope generators to meet continuing clinical demands

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

The low-pressure column chromatographic ^{99}Mo/^{99m}Tc generator system represents an effective and reliable supply of ^{99m}Tc for diagnostic purposes in nuclear medicine. However, the low sorption capacities of the conventionally used materials in addition to the shortage in the production of fission-produced ^{99}Mo of high specific activity restrict their availability. Many alternatives were suggested to overcome the problem. However, the commercial side should not be ignored. The production methods of ^{99m}Tc should be competitive not only in terms of production volume but also in terms of price and applicability for the end user. The use of nanomaterial-based sorbents offers new advantages that could not be achieved with classical materials due to their high sorption capacity, which arises from a higher surface area along with their high radiation resistance and chemical stability. These novel properties improve safety and eliminate proliferation concerns by promoting the use of neutron activated ^{99}Mo of low and medium specific activity without the limitations of the sorbent capacity.

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Production of radioisotopes at Institute for Integrated Radiation and Nuclear Science, Kyoto University

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Keywords: electron linear accelerator, Tc-99m, Mo-99, neutron activation analysis

Institute for Integrated Radiation and Nuclear Science, Kyoto University has been providing radioisotopes for various kinds of research and our group contribute to the research for production of medical radioisotopes using the electron linear accelerator (linac) and geochemical, environmental and other kinds of research by neutron activation analysis (NAA) using Kyoto university research reactor (KUR). The former research has commenced because the shortage in supply of Mo-99 resulting from the shutdown of reactors for its production can be a global issue. We have already reported separation and purification of Tc-99m from Mo-99 produced by electron linear accelerator [1]. Recently, production of not only Mo-99 but also the other radioisotopes, such as Cu-67, has been examined using the electron linac. The latest studies along this line will be reported in the presentation.

Regarding NAA using KUR, geochemical studies are mainly investigated. We are involved in application of neutron activation analysis to micro gram scale of solid samples [2], discussion of the origin of spherule samples recovered from Antarctic ice sheet [3], and radiochemical NAA of halogen elements (Cl, Br and I) in U.S. Geological Survey reference materials [4]. Further studies along this line are in progress and the NAA results of reference materials will be introduced.

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Production of ^{47}Sc with natural Vanadium targets: results of the PASTA project

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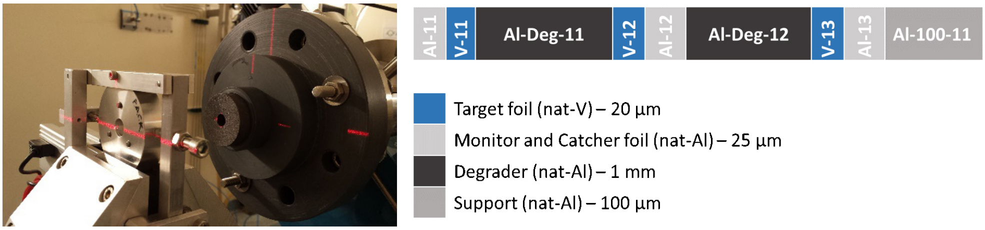
Keywords: scandium-47, production of radionuclides, cyclotron, proton beam

The goal of the PASTA project (acronym of Production with Accelerator of Sc-47 for Theranostic Applications) is the measurement of nuclear cross sections for the production of the theranostic radionuclide ^{47}Sc. The international interest on this radioisotope is underlined by the dedicated Coordinated Research Project (CRP), promoted by the International Atomic Energy Agency (IAEA), focused on *Therapeutic Radiopharmaceuticals Labelled with New Emerging Radionuclides ($_{67}$Cu, $_{186}$Re, $_{47}$Sc)* (F22053). Since at INFN-LNL (Padova, Italy) the infrastructure where the new 70 MeV proton cyclotron was installed in 2015 is under development (beam-lines and laboratories), all the irradiation runs were carried out in collaboration with the Arronax facility (Nantes, France). Nuclear cross sections were measured by using stacked-foils targets, composed by a set of thin metal foils, irradiated by 100 nA proton beams with 70 MeV maximum energy. A previously calibrated High Purity Germanium (HPGe) detector was used for γ-spectrometry, repeating the acquisition of each sample 5 days after the End Of Bombardment (EOB), in order to follow the decay of the radionuclides of interest. The production of ^{47}Sc from natural Vanadium targets was measured, but also the production of different contaminant radionuclides was estimated, including ^{46}Sc, ^{44}Sc, ^{44m}Sc, ^{43}Sc, ^{48}Sc and ^{43}K, ^{48}V, ^{48}Cr, ^{49}Cr, ^{51}Cr. In this work the experimental results will be presented and compared with literature and theoretical estimations of the ^{nat}V(p,x)^{47}Sc,^{46}Sc nuclear reactions; more details on irradiation runs and data analysis will be also given.

Figures



Photograph of the alignment procedure at the Arronax facility (left) and a typical stacked-foils structure (right).

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Authors would thank the LARAMED project at INFN-LNL and the Arronax staff for constant support and helpful discussions.

Standardisation of the emerging medical positron emitter ^{89}Zr

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Keywords: positron emitter ^{89}Zr, absolute standardization, 4πβ(PC)-γ coincidence method, gamma-ray spectrometry measurement, calibration of the ionisation chamber, comparison of results

^{89}Zr is a beta plus and electron capture decaying radionuclide, which presents interest for PET-CT diagnosis in nuclear medicine due to some convenient physico-nuclear and chemical characteristics. As a new radionuclide, its absolute (primary) activity standardisation was tackled only recently [1,2]. That is the reason why this paper describes the establishment of its complete metrological chain, by presenting the following actions: (i) Absolute standardisation by the 4πβ(PC)-γ coincidence method. The difficulties are due to its particular decay scheme, consisting from a mixture of emitted radiations, activating the detectors from the two measurement channels. The beta detector detects positrons, Auger electrons, conversion electrons, x-rays, while the gamma-ray one detects 511 keV annihilation quanta, noncoincident 909 keV (99%) and other higher energy gamma radiations. The method used was based on the measurement of the positrons in the beta channel and annihilation quanta in the gamma one [3]. Important corrections on the measurement data, due to the mentioned radiations, had to be applied. The paper describes in detail the steps of the standardisation: propose an equivalent decay scheme, develop the mathematical formalism applied to it and choose the optimal experimental measurement conditions, perform the measurements. The result is expressed as activity concentration (kBq g^{-1}) on the reference date; a detailed uncertainty budget is presented. (ii) Measurements by high resolution HPGe gamma-ray spectrometry method, which were aimed to determine the possible impurities, to offer an alternative secondary method for the activity measurement and to measure the relative intensities of the emitted gamma rays [4]. (iii) Calibration of the secondary standard, CENTRONIC IG12/20A ionisation chamber, accomplished by two methods: (a) direct measurement of the response, in terms of the ionisation current on activity unit (pA MBq^{-1}), using a P6 vial filled with 5 mL of the absolutely standardised solution; (b) calculation of the efficiency by using a linear least square modelling of data from other measured radionuclides [5].(iv) Comparisons of the experimental and theoretical values of the ionisation chamber responses and of the activity concentration values obtained in the above-mentioned methods. The results agree within their estimated uncertainties.

Acknowledgments:

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Activation cross sections of deuteron induced reactions for production of radionuclides for medical, industrial and biological use

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Keywords: deuteron beam; cross sections; radionuclides; medical, biological and industrial use

Activation cross sections of deuteron induced nuclear reactions for practical applications and to test nuclear reaction models were measured up to 50 MeV. in a few limited case up to 90 MeV.

The investigations were done in a collaboration between the Institute for Nuclear Research, Hungarian Academy of Sciences (Debrecen, Hungary), the Cyclotron Laboratory, Vrije Universiteit Brussel (Brussels, Belgium), the Institute of Neurosciences and Medicine, INM-5: Nuclear Chemistry, Forschungszentrum Jülich, (Jülich, Germany), the Cyclotron Radioisotope Center, Tohoku University (Sendai, Japan) and the Institute of Physics and Power Engineering (Obninsk, Russia).

The targets were irradiated with external beams of the cyclotrons at Debrecen (MGC 20E), Jülich (CV28 and JULIC), Brussels (CGR 560), Louvain La Neuve (CGR 930 Cyclone) and Sendai (AVF 110) mostly up to 50 MeV. The standard stacked-foil irradiation method, off-line gamma ray spectrometry and application of the monitor reactions over the whole energy range were used to determine the cross sections.

The investigation includes around 670 reactions induced on the following 64 target elements: Be, B, C, N, Ne, Mg, Al, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Se, Br, Kr, Sr, Y, Zr, Nb, Mo, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb. A significant part of these data was reported for the first time.

A systematic comparison with the theoretical models allows conclusions on the predictive powers of the different codes used (ALICE-IPPE, EMPIRE-II, GNASH, TALYS, PHITS).

The new experimental data give important information for practical applications in the field of medical radionuclide production, thin layer activation technique, radioanalytical applications, development of accelerator and target technology to produce high energy high intensity neutron fluxes, for space technology and in preparation of dedicated activation data files for different projects at research institutes and nuclear data centers.

Deuterons are compared with other light charged particles with regard to availability, beam parameters, stopping powers and production cross sections. Applications in the field of medical iradionuclide production and tracer studies related to technnological and industrial processes are reviewed.

Tb radionuclides for imaging and therapy: how far have we progressed?

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Keywords: Tb radionuclides, ion exchange chromatography, neutron irradiation, ISOL

Terbium is a unique element, as it provides a quadruplet of radionuclides suited for diagnostics and therapy in nuclear medicine [1]. ^{161}Tb (β^- and Auger/conversion electron emitter, $T_{1/2}$ = 6.9 d) was produced by neutron irradiation of enriched ^{160}Gd [2]. Via the PSI-ISOLDE collaboration, researchers have collected and purified ^{149}Tb (α- and β^+-emitter, $T_{1/2}$ = 4.1 h), used for preclinical therapy studies [2] and PET imaging [3], and ^{152}Tb (β^+-emitter, $T_{1/2}$ = 17.5 h), for preclinical [4] and clinical [5] PET imaging, respectively.

No-carrier-added ^{161}Tb was produced by neutron irradiation of enriched ^{160}Gd targets at the SAFARI-1 and ILL nuclear reactors and the spallation-induced neutron source SINQ, respectively (producing up to 20 GBq product). Mass-separated beams of ^{149}Tb and ^{152}Tb, respectively, were implanted at ISOLDE-CERN into Zn-coated Au foils. With 6 hours of collection and 2 hours decay of co-implanted activities, up to 200 MBq ^{149}Tb could be transported to PSI. Collections of ^{152}Tb lasted 4 to 6 hours and up to 600 MBq ^{152}Tb could be shipped to PSI.

At PSI, the chemical separation was performed using a new set-up and manipulators in a hot cell. The target material containing the Tb nuclide was dissolved in HNO_3/NH_4NO_3. The dissolved nuclides were loaded on to a macroporous strongly acidic cation exchange resin and Tb nuclides eluted using dilute α-hydroxyisobutyric acid (α-HIBA). As an addition, the product eluent was passed through a second resin column, to ensure formulation of the product in chloride form.

Various preclinical studies were performed with regard to imaging and therapy. Various improvements to irradiations, collections, chemical separations, as well as results from in vivo studies, will be presented.

Acknowledgements

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Prompt gamma activation analysis

Upgrade to UT-NETL PGAA system to minimize H background

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Keywords: prompt gamma-ray activation analysis, hydrogen measurement, neutron shielding

The Nuclear Engineering Teaching Laboratory (NETL) at The University of Texas at Austin is home to a 1.1 MW TRIGA Mark II reactor with initial criticality in 1992. The NETL reactor is principally designed as a neutron beam facility and includes a prompt gamma-ray activation analysis (PGAA) system with a cold neutron source and curved neutron guide. This system has been used for measurements of various elements in bulk samples including B, Cd, Cl, Hg, Si, and Na, but has recently been used extensively for measurements of H in steel and semiconductor samples. In these samples, the H content can range from 1-500 ppm. In 2018, the sample chamber and system shielding were redesigned to minimize H background counts and decrease neutron absorptions in the HPGe detector. The system design was simulated using MCNP6, built and installed, and then tested using steel samples. Changes to the design included the following: (1) solid materials except for lead, Teflon® (PTFE), and neutron shielding material (B_4C or Li_2CO_3) were removed from the system or shielded from the detector with a minimum of 20 cm of lead to reduce overall background; (2) air was eliminated as a source of H background by placing the entire sample chamber in a PTFE enclosure purged with high-purity He gas; and (3) a neutron shield was designed, fabricated, and implemented around the HPGe detector that consists of a closed PTFE annulus packed with B_4C or Li_2CO_3 powder to minimize neutron absorptions in Ge while maximizing detector efficiency. The new design resulted in an 80% decrease in H background counts, an 88% decrease in Ge peaks, and a 30% decrease in overall Compton background (as shown in Fig. 1), while maintaining Fe count rates. This paper describes the redesign, implementation, and results of the improved system.

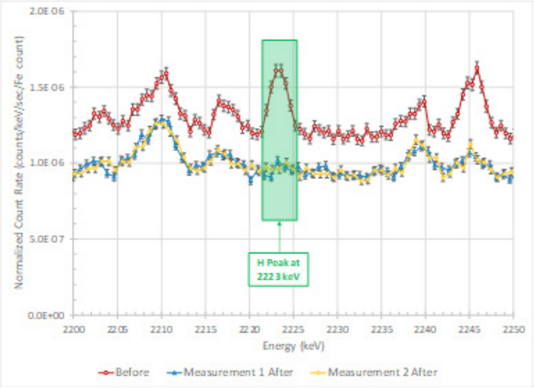

Fig. 1. Measured $^{\text{PGAA}}$ spectrum (counts normalized per count in Fe peak at 1612 keV) for a steel coupon in the UT-NETL system before and after shielding improvements. Two separate measurements (labeled 1 and 2) were performed after the improvements to verify results.

Solving archaeological research problems by prompt gamma activation analyses and complementary techniques

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Keywords: PGAA, archaeological artefacts, Chalcolithic, SW Iberian Peninsula

Archaeology is a field of science focused on the socio-cultural past of man based on the material remains of human activities found during archaeological work/excavations. These materials are often the only remnant of the ancient cultures therefore extremely valuable. Thus, the application of non-destructive techniques is crucial to identify the nature of archaeological artefacts material, particularly those who enable to obtain a set of trace elements that can be used as good fingerprints of raw materials. This study aims to contribute to provenance issues and the identification of the material, by means of compositional studies of both artefacts and potential raw materials (regional and trans-regional) during the Chalcolithic in a very complex and important site in SW Iberian Peninsula. Two types of artefacts were chosen, by its obligatory non-destructive analyses, as well as, by the relevance in identifying what are they made of and where did they come from. The selected artefacts are related with ritual and symbolic activities, comprising a set of cylindrical and anthropomorphic idols and a set of beads. Macroscopic observations indicate that the idols are made of marble or limestone suggesting different origins for these artefacts since both rock types do not occur locally, and that the blackish beads are stone made.

Non-invasive nuclear analytical technique was used at the Budapest Neutron Center, namely Prompt Gamma Activation Analysis (PGAA). In the case of beads the results were complemented by Infrared spectroscopic measurements (FTIR) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectrometry (SEM/EDX).

PGAA proved to be a successful method to determine the bulk composition of the samples, and this way to identify marbles as the raw materials of the idols originating from different geological sources [1, 2]. Results also show that beads are made with shells that were submitted at high temperatures, most probably during funerary rituals [3]. It is important to further enhance the significant results obtained for the archaeological discussion of interaction networks during Chalcolithic in SW Iberia.

Acknowledgments

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Neutron-based elemental analysis of gravels and other concrete-additives

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Keywords: PGAA, NAA, complementarity, activation assessment

Concrete structures of nuclear power plant buildings, research or training reactors, and facilities that use beams of particles can be exposed to high doses of energetic radiation that influence not only the mechanical properties, but also the level of radioactivity of during their service period. Due to the neutron radiation field, certain key isotopes with high-neutron-capture-cross-section can become highly radioactive. Isotopes with long half-life, that remains radioactive long after the reactor shutdown and causing difficulties at the decommissioning phase, must be specially considered.

The objective of this study is to find the proper recipe and the suitable set of ingredients to produce radiation-resistant concretes that are at the same time with low activation susceptibility. To explore the domestically available raw materials, the Hungarian gravel and sand mines (16 mines from 4 different region) were systematically sampled. Different rocks used as additives, as well as several standard types of cements were collected and analyzed for elemental composition and impurities. Major, minor and trace element concentrations of the samples were determined by means of two neutron-based analytical techniques, i.e. prompt gamma activation analysis (PGAA) and neutron activation analysis (NAA), performed at MTA Centre for Energy Research. Complementary X-ray fluorescence (XRF) measurements were also done, to reflect the present industrial practice. However, NAA and PGAA have major advantages over XRF, as they probe exactly the set of isotopes responsible for the radioactivity, with an excellent representativity and metrological quality. Macroscopic, polarizing microscopic investigations, as well as heavy mineral studies have been done to complete and support the results of elemental analysis.

From methodological aspects, this database has highlighted the complementarities and the synergies between the three methods. On the other hand, the outcome of the geological survey pointed towards the conclusion that trace elements with rather long half-lives (2-13.5 y), e.g. Cs, Co, Eu, are enriched in so called heavy minerals (e.g. ilmenite, magnetite, amphibole, rutile, pyroxene, zircon), the accessory constituents (<5%) of the sand and gravel. It was also found that the particle size has an effect on the trace element concentrations: it decreases with increasing particle size, so a crushed larger-particle-size fraction of gravel is recommended instead of sand, to prepare low activation susceptibility shielding concrete. Petrological and geochemical studies revealed that the gravel and sand from the NW Hungarian region has the lowest activation susceptibility.

Acknowledgments

This research was financially supported by the National Research, Development and Innovation Fund of Hungary, in the framework of V4-Korea RADCON collaboration (Grant Number: NN 127102). L.Sz. thanks for the János Bolyai Research Fellowship of the Hungarian Academy of Sciences.

Measurement of the ^{139}La(n,γ) reaction using PGAA and nuclear structure of ^{140}La

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Keywords: prompt gamma activation analysis, level densities, photon strength functions, nuclear structure

The nucleus ^{139}La is an abundant fission product in thermal- and fast-neutron-induced fission of ^{233,235}U and fast-neutron-induced fission of ^{239}Pu. Neutron-capture cross sections for this isotope are therefore an important component for nuclear reactor fuel-related applications. To help address this need, we have measured partial gamma-ray production cross sections for the ^{139}La(n,γ) reaction using guided beams of thermal and cold neutrons incident upon lathanum compounds at the Prompt Gamma Activation Analysis facility of the Budapest Research Reactor. Several nuclear level-density and photon strength function models have been used to assess the statistical-decay properties of the compound nucleus ^{140}La, providing insight into the quality and completeness of the measured data. Furthermore, from the measured reaction cross sections, in conjunction with the statistical-model analysis and an evaluation of the available nuclear structure data for ^{140}La, we have been able to both confirm and determine new spin-parity assignments for many of the low-lying levels populated in this nucleus [1].

This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Numbers DE-NA0003180 and DE-NA0000979. This work is also supported by the Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231 for the US Nuclear Data Program, and the Lawrence Livermore National Laboratory under Contract no. DE-AC52-07NA27344. Additional support was received through the Undergraduate Research Apprentice Program and the Nuclear Science and Security Consortium. The access to the Budapest PGAA facility was supported by Project No. 124068 of the National Research, Development and Innovation Fund of Hungary, financed under the K17 funding scheme.

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Assessment of neutron self-shielding and gamma self-absorption of materials in a white-beam of guided neutrons

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Keywords: PGAA, heterogeneous objects, neutron attenuation, gamma self-absorption

The main advantage of prompt gamma activation analysis (PGAA) is that valuable objects can be analyzed without sampling, even in depth. Neutron self-shielding and gamma self-absorption corrections are routinely applied in case of homogeneous and regular-shaped samples (e.g. powders, metal slabs) [1]. For structured samples, such as layers, or blocks of distinct materials, this simple calculation is not directly applicable, so an extended analytical formula was derived.

Further, the neutron attenuation coefficients required in these calculations are tabulated for the thermal neutron energy only, and not for a polychromatic thermal or cold neutron beamline. These neutron attenuation coefficients for a given beam could be directly determined by neutron radiography, where the transmission of the object is measured, or by neutron tomography, where the pointwise attenuation coefficient is the final result of the 3D reconstruction.

A set of benchmark objects were created from two or three layers of metals, as well as 3×3×3 unit cubes of typical materials, such as Cu, Fe, PTFE, graphite, Pb, Sn, limestone. These represented the major application fields of the Budapest PGAA facilities [2]. They were measured in various geometrical arrangements to generate position-sensitive PGAA and imaging data for validating the calculations of neutron-beam interactions of structured objects. As many of these materials emit gamma-rays at several energies, the effect of gamma-ray self-absorption can also be observed on the identical samples.

Acknowledgments

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Neutron-induced elemental analysis and imaging for archaeometry

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At the prompt gamma activation analysis (PGAA) facility of the Heinz Maier-Leibnitz Zentrum (MLZ) more non-destructive neutron-induced methods are being used for archaeometry. The conventional PGAA provides the bulk composition – for each element the result is a mass fraction averaged over the irradiated sample volume. However, it provides information neither on the distribution of the elements nor the inner structure of an object. Neutron tomography (NT) offers spatial resolution in the range below 100 µm, but provides only basic hints about the elemental composition (absorption coefficients). Therefore, these two methods are combined to obtain the complementary information. As a further step, spatially resolved PGAA – the so-called prompt gamma activation imaging (PGAI) – can be applied. At the MLZ's PGAA facility, it is possible to change the setups for PGAA, PGAI and NT with little effort. We present the investigation of the so-called Celtic rattle rings as an example to show what is possible with the combination of bulk PGAA and NT. We also discuss the opportunities and the limitations of PGAI with the examples of analyses of ancient Roman objects. For instance, it was possible to analyze with PGAI and NT the distribution of the major elements with a resolution in the mm-range and visualize the inner structure of the objects with a resolution below a millimeter. In this way, a closed bronze capsule was analyzed and its content was identified. Finally, we give a short overview about the other recent archaeometry projects and further plans in this field at the PGAA facility of the MLZ.

Quantification of uranium dioxide fuels mixed with boron nitride by using Prompt Gamma Activation Analysis

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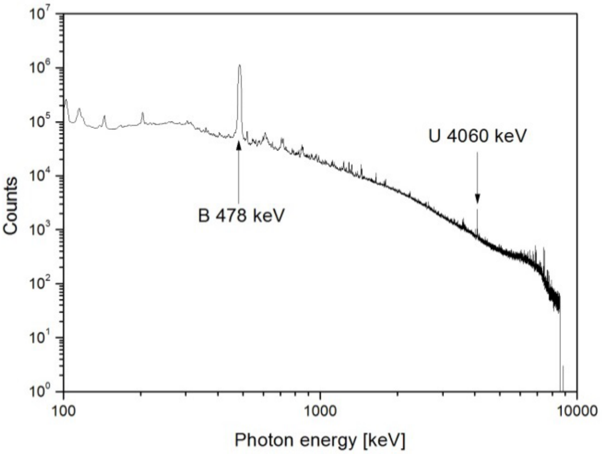
Keywords: Prompt Gamma Activation Analysis, boron, uranium fuels, HYPERGAM

Uranium dioxide or urania sintered pellet is the most widely used uranium fuel. It includes between 1 and 5 wt% of U-235 that releases fission heat in the fission process after absorbing neutrons. Combustible pellets, including neutron absorption additives, are used to control the reactivity of the reactor core. Rare earth elements such as Gd, Ce, and Er have been used as neutron absorption additives. Today, the supply of rare earth elements is not as stable as in the past, and the use of boron elements as neutron absorbers in urania fuels has been attempted since the late 1960s, not rare earth elements. However, boron is bound with oxygen during the sintering process to form boron oxides (B_2O_3) and boron hydroxide (HBO_2 and HBO_3), which have high variability. Boron nitride (BN) is one of the candidates for the additives of urania fuels. The Prompt Gamma Activation Analysis (PGAA) was used to quantify the boron and its volatility in the mixture of urania and boron nitride compound depending on the thermal treatment conditions. Measurements were made using the cold neutron PGAA in the Korea Atomic Energy Research Institute. HYPERGAM with a subroutine of Doppler-broadened peak analysis for boron was utilized.



Figures 1. Typical prompt gamma spectrum for the mixture sample of the uranium dioxide and boron compounds.

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This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korea government (MSIP) (NRF-2018M2A2B3A01071573).

Compositional studies of functional orthodontic archwires using prompt-gamma activation analysis at a pulsed neutron source

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Keywords: PGAA, neutron time of flight, peak interference, neutron energy selection, archwires

Prompt-gamma activation analysis (PGAA) measurements were carried out at the ISIS Spallation Neutron Source on two sets of functional commercial stainless steel orthodontic archwires, aiming at providing insights into the elemental and isotopic composition differences of two nominally equivalent archwires. The results were compared to those obtained from parallel cold neutron PGAA measurements on the same samples at the Budapest Neutron Centre in order to test the current status of PGAA at a pulsed neutron source and eventually to inform improvement in set-up and acquisition methods. In addition, time-resolved PGAA (T-PGAA) that combines PGAA and neutron time-of-flight methods was applied, allowing the measurement of the neutron energy dependence of the PGAA spectra. The advantages of this technique were demonstrated to be that through incident neutron energy selection, spanning 0.07–67.94 eV, enhancement or decrease of specific gamma lines associated with isotopes of interest could be achieved. These were shown to reduce peak interference and to increase the signal-to-background ratio for certain species in order to facilitate accurate elemental identification. Suggestions for potential performance improvement for this evolving technique in order to expand the capabilities of integrated diffraction, spectroscopy and elemental analysis stations at pulsed neutron beamlines are proposed.

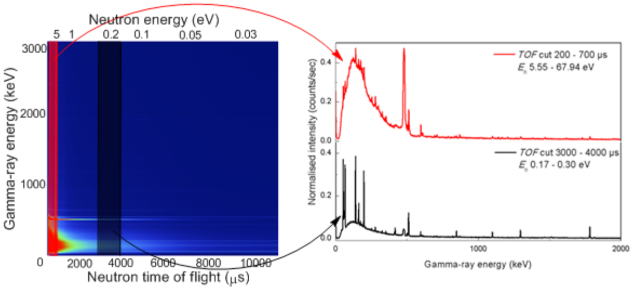

Fig. 1. Count intensity map of γ energy vs. neutron time of flight spectrum of the Azdent samples (left) and the two T-PGAA spectra (right) obtained by neutron time-of-flight selection of 200–700 ms (red) and 3000–4000 ms (black).

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Radioecology and environmental radioactivity

One-pot synthesis of three-dimensional amidoximated polyacrylonitrile nanoparticals/graphene composite hydrogel (PAO-GH) for selective uranium extraction from saline lake brine

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Keywords: uranium, hydrogel, extraction, salt lake brine

In present study, polyacrylonitrile nanoparticals/graphene composite hydrogel (PAO/GH) was prepared through one-pot reduction of graphene oxide and simultaneous enwraping nano-polyacryloniyrile (n-PAN) to the hydorgel structure, follwed by transfroming nitrile groups to amidoxime groups through reacting with hydroxylamine hydrochloride. The obtanied PAO/GH shows a three-dimensional (3D) porous network structure and was characterized by SEM, XRD, FTIR, BET, TGA and Raman analysis. By comparing with the raw grahphene hydrogel (GH) contaning no nano-PAN, the characteization results showed that the enwrapment of PAO nanoparticles to the hydrogel structure not only introduced new amdoxinated functional groups but also led to the partial aggregation of the graphene sheets. The effect of pH, ion strength, contact time and initial U(VI) concentration on U(VI) sorption by GH and PAO/GH, as well as the reusability of PAO/GH were investigated with batch experiments. The kinetic and isothermal studies were also performed by model simulation. Moreover, uranium extraction from brine water acquired from the Salt Lake Potash producing process was discussed and the maximum uranium sorption capacity of PAO/GH for real salt lake sample was found to be 3.5 mg/g, which is in the relative higher range of the investigated uranium sorption materials for seawater uranium recovery[1]. Considering the high uranium extraction capacity and good reusability of PAO/GH, the prepared composite hydrogel may be used as a potential sorbent for obtaining uranium resource from salt lake brines.

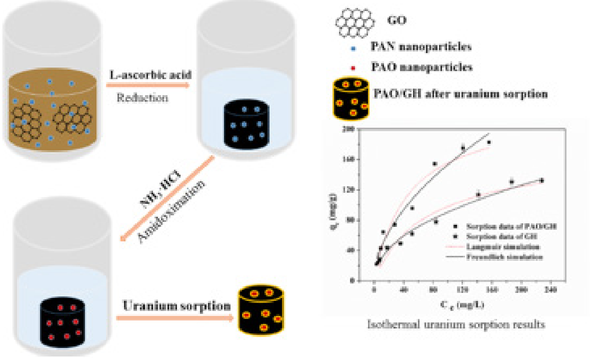

Fig. 1. The schamatic PAO/GH preparation process and the isothermal uranium sorption results

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Sorption of pertechnetate anion by cation modified bentonite

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Keywords: pertechnetate anion, modified bentonite, nuclear waste treatment, anion sorption

Long-lived low- and medium-level radioactive waste and spent fuel assemblies are difficult to store because fissile products can get into the environment. Natural geological barriers do not bind anions from the fission products of ^{235}U [1]. Among the anionic fission products, our work dealt with ^{99}Tc, labeled with ^{99m}Tc radioactive isotope, which has a half-life of 6 hours. The technetium has no stable isotope, it is hard to bind, very little is known about its chemistry, but it can be assumed that it is similar to elements in VII B column (e.g., Mn, Re). Rhenium is quite expensive, so Ca-bentonite was modified with the cheaper manganese.

If it is assumed that $^{99m}TcO_4{}^{-}$ ions react similarly to Mn (II) ions as MnO_4^- ions, then the radionuclide can theoretically be precipitated in $^{99m}TcO_2$ form, thereby it can be sorbed. Therefore, the sorption of $^{99m}TcO_4$ ions was studied on manganese (II) ions modified bentonite. The main purpose of our work was to determine the amount of manganese (II) bentonite and the conditions under which it can bind pertechnetate ions. Our experiences would be interpreted focusing on the pH and redox potential values that determine the chemistry forms, and on thermodynamic data.

The first step was to modify the Ca-bentonite. Mn-bentonite was prepared; the Mn content was $7x10^{-4}$ mol/g, which is 86% of the cation exchange capacity. The sorption of pertechnetate ions were carried out at 4 pH ranges.

From the redox potential and relative binding values, it can be seen that the binding was the most effective in the pH range of 4.6-4.7, approx. 25%. Manganese (II) -bentonite binds pertechnetate ions to a small extent but to a large majority of the results reported so far in the literature.

Similar experiments were carried out with Sn(II) and Cr(III) modified bentonite.

Acknowledgments

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Sequential extraction of Th, U, Ra, Pb and Po for radioactivity assessment in mining residues

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Keywords: extraction, resins, TRU, Sr-resin, Ra-01, AG50Wx8, mining industry

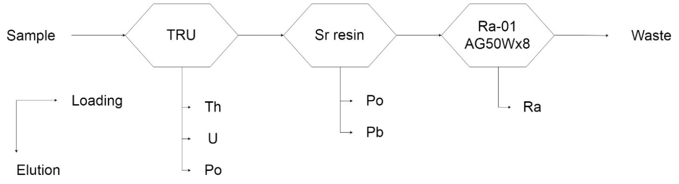
Simultaneous separation and measurement of main radionuclides from uranium and thorium decay series has become one of the challenges encountered by radiochemists with respect to limits imposed by regulators. In fact, the current gamma screening for radioactivity assessment may not be relevant when samples are flirting with governmental regulations [1] due to uncertainties reaching up to 20% [2]. In addition, for such analyses, secular equilibrium is speculated, which is often not realistic, due to the nature of the mechanical and chemical processes performed on the solid in order to extract valuable metals.

Thus, to provide a relevant analysis, major elements from the uranium decay series must be quantified. By doing so, secular or transient equilibrium may be highlighted, and precise levels of activity could be calculated. The targeted radionuclides required by the provincial regulators [3] are : ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po.

Actually, reliable methods have been developed to quantify one or few specific radionuclides from the natural uranium and thorium decay series. However, they lack versatility, robustness and rapidity to be applicable to the mining industries. Moreover, most of the published methods could only be applied to water or diluted samples as they often neglect matrix interferences [4], and thus soils or mineral samples could not be analysed.

The proposed methodology consists in a sequential extraction using extraction and cationic resins (TRU, Sr*Spec, Ra-01 and AG50Wx8). The eluted fractions are then analysed by either ICP-MS/MS or alpha spectrometry. Chemical recoveries are approximately 95% for each analyte in surrogate solutions. Performances with respect to the nature of the loading and elution phase, flow rate, amount of resins as well as the sequence in which they are used will be presented.

Figure



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Retrospective analysis of ^{90}Sr in roe deer antlers originating from north-west Germany

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Keywords: roe deer, antlers, ^{90}Sr, strontium

Sr-90 ($t_{1/2}$= 28.9 y) is a bone seeking pure beta emitter with a high dose coefficient. Antlers of Cervidae are considered effective biomonitors for radiostrontium [1]. Antlers originating from Lower Saxony, Germany, and covering a broad range of the nuclear weapons testing period were collected from hunters. The roe deer (Capreolus capreolus) loses the antlers yearly. Therefore, the level of Sr-90 in the antlers represents the uptake during a single year. Samples from the years 1960-1971 and 1997 as well as from 1913 (as a sample of the pre-nuclear weapons testing period) were collected. In total, 22 antlers were analysed. After challenging sample preparation by sawing and ashing, the classical radiostrontium separation method based on several precipitation steps was applied [2]. The prepared strontium sulphate was measured repeatedly using a low-level proportional counter. The mean value of the Sr-90 activity concentration of the antlers from that region in the 60s was 450 ± 260 Bq/kg dry weight. The results showed a slight correlation with the accumulated annual fallout deposition of ^{90}Sr for the region at that time. There is no correlation between calcium and ^{90}Sr content in the antlers.

Figures

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Determination of mobility and speciation of ^{129}iodine in the soil vadose zone using long-term column experiments

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Keywords: iodine sorption, soil column, vadose zone, speciation

^{129}I is emitted continuously in large amounts by reprocessing plants in La Hague and Sellafield, which lead to an increase of the isotopic ratios ^{129}I/^{127}I from 10^{-12} in the pre-nuclear age to 10^{-7} or above in parts of Europe, today [1]. Due to its long half-life (15 Mio y) and rather high mobility, ^{129}I is also an important fission product to be considered for the long-term assessment of nuclear waste disposal. Many aspects of iodine chemistry in the environment are already known [2], particularly the dominant role of organics and clay in iodine soil interaction. However, detailed process understanding, relevant for radioecological and geochemical modelling, is still missing for many aspects [3]. We report on long-term experiment with undisturbed natural soil columns of approx. 20 cm length, proving upwards migration of iodine in the vadose zone. In contrast to previous studies [4, 5], inhomogeneous soil columns were extracted from natural soil matrix and prepared for the experiments.

Relative iodine amounts (correlated with the added amounts of ^{125}I tracer) increased by factors ranging from 0.25 to 41 in the retardation zones of 4 to 14 cm above solution level. The experimental setup contained soil columns that were kept in contact with iodine solution over a period of 180 days at constant solution level at the bottom of the soil column. To achieve a homogeneous distribution of iodine throughout the column by capillary action, an air filled space is kept on top of the soil inside the column. Furthermore, we performed speciation for different reference soils with selective sequential extraction at low concentrations of $[I] = 10^{-8} – 10^{-4}$ M and XAS measurements at concentrations of $[I] = 10^{-4} – 10^{-2}$ M. Iodide shows rapid transformation into organo-iodine species (<24 h contact time), while iodate proves slow sorption (>30 days contact time), indicating chemical transformation processes before sorption to either soil matrix or soil organic matter. Concluding, we present combined results on iodine migration in undisturbed soil columns and give first insight into iodine speciation in German reference soils [REF].

Figures

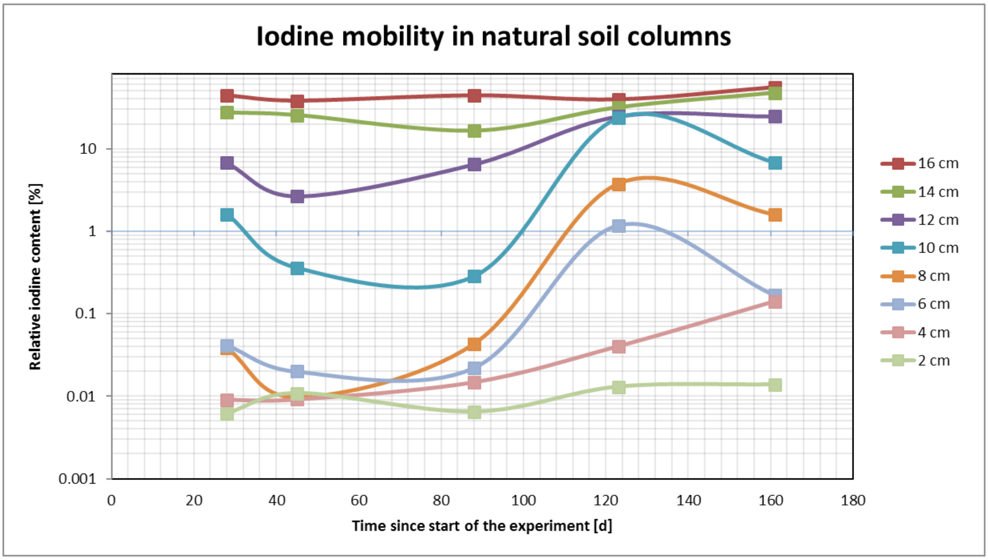

Fig. 1: Relative iodine amount in 18 cm undisturbed soil columns over period of 180 days displayed in 2 cm segments.

Acknowledgments

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Radiation chemistry as a tool in chemical evolution processes

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Keywords: chemical evolution, ionizing radiation, HCN, nucleic acid bases, carboxylic acids

Simulation experiments related to the primitive scenarios have been proposed to have an insight into the possible mechanism for which organic molecules were formed before the appearance of living forms. The simulations are bases in the Oparin-Haldane hypothesis that states that life originated by the abiotic synthesis and subsequent accumulation of organic compounds, through a series of physical and chemical processes, collectively known as Chemical Evolution.

To this end, we studied the radiation-induced reactions of different compounds of biological importance such as HCN, nucleic acid components and carboxylic acids in the presence of a mineral surface. Our results strongly reinforce the possible central role of mineral surfaces in the process of chemical evolution on the early Earth and extraterrestrial environments, and especially, we emphasized that the study of chemical evolution can be a rewarding domain for radiation chemistry to transfer some of its achievements.

Acknowledgments

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Environmental fate of bentonite colloids in aqueous media: Stability and transport

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Keywords: environmental fate, bentonite colloids, stability, transport

Colloids associating with radionuclides provide an important mechanism for radionuclide migration, the mobile colloids in aquifer can enhance the transport of radionuclides toward to geosphere, while the aggregated colloids increases the probability of colloids settlement in porous media due to the increased steric effect and deposition velocity. Therefore, the knowledge on environmental fate of mineral colloids concerning colloidal stability and migration is essential to understand the geological fate of colloids as well as colloids-carried radionuclides. In China, bentonite from Gaomiaozi region (Inner Mongolia, China) has drawn widely concerns as a buffer material in high-level radioactive waste repository. Erosion of the back-filled bentonite blocks by flowing in-situ groundwater is expected to produce bentonite colloids easily. In present work, the stability of bentonite colloids, the sorption characters of Eu(III) on bentonite colloids, and the diffusion behavior of bentonite colloids in quartz column were systematically investigated under various environmental conditions. Results show that the stability of is sensitive with water chemistry conditions, humic substance can significantly promote the colloidal stability. Eu(III) displays great affinity on bentonite colloids under wide environmental conditions. The transport and mobility of Eu(III) in saturated quartz column is highly correlated with the colloidal stability, which is related with the water chemistry at the subsurface. Knowledge from current work can provide an improved understanding on environmental behavior of bentonite colloids as well as a vital reference for safety assessment of high-level radioactive waste repository.

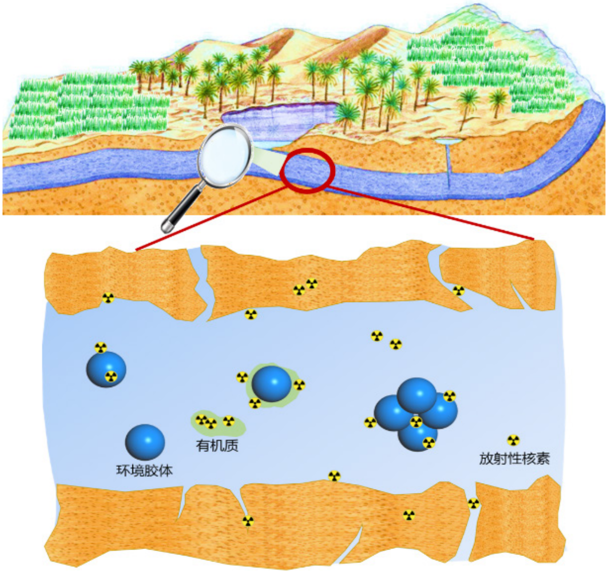

Figure 1. The sketch of environmental behavior of colloids in aquifer.

Influence of calcium on uranium and neptunium sorption on clay minerals at (hyper)alkaline conditions

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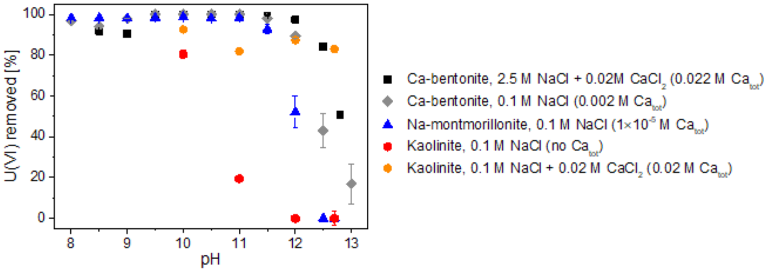
Keywords: calcium, U(VI), Np(V), Np(VI), adsorption, surface charge

Our previous experiments have shown that U(VI) is retained very strongly by Ca-bentonite in the pH range 10-12. Different spectroscopic techniques (site-selective TRLFS, EXAFS) have proven that the underlying retention mechanism under the given conditions was adsorption (not precipitation) despite the negative mineral surface charge and the anionic character of prevailing aqueous U(VI) species. It was hypothesized that attachment is facilitated by mediating calcium cations which are present in the solution. Therefore, the influence of calcium on the sorption of U(VI), Np(V) and Np(VI) at alkaline conditions was systematically studied. These radionuclides were selected as their aqueous speciation at high pH values is characterized by the predominance of anionic hydroxide species. Furthermore the adsorption of ^{45}Ca on clay minerals and the resulting effect on the mineral surface charge was examined.

It was found that ^{45}Ca adsorbed almost completely on Ca-bentonite between pH 8 and 13. Zeta potential measurements showed a partial compensation of the strongly negative surface charge of Ca-bentonite upon introduction of calcium. Hence, calcium is present at the surface, offering possible sorption sites for anionic uranium and neptunium species. Batch sorption experiments at different calcium concentrations revealed enormous effects on the retention of U(VI), Np(V) and Np(VI) between pH 10 and 13. Exemplarily shown for U(VI) in the figure below, the strong retention could not be observed in the experiment with kaolinite, where calcium was completely absent. Consequently, calcium is a crucial factor for the safety assessment of deep geological radioactive waste repositories, where (hyper)alkaline conditions evolve due to cement degradation.



Percentage of U(VI) (5×10^{-7} M) removed from solution by sorption on Ca-bentonite (10 g/L), Na-montmorillonite (10 g/L) and kaolinite (0.5 g/L) as a function of pH. Different total calcium (Ca$_{tot}$) concentrations are achieved by addition of CaCl$_2$ to the background electrolyte or occur due to leaching from the different minerals.

Acknowledgments

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40-year seasonal variation of Tc-99 and Cs-137 in Danish marine environment: implication for environmental monitoring and tracer studies

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Keywords: seaweed, time series, seasonal variation, Tc-99, Cs-137

This work reports comprehensive time-series for ^{137}Cs and ^{99}Tc in seaweed (*Fucus vesiculosus*) and seawater samples collected from Danish coasts (Klint and Hesselø) during 1973-2016. The impact of radioactive discharges from the two European nuclear reprocessing plants (La Hague and Sellafield) and release from Chernobyl accident on the Danish marine environment are clearly detected. The overall results confirm that ^{137}Cs in Danish waters is mainly due to discharges from reprocessing before 1986, and dominated by fallout from the Chernobyl accident since May 1986, while the major source of ^{99}Tc is from ^{99}Tc discharged from La Hague before 1994 and from Sellafield since 1995. Interesting seasonal variations are observed for both ^{99}Tc and ^{137}Cs concentrations in *Fucus vesiculosus,* but with very different patterns which are related to the source terms and metabolic processes of ^{99}Tc and ^{137}Cs in seaweed, as well as oceanic and weather conditions. This study further demonstrates that seaweed serves as an excellent bio-indicator for radioactive pollutants in the marine environment.

Assessment of radiation hazards for athletes or visitors of the Tokyo 2020 Olympic Games

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Keywords: Olympic games, Tokyo 2020, ^{137}Cs, ^{90}Sr, Fukushima, tap water

The Fukushima nuclear accident happened in the aftermath of a powerful earthquake that happened on March 11, 2011 and triggered a tsunami that travelled over eastern Japan with devastating consequences. The tsunami waves also damaged the cooling systems of the Fukushima Daiichi nuclear power plant (FDNPP). A number of other processes resulted in the release of significant amounts of radioactive material. Two big radioactive plumes carried volatile nuclides (e.g. ^{131}I, $^{134+137}$Cs etc.) to the south and the north-west of FDNPP. This caused contamination of various areas of Japan (Fig. 1).

Nine years after the accident, the 2020 Olympic Summer Games will take place in Japan. Olympic venues will include areas, which have been moderately contaminated through the radioactive releases. Many people still have concerns about being part of the games as athletes or visitors.

To assess the radiation hazards for visitors and athletes, various water samples have been collected at the Olympic venues in 2016. The sample material included tap water, bottled water, and surface water samples from the prospective locations of the 2020 Olympic Summer Games. Also air dose rates were determined in Febuary 2018.

Isotopes of interest were ^{90}Sr and ^{137}Cs. Radiocesium were measured by gamma spectrometry (HPGe). Prior to measurement, all samples were filtered (2-4 µm mesh). Measurements were performed by low-level gamma spectrometry in an underground laboratory (Felsenkeller, Germany). For the measurement of ^{90}Sr, the water samples were pretreated by solid phase extraction using SR resin (TRISKEM^{TM}). Afterwards, the activity was determined via LSC (HIDEX 300SL).

In the "Olympic" water samples, detection limits of ^{137}Cs were in the range of 3 mBq/L, however, this low detection limit was exceeded only in one case. ^{90}Sr levels were all under the limit of detection.

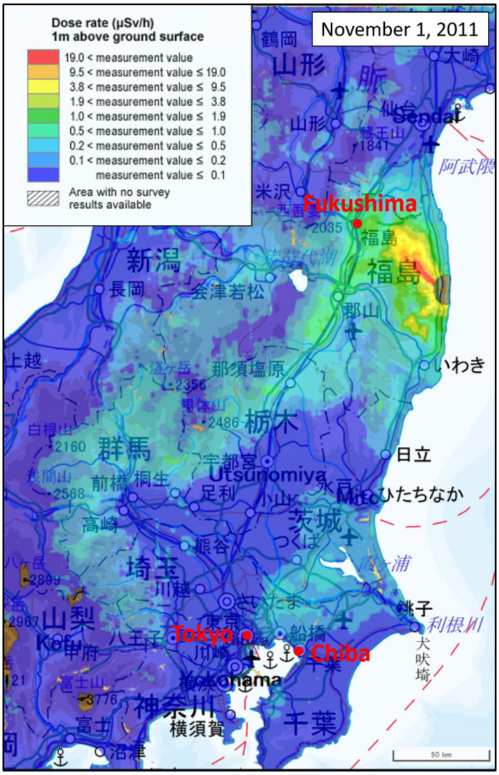

Figure 1. Doserate in Japan at November 1, 2011, after Fukushima desaster. Modified after [1]

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Polonium ^{210}Po, lead ^{210}Pb and uranium (^{234}U, ^{238}U) in food products

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Keywords: food, ^{210}Po, ^{210}Pb, uranium, effective radiation dose

Air, airborne particles and food are the main sources of chemical elements, among them also natural and artificial radionuclides are consumed. The intensity of radioisotopes intake depends on the place of residence, local radiation quantity, diet habits, and food origin. In Poland, statistically, among natural radionuclides in the air the most important is ^{222}Rn, and gives the most significant amount of the radiation dose (about 40%; 1,2 mSv)

Presented are the results on polonium ^{210}Po, radiolead ^{210}Pb as well as uranium (^{234}U, ^{238}U) determination in different food products. So far, during annual radiation doses evaluations in Poland, the most often consumed food products were taken into account. Among naturally occurring radionuclides, their potential ingestion and internal expose, the most important seems to be ^{210}Po and its parent nuclide ^{210}Pb. The studies showed there are some food products (additives, supplements) available that gives a significant amount of radionuclides while having a completely insignificant contribution in the entire diet: mineral supplements (12 μSv), mushrooms (7 μSv) or herbs (10 nSv).

Acknowledgments
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On the use of sediment records to reconstruct historical discharges from a nuclear facility in Sweden

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Keywords: cesium, cobalt, europium, plutonium, americium, curium, sediments, dating

Radioactive releases from Swedish nuclear facilities are reported to and supervised by the Swedish Radiation Safety Authority (SSM). One of these nuclear facilities is Studsvik, located in the Trosa archipelago. Data on annual liquid radionuclide discharges from this facility are available, which gives an excellent opportunity to examine behavior of artificial actinides in the marine environment. The recipient bay, Tvären, has high sedimentation rates (~1cm/y) and undisturbed sedimentation bottoms that enables detailed sediment chronology studies. By comparing inventories of different radionuclides in the sediment cores and the discharge data combined with sediment dating, a validation of the discharge records can be done.

We will present radiometric sediment core data for a suite of radionuclides; γ-emitting nuclides: ^{60}Co, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{154}Eu; α-emitting nuclides: ^{238,239,240}Pu, ^{241}Am, ^{243,244}Cm and β-emitting nuclides: ^{55}Fe, ^{63}Ni, ^{90}Sr. The sediment cores have been dated using a ^{210}Pb model assuming constant ^{210}Pb flux and initial concentration. The obtained actinide data show high activity concentrations for ^{238}Pu and ^{241}Am (up to 56±2 Bq/kg and 65±7 Bq/kg dry mass, respectively), and unique ^{238}Pu/^{239,240}Pu and ^{241}Am/^{239,240}Pu activity ratios (0.2-1.6 and 0.4-1.5, respectively). ^{234}U/^{238}U and ^{235}U/^{238}U activity ratios suggest natural origin of uranium isotopes in Tvären. Our results indicate that the sediments are suitable for reconstructing the history of the nuclear operation discharges in the marine environment.

Uptake and elemental distribution of radiosilver and radiocesium in Shiitake mushrooms

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Keywords: radiocesium; radiosilver; substrate-fruit body uptake; elemental distribution

The ingestion of radionuclides is considered one of the main pathway for long-term internal exposure for humans. For calculating the uptake of these radionuclides in case of accidential releases from nuclear accidents or even nuclear waste repositories, knowledge about the migration of the radionuclides along the food chain is of high importance. Mushrooms are well known to highly accumulate radiocesium in case of releases with long-term effects on the environment, especially in the forest ecosystem [1, 2]. However, the accumulation of radiosilver isotopes ^{108m}Ag ($T_{1/2}$= 438 a)and ^{110m}Ag ($T_{1/2}$= 250 d) in mushroom are scarely studied.

Methods: Shiitake mushrooms were grown on woodchips incubated with Shiitake mcyelium. The substrate was contaminated one time with 100 kBq ^{137}Cs and 900 Bq ^{108m}Ag, respectively. The mushrooms were grown consecutively in 4 cycles and the fruit body were harvested and measured by gamma spectrometry. Cross-sections of the fruit body were used to expose a X-ray film for autoradiography (Figure 1: ^{137}Cs mushroom, 4 weeks exposure). For the exact activity determination, the respective stable isotopes were quantified via LA-ICP-MS. *Results:* Radiocesium was highly accumulated into the mushroom, where the main fraction was found in the spores. Radiosilver accumulation was mainly found in the mushroom stem.

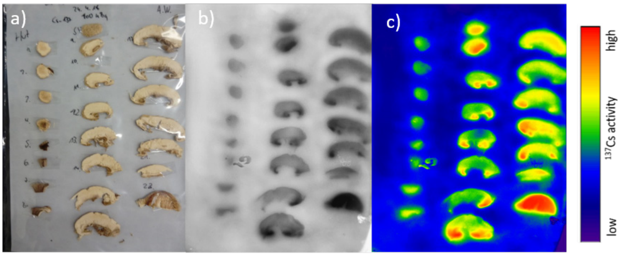

Figure 1: a) Cross sections of 5 kBq radiocesium-containing Shiitake mushroom fruit bodies, b) autoradiograph after 4 weeks, c) Contour plot of the autoradiograph.

Acknowledgments

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Impact of water chemistry on the stability and aggregation of bentonite colloids

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Keywords: bentonite colloids, stability, aggregation, water chemistry

Colloids existing in soils and groundwater aquifers can facilitate the transport of environmental contaminants including radionuclides as well as hydrophobic organic compounds. The mobility of colloids depends strongly on dispersion and aggregation of the particles. Therefore, the environmental fate and stability of colloidal bentonite particles under various conditions are crucial for assessing the safety of radioactive waste repository. In China, bentonite from Gaomiaozi region (Inner Mongolia, China) has drawn widely concerns as a buffer material in high-level radioactive waste repository. Erosion of the back-filled bentonite blocks by flowing in-situ groundwater is expected to produce bentonite colloids easily.

In present work, aggregation of bentonite colloids were investigated by the photon correlation spectroscopy (PCS), effect of water chemistry such as pH, background electrolytes (including Eu3+, Ba2+, Sr2+, Ca2+, Mg2+ and Na+) and humic substance on colloidal aggregation were discussed in detail, and the DLVO model were employed to demonstrate the aggregation process. Results showed that the stability of GMZ Na-bentonite colloids was dependent significantly on cations concentrations and pH values, while slightly on colloids concentrations and anions concentrations, aggregation was getting obvious and kinetically fast when increasing either salinity or acidity. The presence of humic acid enhanced colloidal stability and thus acted as an unstable role in repository terrains. The results in present work can provide a fundamental understanding on environmental behavior of bentonite colloids as well as a vital reference for safety assessment of high-level radioactive waste repository.

Figure

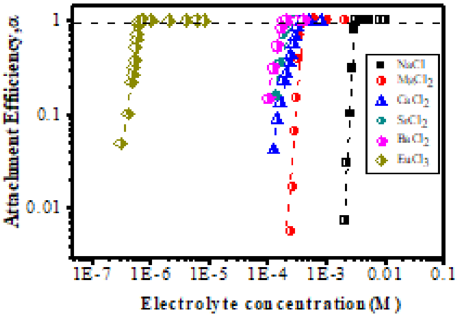

Fig. 1. Attachment efficiencies of bentonite colloids as a function of different cations concentrations. The dashed lines represent a visual guide to distinguish the reaction-limited and diffusion-limited regimes.

Acknowledgments

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Day-resolution temporal variation of iodine isotopes (^{127}I and ^{129}I) in aerosols from Xi'an, China during 2017-2018

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Keywords: Aerosol, ^{127}I, ^{129}I, air pollution, nuclear environmental safety

The high-resolution daily changes of ^{127}I and ^{129}I are now investigated in aerosols in northwest China (Xi'an city) during 2017-2018. There exist obvious seasonal fluctuation and two significant periods for both the two iodine isotopes (Fig.1). The mean ^{127}I concentrations were 10.6 ± 6.0 μg m^{-3} in winter, about three times higher than the value of 3.61 ± 1.49 μg m^{-3} in summer. The level of ^{129}I in winter was about two times higher than spring, fall and the whole year, 3.3 times higher than summer. ^{129}I/^{127}I atomic ratios fell within in a wide range of (10.6-743) ×10^{-10}, with a mean of (101 ± 129) ×10^{-10}, which provides an atmospheric ^{129}I/^{127}I background level in northwest China for the purpose of nuclear environmental safety monitoring. ^{127}I concentrations is found to be strongly positively correlated with air quality index (AQI). The high and low levels in northwest China are controlled by the ^{129}I-enriched Westerly and East Asian winter monsoon and ^{129}I-poor East Asian summer monsoon, respectively. Except the climate reason, the temporal variation of ^{129}I indicates that topographic and metrological conditions in Xi'an are of secondary importance for deposition of ^{129}I. Five ^{127}I peaks fairly coincided with one sand and dust storm in spring, as well as four heavy haze episodes in winter.

This study would have insights into nuclear safety monitoring and air pollution control strategy. Further investigations are expected to focus on the speciation of iodine isotopes especially during heavy haze events for mechanism study of iodine's impact on air pollution.

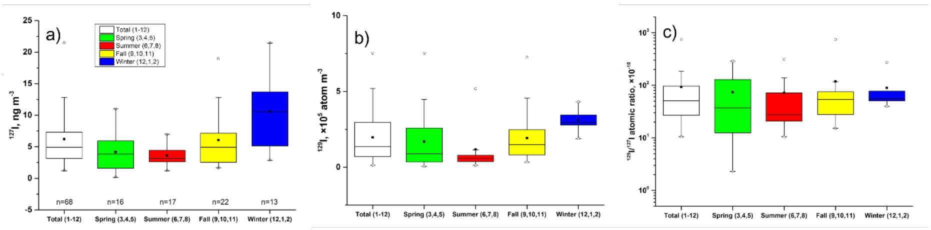

Fig. 1. Seasonal variation of ^{127}I (a), ^{129}I (b) and ^{129}I/^{127}I atomic ratios (c) in aerosols collected in Xi'an, China from March 2017 to March 2018.

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Radiolabeled compounds and radiopharmaceuticals

New promising modified peptide with DOTA-NHS-ester labeled with Ga–68 as early cancers diagnostic tool

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Keywords: Peptide, Cancers, Diagnostic, Ga–68

Integrin family consists of 24 different hetero-dimerized transmembrane receptors which play an important role in many physiological and pathological processes including cell survival, growth, differentiation, migration, inflammatory responses, platelet aggregation, tissue repair and tumor invasion (*1*). There are two major targets for angiogenesis imaging with Positron Emission Tomography (PET); vascular endothelial growth factor receptor (VEGFR) and integrin αvβ3. VEGFR is the most significant and potent stimulator of angiogenesis and integrin αvβ3, a heterodimeric cell surface receptor, plays a significant role in angiogenesis by allowing cells to interact with the extracellular matrix, contributing to the migration of endothelial cells.

In our present study we select a short peptide, containing eight amino acids domain and having affinity towards the αvβ3 integrin receptors over expressed in angiogenesis, and introduce various modifications and then been labeled with ^{68}Ga.

[^{68}G]-DOTA-Peptide was prepared in good radiochemical yield and high radiochemical purity. The product might be a promising for noninvasive imaging of integrin $\alpha v\beta_3$ expression which will be a possible target for early cancer diagnosis. Labelling procedure, purifications and initial in vitro work will be presented.

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Preparation of [^{18}F]ALX5407 via alcohol-enhanced Cu-mediated radiofluorination

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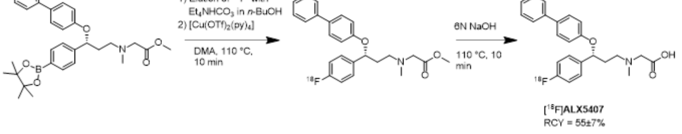
Keywords: glycine transporter type 1 inhibitor, Cu-mediated ^{18}F-fluorination, alcohol enhanced

Glycine is an inhibitory neurotransmitter and a positive modulator of glutamatergic neurotransmission. Extracellular concentration of glycine is regulated by the glycine transporters (GlyT$_{1–3}$). Alterations in GlyT$_1$ and GlyT$_2$ are linked to the pathogenesis and/or treatment of neurological disorders, like schizophrenia, alcohol dependence, pain, epilepsy, breathing disorders and hyperekplexia. ALX5407 is a highly potent and selective antagonist of GlyT$_1$ transporters. Whereas the preparation of ^{11}C-labeled ALX5407 has been already reported no protocol for the production of the radiofluorinated ALX5407 has been published so far. Herewith we disclose the radiosynthesis of [^{18}F]ALX5407 using the protocol of alcohol-enhanced Cu-mediated radiofluorination recently developed in our group.

The chiral aryl pinacol boronate precursor was prepared starting from 1-(4-bromophenyl)-3chloropropan-1-one: the reduction step was followed by Mitzunobu reaction of the resulting alcohol with 4-phenylphenol and thereafter by amination with sarcosine. Finally Miyaura borylation with bis(pinacolato)diboron afforded the desired radiolabeling precursor in 19% yield over four steps. The key step, reduction by catalytic asymmetric hydrosilylation, afforded the corresponding intermediate as the (*S*)-enantiomer in 96% *ee*, whereas the clean inversion of the stereogenic center by Mitzunobu reaction yielded in the desired (*R*)-enantiomer. Radiosynthesis was carried as follows: ^{18}F^{-} (0.1–5 GBq) was loaded onto an anion exchange resin, eluted with a solution of Et_4NHCO_3 (1 mg, 0.7 μmol), in *n*-BuOH (400 μL) and added to a solution of the radiolabeling precursor (15 mg, 30 μmol) and $Cu(OTf)_2(py)_4$ (20 mg, 30 μmol) in DMA (800 μL). The resulting mixture was incubated under air at 110 °C for 10 min furnishing the radiolabeled intermediate in 60% RCC. The latter was hydrolysed with 6 m NaOH at 50 °C for 10 min affording after HPLC purification and formulation [^{18}F]ALX5407 in an ready to use form in a RCY of 55% within 120 min. Alcohol-enhanced Cu-mediated ^{18}F-fluorination provided [^{18}F]ALX5407 in amounts sufficient for its careful preclinical evaluation.

Figures



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Towards a stronger halogen bond involving At – Investigation of halogen-bonded adducts of AtI and Bu_3PO

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Keywords: astatine, halogen bond, competition experiments, relativistic quantum mechanical calculations

Astatine (At, Z=85) is a radioelement belonging to the halogen group. Since its discovery, the basic chemistry of astatine has remained poorly known, mainly due to its rarity and radioactive nature [1]. One of the astatine isotopes, At-211, is considered as a promising candidate for targeted alpha-immunotherapy because of its suitable physical properties (half-life time of 7.2 h and 100% alpha emitter). A prerequisite is to efficiently label carrier-targeting agents with At-211, which requires knowledge on astatine chemistry and to investigate its reactivity.

A halogen bond corresponds to the interaction between an electrophilic region of a halogenated compound R-X (called halogen-bond donor) and a Lewis base B (called halogen-bond acceptor) [2]. Recently, some of us have evidenced the very first halogen bonds involving astatine, that is between the astatine monoiodide (AtI) and nine Lewis bases [3]. The associated equilibrium constants (log K_{BAtI}) were measured through liquid/liquid competition experiments, and compared with the ones obtained for the diiodine donor (pK_{BI2}) [4]. The comparison reveals a quasi-proportional relationship between both sets of constants. The present work aims at extending the previous halogen-bond scale and looking for stronger halogen-bond acceptors for AtI. To this end, the Lewis base tri-n-butylphosphine oxide (Bu_3PO) was selected. It is expected to possess a large log K_{BAtI} value since it possesses a relatively large pK_{BI2} one [4]. In contrast with the previous study, Bu_3PO exhibits a distinct behavior: it can not only lead to 1:1 adduct (B···AtI), but also to 1:2 one (B_2···AtI). The equilibrium constant for the formation of the 1:1 adduct is 4.16 ± 0.34, which is in good agreement with the theoretical calculations. For now, it is the strongest halogen-bond involving At that has been reported. The nature of the 1:2 adduct, which is quite original from a chemist's point of view, will be revealed by means of relativistic quantum mechanical calculations.

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Improved radioiodination of sodium hyaluronate

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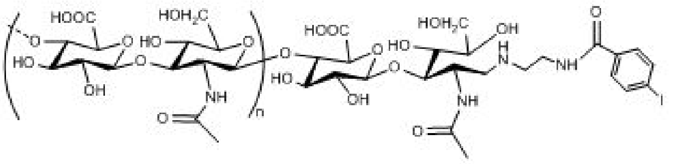
Keywords: radioiodination, hyaluronic acid

Hyaluronic acid (HA) is a polymer of disaccharides made of D-glucuronic acid and D-N-acetylglucosamine moieties which are linked by alternating β-1,4 and β-1,3-glycosidic bonds.[1] HA is found in the body fluids and tissues of most living organisms.[2] This highly hydrophilic molecule binds a thousand times its volume of water,[3] and is commonly used as a medicine. For instance, it is used for pain relief and promotion of joint recovery following arthroscopy or joint lavage. It acts as a temporary substitute for synovial fluid, restoring normal physiological functions.[4]

In order to investigate its synovial fluid functions, sodium hyaluronate with a molecular weight of 300 KDa was radioiodinated via a tributyltin intermediate and formulated following SPECT/CT imaging. In this presentation, an efficient synthetic approach and instrumental analysis for the radioiodinated HA (Fig.) will be presented.

Figure



Structure of radioiodinated hyaluronic acid

Acknowledgments

This work was supported by KBIO HEALTH and KAERI.

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Thermochromatographic isolation of ^{45}Ti from irradiated Sc

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Keywords: Titanium-45, Radiochemical separation, Titanium(IV)chloride

Titanium-45 (^{45}Ti, $t_{1/2}$ = 3.08 h) is an important non-standard radio nuclide exhibiting favorable decay properties for PET imaging due to its relatively low maximum positron energy (E_{max} =1040 keV, E_{avg}= 439 keV) and high β^+ intensity ($I_{\beta+}$ = 84.8%). Furthermore, ^{45}Ti might be of high interest since titanium(IV) complexes with high therapeutic anti-cancer potential have been reported[1,2]. Therefore, labelled Ti-complexes have the potential to gain information about the biodistribution and therapeutic efficiency of Ti-complexes.

However, application of ^{45}Ti is hampered by the lack of separation methods which enable to obtain ^{45}Ti in a chemical form suitable for radiometal complex syntheses. The aim of this work was to isolate ^{45}Ti from scandium by the formation of volatile [^{45}Ti]titanium(IV) chloride, which can be used for further conversions and the synthesis of tetravalent titanium complexes.

For ^{45}Ti production a scandium metal disc was irradiated with 16 MeV protons. The irradiated scandium was heated in a stream of chlorine-argon gas to 900°C yielding scandium(III) chloride and [^{45}Ti]titanium(IV)chloride. Both compounds can be separated by exploitation of their different sublimation points. Hereby, [^{45}Ti]titanium(IV)chloride was trapped at -29°C either directly in a dry vessel or in dry acetonitrile while the scandium(III)chloride was deposited before. First experiments showed a ^{45}Ti-recovery of 25%. The trapped [^{45}Ti] titanium(IV)chloride was directly used for further conversions.

To demonstrate the reactivity of trapped [^{45}Ti]titanium(IV)chloride, the complex ligand FL^4 was added to afford the hydrolytically stable [^{45}Ti]Ti(IV)salan complex [^{45}Ti]TiFL^4. The reaction was carried out in the trapping vessel using dry acetonitrile as a solvent at -29°C in 30 min reaction time. N-ethyl-N-(propan-2-yl)propan-2-amine (DIPEA) was used to activate the salan ligand and to neutralize formed HCl. The radiolabelled complex was obtained in a RCY of 40% (HPLC) and its identity and purity was determined by HPLC analysis using a non-radioactive standard as a reference.

The thermochromatographic work up of the scandium target enabled the isolation and recovery of ^{45}Ti as the corresponding ^{45}Ti-tetratchloro compound which in the future can be converted to clinically relevant complexes.

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Use of a new cation exchange resin for the separation of ^{64}Cu from proton irradiated ^{64}Ni

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Keywords: copper-64, cyclotron, radionuclide separation, positron emission tomography (PET)

^{64}Cu, an intermediate-lived positron emitter ($T_{1/2} = 12.7$ h), is one of the most attractive radiotracer for positron emission tomography and a promising radiotherapy agent.

In this work, a reliable and robust method for the production of ^{64}Cu was developed. ^{64}Cu was produced via the ^{64}Ni(p,n)^{64}Cu nuclear reaction at the research cyclotron facility (Injector 2) of Paul Scherrer Institute. Targets were prepared electroplating enriched ^{64}Ni on Au foil with more than 98% efficiency. After irradiation, the target was dissolved and ^{64}Cu was chemically separated from other elements via column chromatography using AG MP-50 cation exchange resin. The entire process was performed in a hot cell. Chemical purity of Cu and Ni fractions was determined by ICP-MS. ^{64}Ni could be re-used without further purification. The use of AGMP-50 cation exchange resin improved the quality of the final product, i.e. lower Ni and Co content, compared to the common used AG1X8 anion exchange.

The resulting product was labelled with NODAGA-RGD at specific activity up to 500 MBq/nmol°peptide. Preclinical studies have been performed using the obtained product, using albumin-binding folate [1] and PSMA [2].

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Novel ^{18}F-labeled D$_4$-receptor ligands

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Keywords: dopamine, D4 receptor, PET, fluorine, autoradiography, schizophrenia

The dopamine D$_4$-receptor subtype is discussed to be involved in the development of neurodegenerative diseases such as schizophrenia. Specific PET-tracers for more detailed preclinical and clinical investigations are still missing so far. The objective of this work was to develop a D$_4$-selective radioligand, which is not accessible by conventional radiochemical methods. The selected lead structures exhibit high D$_4$R subtype selectivities and a suitable Log*P* values, rendering them attractive for the development of a D4-selective radioligand for PET-imaging. 2-[^{18}F]Fluorophenylpiperazine [^{18}F]**3** (2-[^{18}F]FPP) was obtained by copper-mediated radiofluorination of the Boc-protected precursor **1** followed by deprotection. Subsequently, the desired D$_4$R-radioligand was obtained by reductive amination with 7azaindole3-carbaldehyde using NaBH$_3$CN as reductant. *In vitro* autoradiography was performed on horizontal rat brain slices with the radioligand [^{18}F]**4** to evaluate the binding profile. Additionally, precursor **5** (fig.2) was radiolabeled under the same Cu(II)-mediated conditions. [^{18}F]**2** was prepared in a RCY of 30-80% within 10 min. The reductive amination of [^{18}F]**2** with 7azaindole3-carbaldehyde at 80 °C afforded the desired D$_4$R-radioligand in a RCY of 35 % over three steps, carried out as a one-pot procedure. Autoradiographic examination of [^{18}F]**4** could not reveal discrete accumulation in specific brain areas (fig. 1.II). The radioligand [^{18}F]**6** was obtained within 10 min in a radiochemical yield of 7 % (n = 2). Due to the first in vitro evaluation results of this candidate, the specificity of the tracer appears to be too low as no distinct accumulation in the brain could be found. Automatization of the radiosynthesis on both radiotracers are planned. Additionally, further developments by *in silico* supported refinement of the lead structures, to increase D$_4$-(subtype)specific binding, are in progress.

Figures

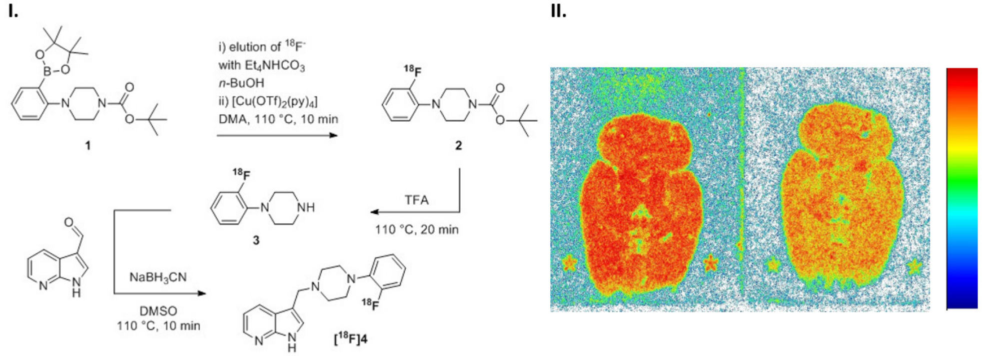

Fig. 1: I) build-up radiosynthesis of the D_4R-radioligand [^{18}F]**4**. II) autoradiography with [^{18}F]**4** (2.5 kBq/mL) on horizontal rat brain slices (Left: without additional blocking agent, showing the total binding profile. Right: with **4** (5 µM) as additional blocking agent, displaying nonspecific binding).

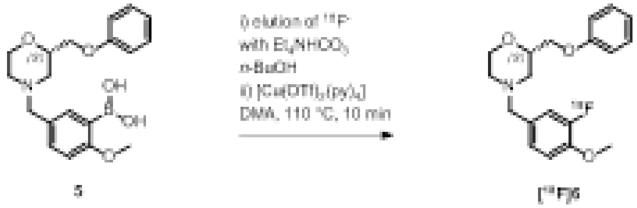

Fig. 2: Cu(II)-mediated radiosynthesis of the D_4R-radioligand [^{18}F]**6**.

Separation, speciation

Use of bifunctional compounds N, P for extracting uranium from aqueous solutions of nitric acid

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Keywords: uranium, zirconium, solvent extraction, nitric media

A new series of N, P bifunctional ligands was found to give excellent extraction properties for uranium from a nitric media [1]. Two of them, which only differ by the presence of an alkyl chain between their reactive sites, gave interesting performance in terms of extraction and selectivity towards zirconium. We could observe that the separation factor U/Zr increased from 21.7 for the unbranched molecule to 220 for the branched one.

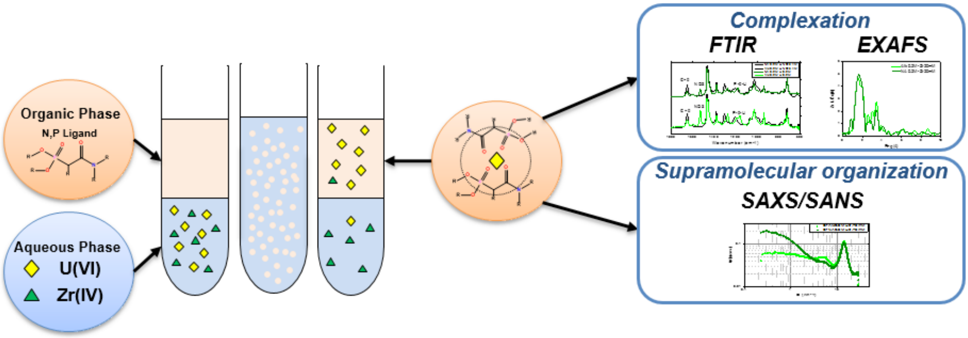
Based on the know-how of the LTSM group in the field of bifunctional ligands synthesis and study and of the CEA / DMRC teams in the data acquisition on major actinides [2], [3], the objective of this study was to explore the capacity of these new molecular architectures for uranium and zirconium extraction, and to understand their extraction mechanisms.

The extraction of cations, acid and water by the new bifunctional ligands were characterized by ICP-AES, coulometry and potentiometry. The molecular structures of the complexes were probed with different techniques such as infrared spectrometry and EXAFS. The organization of the ligands in supramolecular aggregates was assessed by X-ray and neutron scattering measurements, and related to their extraction properties.

It is indeed now well established that the mechanisms underlying the liquid-liquid extraction processes are based not only on the chelating properties of the extracting molecules but also on their capacity to form supramolecular aggregates because of their amphiphilic nature [4] [5] [6]. This study concentrates therefore on both molecular and supramolecular mechanisms to understand and master both chelation and self-assembly properties of these molecules in order to optimize extraction processes.

Thanks to the applied techniques, the influence of this alkyl chain on the selectivity has been put in regards with the complexation of the ligands with the uranium and zirconium and also, with the supramolecular organization in the organic phase.

Figure



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Separation of Fe and Co from decontamination media using ionic liquids

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Keywords: ionic liquids, liquid-liquid extraction, decontamination, radioactive waste

Any decontamination process always generates large volumes of the secondary waste containing the removed contaminants. The main part of this type of waste is usually represented by liquid waste containing low amount of the radioactive substances (usually ILW or LLW types) but its volume is rather large. Therefore strong demand for new technologies capable to remove the radionuclides and recycle the residue exists. One of the possible ways could be the use of the ionic liquids. Ionic liquids (ILs) are the salts with the melting point below 100°C composed of cations (organic including imidazolium, pyridinium, pyrrolidinium, ammonium and phosphonium) and anions (either organic or inorganic) [1] where at least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice. Compared to traditional solvent-extraction behaviour, the metal-ion partitioning in ionic liquid-based extraction systems exhibits high complexities and the designability of ionic liquids could offer a powerful tool for the separation of radionuclides from decontamination solutions [2]. The main aim of this work was to develop a new separation method based on the ionic liquids application for the separation of radionuclides from this type of waste. The proposed two-step separation method consists of extraction of radionuclides from the solutions containing organic complexing agent, such as oxalic and/or citric acids which are usually present in decontamination solutions, by using the ionic liquids, followed by the separation of radionuclides from ionic liquids by electrodeposition. Several parameters strongly influencing the efficiency of extraction (pH of aqueous phase, different type of ionic liquids, concentration of extractant and presence of organic complexing agents) were studied in detail. The conditions for reextraction by electrodeposition were tested as well. It was found out that the method consisting of extraction using ionic liquid and 8-hydroxyquinoline as extractant followed by reextraction by electrodeposition could be very effectively used for the removal of metals and radionuclides even from the organic complexing agents like oxalic or citric acid and represents very promising system for potential recycling of decontamination solutions and thereby reduction of the volume of the the final waste.

Acknowledgments
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Homogeneous liquid-liquid extraction of europium from aqueous solution with [DHbet][Tf_2N] and [THbet][Tf_2N] ionic liquid

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Keywords: homogeneous extraction, europium, complex formation, ionic liquid

Comparing with the traditionally immiscible two-phase extraction, the homogeneous liquid-liquid extraction technique shows potential in industrial separation engineering due to nearly infinite contact interface. In this work the ionic liquid (IL) compounds such as N-(carboxymethyl)-N,N-dimethylethanaminium bis-trifluoromethane-sulfonimide ([DHbet][Tf_2N]) and N-(carboxyethyl)-trimethylammonium bistrifluoromethane-sulfonimide ([THbet][Tf_2N]) were synthesized. The homogeneous extraction behaviors of europium with two ILs were studied as functions of solution pH, ionic strength, contact time, and initial europium concentration. The results indicated that both homogeneous extractions were dependent on pH and independent on ionic strength. The extraction capacities for [DHbet][Tf_2N] and [THbet][Tf_2N] were 3.29 mmol/L and 3.16 mmol/L, respectively. ILs could be recovered using 1.0 M hydrochloric acid. The mole-ratio method indicated the formation of a mononuclear complex between the europium ion and IL. Total europium extraction efficiencies of more than 91% for [DHbet][Tf_2N] and more than 90% for [THbet][Tf_2N] were obtained by quadruple-stage countercurrent extraction. The result proves the feasibility of the homogeneous liquid-liquid extraction technique as an alternative option for europium separation from aquatic solution.

Acknowledgements

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Dropwise analysis of extraction chromatography resins utilizing an on-line mass spectrometry approach

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Keywords: LC-MS, extraction chromatography, separation, mass spectrometry, ICP-MS, dropwise

Extraction chromatography and mass spectrometry are both heavily utilized techniques in the analysis of nuclear materials. The advent of hyphenated techniques that combine chemical separations and the resulting measurements into one continuous stream has greatly reduced the time required and the waste produced in many processes. However, minimal effort has previously been put into developing this technique for extraction chromatography and mass spectrometry. Coupling an Idaho National Laboratory built separation apparatus known as the Gas Pressurized Extraction Chromatograph (GPEC) to a Quadrupole-Inductively Coupled Plasma-Mass Spectrometer (Q-ICP-MS) allows for analysis of samples as they are being separated. This eliminates the wasteful, time consuming, and potentially error-introducing sample preparation steps needed when the two methods are employed separately. By observing the separation as it occurs, the researcher is able to fine-tune the process in order to achieve the resolution necessary to generate measurements completely free of isobaric interferences, thus leading to more accurate and reproducible data. Incorporating a drop collection apparatus provides data on much smaller elution volumes than what was practical in the past. The data produced by this technique, in a fraction of the time that other methods require, can be used to develop better separation schemes for various nuclear fuel cycle samples that require the use of extraction chromatography resins.

Acknowledgments

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Automated system applicable for radiochemical separation

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Keywords: automation, radiochemical, separation, extraction

The analytical methods used for radionuclides are of great interest in the study of environmental radiation because the public is extremely concerned with environmental radioactivity near nuclear facilities. The analytical methods used for working with decommissioning wastes are also of great interest in the nuclear industry. For effective decommissioning of nuclear facilities, the radiological characterization of the waste is essential for its disposal.

The conventional analytical methods used for radionuclides have undergone much development in the past ten years. In particular, the commercialization of resin based on extraction chromatography (for example, Sr-resin) has brought about savings in time and improvements in safety while using such methods. Because such resin can be applied for column chromatography, radiochemical separation with such resins can be performed using valves and pumps. We have developed an automated radionuclide separation system named *KXT-S* (**K**AERI developed e**X**traction **T**echnique-**S**tandard). It can treat up to eight samples simultaneously in single column mode, and up to four samples sequentially in tandem column mode.

In this paper, we present an application of *KXT-S* for determining radioactive strontium and cesium in environmental samples. In addition, we describe *KXT-20*, which allows up to 20 samples to be continuously separated. With application of the PS-resin developed by UB (University of Barcelona), *KXT-20* shows very high throughput when it comes to the analysis of radionuclides. Figure 1(a) shows a schematic diagram of *KXT-S*, whereas Fig. 1(b) shows a conceptual design of *KXT-20*.

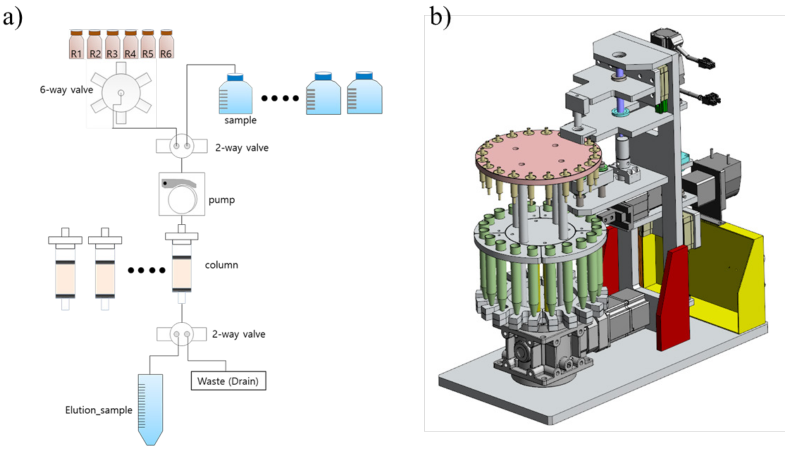

Figure 1. (a) Schematic diagram of an automated radionuclide separation system and (b) conceptual design of *KXT-20*

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Alpha spectrometric determination of polonium-210 for ultra-trace state: Comparative study between extraction and preconcentration techniques

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Keywords: alpha spectrometry, Polonium-210, Cloud point extraction, Drinking water analysis

Polonium-210 is one of the most concerning radionuclides for human being. The major part of ^{210}Po found into the different compartments of our environment origins from natural sources, this radioisotope being part of ^{238}U decay series. From its ubiquitous nature, ^{210}Po can affect a wide range of ecosystems, mainly aquatic environments and water supplies.[1] This radiocontaminant can be naturally released, amongst other processes, from radon-222 emanations or via decay of dissolved radium-226 present in sea water.[2] On the other hand, human activities, including power plants, phosphate or uranium mining, can also release locally significant amount of ^{210}Po,[3] resulting in contamination of surrounding aquifers as well as food chain.[4] Polonium-210 has also been known to cause severe effects on human cells and DNA due to its highly radioactive nature and high kinetic energy. Its radiotoxicity translates into extremely low maximum acceptable concentration of ^{210}Po for drinking water (100 - 200 mBq L^{-1}), the lowest among the naturally occurring radionuclides, prescribed by national (Health Canada) and international (World Health Organization (WHO)) regulators.[5-6] This last feature pose a challenge for its rapid and precise determination by radiometric approach.

The purpose of this research is to highlight the differences between two polonium extraction and preconcentration systems. A commonly used technique in radioanalytical chemistry, extraction chromatography (using N,N,N',N'-tetraoctyl diglycolamide (TODGA)[7]), will be compared with an emerging technique, cloud point extraction. This novel analytical technique is well-suited for radioanalytical measurements as it is environmentally benign while being simple to perform, rapid and inexpensive. For the sake of comparison, the two extraction techniques will be performed with a DGA analog which has demonstrated a strong selectivity for polonium. The coupling of these extraction techniques with alpha spectrometry (α-spec) to achieve the necessary sensitivity in order to carry out the analysis of ^{210}Po in the ultra-trace state, while maintaining a good sample troughput, will also be presented.

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The disposal of highly acidic spent nuclear fuel solutions

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Keywords: extraction chromatography, spent nuclear fuel, ion exchange, cesium, lanthanides, actinides

During previous analytical studies at Paul Scherrer Institute ca. 30 l of acidic waste containing spent nuclear fuel was produced. These have been stored at Hot Laboratory for several decades and now they need to be disposed. In order to fulfill the requirements for cementation, the dose rate, salt content, acidity and volume have to be reduced. Therefore, the main gamma dose emitters (e.g. Cs isotopes) need to be removed. Afterwards uranium and plutonium isotopes should be removed to avoid the criticality issue during the volume reduction (e.g. evaporation). Beside that the extraction and separation of lanthanides and minor actinides isotopes is desirable for scientific purposes. Extraction chromatography was evaluated for separation processes due to its selectivity and operational simplicity. Several sorbents were tested by batch and column methods to select the most suitable sorbent for selective Cs-removal. Batch tests results indicated that AMP (ammonium molybdophosphate), AMP_PAN (AMP is bound with polyacrylonitrile) and AMP/SiO_2 (AMP is immobilized on silica gel) are promising. The column studies showed the high feasibility of AMP_PAN resin for column operation. TBP impregnated resin was evaluated in order to extract U and Pu from the solutions. Dependence of uranium and plutonium uptake by resin was tested in wide range of HNO_3 concentrations. For extraction of lanthanides and minor actinides (Am, Cm) DGA resin was evaluated over the range of HNO_3 concentrations (1mM - 4M) for the loading behavior. In order to separate lanthanides from minor actinides, stripping tests were performed with hydrophilic BTP as a selective complexing agent for actinide elements. Performed tests allowed us to develop the flow sheet for treatment of solutions in order to both fulfill criteria for disposal as well as extraction of scientifically interesting isotopes. Based on the flow sheet pilot device will be built for preliminary tests with diluted solutions.

Separation of ^{93}Mo from irradiated Nb

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Keywords: ^{93}Mo, Nb, $Fe(OH)_3$, Al_2O_3, HF, LSC

Scientific interest in ^{93}Mo is increasing, as it is an important radionuclide in radioactive wastes, which originate from decommissioning of nuclear reactors. However, very few methods for its separation and determination are available in literature; and even its nuclear data are not very well known (for example, its half-life is reported as $(4.0 \pm 0.8) \times 10^3$ years with rather high uncertainty (20%)). In present work, a fast and effective method for separation of Mo from Nb was developed and applied to prepare a pure solution of ^{93}Mo.

The separation method consists of dissolution of the sample, precipitation of Nb_2O_5 and $Fe(OH)_3$, and chromatographic purification of Mo using alumina (Al_2O_3) column. For method development, model experiments with inactive materials were performed. Concentrations of stable Mo and Nb in the solutions from the experiments were measured using ICP-AES (Varian Vista AX CCD). The role of NH_3 in the precipitation step was investigated. To develop an effective chromatographic separation method, the sample was prepared in HNO_3 and HF for loading onto the column, and NH_3 of different concentrations were used for eluting Mo from the column. In the model experiments, recoveries of Mo were ≥ 75%, decontamination factors for Nb were $\geq 10^5$.

This method was successfully applied to separate ^{93}Mo from irradiated Nb, that was taken from a target chamber of a GE Healthcare PETtrace 800 cyclotron. (Long-time irradiation of ^{93}Nb with protons produces ^{93}Mo through the reaction ^{93}Nb(p,n)^{93}Mo.) After the separation, a purified ^{93}Mo solution was obtained, which can be used for further research related to this radionuclide (for example for a more precise determination of its half-life). The separated ^{93}Mo was measured using ultra-low level liquid scintillation spectrometer (Wallac Quantulus 1220).

Acknowledgments

The authors are grateful to Mikael Jensen (Center for Nuclear Technologies, Technical University of Denmark) for providing the irradiated Nb.

Recovery of thorium and uranium from tin smelter slag by bisulfate roasting and leaching

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Keywords: tin slag, thorium, uranium, decontamination, roasting

Slag as secondary product (waste) of tin smelter still contains not only valuable elements e.g. Ti, Nb, Ta, Zr, Hf and rare earth elements, but also radioactives such as Th and U, which grade reaching 0.36% and 500 ppm, respectively. Both radioactive elements are accumulated in the slag phase since the raw materials used in smelting i.e. cassiterite minerals, is closely associated with Th and U containing monazite. Due to valuable element content, the slag becomes major of interest in mineral processing industries, hence the slag needs to be decontaminated before it could be processed further.

Common approach to reduce Th and U content from the slag using leaching process is considered ineffective due to association of Th and U with refractory elements e.g. Si and Ti in the slag. To break down the refractory phases, the roasting approach by using fusing agent is required in order to release Th and U so that they could be leached out using mild lixiviant.

In this research, potassium hydrogen sulfate ($KHSO_4$) and sulfuric acid 1 M was used as fusing agent and lixiviant, respectively. The parameters studied includes molar ratio between fusing agent and refractory elements in slag, roasting temperature, roasting time, particle size and sulfuric acid concentration in lixiviant. The studies so far demonstrated that optimum condition in Th and U removal occurred at molar ratio 6, roasting temperature 400 °C, roasting time 3 hours, slag particle size less than 74 micron. The optimum condition resulted in 44% Th and 34% U removal. These figures are significant compared to the results using direct leaching without roasting, which are 18% and 0.1% for Th and U, respectively.

Extraction of natural radionuclides with ionic liquids

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Keywords: natural radionuclides, ionic liquids, extraction, loading capacity

Ionic liquids (ILs) are salts with a low melting point (below 100 °C) and they are composed of completely dissociated large ions. ILs have many advantages and they are of growing interest in the field of green chemistry. Some of the unique properties of the most widely studied ILs include the large liquid temperature range, high thermal stability, electrical conductivity, and tunable physical properties.[1] Especially the extraction of uranium by using ILs is of enduring interest in the literature as it may also be relevant to spent fuel reprocessing.[2,3]

The presented work is part of a project dealing with purification processes for drinking and waste water. The aim of our work was the extraction of Uranium, Th-234, Ra-226, Pb-210 and Po-210 from aqueous solutions with 11 different ILs, composed from 3 cations ([N1888], [P1888] and [PR4]), and 6 anions ([Ant], [HNBA], [C6SAC], [ASA], [PTB] and [TS]). Additionally to the extraction efficiency we investigated the time necessary for satisfying extraction and the maximum uranium load that can be taken up by the respective IL. We found that also the anion of the uranyl salt strongly influenced the uptake of uranium.

Furthermore, a successful back-extraction of the radionuclides from the IL is desirable in order to be able to re-use the IL for several times. Investigations in our laboratory demonstrated that complete extraction of uranium and Po-210 from water is possible with many ILs, while Th-234, Ra-226 and Pb-210 are extracted only with poor yields.

Figures

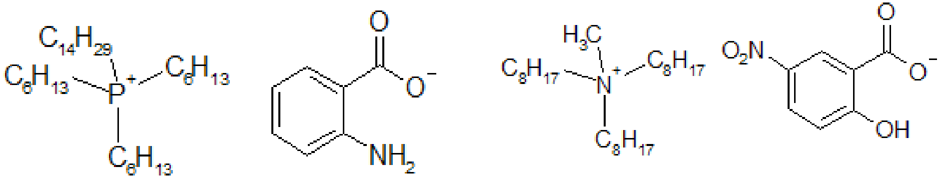

Figure 1: some of the ILs investigated: [PR4][Ant] and [N1888][HNBA]

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Poster Presentations

Actinide analytical chemistry

Actinides reduction in SNF reprocessing studied with UV-Vis spectroscopy and chemometrics

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Keywords: actinides, reduction, UV-Vis spectroscopy, PUREX

Various forms of PUREX process include important stages of uranium, plutonium and neptunium separation. This separation is based on different partitioning of actinides in different oxidation states: Pu(IV) and Pu(VI), Np(IV) and Np(VI) can be easily extracted with tributylphosphate, while Np(V) and Pu (III) are almost cannot. Reduction of Pu(IV) into Pu (III) is usually performed with hydrazine derivatives and kinetics of this process strongly depends on conditions. PUREX process optimization in reprocessing industry requires a thorough study of this kinetics. There are plenty of kinetic data on pure solutions, however it is known that in presence of technetium and iron kinetics of reduction may be seriously disturbed [1,2]. There is a strong interest in industry for elucidation of numerous details regarding this process [3, 4]. Optical spectroscopy seems to be an obvious tool to study process kinetics when metals are involved, however in real complex media there are numerous effects from gas bubbles, colloid particles and other impurities which hinders significantly a straightforward approach. We report the application of multivariate curve resolution – alternating least squares (MCR-ALS) [5] to analyze reduction kinetics of Pu and Np in presence of technetium and iron. UV-Vis spectral measurements were performed in several series of solutions closely mimicking the real reprocessing media. The resulted spectra were extremely noisy and complex due to gas formation (nitrogen from hydrazine) and individual metal bands were not clearly visible to make any processing. Extensive smoothing and baseline correction with asymmetrical least squares algorithm [6] followed by MCR-ALS procedure applied to multiple data sets allowed for obtaining clear concentration profiles of reduced and oxidized forms of neptunium and plutonium. Moreover it was possible to judge on the effect of iron in technological solutions and to determine optimal conditions for operation. The details of the study will be reported in the presentation.

Acknowledgments
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Fusion melting and chemical separation of Am, Pu and Sr from barite concrete

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Keywords: barite concrete, actinides, strontium, hydrofluoric acid, borate fusion, chemical separation

The determination of the radionuclide vector of shielding concrete is a key point in the context of decommissioning nuclear facilities. Barite is a component often used to reinforce concrete, resulting in a density of more than 3 g/cm^3. This material presents a challenge to prepare for nuclide-specific analysis to determine alpha and beta emitters. A classical, but hazardeous chemical route is to digest a barite concrete sample by using hydrofluoric acid (HF). However, due to safety concerns it is highly desirable to have a procedure which avoids the use of HF altogether.

The aim of this study was first, to adapt a fusion melting technique for barite concrete without the use of HF. Secondly, to develop a suitable chemical separation sequence to analyse the radionuclides ^{238}Pu, ^{239,240}Pu, ^{241}Am from the actinide group and ^{90}Sr. A borate fusion technique using Li metaborate / Li tetraborate (80/20 w/w%) was used, which completely dissolves the concrete sample (Croudace et al., 1998; Jäggi and Eikenberg, 2009).

Preliminary experiments with inactive barite concrete and ^{241}Am tracer have shown a complete recovery of 99% of the tracer activity in the HNO_3 solution obtained from the fusion melting process.

For the subsequent chemical separation and preconcentration of the actinides, DGA resin (Triskem) was used. After the elution from the DGA resin, Pu isotopes were purified using an anion exchange resin AG 1-X2 from BIO-RAD. The plutonium eluate was electrodeposited and the activity concentration of the Pu isotopes was subsequently determined by alpha-spectrometry.

Am does not adhere to the BIO-RAD AG 1-X2 resin. It was purified by using the two resins UTEVA/DGA (Triskem) in sequence. Since also lanthanides can be present in barite concrete, an additional purification step was added using a TEVA resin (Triskem). Am was then eluted from the TEVA resin, eletrodeposited and its activity concentration determined by alpha-spectrometry.

Strontium does not adhere to the DGA resin and passes quantitativly through the column. It was then separated by $CaCO_3$ precipitation and further purified by using a Sr resin (Triskem). Finally, the ^{90}Sr activity concentration was quantitatively determined by observing the ^{90}Y ingrowth by liquid scintillation counting.

In summary, the tracer recovery for ^{85}Sr was 63% ± 7.8%, for ^{242}Pu 73% ± 5.7% and for ^{243}Am 79% ± 22.3%. It could be demonstrated that fusion melting of barite concrete, with subsequent total dissolution and radionuclide separation worked well without the use of hydrofluoric acid for the determination of the activity concentrations of various radionuclides.

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Theoretical studies on the actinide endohedral borospherenes

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Keywords: actinides, aromaticity, density functional calculations, metalloborospherenes

Since the discovery of the first all-boron fullerenes $B_{40}^{-/0}$,[1] metal-doped borospherenes have been received extensive attention.[2] So far, in spite of theoretical efforts on metalloborospherenes, the feasibility of actinide analogues remains minimally explored. Here we report a series of actinide borospherenes AnB_n (An=U, Th; n=36, 38, 40) from DFT-PBE0 calculations.[3] All the AnB_n complexes are found to possess endohedral structures ($An@B_n$) as the global minima. In particular, $U@B_{36}$ (C_{2h}, ${}_3A_g$) and $Th@B_{38}$ (D_{2h}, ${}_1A_g$) exhibit nearly ideal endohedral borospherene structures. The C_{2h} $U@B_{36}$ and D_{2h} $Th@B_{38}$ complexes are predicted to be highly robust both thermodynamically and dynamically. Bonding analysis indicates that $U@B_{36}$ and $Th@B_{38}$ can be qualified as 32-electron systems, and $Th@B_{38}$ exhibits 3D aromaticity with σ plus π double delocalization bonding. The results demonstrate that doping with appropriate actinide atoms is promising to stabilize diverse borospherenes, and may provide routes for borospherene modification and functionalization.

Acknowledgments

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Analytical methods and detection techniques

Estimation of uncertainty in concentration measurement processes of iodide ion and molecular iodine

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Keywords: measurement uncertainty, iodide ion, molecular iodine, UV-VIS spectrophotometer

The importance of the measurement uncertainty is increasingly emphasized in the analytical areas, since the measurement uncertainty should be considered when the analysis data are used as part of a basis for making some decisions. In nuclear field, iodine is one of the important elements to be considered, because most of iodine isotopes are radioactive and can be changed into volatile species. Among the iodine species, non-volatile iodide ion (I^-) and volatile molecular iodine (I_2) are representative species when distinguished by their volatilities. In this study, we estimated the measurement uncertainties, which was occurred in the process of the concentration determinations of I^- and I_2 with using UV-VIS spectrophotometer. The concentrations of I^- and I_2 were determined by using 228 and 309 nm absorption wavelengths, respectively. An I_2 separation process by toluene extraction was added before the UV-VIS absorption measurement. From the consideration of all measurement processes, the uncertainty sources were determined to be the values of volume, I^- and I_2 molar masses, purities of standard materials, numbers of repeatability and the calibration equations. It was found that the uncertainty of calibration equation was the most influential source in the processes of I^- and I_2 concentration measurement.

A study of the characteristics of inorganic scintillators for radiation monitors

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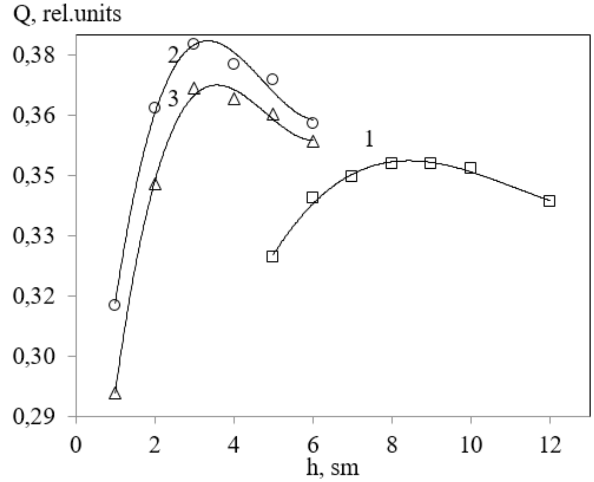
Keywords: radiation monitor, scintillator, detection threshold

Development of a radiation monitor for detection of a smaller amount of nuclear materials and radioactive substances is a complicated problem. One of the methods for solving it consists in substituting higher-efficiency materials for organic scintillators and haloid crystals that are widely used in radiation monitors. Today, there are a number of high-sensitivity scintillating materials that can replace widely used scintillators. In this study, we carried out investigations of the applicability of inorganic scintillators in radiation monitors with the aim of lowering the detection threshold. The evaluation of the effective thickness of a scintillator for a radiation monitor is presented.

Figures



1 – CsI:Tl; 2 – BGO; 3 – CWO

Dependence of the quality factor on the thickness of the scintillator during registration ^{235}U

Study for beta coincidence spectroscopy

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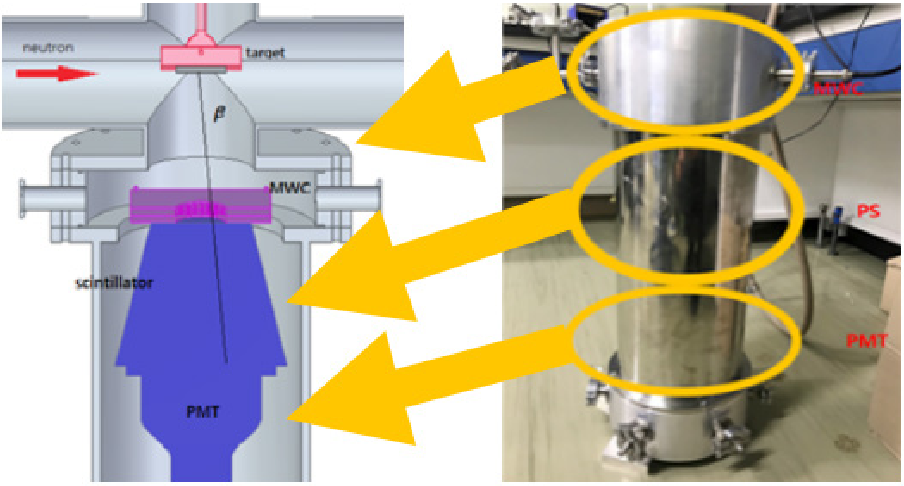
Presented by Jong-Hwa Moon

Keywords: beta coincidence spectroscopy, positron annihilation spectroscopy, measurement of positron yield

Positron annihilation spectroscopy (PAS) has been well-known as a useful tool to investigate the microstructure of materials. KAERI has been studying in-beam PAS system construction based on HANARO research reactor. Measurement of positron yield is considered to be part of the PAS. In this study, we present a beta (positron) coincidence spectroscopy for more accurate measurement of positron yield. Because the important technique in a measurement of positron yield is to eliminate gamma-ray background interference within the beta-ray signal efficiently, we benchmarked the beta coincidence spectroscopy designed by N. Haag, et. al.'s research[1] and used a beta-gamma coincidence counting method. Neutrons provided in beam tube are used to induce (n, γ) interaction at the target to emit beta particles and gamma-rays. In this process, positron is generated by pair production. The principle of beta coincidence spectroscopy: In low-density gases (1) most of the neutrons and photons pass through without interaction and (2) the electrons produce a measurable signal. The beta coincidence spectroscopy implemented using this principle consists of the following sub-detectors: (1) gas-filled multi wire chamber for gamma-ray suppression, (2) plastic scintillator for obtaining the energy spectrum of all beta particle emission processes and (3) photomultiplier. Currently, the beta coincidence spectroscopy has been installed and its performance is being evaluated. In further research the performance of the beta coincidence spectroscopy will be optimized with the measurement of positron yield in ^{63}Ni and ^{90}Sr beta sources instead because the positron production using reactor is in progress.

Figure



Design of beta coincidence spectroscopy

Acknowledgments

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Analysis of radionuclides in Martian meteorites using nondestructive low-level HPGe gamma-ray spectrometry

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Keywords: Chassigny, Nakhla, cosmogenic radionuclides, primordial radionuclides, coincidence-anticoincidence gamma-ray spectrometry

Martian meteorites were produced by impacts of asteroids or comets on the Mars planet, orbiting then for the order of million years around the Sun, and afterwards they finally landed on the Earth. They carry information on the composition and characteristics of Mars surface and subsurface depending on the ejection depth, thus representing unique samples as currently there are no other possibilities to investigate the subsurface of Mars. Cosmogenic radionuclides found in meteorites are products of interactions of cosmic-ray particles with their bodies. They have been widely used to study the origin of meteorites, their orbital history, and cosmic-ray exposure ages, as well as temporal and spatial variations of cosmic rays. We focused specifically on long-lived cosmogenic radionuclides with half-lives above 10 years, and on primordial ^{40}K and on ^{232}Th and ^{238}U (determined using their radiogenic products), which can be analysed non-destructively using high-sensitive HPGe gamma-ray spectrometry. Two meteorites of Martian origin (obtained from the Vatican Observatory) – Chassigny (15.79 g) and Nakhla (153,67 g) were analysed in the Low-level gamma-spectrometry laboratory of the Department of Nuclear Physics and Biophysics of the Comenius University in Bratislava, comprising a large volume lead-iron-polyethylene-copper passive shield housing HPGe detector (70% relative efficiency), NaITl (10 cm dia and 10 cm long) detector for coincidence measurements, and a plastic scintillation detector for anticosmic active shielding [1]. Detailed descriptions of the procedures and calibration of large volume samples are given by [2]. Although accelerator mass spectrometry (AMS) has considerably improve detection limits (especially for beta-emitters such as ^{10}Be and others) and also decreased the required sample size necessary for analysis, the necessity to analyse samples destructively is problematic for such extraordinary samples as Martian meteorites. The low-level gamma-ray spectrometry is a nondestructive technique enabling the analysis of large-volume samples, especially those of high scientific value. Results of analysis of cosmogenic and primordial radionuclides in Chassigny and Nakhla samples will be presented, focusing then on their pre-atmospheric sizes and cosmic-ray exposure ages with implications for their Martian origin.

Acknowledgments

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Dose verification and comparison on flattening filter free beam and flattened beam of IMRT and VMAT using a 3D N-isopropyl acrylamide gel dosimeter

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Keywords: NIPAM gel dosimeter, Optical CT, IMRT, VMAT, flattened beam, flattening filter free beam, gamma evaluation

Polymer gel dosimeters (PGDs) have been widely studied for use in the pretreatment verification of clinical radiation therapy. However, the suitability of PGDs for complex radiation treatment plans or high-dose-rate radiation treatment plans remain unclear. This study aimed to investigate the dosimeter characteristics using photon beam with and without flattening filter of intensity-modulated radiation therapy (IMRT) and Volumetric modulated arc therapy (VMAT) by using 3D N-isopropyl acrylamide (NIPAM) polymer gel. A self-developed optical computed tomography (Optical-CT) was used as a readout tool. Twelve cylindrical acrylic phantoms (10 cm in diameter, 10 cm in height, and 3 mm in thickness) were filled with NIPAM gel and was used to measure the dose distribution of a clinical case of IMRT and VMAT irradiation by using the Elekta Versa HD treatment machine. In current study, a clinic case of brain tumor was modified as the experimental TPS. The irradiation energies for IMRT and VMAT were set as 6 MV photons, but their irradiation angles and dose rates differed during irradiation. The irradiation angles of IMRT were15°, 45°, 105°, 180°, 210°, 240°, 270°, 300° and 330°, and the dose rate was fixed at 600 cGy/min with flattened beam (FF) and the dose rate was fixed at 1400 cGy/min with flattening filter free beam(FFF). VMAT rotated continuously during irradiation, and the dose rate varied from 330 cGy/min to 600 cGy/min with FF beam and the dose rate was fixed at 1100 cGy/min to 1400 cGy/min with FFF beam. Gamma evaluation was performed between TPS and the measured dose map by using optical-CT. For the 3%/3 mm criteria, the passing rates of both IMRT and VMAT at 24, 48, 72, 96 h post irradiation were higher than 95%. The isodose lines of IMRT and VMAT were consistent with those of TPS from 40% to 90%. Scattering and edge enhancement effects are main factors that cause dose inaccuracy in the edge region and reduced passing rates. Considering dose rate dependence, we performed irradiation with variable dose rates by using

VMAT. Results showed that the dose distribution of NIPAM gel was consistent for various dose rate for both IMRT and VMAT radiation. The passing rates were almost the same for IMRT and VMAT irradiation with and without flattening filter. This study reveled that the performance of VMAT is superior than IMRT because VMAT radiation has shorter radiation time than IMRT radiation. In addition, NIPAM gel dosimeter is suitable for high dose rate radiation and is also used for clinical pretreatment verifications.

Feasibility study of in-beam positron annihilation spectroscopy at HANARO research reactor

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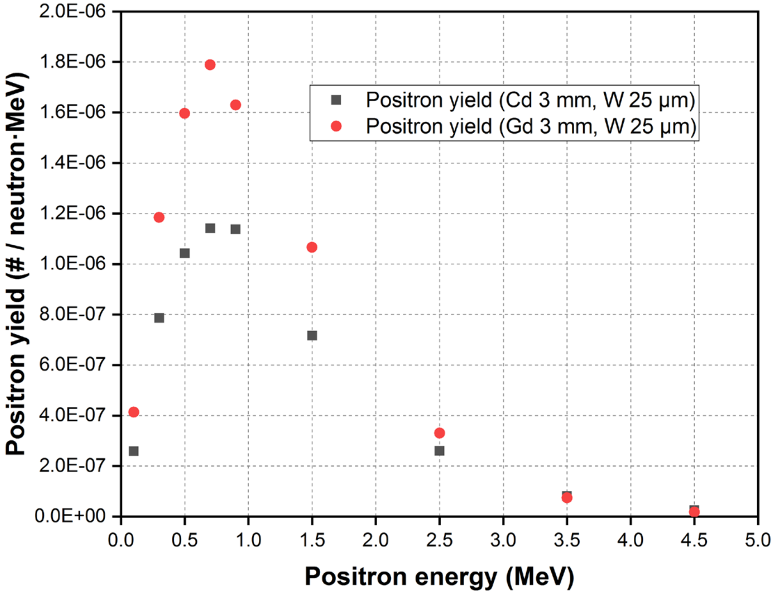
Keywords: positron annihilation spectroscopy (PAS), vacancy defect, research reactor, Monte Carlo simulation

Positron annihilation spectroscopy (PAS) is one of the powerful tools to investigate the small concentration of vacancy-type defects in materials. In classic PAS, radioactive isotopes such as ^{22}Na have been typically used as a positron source. However, conventional radioactive isotope-based PAS system is limited in intensity due to the self-absorption of the positron in the source material. The yield of this positron beam system ranges between 10^4 and 10^6 positrons/cm^2·s, which requires long measurement time. The intense positron beams using a research reactor can solve this problem. The reactor-based PAS system generates the positron beam from positron-electron pair production after thermal neutron capture reaction in ^{113}Cd. We applied the reactor-based PAS system into HANARO research reactor in Korea Atomic Energy Research Institute (KAERI). The calculated thermal neutron flux in the reflector region of HANARO was 6.9×10^{14} neutrons/cm^2·s with 30 MW thermal power. The neutron beam with the calculated energy spectrum was incident to the simple positron converter. Two positron converters were modeled using cadmium and gadolinium sheets. The thickness of a cadmium/gadolinium sheet was 3 mm to convert thermal neutrons into gamma rays. Behind the cadmium/gadolinium sheet, a 25 μm tungsten foil was added for positron beam generated by pair production. The calculated positron flux of the cadmium and gadolinium converters from the neutron flux was 1.32×10^9 and 6.24×10^9 positrons/cm^2·s, respectively. We performed the feasibility study of in-beam positron source at HANARO. It was possible to generate the intense positron beam, which satisfied three-order higher positron flux compared to the conventional ^{22}Na source.

Figure



Positron yield from neutron capture reaction in HANARO.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korea government (MSIP) (NRF-2017M2A2A6A05018529).

^{210}Po determination in industrial air filters

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Keywords: ^{210}Po, aerosols, radiation protection

^{210}Po is a natural radionuclide originating from the Uranium – Radium decay chain. The presence of ^{210}Po in the atmosphere results from ^{222}Rn exhalation followed by series of radioactive decays. Average natural concentration of ^{210}Po in air is 50 μBq/m^3 and does not pose any radiation hazard [1]. On the other hand, various industrial processes lead to abnormal concentration of natural radionuclides in products, waste materials or flue gas. These materials are known as TENORM (Technologically Enhanced Naturally Occurring Radioactive Materials). The most important sources of TENORM are: mining, ores and minerals processing, coal combustion.

The aim of this work was to develop a method for determination of radioactivity of ^{210}Po in industrial air, by measuring indoor air filters.

Particulate matter were aspired from different locations in industrial plant on Petranov and glass fiber filters. Each filter was weighted and cut into smaller samples to allow multiple analysis. In order to determine the content of ^{210}Po number of extraction methods were applied. Reference activity of ^{210}Po was established by total dissolution of a sample with microwave digestion system. The extracts were concentrated and mixed with Ultima Gold^{TM} AB scintillation cocktail and counted with a liquid scintillation counter (LSC) or did undergo radiochemical procedure, plating of polonium on silver disc and counting with alpha spectrometer equipped with PIPS detector. In this work comparison of different extraction techniques was presented.

Acknowledgments

This work was partially supported by the founds of Polish Ministry of Science and Higher Education within the framework of carmarked subsidy for young scientists – decision no 212727/E-78/M/18.

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Study on better kind of collector medium in application of geogas measuring for uranium prospecting

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Keywords: geogas, collector medium, deeply concealed deposits, uranium prospecting

The element anomalies on the ground are usually caused by concealed uranium deposits existing dispersedly in the vertical strata from deep layers to shallow ones. Geogas measuring is one of the prospecting methods with indicating capacity for deeply concealed uranium deposits, figure 1 for its gas pumping schematic. The collector medium is so important for geogas prospecting that collecting abilities of foam plastic (solid) and nitric acid (liquid) ware comparative studied on the known profile No.64 in Xiangshan area. The uranium element concentration in above two media respectively determined by Inductively coupled plasma mass spectrometry (ICP-MS) is shown as figure 2. On the known profile, uranium anomalies indicated by determining results of nitric acid samples could be distinguished distinctly, but uranium anomalies indicated by determining results of foam plastic samples did not. For nitric acid samples, uranium anomaly I and uranium anomaly II appear in position of 750m and 1350m along the known profile, respectively. Anomaly in the range from 1000m to 1200m could be caused by the geological structure there. In consideration that uranium is the mainly determining element in geogas prospecting, liquid nitric acid is one better kind of element collector in application of geogas measuring for uranium prospecting on the basis of above research results.

Figures

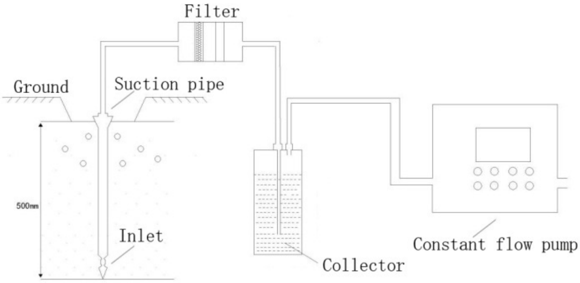

Figure 1. Schematic diagram of dynamic geogas pumping

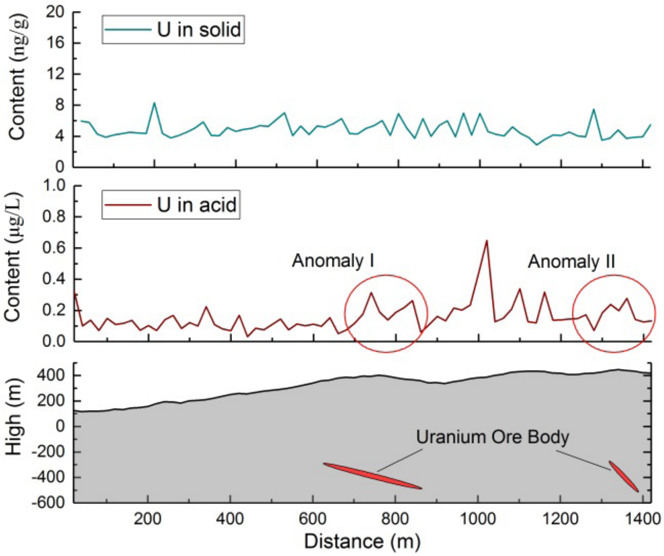

Figure 2. Anomaly profiles of uranium indicated by determining results of solid & liquid collectors

Acknowledgments

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Education in radiochemistry

E-Learning in neutron activation analysis: a challenge to preserve the expertise

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Keywords: e-learning, neutron activation analysis, education

In the past several years the International Atomic Energy Agency (IAEA) has been involved in the development of a detailed E-Learning on-line course in neutron activation analysis. Existing books and guidance documents on the concepts and execution of NAA [e.g., 1-6] are apparently not sufficient to ensure the timely transfer of knowledge on the practice of NAA. The IAEA E-learning tool will not have teachers as points of contact with learners in up to fifty-five Member States with different skillets going online to follow the course. And thus a lot of the success of such an endeavor relies on the individual's self-motivation to study effectively and use additional information on the internet or library to assess published articles and review papers. The over view E-learning scheme is described below.
Up to seven modules are grouped in the following order.

1. Introduction
2. Basic Nuclear Physics
3. Instrumentation
4. Calibration
5. Quality
6. NAA Practice
7. Varieties

Curre.ntly there are 166 registered users on-line from over 40 Member States, 150 CDs distributed, and the off-line version has been was downloaded 85 times. There was a total 2111 activities completed on-line where an activity is going through a lecture of successfully completing a quiz. A map with the countries with enrolled E-learners on-line (gray), or only via CD (green) is shown Figure 1 while the subsection of activities is shown in Figure 2.

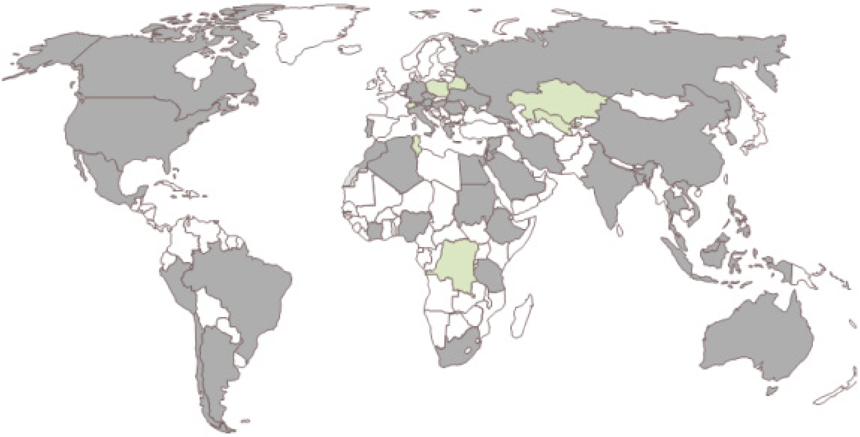

Figure 1. Countries invloved

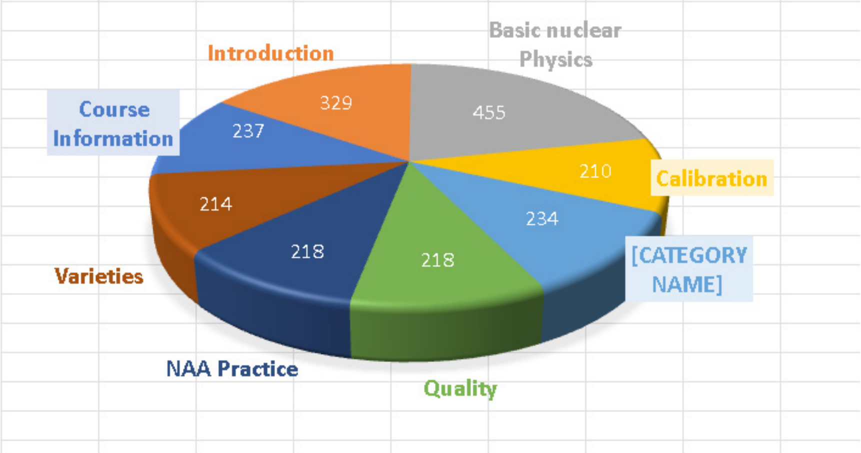

Figure 2. Activities completed on-line in the IAEA E-Learning in NAA.

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Patent trend analysis of radioactive liquid treatment technology

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Keywords: patent, IPC, radioactive liquid treatment technology

As the world's largest source of technical information, patents contain more than 90% of the world's technical intelligence. This paper analyzes the radioactive liquid treatment technology from the perspective of patent. A series of researches are being carried out around the world in the field of radioactive liquid treatment technology, the number of patent applications has grown rapidly. In a worldwide patent database published in various countries, using the IPC(international patent classification) code G21F9/04 which means "radioactive liquid treatment technology" as a search strategy for patent retrieval. As of January 14, 2019, 1689 related patents have been preliminarily retrieved. This paper analyzes the patent applicants, the country of patents, the technical field of patents and the patent application quantity, in order to get the development of patented technology in the field of radioactive liquid treatment technology. It is hoped that this paper can provide a new perspective for technicians in related fields to understand the development trend of radioactive liquid treatment technology.

Figures

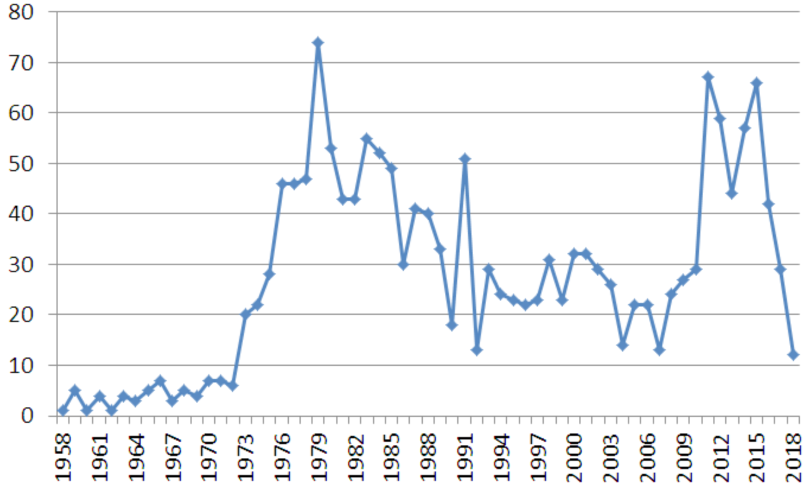

Figure 1. year and number of patent application schematic diagram

Acknowledgments
We thank the CINIE for financial support. We received helpful comments from Zhang Chundong, Wei Guanggang, and many others including members of the nuclear industry patent center. All results have been reviewed to ensure that no confidential information is disclosed.

I-131 Production, release, and measurement

Global ^{131}I activity concentration trends and distributions

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Keywords: ^{131}I, environmental radioactivity, aerosol, CTBT, IMS

This work provides a time history and analysis of ^{131}I atmospheric aerosol concentrations as monitored by the International Monitoring System (IMS) as part of the Comprehensive Nuclear-Test-Ban Treaty (CTBT). The IMS consistes of up to 80 radionuclide stations measuring atmospheric aerosol concentrations for 24-hour measurement cycles. ^{131}I is a fission product and is produced through fission. The most common usage of ^{131}I is for radiotherapy and medical imaging procedures. One of the most common applications for medical ^{131}I is the treatment of hyperthyroidism. The goal of this work is to examine more than a decade of global atmospheric aerosol ^{131}I concentrations. Local and global trends will be identified. Seasonal and long-term trends will be examined as well. Special events including the Fukushima Daiichi nuclear accident.

Liquid scintillation and analysis of long-lived radionuclides

Determination of Ca-41 in electrochemically acquired samples

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Keywords: calcium-41, electrochemically sampling, LSC, radioactive waste

An LSC spectrometric method has been developed for determination of Ca-41 in electrochemically acquired samples from contaminated metal surfaces originated from the Paks Nuclear Power Plant. The aim of measurements is to determine the isotopic inventory of the special solid radioactive waste generated in nuclear power plant during recovery of nuclear incident. The results are necessary for determining the environmental impact of final disposal of radwaste as input for the safety analysis of the repository.

The sampling was conducted electrochemical sampling. During the sampling procedure, following the impregnation of the 40 mm diameter sampling disk (tissue) with electrolyte, the sampling was made by pressing it to the surface to be sampled, then passing electric current through the contact.

The part of radioactive waste came from damaged nuclear fuel, therefore the samples contains fission and activation products, and also contain TRU isotopes from nuclear fuel. So, the main task of the measurement was the development of a proper radioisotope separation process.

The sampling disk was digested during a combined procedure and performed the separation of the Ca-41 using 10 ml quantity of the resulting solution. The solution was purified on TRU resin, applying 8 M HNO_3 onto the column. As the next step of the separation, using H_2SO_4, we made $CaSO_4$ residual, then using 1M HCl and 7M NaOH, the $Ca(OH)_2$ residue was filtered. The chemical yield was determined using $CaCl_2$ carrier. We solved the residue in 1M HCl and placed it into a scintillation vial, and using $GSLT^2$ scintillation cocktail, we measured it using Quantulus 1220 LSC device. ERM-AE701 reference material was used for calibration and validation. The results of the samples from different surfaces (13 pcs) varied between 120.9 ±1.81 and 229.9 ± 2.3 Bq.

By this developed method, the Ca-41 activity value may be reliably determined on samples from metal surfaces. In addition to the radioactive waste management the method may also be suitable for checking decontamination procedures too.

Determination of ^{210}Pb by liquid scintillation counting of ^{210}Pb and its progenies

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Keywords: LSC, ^{210}Pb, ^{210}Bi, ^{210}Po, measurement

Lead-210 is relatively long-lived (half-life: 22 years) beta emitting radionuclide of the natural ^{238}U decay series. The analysis of ^{210}Pb is required in many fields for example NORM related research, geochronology, radioecology, and marine biogeochemistry. For determination of ^{210}Pb various analytical methods have been used such as gamma-spectrometry by measuring the 46.5 keV photon emitted during ^{210}Pb decay, alpha-spectrometry through the determination after ^{210}Po ingrowth, and the methods by measurement of ^{210}Pb or its immediate daughter ^{210}Bi by proportional counting. However, these methods show disadvantages such as poor counting efficiency, self-absorption in the sample for gamma-spectrometry and long waiting time for ingrowth of ^{210}Bi and ^{210}Po, respectively, for proportional counting method and alpha-spectrometry. Meanwhile, liquid scintillation counting method offers limit of detection comparable to those achieved by alpha-spectrometry and have no need to wait for ingrowth of ^{210}Bi or ^{210}Po.

Generally used liquid scintillation counting methods for ^{210}Pb determination involve liquid scintillation counting of ^{210}Pb after elimination of ^{210}Bi interference using double energetic window method or measurement of ^{210}Pb immediately after separation to minimize the effect of ^{210}Bi ingrowth. In this study a novel method for determination of ^{210}Pb by liquid scintillation counting using spectra regions of ^{210}Pb, ^{210}Bi, and ^{210}Po was established.

To prepare calibration standard of ^{210}Pb, extraction chromatography using Sr-resin was conducted. The chemical recovery was determined by gravimetric method with lead oxalate precipitation. The lead oxalate was dissolved in 1 mL of 6M HNO_3 and mixed with 15 mL of ULTIMA GOLD AB scintillator cocktail. The standard sample was measured repeatedly over time after chemical separation of ^{210}Pb from its progenies for estimation of gradually increasing detection efficiency caused by ingrowth of ^{210}Bi and ^{210}Po. Furthermore, the separated ^{210}Pb standard solution with varied quenching effects were prepared by adding different amount of CCl_4 to the standard solution for quenching correction of detection efficiency.

The measured counting efficiency of ^{210}Pb with its progenies was 79% at the time of 30 hours after separation and gradually increased with time. After 39 days from separation time, the counting efficiency was increased up to 171% by ingrowth of ^{210}Bi and ^{210}Po. The detail experimental results about quenching effect, method validation and optimization will be discussed during presentation.

The newly established method for ^{210}Pb determination can be used for analysis of the sample with extremely low activity concentration due to the increased detection efficiency. Moreover, this method allows accurate measurement during the ingrowth of ^{210}Bi and ^{210}Po after separation.

Design of a LabVIEW-based virtual instrument system for gaseous carbon-14 monitoring by on-line liquid scintillation

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Keywords: LabVIEW, virtual instrument, digital coincidence, LSC, on-line monitoring, carbon-14

The gaseous carbon-14 (C-14), released from the ventilation system of nuclear power plants and from the radioactive waste containers in storage facilities, should be regularly monitored for environmental regulatory compliance and for radiation protection of facility workers. The classical methods of C-14 gas monitoring are based on the on-site gas sampling with a commercially available or a in-house designed C-14 bubbler system, and the off-site assays of collected gas samples with the commercial liquid scintillation counters (LSC). The typical LSC systems are so huge and heavy that these instruments are difficult to use for on-line measurement of gaseous C-14 in the field. Recently, a full digital approach to the portable LSC systems based on the coincidence acquisition methods with two or three PMTs have been developed for the in-situ measurement of radionuclides [1,2]. In addition to hardware installation, control software is also required for performing sequences of operations automatically and for the individual control of all instrument components. National Instrument's LabVIEW is a graphical programming language and a powerful tool for the instrumentation control, data acquisition and data analysis. LabVIEW has been successfully applied to the automated fluid handing system [3].

In this study, the conceptual designs of an automated C-14 gas collection system, a digital coincidence LSC system and its virtual instrument system based on the LabVIEW platform were described for the on-line monitoring of the gaseous C-14 effluents from the nuclear facilities.

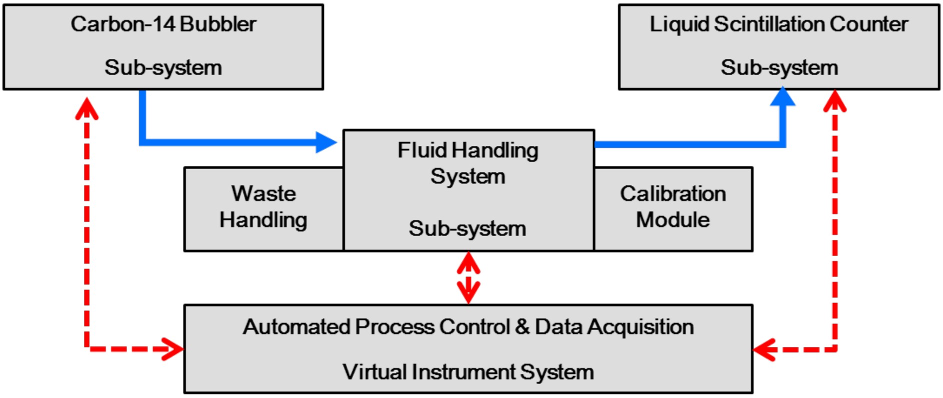

Fig. 1. Block diagram of an automated C-14 gas on-line monitroing system

Acknowledgments

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No.20181520302310).

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Development of a method for determination of ^{222}Rn in water by liquid scintillation counting

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Keywords: ^{222}Rn analysis, LSC, drinking waters, calibration with ^{226}Ra

The aim of this work was to develop, validate and introduce a method for ^{222}Rn determination in water samples by liquid scintillation counting (LSC). This task has become particularly important due to the EC Directive (2013/51/Euratom) requirements and subsequent polish regulations concerning monitoring of water intended for human consumption (Regulation of the Minister of Health of November 13, 2015). According to these regulations radon activity concentration determination is one of the main analyses of radioactive substances carried out for the purpose of assessing the quality of water intended for consumption, which are performed to protect the health of general public.

The applied method was based on the injection of a small amount of water sample under the surface of the organic, water – immiscible scintillation cocktail Mineral Oil Scintillator (PerkinElmer, USA). Due to its high solubility in organic solvents ^{222}Rn is extracted to the cocktail which allows to separate it from ^{226}Ra remaining in the aqueous phase. Measurement in the liquid scintillation counter is performed after 3 hours to establish the radioactive equilibrium between^{222}Rn and its short-lived progenies (^{218}Po, ^{214}Po, ^{214}Pb, ^{214}Bi) .

All measurements were performed using liquid scintillation counter Tri-Carb 3180 TR/SL (PerkinElmer, USA) in glass vials, applied sample to scintillation cocktail ratio was 10:10.

In this work measurement parameters such as measurement mode, discriminator setting and overall efficiency were established by preparing test samples with a known amount of ^{226}Ra standard solution (Czech Metrology Institute) and of similar composition to the real samples. Measurements of test samples were carried out at least 25 days later after the ingrowth of ^{222}Rn in secular equilibrium with ^{226}Ra.

The conducted studies and validation have shown that the investigated method meets the established criteria concerning linearity, repeatability and trueness and is characterised by mean efficiency (refering to three alpha emitting particles and determined in alpha/beta discrimination mode) of 2,67 ± 0,11. Obtained detection limit of 0,58 Bq□dm^{-3} was in compliance with the EC Directive (2013/51/Euratom) requirements. Accuracy of the developed method of ^{222}Rn determination was proven by participation in interlaboratory comparisons.

The conducted analyses have demonstrated that the developed method is applicable to the measurements of radon activities concentration in water in the working range of 1-4500 Bq□dm^{-3}.

Acknowledgments

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Application of the absolute method for determination of tritium and radiocarbon in groundwater from radioactive waste facility

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Keywords: quenched samples, radiocarbon, TDCR, tritium

The triple-to-double coincidence ratio (TDCR) technique is a primary method used for the standardization of beta-emitters and radionuclides decaying by electron capture mode. Developed three decades ago this liquid scintillation counting method was continuously improved and became one of the most important tools in the radionuclide metrology. By using the TDCR method, the activity of low-energy beta emitters such as tritium and radiocarbon may be determined with standard uncertainties not exceeding 1.5 % ($k = 2$). This implies the use of the precise absolute activity measurement in combination with other low-background instruments for detection and quantification of different beta-emitters present in a single sample. The application of the TDCR instrument and an ultra low-level apparatus Quantulus-1220 for the standardization of ^{36}Cl, ^{55}Fe, ^{63}Ni and ^{90}Sr at different activity levels was demonstrated in literature.

Monitoring results in groundwater near a radioactive waste storage facility revealed that tritium might be present in groundwater together with radiocarbon at highly variable activity ratios of these two radionuclides. The separation of radiocarbon from the water samples is a time consuming activity when number of yearly analyses reaches one hundred. To support prompt and reliable monitoring results the double label liquid scintillation counting method was developed. Original groundwater samples may vary in impurities level which affects a quenching of LSC samples prepared for direct measurement. The TDCR device was used for the standardization of tritium and radiocarbon reference solutions which were applied for calibration of the secondary instrument at varying quench levels typical for original groundwater samples. The quench value was assessed with the aid of the Quantulus-1220 instrument as the external sequential quench parameter SQP(E).

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Preset of the PSA value for 1220 Quantulus™ LSC

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The Liquid scintillation counting LSC can be used for simultaneous measurement of gross alpha and gross beta activity concentration in low level liquid effluent samples. To optimize the gross alpha and gross beta analysis, the calibration methodology for 1220 Quantulus™ LSC based on PSA technique using ^{239}Pu and ^{40}K as alpha and beta standards respectively was described in detail (Fig. 1 and Table1.).

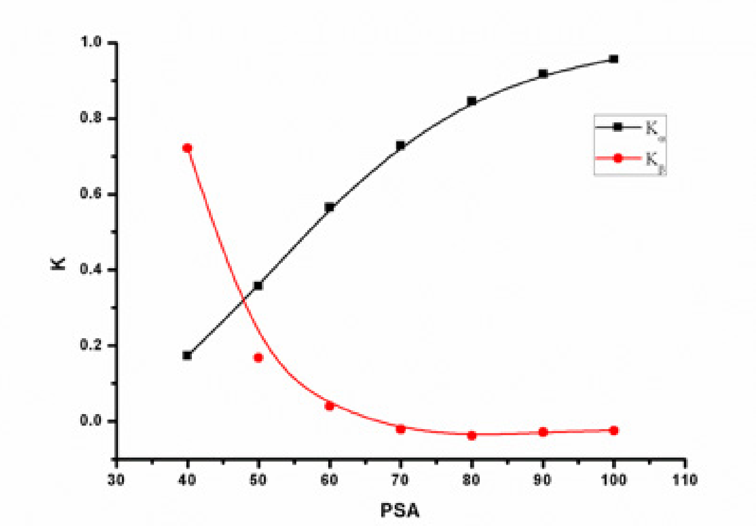

Fig. 1. Optimal PSA dependence on radionuclide (^{239}Pu and ^{40}K) activity concentration, obtained with ULTIMA GOLD AB cocktail.

Table1. K_β and K_α value different preset PSA

^{40}K			^{239}Pu		
SP11	SP12	$^aK_\alpha$	SP11	SP12	$^aK_\beta$
4.88	10.39	0.680	0.75	165.64	0.005
8.54	6.51	0.433	2.11	164.48	0.013
11.65	3.20	0.215	4.77	163.86	0.028
13.49	1.30	0.088	12.38	154.49	0.074
14.36	0.55	0.037	18.81	147.74	0.113

a. K_α= SP12 / (SP11 +SP12); K_β = SP11 / (SP11 +SP12).

Quantulus 1220 ultra-low background liquid scintillation spectrometer was used in this work. Alpha sources for measurement were prepared from a standard solution of ^{239}Pu, with nominal activity of (0.068) Bq/ml. Beta standard radioactive sources (^{40}K) were prepared from a standard solution of K. All LSC samples were prepared in 20 ml high performance glass vials, with 8 ml of active solution and 12 ml of scintillation cocktail. The method of setting the PSA test describes in Fig.1 and Table1. Optimal PSA was 47 which dependence on radionuclide (^{239}Pu and ^{40}K) activity concentration, obtained with ULTIMA GOLD AB cocktail.

For the preset the PSA value in different quenching samples, quench standards were prepared with 8 ml of active solution and 12 ml of scintillation cocktail, adding the increasing amounts of nitric acid (8 M HNO_3). The quenching effect on the PSA value was exhibited on Fig.2. These equations were used to confirm the PSA value of every measuring sample.

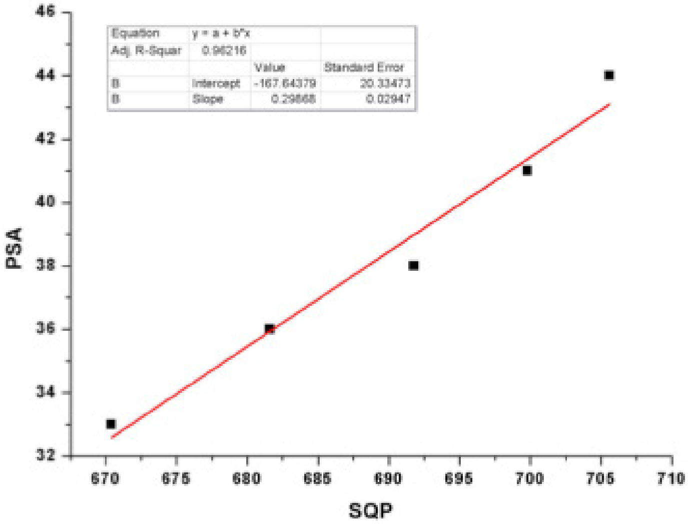

Fig. 2. The lines fitted to the PSA value vs. SQP(E).

In conclusion, we can detect alpha/beta emission simultaneously in the same sample though preset of the correct PSA value and the best PSA value can preset by the experiment. At PSA measuring way, HNO_3 as a quenching agent to simulate calculation PSA value was more becoming and quench calibration curves maybe can utilize as an effective method for the PSA value calculation and applied in the detector of gross alpha and gross beta.

Mass spectrometry

The first AMS laboratory in the Czech Republic – the CANAM infrastructure extension

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Keywords: accelerator mass spectrometry, CANAM infrastructure, radiocarbon, actinides, fission products, cosmogenic radionuclides

Building the first accelerator mass spectrometry (AMS) laboratory in the Czech Republic has recently been started in co-operation of the Nuclear Physics Institute (NPI) of the Czech Academy of Sciences (CAS), the Faculty of Nuclear Sciences and Physical Engineering (FNSPE) of the Czech Technical University in Prague and the Institute of Archaeology of the Czech Academy of Sciences, Prague (IAP). The laboratory will be located on the premises of NPI in Řež and equipped with a multi-isotope low energy AMS system, a complex of new laboratories, including the class ISO 7 clean laboratory, and offices. The AMS system should be capable of measuring low levels of ^{14}C, cosmogenic radionuclides ^{10}Be and ^{26}Al, actinides, namely isotopes of U and Pu, and selected fission products, e.g., ^{129}I.
The application fields of ^{14}C measurement will involve

- Radiocarbon dating in archaeology, paleoecology and other disciplines
- Bomb peak dating for environmental protection and forensic medicine
- Environmental and geological studies, detection of environmental changes
- ^{14}C in the vicinity of nuclear power plants
- ^{14}C in atmosphere and other ^{14}C environmental levels (reference background values)
- Green vs. fossil carbon ^{14}C in fuels (HVO), pharmaceuticals, foods and chemical industry
- Microdosing of pharmaceuticals labeled with ^{14}C

The applications of ^{10}Be and ^{26}Al measurement will involve

- Geochemistry and paleoclimatic change studies (sediments, rocks, glaciers, …)
- Age determination of meteorites and other extraterrestrial materials

The measurements of actinides and fission products will be applied for

- Geochronology, environmental control and monitoring
- Natural fission and neutron reactions
- Nuclear forensics and Safeguards, undeclared nuclear activities, nuclear weapon explosions

The new AMS laboratory will complement the existing NPI infrastructure Centre of Accelerators and Nuclear Analytical Methods (CANAM) that currently comprises the following laboratories – Laboratory of Cyclotron and Neutron Generators, Laboratory of Tandetron, and Neutron Physics Laboratory at NPI. In addition, this new AMS laboratory will also substantialy improve capabilities of joint NPI and IAP radiocarbon laboratory CRL as well as FNSPE radioanalytical laboratories. AMS laboratory will develop into the fourth laboratory of CANAM and should become operational during 2020.

Acknowledgement

This work is realized within the EU, ESIF, OP RDE, MEYS project Nr. CZ.02.1.01/0.0/0.0/16_019/0000728: “RAMSES - Ultra-trace isotope research in social and environmental studies using accelerator mass spectrometry“ .

Mössbauer spectrometry

Study of structural changes for SUS316L using the Positron Annihilation Lifetime Spectroscopy (PALS)

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Keywords: positron annihilation spectroscopy, PALS, SUS 316L, lifetime

The RI positron annihilation spectroscopy system gives us many informations of material such as the presence of defects, the structural changes, and the dislocations of molecules, etc. The austenitic stainless steel 316L (SUS316L) with a thickness of 1 mm (1T) and 4 mm (4T) were prepared using the extrude method. Also, as-prepared samples were annealed at 300 and 700 °C. The positron lifetime was measured to clarify amounts of defects and dislocations in the extrude samples as a function of thickness. The recovery effects of samples heated at 300 and 700 °C were detected using PALS. ^{22}Na wrapped in Ni-foil with a thickness of 2.5 μm was used as a positron source. To prohibit any errors of analysis, a sufficient number of counts were collected for 80,000 seconds (approximately 22 hours). The obtained spectra are shown in Figure 1. The gradient for the right side of the graph for 1T is less than that of 4T sample. It means that lifetime components of the 1T are longer than 4T. The mean lifetime decreased from 331 ps to 247 ps for 1T and 4T, respectively. The same trend was observed in the annealed samples. It can be attributed to the structural deformation as a result of manufacturing processing. With same thickness, the gradients after the peak on the graph for the annealed sample is increased compared to the as-extrude sample. The reason why the slope of the spectrum is further accelerated in the annealed state can be considered as the vacancy-type defect such as the dislocation generated in the sample is repaired during the annealing process.

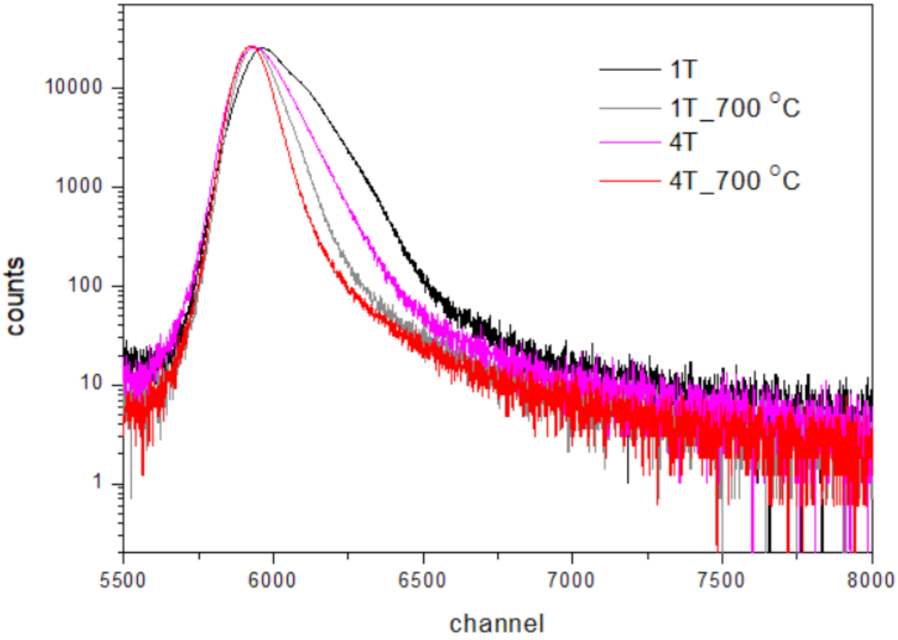

Figure 1. Positron annihilation spectra for the as-extruded and the annealed SUS316L with a thickness of 1mm (1T) and 4 mm (4T).(These are preliminary spectra. Y-axis is expressed as log-scale.)

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korea government (MSIT) (NRF-2017M2A2A6A05018529), and and by the R&D program of Korea Atomic Energy Research (KAERI).

Development of non-destructive isotopic analysis method using negative muon

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Keywords: muonic atom, isotopic analysis, muonic X-ray, non-destructive analysis

A negative muon is one of the elementary particles with the same charge and 206 times higher mass than that of an electron. When a muon is captured by an atom, a muonic atom that has the muon in a muon atomic orbit instead of an atomic electron is formed. The captured muon emits muonic X-rays during deexcitation process after muonic atom formation and finally reaches to muonic 1s state. Due to a large mass of a muon, muonic X-rays have very high energies. Using these high energy X-rays, non-destructive elemental analysis method including light elements for bulk materials has been developed [1].

As well as elemental composition, isotopic abundance provides very important information in various scientific fields. Because muon atomic orbit is very close to the nucleus, the energy of muonic X-ray, especially KX-ray, has large isotope shift. That is, from precise muonic X-ray measurement, isotopic abundance can be identified. In this study, we conducted non-destructive isotopic analysis for lead samples using negative muon.

The muon irradiation experiments were carried out at D2 beam line in J-PARC/MLF. We prepared two lead samples with different isotopic abundance; ^{nat}Pb(^{208}Pb: 51.5%, ^{207}Pb: 22.3%, ^{206}Pb: 24.7%, ^{204}Pb: 1.4%) and ^{208}Pb(^{208}Pb: 99.57%, ^{207}Pb: 0.35%, ^{206}Pb: 0.01%, ^{204}Pb: 0.07%). Muonic X-rays emitted after formation of muonic atom were measured by high-purity Germanium detectors.

The muonic X-ray spectrum is shown in Figure 1(a). The expanded spectra of muonic KX-ray region is also shown in Figure 1(b). Muonic KX-ray peaks from ^{nat}Pb sample had wide width in contrast to these from ^{208}Pb. The high energy components in ^{nat}Pb sample were identified as ^{207}Pb and ^{206}Pb from the peak energies [2]. From muonic X-ray intensity, we determined isotopic abundance of ^{208}Pb, ^{207}Pb and ^{206}Pb as 50.2±2.4%, 23.3±2.1% and 24.1±1.9%, respectively for ^{nat}Pb sample, these values are consistent with the isotopic abundance determined from mass spectroscopy.

Figures

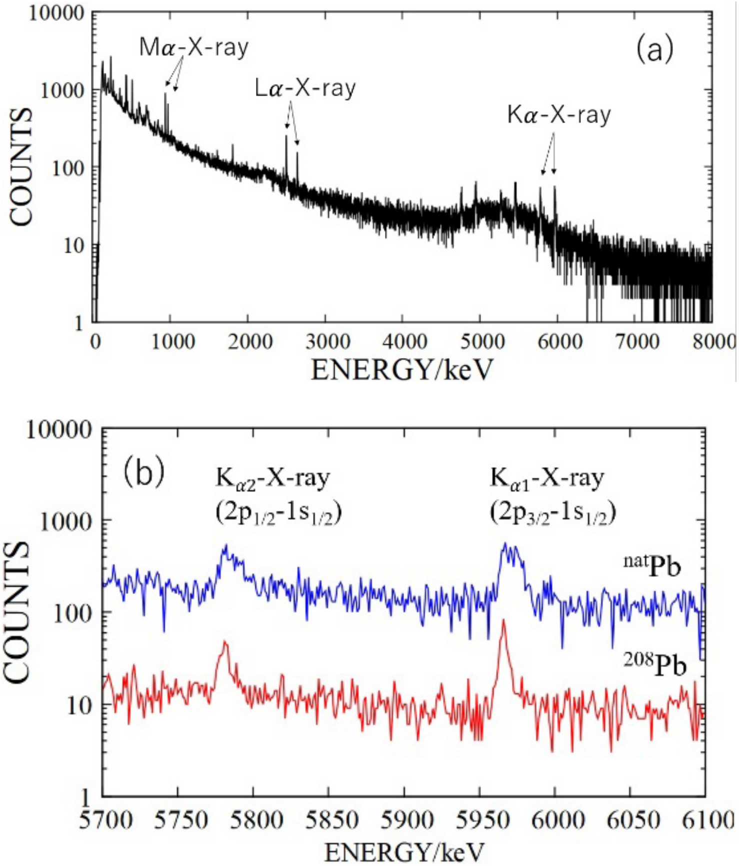

Figure 1. (a) ^{nat}Pb muonic X-ray spectrum, (b) ^{nat}Pb and ^{208}Pb muonic KX-ray spectra (5700-6100 keV)

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Mössbauer spectrometry driven speciation analysis of iron in human brain

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Keywords: Mössbauer spectrometry, *Globus Pallidus*, hyperfine interactions, speciation of iron

This contribution aims at speciation analysis of iron in human brain. Samples of *Globus Pallidus* were extracted post mortem according to the Helsinki Declaration. They were lyophilized (dried in a vacuum) thus providing powder forms. As a principal method of study, ^{57}Fe Mössbauer spectrometry (MS) in transmission mode was used. This technique enables simultaneous examination of both structural arrangement and magnetic states of iron atoms located in the samples. MS experiments were performed at room (~300 K) and liquid helium (4.2 K) temperature. Room temperature Mössbauer spectra show doublet-like features. Such behaviour is typical for fluctuating magnetic moments that acquire arbitrary positions. On the other hand, low temperature MS measurements show significant contributions of sextets that confirmed the expected superparamagnetic behaviour of Fe^{3+} atoms in several species.

Elemental composition of the studied tissues was checked by atomic absorption spectrometry and by neutron activation analysis.

Acknowledgments

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Denitration of simulated radioactive liquid wastes

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Radioactive liquid wastes (HRLW or MRLW) containing great amounts of nitric acid (~ 4 to 7 M) that are generated in nuclear fuel cycle are very undesirable by-product. Denitration of highly acidic radioactive liquids has several adventages. Partial denitration with organic reducens of highly radioactive wastes stored in steel tanks has been used to reduce the corrosion of steel and to minimaze the volume of liquid. Also, denitration reduces volatilization of some radioisotopes, for example, radioactive ruthenium (^{106}Ru) transform from volatile RuO4 form to involatile RuO_2. The gradual increase of pH during the denitration can be used to separate certain radioisotopes which can be utilized in some other technologies. In the present work we investigated some aspects of denitration of simulated radioactive liquid wastes. Denitration of HNO_3 with formic acid was investigated for different (HCOOH)/(HNO_3) ratios. The changes in the induction time, pH-increase and volume decrease were determined. The denitration of two simulated radioactive liquid wastes were also investigated. It was shown that by denitration of these liquids near neutral pH-values can be obtained. The XRD and Mössbauer analysis of the solid phase formed, after excess of HCOOH was oxidized with H_2O_2, showed dominantly the presence of amorphous phase, goethite and hematite, which phases also could be removed with the zeolite carrier due to increased pH of the liquid.

Chemical environmental effect on muon capture processes for iron compounds

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Keywords: muonic atom, muonic X-ray, muon capture process, chemical effect

Muonic atom is one of the exotic atoms having one negatively charged muon in muon atomic orbit. When a muon is stopped in a substance, a muonic atom immediately forms due to larger binding energy of atomic muon than that of atomic electron. In the formation process of muonic atom, chemical environmental effect has been known; muon capture probability for individual atom and initial muon atomic level (principal and angular momentum quantum numbers) just after muon capture are completely different by molecule. For example, per atom muon capture probabilities for nitrogen and oxygen atoms are completely different by each nitrogen oxide molecule such as NO, NO_2 and N_2O [1].

In this study, muon capture processes for iron compounds were investigated. Muon capture ratios and initial muon atomic levels were determined through muonic X-ray measurement emitted after formation of muonic atoms.

Muon irradiation experiments were carried out at M1 beam line in RCNP-MuSIC, Osaka University. We prepared five iron compound samples, Fe(metal), Fe_2O_3, FeO, FeS and $FeCl_2$, for muon irradiation. Muonic X-rays emitted from muonic atoms were measured by high-purity Germanium detectors. Duration times of muon irradiation were about 4 hours for each sample.

Figure 1 shows muonic X-ray spectrum for Fe_2O_3 sample. Muonic X-rays from muonic iron and oxygen atoms were clearly identified. We determined muon capture ratio for each atom from total intensity of muonic X-rays. The initial muon atomic levels can be estimated from muonic X-ray intensity patterns such as K_α/K_β X-ray ratio using calculation of muon de-excitation process [2]. In the case of metal iron sample, the captured muon has small angular momentum quantum number rather than other iron compound samples.

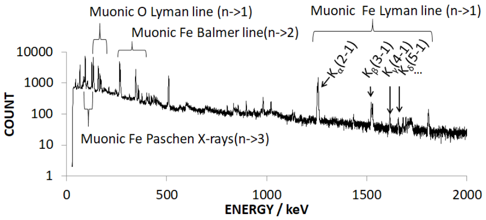

Figure 1: Muonic X-ray spectrum for Fe_2O_3 sample together with assign of each peak.

Acknowledgments

This research was supported by the Grant-in-Aid for Scientific Research (C) (18K11922).

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Study of exchange interaction strength of $Y_{3-x}R_xFe_5O_{12}$ (R= La, Na, and Gd) using Mössbauer spectroscopy

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Keywords: rare-earth doped YIG, Super-exchange interaction, Intra-lattice exchange interaction

The magnetic hyperfine field of single phased garnet $Y_{3-x}R_xFe_5O12$ (R=La, Nd, and Gd) was studied using Mössbauer spectroscopy. The Gd^{3+} and Nd^{3+} are magnetic heavy rare earth ion, and light rare earth ion, respectively. While La^{3+} is non-magnetic ion. The Curie temperature was slightly increased substituting rare earth ions such as Gd, Nd, and La with a relatively larger ionic radius than those of Y (yttrium). The magnetic hyperfine fields (H_{hf}) are slightly decreased, as rare earth ions are substituted into YIG. The ionic radius of doped ion in 24(c) site has more immediate and vital influence on the magnetization. This implies that the bond angle of $Fe_{16(a)}$-O-$Fe_{24(d)}$ is changed, as the 24(c) site is substituted to rare-earth ions with large ionic radius. However, heavy rare earth ion of Gd^{3+} doped YIG shows the lowest values of H_{hf} at low temperature. The intra-lattice exchange link was focused to clarity magnetic properties of R-YIG (R=La, Nd, and Gd).

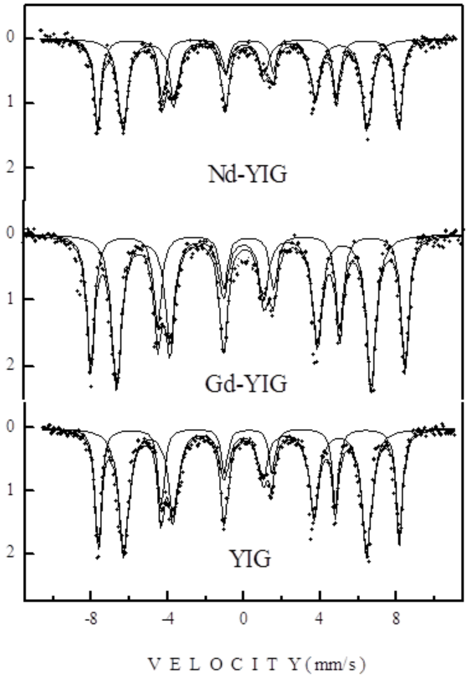

Figure 1. Mössbauer spectra of R-YIG measured at 293 K

Acknowledgments
This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korea government (MSIT)(NRF-2017M2A2A6A05018529).

Neutron activation analysis

Total, bioaccessible and speciation analysis for iodine at nanomolar levels with low measurement uncetainties in nutritional materials by neutron activation at the Dalhousie University SLOWPOKE-2 Reactor Facility

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Keywords: iodine, foods, neutron activation

Iodine is considered an essential trace element for humans. Iodine plays very important roles in the synthesis of thyroxine (T4) and triiodothyroxine (T3) hormones which control oxidation/reduction ratio in cells and are responsible for many functions such as metabolism, blood circulation, muscle activity, and thermoregulation. Deficiency of iodine can lead to goitre disease commonly referred to as iodine deficiency disorder (IDD). The World Health Organization estimates that about 1.6 billion people around the world are at a risk of IDD. Excessive iodine intake can induce hypothyroidism and may contribute to autoimmune thyroid disease in susceptible individuals over the age of 40. Marine fish, seaweeds, eggs and milk are generally the richest sources of iodine in diets. Milk provides 16-30% of the daily dietary iodine intake. Iodine levels in other foods tend to vary quite a bit. Iodide is the most common form of iodine in foods and readily bioavailable. A considerable portion of iodine in muscle meats is bound to proteins although that in milk is not. Much of the iodine in fish is in inorganic form and highly bioavailable. Obviously, total iodine, its chemical species and bioavailable fraction are of much interest in both nutritional and toxicological studies. The determination of iodine at trace levels with high precision and accuracy in nutritional materials is a rather difficult task. To study total, bioaccessible fraction, and speciation of iodine in nutritional materials we have developed several neutron activation analysis (NAA) methods over the decades in our laboratory using the Dalhousie University SLOWPOKE-2 Reactor (DUSR) facility and are summarized here. These NAA methods include instrumental NAA (INAA), epithermal INAA (EINAA), INAA-anticoincidence (INAA-AC), EINAA-anticoincidence (EINAA-AC), Pseudo-cyclic INAA (PC-INAA), PC-INAA-anticoincidence (PC-INAA-AC), PC-EINAA-anticoincidence (PC-EINAA-AC), k_0-INAA, Preconcentration NAA (PNAA), and radiochemical NAA (RNAA). We have evaluated these methods for interference, rapidity, accuracy, precision, overall expanded uncertainty, and detections limits.

Neutron shelf-shielding effects and analysis of rare-earth elements during NAA

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Keywords: neutron activation analysis, neutron self-shielding, rare-earth elements

Determining concentrations of elements with large absorption cross sections can pose a challenge when conduction neutron activation analysis (NAA). Elements such as europium and samarium, whose stable and unstable (created during NAA) isotopes have large cross sections, can result in noticable flux depressions within a sample, which curtails the amount of activated target atoms within a sample. Thus, the analysis of specimens which contain high concentrations of multiple large cross section isotopes will often interfere with attempted measurment. The current work utilizes research from Stewart and Zweifel [1,2], who initially began the developement of an expression for calculating thermal neutron self-shielding, and the more refined expressions which have be more recently created [3-5]. The usage of Monte Carlo N-Particle (MCNP) code has been implemented in order to verify the experimental data. By diluting NIST certified standard lanthanoid solutions, it was possible to create varying concentrations of rare-earth element solutions. These were then irradiated for 30 minutes in a TRIGA reactor rotory specimen rack at a nominal flux of 4.5 x 10^{12} n cm^{-2} s^{-1}. Figure 1 depicts the determination of the activity of the europium samples using an hyperpure germanium detector. It is evident that for these stable isotopes there exist significant self-shielding which distorts the measurments, particularly when there are several of such isotopes present. Our goal is set up an iterative algorithm that accounts for a range of concentrations of rare earth elements in various geological and mining materials such as phosphate and bauxite.

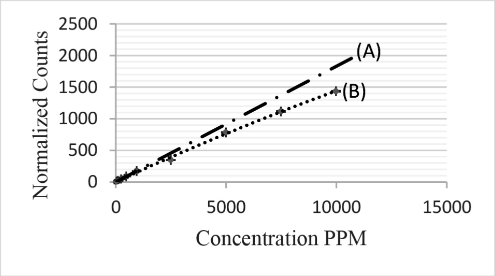

Figure 1: Self-sheilding effects of natural europium at increasing concentrations in an aqeous solution. Where (A) is a typical linear relationship, extrapolated from low concentrations of europium, which is exhibited by most stable isotopes have low neutron absorbing cross sections. And where (B) is experimentally attained results.

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Neutron activation analysis using Kyoto university research reactor

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Keywords: neutron activation analysis, GSJ certified geochemical reference material, ICP-MS, ICP-AES

In Institute for Integrated Radiation and Nuclear Science, Kyoto University, a programme for the cooperative use of Kyoto university research reactor (KUR) has been promoted. Among various kinds of research using KUR, studies using neutron activation analysis (NAA) is also carried out. We contribute to geochemical, environmental and other kinds of research by NAA. One of our studies is NAA of the certified geochemical reference materials prepared by the Geological Survey of Japan (GSJ). Those materials are also subjected to ICP-MS and/or ICP-AES. We are also involved in radiochemical NAA of halogen elements (Cl, Br and I) in Canadian reference materials. The latest studies along this line will be reported in the presentation.

Neutron activation analysis and data mining techniques to discriminate beef cattle feed

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Keywords: cattle feed, classification algorithms, cattle rearing, geographical origin

The feeding method implemented in Brazil today using maize and soy supplementation is a sustainable and competitive alternative to beef cattle rearing. In order to identify geographical origin of beef, it is important to consider the effect of feeding in the beef mineral composition. Samples of two types of feed offered to cattle at finishing stage at the "Beef Passion" production farm, Nhandeara, SP, Brazil, were collected during fourteen consecutive days. The first was composed by corn germ (30%), citrus pulp (29%), corn silage (17%), corn grain (13%), almond meal (7%) and "Núcleo NB Performa" salt (4%) and the second by corn grain (30%), citrus pulp (22%), corn germ (20%), corn silage (16%), soybean (7%) and "Núcleo Nutron Wagyu" salt (5%). All the vegetal components of the feed were produced in the same biome Cerrado. Neutron activation analysis was used to determine Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Mo, Na, Rb, Sc, Se, Sm, Sr, Th, and Zn. A data mining study using classification techniques as Classification and Regression Tree (CART), Multilayer Perceptron (MLP), Naive Bayes (NB), Random Forest (RF) and Sequential Minimal Optimization (SMO), on the 10-fold cross validation, allowed to developing predictive models capable of discriminating cattle feeds.

Very good performances were achieved for the CART, RF, MLP, NB and SMO with, respectively, 86%, 89%, 100%, 96% and 96% prediction accuracy. The Chi-square and F-score showed that Cs, Se and Sc are, in this case, the three most important elements to discriminate the cattle feeds in this study.

	RF	SMO	MLP	NB	CART
Variable subset	{Cs, Se, Sc}	{Cs, Se, Sc}	{Cs, Se, Sc}	{Cs, Se}	{Cs}
Accuracy (%)	89	96	100	96	86
Sensitivity (%)	93	100	100	100	93
Specificity (%)	86	93	100	93	79
ROC Value (%)	98	96	100	99	85

Table 1. Detailed performance obtained by RF, SMO, MLP, NB AND CART for cattle feed discrimination

Acknowledgments
We wish to thank the Coordination of Improvement of Higher Level Personnel (CAPES) for the scholarship and the ”Beef Passion” for offering technical support whenever necessary.

Nuclear forensics

Fallout and deposition of cesium-137 in Aragats Massif, Armenia

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Keywords: ^{137}Cs, Aragats massif, topsoil, dry atmospheric depositions, moss, snow survey

The overall goal of radioecological monitoring launched in Armenia in 2015 was to reveal the distribution patterns of artificial and natural radionuclides in trough Armenia. This particular study aims at assessment of fallout and deposition of ^{137}Cs by altitudinal belts in Aragats massif, the highest point of present-day Armenia (4090 m above sea level).

Dry atmospheric depositions, snow, mosses and soil were collected from the southern slope of Aragats massif in 2016-2018. Dust was collected on Petryanov's filters in 5 monitoring stations situated at 854, 1208, 1281, 2032 and 3200 m above sea level. Snow, soil and mosses were collected from 14 sampling locations at 900-3200 m a.s.l. at a sampling interval of 200 m by altitude. Snow was collected prior to the main thawing in February-April 2017. 15 L volume plastic buckets pre-cleaned with 5% nitric acid were used for the transportation of snow samples. Undisturbed soil was sampled with the stainless still scoop from a depth 0-5 cm. 5-8 subsamples of topsoil were mixed in order to obtain a representative bulk sample. Mosses were collected manually into polyethene bags.

Ones at laboratory snow was melted in room temperature and filtered. Filtrate was preconcentrated on the ion exchange resin. Soil was disaggregated and sieved (2 mm), 700-1000 g of each homogenized sample was placed in Marinelli beaker and kept sealed. Mosses were cleaned manually and dried at room temperature to a constant weight, then packed into plastic beakers. All environmental samples were analysed using high purity Germanium detector coupled to a DSA-1000 multichannel analyser (Canberra). Background gamma radiation levels were measured once a week. Genie 2000 software was used for correction for background and Compton contribution of obtained gamma spectra.

^{137}Cs loading in dry atmospheric deposition varied from 9.0E-03 (at 846 m) to 4.3E-02 (at 3200 m) Bq/m^2 per day. In snow dust loading of ^{137}Cs varied from 2.56E-01 to 1.247E+00 Bq/m^2 per day respectively.

Activity concentration of ^{137}Cs in snow (filtrate and dust) and dry deposition exhibit positive correlation with the altitude. Regularity of distribution by altitude was not observed for activity concertation of ^{137}Cs in mosses. The maximal activity of ^{137}Cs: 1.01E+02 and 1.16E+02 Bq/kg was detected at 1600 and 1800 m respectively. In soil activity concentration of ^{137}Cs exponentially increased from 11.0 to 350 Bq/kg by altitudinal belts. A strong positive correlation was observed between activity concentrations of ^{137}Cs in soils and its loading in dry atmospheric depositions and snow dust.

New understanding of radionuclide distribution serves as essential information for detection of new radionuclides input to the environment. Ongoing studies are aimed at assessing of background and baselines of radionuclides in different environmental media through Armenia.

Acknowledgments

This research was implemented in the frames of a grant #15T-1E061 “Radioecological Monitoring in the Area of the Republic of Armenia – REMA” 2015-2017, and #18T-1E311 “Radioecological Monitoring in Armenia: Phase II – REMA II” 2018-2020 under support of Committee of science to the Ministry of Education and Science RA.

Adsorption of tracer gases in geological media: Experimental benchmarking

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Keywords: prompt gamma-ray activation analysis, hydrogen measurement, neutron shielding

Analysis of atmospheric radioactive noble gas concentration plays a crucial role in the detection of covert underground nuclear explosions. Their high mobility and isotopic signatures support detection significant distances away from a detonation site as well as provide the ability to distinguish weapons derived xenon from peaceful background sources. The presence of both natural geological and manmade containment can however impede transport and introduce uncertainty. This work therefore examines the interaction of xenon with geological barriers by experimentally benchmarking previously constructed models.

Two noteworthy large scale field experiments have attempted to replicate radio-noble gas transport following a nuclear event by injecting radioxenon in a subsurface explosive cavity and analyzing gas samples either in the atmosphere [1] or withdrawn from the shallow subsurface [2]. In both of these experiments, the amount of gaseous xenon detected at the surface fell short of expectations, indicating an unexpected loss mechanism exists. Furthermore, in situ xenon measurements in one experiment [2] observed concentrations an order of magnitude higher than that of the corresponding gas samples. Later independent analyses characterizing xenon adsorption on geological media [3] suggest the observed discrepancy could be a result of xenon being retained underground in the adsorbed phase. Previous lab scale experiments and ancillary models predicted adsorption of xenon onto geological media, thus providing plausible explanation for decreased xenon concentration at equilibrium [3, 4]. This work sought to experimentally verify those predictions by analyzing the transport of xenon in comparison to the commonly used gaseous tracer sulfur hexaflouride though a two-bulb diffusion apparatus adapted for the study of geologic media. Novel to this work is the timescale over which these experiments were carried out, allowing the system to reach equilibrium, rather than relying on numerical models to treat the equilibrium concentration of each gas as a fit coefficient. These experimental results prove that when the close diffusion system does finally reach equilibrium the xenon concentration does in fact fall below that of the SF_6 tracer, confirming the models suggesting a great fraction of xenon absorbs to the media.

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Age determination of uranium sample by ^{231}Pa/^{235}U radiochronometer

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Keywords: uranium age, ^{233}Pa spike, calibration, ICP-MS please follow the style and articulation

Developing different model age determination methods of uranium sample could get more information on insight into source and suspected use in nuclear forensic investigation. A procedure for the determination of model age of uranium sample using ^{231}Pa/^{235}U radiochronometer was reported. The purifed ^{233}Pa solution to be used as spike was separated from ^{237}Np solution using two TRU resin columns and two silica gel columns, which was calibrated by CRM U100. Model ages of CRM U010 and IRMM 1000 were presented. The model age of IRMM1000 using ^{231}Pa/^{235}U radiochronometer was inconsistent with the literature reported results by ^{230}Th/^{234}U radiochronometer which was consistent with production date of uranium material.

A novel chronometry technique to date nuclear fuel based on long lived Cm isotopes

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Keywords: nuclear forensics, dating, hot particles, Cm-isotopes

Dating of nuclear fuels or hot particles has become an important tool in nuclear forensics. Combined with other tests such as physical properties, isotopic composition, and impurity signatures, dating may help revealing the origin of a nuclear material and ultimately when, where, and how it was removed from regulatory control. Age dating of irradiated fuel determines the time since last irradiation and usually relies on a parent/daughter ratio such as ^{60}Co/^{60}Ni, ^{234}U/^{230}Th, ^{241}Pu/^{241}Am or ^{233}U/^{229}Th. The parent/daughter method can be very precise but it requires complex chemical separation of two different elements and thus the use of a chemical yield tracer (or spike) for each element.

We present a new post-irradiation chronometry model that is based on Cm-isotopes only. The advantages of the method is that it relies only on the measurement of two isotopic ratios of a single element. Thus, no isotopic yield tracer is required and no environmental or other fractionation effects need to be considered e.g. in case a geochemically altered material is found in the environment.

In a nuclear reactor the long lived Cm isotopes ^{245}Cm ($T_{½}$ = 8.5 kyr) and ^{246}Cm ($T_{½}$ = 4.8 kyr) are formed by neutron activation of ^{244}Cm ($T_{½}$ = 18.1 yr). Therefore, a correlation exists between ^{245}Cm/^{246}Cm and ^{244}Cm/^{246}Cm ratios (Fig. 1). When the fuel is removed from the reactor production of Cm isotopes ceases, and ^{244}Cm decays comparably rapid, while ^{245}Cm/^{246}Cm stays constant over several hundred years.

We developed a chemical protocol to extract Cm from irradiated U and U/Pu nuclear fuels. To calibrate the method, Cm-isotopes were extracted and measured from different fuel types with known age. The measurements were carried out with compact accelerator mass spectrometry (AMS) at ETH Zürich. The measured and decay corrected ^{244}Cm/^{246}Cm and ^{245}Cm/^{246}Cm ratios (data points in Fig. 1 provide a preliminary calibration curve for the dating method. In the presentation, the potential, the uncertainties, and the possible fields of application of the novel method will be discussed.

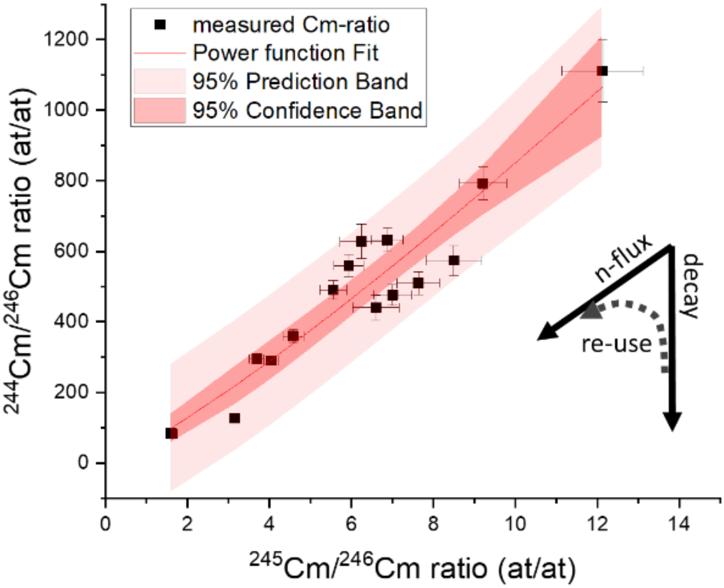

Figure 1: Measured and decay corrected Cm-isotope ratios (data points) from different irradiated U-fuels of known age. The inset explains the general concept of Cm-dating.

Isotopic composition of commercially available uranium chemicals – Part II

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The isotopic composition of commercially available uranium chemicals continues to be of interest to the International Atomic Energy Agency (IAEA) as it can provide valuable reference information. Further to dedicated studies on the subject, where uranium chemicals currently available in the marketplace were analyzed, the IAEA also seeks to analyze uranium chemicals in use in laboratories but which may no longer be available for purchase. Samples of uranium chemicals in use by several laboratories were analyzed to determine the uranium isotopic composition using particle analysis by thermal ionization mass spectrometry (TIMS) or using bulk measurements by either inductively coupled plasma mass spectrometry or TIMS in the modified total evaporation mode. All of the chemicals sampled and analyzed were determined to consist of uranium depleted in ^{234}U and ^{235}U; some of them contain levels of ^{236}U indicative of irradiation. Model scenarios are presented for a combination of uranium irradiation and enrichment processes, which may have resulted in depleted uranium tails materials with such compositions.

Development of nuclear forensics in Kazakhstan

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Keywords: nuclear physics, nuclear-physical methods of analysis, ionizing radiation sources

The activities of nuclear forensics in Kazakhstan are mainly performed in the Institute of Nuclear Physics.

One of the main activities of the Institute of Nuclear Physics is development and application of the nuclear-physical methods for analysis of the environmental objects including mineral raw materials. Having retained the intellectual and scientific capabilities through the collapse of the Soviet Union, in recent years the Institute was able to upgrade the scientific instruments and methodological frameworks in this area and to gain the valuable experience in development of the instrumental methods of elemental and radionuclide analysis. Currently, the complex of nuclear-physical methods of analysis is available in the Institute of Nuclear Physics, established on the existing spectrometric and analytical equipment, including the methods of elemental analysis such as neutron activation analysis, X-ray fluorescence analysis, inductively-coupled plasma mass spectrometric analysis and the complex of instrumental and radiochemical methods of analysis of radionuclide and isotopic composition.

The Institute of Nuclear Physics has designed and developed the special hardware-and-methodological system providing the forensics examination of various nuclear and radioactive materials and products. The wide range of available equipment and procedures is applied for study of the materials/products received for examination.

The Institute is licensed for handling of ionizing radiation sources, radioactive substances and waste, and for providing the services in nuclear energy application, including determination of radionuclides in the materials, environment objects; it operates necessary technical equipment for the wide range of analytical research in applied nuclear physics, including the specialized laboratories and the qualified staff of former "weapon" specialists with experience in similar work. The Center of Complex Ecological Research in the Institute of Nuclear Physics is accredited to meet the requirements of Standard ISO/IEC 17025 - 2009 "General requirements for competence of testing and calibration laboratories".

The quality of analyses is confirmed by successful participation in many international interlaboratory comparisons and professional tests organized by IAEA.

Lately, the international cooperation of INP is dynamically developing in nuclear forensics. Many workshops, trainings and conferences have been held in Kazakhstan. We can note the scientific practical conference "Development of the analytical plan to support nuclear forensics" (Almaty, 2015), which was supported by DOE with participation of the specialists from several US National Laboratories.

The representatives of our Institute have participated in several meetings of the International Technical Working Group.

The Inter-laboratory comparison study of nuclear materials from the Lawrence Livermore National Laboratory, US DoE has been completed. We have participated and continue to participate in various exercises "Csodaszarvas: Mystic Deer", "Galaxy Serpent", CMX-5, CMX-6.

Now the partner project of the International Science and Technology Center "Advancement of material-technical and regulation-methodological framework for Nuclear and Radiologic Materials Forensics in the Republic of Kazakhstan" is being implemented jointly with the US Lawrence Livermore National Laboratory.

And undoubtedly it is necessary to mention the IAEA project, within which our visit was organized to your laboratory.

Analysis of Pb, Sr and Nd isotopes in UOC for nuclear forensics

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A comparation analysis of the characteristics of uranium ore concentrate samples has been carried out among four nuclear forensic research groups. The characteristics of the analysis included micro-morphology, chemical composition, uranium content, uranium isotope abundance, impurity element content (Al, Cr, Fe, Pb, Ti, Zn, Mo, Nb, Sb, Sn, Ru, Ta, Th, Ni, Mn, etc.), Pb, Sr, Nd isotope abundance, etc. Through the comparation analysis of uranium ore concentrate samples, hope to establish the impurity element separation and elements content, isotope analysis process of uranium ore concentrate samples in nuclear forensic study, and establish a standard analysis method for the domestic uranium ore concentrate database data.

Standard analytical procedure include sample dissolution, separation of uranium from impurity elements, measurement of uranium isotope and that of impurity elements content, separation of Pd, Sr and Nd, and Pd, Sr, Nd isotope abundance measurement. The incomplete dissolution of samples or the formation of suspension will lead to the loss of target impurity elements in samples, especially in some insoluble uranium ore concentrate samples. HF is added to the sample along with concentrated HNO_3 when dissolving. However, CaF_2 precipitation formed between HF and Ca coming from uranium ore concentrate, which carries some impurity elements out of the solution, resulting in inaccurate measurement results of impurity elements content. Therefore, HF dosage should be controlled when dissolving, considering CaF_2 precipitation is difficult to form under low fluorine concentration. TBP or UTEVA resins are used to separate uranium from impurities. The eluent and analytic solution are used to measure the content of impurities and uranium isotopes respectively. Sr and Pb were separated from the eluent by Sr resin and Nd was separated from the eluent by LN resin. The separated uranium analytical solution, leaching solution containing Pb and Nd were measured by MC-ICP-MS with $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{142}Nd/^{144}Nd$, $^{143}Nd/^{144}Nd$, $^{145}Nd/^{144}Nd$, $^{148}Nd/^{144}Nd$, $^{150}Nd/^{144}Nd$, and the leaching solution containing Sr was measured by TIMS with $^{87}Sr/^{86}Sr$. The established separation and analysis process will be used as a routine domestic method of the uranium ore concentrate analysis in nuclear forensics.

Age determination of uranium in mine tailing using Inductively Coupled Plasma Mass Spectrometry for nuclear forensic

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Keywords: age determination, nuclear forensics, Inductively Coupled Plasma Mass Spectrometry, uranium

Illicit trafficking of radioactive material and especially nuclear material (thorium, uranium, and plutonium) has been an issue of concern since the beginning of the 1990s, when the first seizures of nuclear material were reported to the International Atomic Energy Agency. The radioactive decay of the uranium isotopes provides a chronometer that is inherent to the material, which allows us to calculate the time elapsed since the last chemical separation. In this work, the samples selected for investigation originate from different South African uranium mine tailings. In South Africa, uranium is extracted from the Mine Waste Solutions (MWS) tailing retreatment operation and uranium is produced as a by-product of gold or copper mining. The aim of this study was to determine whether the impurities measured in a particular sample can be used to attribute the sample to the time elapsed since the last chemical separation took place and to the production or reprocessing plant.

Interaction of rse «inp» with RK law enforcement authorities in prevention of illegal trafficking of nuclear materials/radioactive substances

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Keywords: illegal trafficking, nuclear forensics, interaction

The effectiveness of the measures for combating illicit trafficking of nuclear and radioactive materials considerably depends on the level of interaction between the various agencies and organizations involved in various stages of detection, suppression and response. The legal norms and legislation in Kazakhstan determine the procedure for participation and involvement of the expert and scientific centers in assisting the law enforcement agencies in the activities on prevention of illicit trafficking of nuclear and radioactive materials beyond the regulatory control.

In this regard, the specialists of INP have developed, implemented and continue to improve the methods of interaction with state law enforcement agencies in this area.

Thus, in addition to training of the law enforcement officials on the basics of radiation safety, the rules for NM/RS handling and the practical application of primary radiation monitoring equipment, the specialists of the Institute regularly provide assistance for the law enforcement agencies in organizing the activities on combating illicit trafficking of nuclear and radioactive materials.

In particular, the technical experts are directly involved at the site of the radiological incident, in order to assess the radiation risks and provide radiation safety; they perform primary study of the object and its identification, make recommendations for package and temporary storage of the seized items or substances, and also perform transportation of NM/ RS for the special study, the results of which are used for preparing the report, submitted to the investigating authorities and referred to the criminal case as evidence.

The Institute considers the following points as high priority areas for development:
- Improvement of the regulatory framework;
- Establishment of the national database of nuclear and radioactive materials;
- Development of expert, research laboratories;
- Unification of the special studies of NM/RS;
- Establishment of the storage site for NM/RS seized from illicit trafficking;
- Establishment of the Nuclear Forensics Center in INP.

The procedures for interaction were developed within the framework of the ISTC Project K-2400 "Advancement of material-technical and regulation-methodological framework for Nuclear and Radiologic Materials Forensics in the Republic of Kazakhstan" under support of the Lawrence Livermore National Laboratory and financial support of the US Department of Energy.

Experience of collaboration in field of creating and development of armenian national nuclear forensic lab

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Keywords: alpha spectrometry, gamma spectrometry, nuclear forensics, radioactive sources

Introduction

After disintegration of the USSR, in Armenia developed a situation when at the enterprises using the radioactive sources, the control over sources has been extremely weakened for the following reasons:

The majority of the industrial enterprises and scientific research institutes of federal submission, including so-called "enterprises of military department", from the end of 80th years practically did not work. Further process of renewal of manufacture was accompanied by active alienation of the equipment without taking into account radioactive sources of scientific and industrial purpose.

- In the beginning of 90th years in Armenia there was no corresponding body of state management on supervision of radioactive sources. The centralized lists of the account and the control of radioactive sources of industrial and medical assignment have been lost. Therefore, the actual process of the account from Regulatory body of RA was carried out on the basis of own studies within the framework of developed statutory acts, this process proceeds and now.
- In connection with shutdown of the enterprises, they do not have possibility for realization of the appropriate control over the sources because of absence of the means and experts of corresponding qualification.

There are a set of the facts confirming the above-mentioned. In particular, known many cases, when sources (highly active) have been found at the persons, who practically nothing represented about the danger to which they and their environment were exposed. The situation becomes more complicated because of circumstance that radioactive sources can become a subject of illegal trade or be used by people which are not suspecting about their danger. Many cases when during the transportation through border, the radioactive sources and radioactive materials have been found in cargoes of scrap metal are known.

The present situation represents real danger for workers of the enterprises, population and environment. It is necessary to note one more (though also improbable, but possible) aspect of this problem. The problem is that the threat of radiation terrorism in view of a developed situation (the let-down of control over the radioactive sources) is rather high. Cases (in particular, in the Chechen Republic) are known when terrorists threatened to use the radiation weapon against the population. According to IAEA - for the period since January 1st 1993 to

2003 335 confirmed incidents with radioactive materials are known. In most cases they were in the form of the closed radioactive sources. The data resulted in IAEA documents indicates that the confirmed incidents, with nuclear materials, since 1993, have sharply gone on a loss [V.Orlov IAEA BULLETIN, v. 46, N_o 1, June 2004, p.53]. At the same time the number of incidents with radioactive materials has increased in comparison with 2003 more than twice.

Below are described a few incidents involving the illicit trafficking of radioactive materials in Armenia.

- In 2009 in Institute of Physical Researches of Academy of sciences RA the unknown robbers crack the door of the room in which the K-1200 device containing radioactive cobalt-60 was placed. Fortunately, they could not take out the sources from the device. For that moment its activity was 468,06 curie or $1{,}73210^{13}$ Bq.
- The incident which has occurred in January, 2009 on Megry custom-house (the border with Iran) is remarkable. At inspection of a truck with a lead waste has been fixed the excess of a limit of a dose rate on the transport monitor. Three bags with a lead waste were delivered to laboratory. The further analysis has shown that in lead waste there was source Am-241. Capacity of a neutron stream from a source was equal 10^7 neutron/s. This incident is remarkable that the owner knew about presence of a source and tried to hide it from customs officers, carefully packed it in some layers of sheet lead.
- In May 2009 during carrying out the radiation monitoring in village Noraduz was revealed, that premises of a auto repair shop and territory adjoining to it (the area of 300 square meters) were polluted by a radioactive isotope caesium-137. Gamma-radiation intensity in premises made from 900 to 1200 μSv/h. Gamma-radiation intensity in adjoining territory was equal 600-800 μSv/h. Four persons (the owner of a auto repair shop, his son and two technicians) have received the doses of an internal irradiation exceeding the admissible sizes. The internal dose for owner's son was 128 mSv/year, another person's internal dose make from 7 to 12 mSv/year. Premises of a auto repair shop and adjoining territory have been decontaminated, now the gamma-radiation intensity in these territories is lowered to admissible level. The owner of a auto repair shop, his son and two technicians have received corresponding medical aid. The analysis of information has shown, that someone of the listed persons (most likely the son of the owner of a repair truck as his internal exposure dose was in 10-12 times more than at the others) has found a radioactive source and has opened it in a auto repair shop. As a result of it there was a pollution of premises and territory, and also people exposure. Criminal investigation of this incident was made. Fig. 1 shows the number of incidents, related to the illicit trafficking of radioactive materials in Armenia for the period of 2006-2016. In Fig. 2 are shown location of discovered radioactive sources and materials.

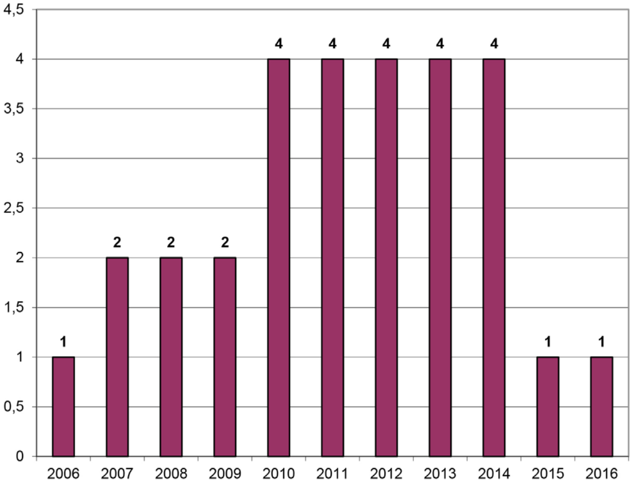

Fig. 1. The number of incidents related to the illicit trafficking of radioactive materials in Armenia, 2006-2016

Fig. 2. Location of discovered radioactive sources and materials

In all cases of revealing of the illegal manipulations with radioactive sources and materials arise a necessity of their identification, and realization of the established procedures, connected with describing these sources, for providing the data for prosecution and excitation of judicial actions.

In Armenia there was no specialized laboratory intended for the decision of such problems. Therefore, the initiative group of the Department of Radiation Protection (laboratory of radiation monitoring) of the Armenian Nuclear Power Plant has made a decision of carrying out the expert examinations of identified radioactive materials and sources, and also execute radiation monitoring of the enterprises and territories of Armenia, with the purpose of searching the orphan radioactive and nuclear sources and materials. During all period of monitoring the initiative group closely cooperated with National Security Service, law enforcement agencies and nuclear regulatory body.

The laboratory of radiation monitoring received the state licenses on: export of radioactive and nuclear sources and materials; storage of radioactive and nuclear sources and materials; transportation of radioactive and nuclear sources and materials. Besides were developed the program of safe transportation of radioactive sources and the emergency procedures in case of the emergency situation.

Members of initiative group participated at the training course on search and detection of radioactive and nuclear materials in August, 2006, organized by Sandia National Laboratory of the USA and has corresponding certificates.

Establishment of the Armenian Nuclear Forensic Laboratory

In 2012 ANPP laboratory received CRDF grant for the project "Establishment of the Laboratory for Technical and Forensic Analysis of Nuclear and Radioactive Materials (NFL) in the Republic of Armenia" in framework of the Preventing Nuclear Smuggling Program of the United States. In framework of this project, the laboratory received modern gamma spectrometric equipment (stationary and portable) as well as an installation for measuring total alpha and beta activity (Ultra low-background cryostat 7500SL; Falcon 5000 HPGe-based portable identifier; iMatic™ Gas-less Automatic Alpha/Beta Counting System; Alpha spectrometer). During realization of the project the package of documents and instructions regulating the laboratory activity, has been developed.

In order to create and develop the NFL, the ANPP provided the laboratory with several rooms with a total area of 90 m^2, provided electric power supply, water and constant security. Furthermore, the ANPP provided individual, search dosimeters and other radiation devices to the laboratory. The ANPP constantly supplies the laboratory with the necessary sources for the calibration of gamma spectroscopy facilities. Currently, 5-6 people participate in activity of the laboratory. It should be noted that they all have their primary work at the Armenian NPP and are involved in NFL activity as needed, and they do not receive payment for this work. During project realization and later, we constantly got support from curators of the project (Ms. Antsiferova, Ms. Dace Sarma, Mr. Matthew Fargo from CRDF Global), Sarah Fendrich from Counter Nuclear Smuggling Unit, US Department of State and from scientific collaborators (Dr. Michael Palian, Dr. Kevin McLeary and James Blankenship from CBRN Sciences Unit, FBI Laboratory). In the scientific plan we have received the invaluable support from Los Alamos National Laboratory (preparation of samples and alpha spectrometry).

In 2017, under the guidance of the State Scientific Committee of RA between the Armenian Nuclear Power Plant and the State Polytechnic University, a Memorandum of Mutual Understanding was signed which gave the official status to the NFL and enabled scientific organizations and universities in Armenia to participate in supporting NFL activities. The memorandum allowed using the NFL equipment, unique for Armenia, for performing scientific research in other areas. In particular, the Institute of Physical Research of the Academy of Sciences of the R A carried out research of composition of stable isotopes of certain chemical elements in water under the influence of acoustic vibrations using the gamma spectrometer provided by NFL. Besides, NFL participated in radio ecological researches of uranium ore deposits of Kadzharan site. Together with the Center for Ecological-Noosphere Studies NAS RA, studies of the altitude distribution of cesium-137 (Mount Aragats 900 -3200 m) were carried out in Armenia.

Certainly during all time NFL communicate with law and order agencies; continue the expert activity and also carried out monitoring of some territories and the enterprises of Armenia.

NFL current capabilities.

NFL has equipment for implementing basic research methods for radioactive and nuclear materials (gamma spectrometry and alpha spectrometry), as well as for measuring total alpha-beta activity, dose rate, surface contamination and so on. The laboratory also possesses the sufficient equipment for preparation of samples for gamma and alpha spectrometric measurements.

Gamma spectrometry

In the field of analysis of gamma emitters with energies from 0.05 to 3-4 MeV we have no problems with measurements and equipment calibration (by the energy and efficiency).

NFL has long experience in this area (over 15 years). During this period, we have often dealt with sources used in different areas: industrial gamma radiography, fixed industrial gauges, portable gauges (e.g. moisture, density), logging gauges, thickness/fill level gauges, fire detectors, etc. (Co-60, Co-58, Cs-137, Cs-134, Am-241 and so on). Activity - from micro curie to 468,06 curie.

The laboratory can perform expertise using gamma spectroscopic methods of investigation. For this there is a sufficient instrumentation base, documentation and obtained experience. To finally close this question, it is necessary to organize training course for "trainers" (two persons) for training a new generation of experts in this field of knowledge. This will ensure a well-organized training process from the methodological point of view.

Alpha spectrometry

Of reference data and information, which we have received at ITWG workshops, we know that Alpha Spectroscopy is:

- Reliable technique for identification and quantification of alpha emitting radionuclides.
- Useful for nuclear forensics examination:
  - Material identification and quantity
  - Especially useful for Po, Th, U, Np, Pu, Am
  - Uranium enrichment definition.

Currently NFL has equipment for sample preparation for alpha spectroscopic measurements, as well as an alpha spectrometer.

Needs in the field of Alpha spectroscopy

One of the weaknesses of NFL is the lack of skills in alpha spectrometric measurements and sample preparation for such measurements. It is well known that sample preparation for alpha spectrometric measurements is a complex process and greatly affects on accuracy of the data obtained. Laboratory staff needs additional training in sample preparation and alpha spectroscopic measurements.

In solving this problem, we were greatly supported by colleagues from Los Alamos National Laboratory: Stephen LaMont, Lisa Hudston, Michael Harris and Liz Dallas from NNSA. In December 2017, on the basis of NFL, they organized a training course. Training subjects: Detector Settings, Nuclide Libraries, Regions of Interest, Calibration Source Records, Energy and Efficiency Calibration, Verification Performance, Quality Control of Performance Verification, Counting Samples, Data Analyzing. Also due to them, we now have certified Alpha Spectrometry Calibration Sources. Another training subject was Radiochemistry Processing for Alpha Counting.

In October 2018, a training course was organized for experts from Armenia on the basis of Los Alamos National Laboratory on the following topics: alpha-spectrometry by isotope dilution method (ID-AS), separation of uranium and thorium samples, electrodeposition and calculation plan, data review according to the accounts of U and Th, counting parameters on the prepared samples. The training program also included practical laboratory classes. Lecturers - Stephen LaMont, Lisa Hudston, Michael Harris.

Educational activity

Another area of NFL activity is non-technical training of National Security Service officers, customs officers, officers of Ministry of Internal Affairs, officers of public prosecutor's office and Ministry of Emergency Measures. Such training is necessary, since the above-mentioned employees have very little information about radioactive sources and materials, their description and properties. In addition, they are not familiar with the principles of radiation safety. 15 October to 20 December NFL conducted a thirty hours training course for lecturers of the Academy of the National Security Service of Armenia. After completing the course, the certificates and also training materials have been presented to all participants. Topics of lectures: 1- fundamentals of radiation safety; 2 - natural and man-made sources of human exposure; 3 - characteristics of industrial radiological devices, possible threats; 4 - search methods; 5 - areas of radioactive source applications; 6 - legislative and regulatory acts of Armenia related to the treatment of radioactive materials and sources, etc. In 2019 NFL will conduct the same training course for students of the Academy.

Training of new generation of specialists

In Armenia, there is the problem of training of new generation of specialists in the field of nuclear forensics. Currently, no educational institution has any training programs for the training of such specialists. Therefore, the State Scientific Committee of RA, Yerevan State University and the National Polytechnic University of Armenia are currently developing a curriculum for masters in this field. The NFL has practically all modern instruments, necessary for studying the physical properties of radioactive and nuclear materials. Therefore, NFL and ANPP will be able to provide practical training of the methods of measuring the physical characteristics of radioactive materials. In addition, NFL specialists have extensive practical experience in the field of radiation safety and their potential can be used in students education in this field.

Comparison of fission track analysis, SEM-EDX and SIMS for identification and localisation of microscopic uranium particles in environmental samples

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Keywords: fission track, nuclear safeguards, SEM-EDX, SIMS, uranium particles

Mass spectrometric methods such as secondary ion mass spectrometry (SIMS), thermal ionization mass spectrometry, and inductively coupled plasma mass spectrometry are used to measure isotopic ratios of individual uranium particles in environmental samples for nuclear safeguards.[1,2] The first step of the analysis is identification and localization of uranium particles in large quantities of dust and other particles. Subsequently, the particles of interest are relocated and analyzed in the mass spectrometer.

In the present study, fission track analysis, scanning electron microscopy (SEM) with automated particle search mode using energy dispersive X-ray analysis and SIMS with automated particle measurement (APM) mode were used for identification and localization of the uranium particles on the sample. Fission track analysis is based on creation of damage (tracks) inside the detector material caused by the passage of high-energy fission products from uranium particles after irradiation in nuclear reactor.[3] Centers of enlarged "star-shape" fission tracks which correspond to the positions of the uranium particles on the sample were determined by optical microscope. Automated particle search in SEM is based on recognition of particles using back-scattered electrons mode and their chemical analysis by energy dispersive X-ray spectrometer. In the SIMS instrument, automated particle search is based on selection of uranium isotopes of interests (235U, 238U) and recording of the isotopic maps, which reveal positions of particles.

The used methods were compared according to three basic performance parameters: efficiency, i.e. amount of particles found with the given method, relocation precision, and the speed. SIMS with APM is the only method that can determine location and isotopic ratios of U particles in one instrument and it is fast. FTA has high efficiency for finding the particle positions and providing preliminary information about enrichment. The advantage of SEM is the accuracy of particle positions and visualization of particle shapes and sizes.

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Uranium particles analysis using a combination of fission track technique and secondary ion mass spectrometry

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Keywords: uranium particles analysis, safeguard, fission track, FIB-SEM, SIMS

Analysis of isotope ratios in individual U-bearing particles is an effective tool for nuclear safeguard to verify that nuclear materials are used for peaceful purposes only. Every single U-rich particle in μm and sub-μm size range can provide valuable information such as enrichment and reprocessing history and relate it to the place of sample collection. Two main mass spectrometric methods that are currently applied for analyzing the U isotopic composition in international safeguards community are secondary ion mass spectrometry (SIMS) [1] and thermal ionization mass spectrometry in combination with a fission track method (FT-TIMS) [2]. An important preliminary step prior to isotopic analysis of the particles of interest is their identification and location within a large amount of non-specific dust in environmental samples taken from nuclear facilities. For this purpose, fission track technique (FT) was developed and applied by several laboratories [2]. In FT technique, U-containing particles are located via "tracks" of damage created in insulating plastic detector by ^{235}U fission fragments after irradiation in thermal neutron field.

In the presented study, an in-house FT technique combined with focused ion beam scanning electron microscopy (FIB-SEM) was used as a sample preparation and particle identification method for subsequent isotope ratios analysis with SIMS. In the developed FT technique, U particles were deposited on a silicon wafer in a solution of collodium and ethanol. The prepared substrate was covered with a piece of polycarbonate detector Lexan, fixed with specially designed plastic holder and irradiated in the LVR-15 research reactor at Research Centre Rez (Czech Republic). After irradiation, reference marks were made by FIB-SEM to create a coordination system between silicone substrate with particles and detector with fission tracks. Then, the detector was etched to enlarge the fission tracks for position determination in optical microscope. With the aid of location of the tracks and reference marks, positions of U-particles on silicon substrate were relocated using triangulation method [3]. The isotopic analysis of selected particles was performed by SIMS (IMS7f). The isotope ratios ^{234}U/^{238}U, ^{235}U/^{238}U and ^{236}U/^{238}U determined by the described FT-SIMS procedure were in good agreement with the certified values.

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Complex of methods for analytical study of uranium-containing raw materials for nuclear forensics purpose

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Keywords: nuclear materials, nuclear-physical methods of analysis, nuclear forensics, natural uranium

The Republic of Kazakhstan (RK) has a developed complex for mining and processing of raw materials containing natural uranium. In this regard, now in Kazakhstan there is a demand to establish a nuclear forensic database (DB) with information on nuclear materials available in the country, including those based on natural uranium. As in the rest of the world, the competent authorities of the Republic of Kazakhstan need to keep records of nuclear materials in order to identify and establish the origin of materials seized from illicit trafficking.

The main DB components include the radionuclide and elemental "signatures" of materials obtained at all stages of uranium production. This paper provides the study of elemental and radionuclide composition of various materials of the uranium mining and processing cycle using the method of underground borehole leaching (UBL), including the initial uranium raw materials, technological media and solutions.

Using the methods of inductively coupled plasma optical emission spectrometry and mass spectrometry (ICP-MS), instrumental neutron activation analysis and energy dispersive X-ray fluorescence analysis we determined the macro-component (P, Na, Mg, Al, K, Ca, Ti, Mn, Fe) and trace-component composition (As, B, Ba, Bi, Cu, Li, Mo, Ni, Pb, Re, Sb, Th, U, V, W, Zn, Zr) of the studied materials, as well as the content of rare-earth elements. Radionuclide composition (^{234}U, ^{238}U, ^{234}Th) was studied by the methods of alpha- and gamma-spectrometry, the isotope ratio ^{234}U/^{238}U was determined by ICP-MS method.

As a result of the completed study, the characteristic fragments of elemental and radionuclide "signatures" of the uranium-containing raw materials and processing products were identified at the plants of JSC NAC KAZATOMPROM Company, the world leader in natural uranium mining. Based on the obtained "signatures", the individual and group markers were determined for characterization, identification and geochemical binding of the uranium-containing products of uranium mining and production by UBL method at the plants in Kazakhstan.

These studies were performed in the Center of Complex Ecological Research of the Institute of Nuclear Physics within the framework of the ISTC Project K-2400 "Advancement of material-technical and regulation-methodological framework for Nuclear and Radiologic Materials Forensics in the Republic of Kazakhstan" under support of the Lawrence Livermore National Laboratory and financial support of the US Department of Energy.

Nuclear fuel cycle

Large volume airborne contamination monitoring to support nuclear processes deactivation and decommissioning

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Keywords: Savannah River Site, Hanford, Airborne Contamination, Continuous Airborne Monitoring

One of the challenges facing the nuclear industries efforts to bring new nuclear processes online is demonstrating that legacy nuclear facilities can be successfully remediated. The Department of Energy's Hanford Site has recently experienced considerable challenges in its efforts to remediate the Hanford Plutonium Finishing Plant, a facility linked to legacy weapons program processes. Current deactivation and decommissioning (D&D) operations at Hanford have demonstrated a flaw in the current state of the art capability of defining airborne contamination boundaries. Airborne particulate emissions of Pu-239 from contractor D&D operations on the Hanford Pu Finishing Plant were detected well beyond areas controlled for airborne Pu, putting numerous workers at risk for radiological assimilations. Forty-two Hanford workers had positive bioassay results for plutonium uptake. Work areas determined to be free of airborne contamination as measured by state-of-the art continuous alpha monitoring (CAM) systems were later discovered not to be. Airborne contamination was scattered to a such degree that CAM systems were surveying insufficient volumes of air to accurately predict where respiratory protection was required.

This research project is studying the feasibility of using commercially available air purifying systems to screen significantly larger volumes of air for airborne actinide contamination. Commercial household HEPA based air purifying units screen large volumes of air, a simple household unit being looked at for this study could screen a volume of air that would require over 300 commonly used commercially available CAMs. Detection systems are being studied that could be capable of screening the air purifiers pre-filters and HEPA filters for any actinide bearing hot particles that have been captured. Field deployable detection processes focused on x-ray/low energy gamma ray spectrometers (as actinides typically having higher x-ray over gamma emissions) as being compared to sensitivities obtained with screening of gross alpha emissions by scintillation and solid-state detection processes.

Production of radionuclides

Preparation of hafnium targets by electrodeposition

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Keywords: targets, molecular plating, hafnium

At the basic physical setups at the Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research (SHELS, MASHA, DGFRS) superheavy elements are obtained and their chemical properties are researched, neutron-excess and neutron-deficient are obtained, nuclear cross-sections are researched. One of the considerable parts of the experiments are targets, generally from lanthanides, actinides or lead on the 1,5-2μm titanium backing.

Different methods for target preparation, such as chemical deposition, polymer-assisted deposition, sputtering, painting, electrospray, intermetallics and electrodeposition, including molecular plating, are applied [1]. In each case most suitable coating method is chosen according to advantages and disadvantages of known methods. Advantages of electrodeposition are high yield of coating substance and sufficiently uniformity of coating even for complicated target forms. Method of molecular plating is applied successful for a long time for preparing of cyclotron targets [2].

Sometimes it is needed to prepare not lanthanide or actinide target, but, for example, target from hafnium. Techniques of cyclotron targets preparing by electrospray [3] and electrodeposition from aqua solution of urea oxalate [4] and from aqua solution of potassium fluoride [5] are known.

At this work electrodeposition techniques of hafnium plating [4, 5] are tested. Technique [4] is not used for deposition on Ti foil, so we cannot reconstruct all conditions. As the authors note using technique [5] Ti foil is may dissolved partially, but 1,5-2μm foil is dissolved up to the hole. Therefore molecular plating like [2] based on [4] and [5] for hafnium plating is tested.

Aliquot of aqua solution of hafnium at 1M potassium fluoride or at 82,4g/dm^3 oxalic acid is added at cell filled by isopropanol and mixed carefully. Molecular plating is carried out at 990V, current density was 0.5-1.5mA/cm^2. In contrast with [2] deposition is carried out not on a cathode, but on an anode. It should be explained by formation of anion complexes like $[HfF_6]^{2-}$ and $[Hf(C_2O_4)_4]^{4-}$. Yields is 47% in potassium fluoride presence and 75-100% in oxalic acid presence. Prepared with addition of aliquot of hafnium aqua solution at oxalic acid targets are smooth and crack free. Layer up to 200 $\mu g_{Hf}/cm^2$ thicknesses is stay sufficiently crack free under heating to 350-400°C at hot plate on air.

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Excitation functions for alpha-induced reactions on zirconium in the 10–40 MeV energy range

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Keywords: activation cross section, technetium 99m, molybdenum 99, medical testing crisis, helium beam

^{99m}Tc/^{99}Mo is one of the most important radioisotopes used in nuclear medicine for common diagnostic imaging technologies such as single photon emission computed tomography (SPECT). After the worldwide shortage of ^{99m}Tc/^{99}Mo due to the long shutdowns of major nuclear research reactors in 2009–2010, some alternate sources of ^{99m}Tc/^{99}Mo using accelerators have been investigated for stable supply of ^{99m}Tc/^{99}Mo1). In this study, we focused on the production route of ^{99}Mo via the ^{96}Zr(α,n)^{99}Mo reaction using a low energy accelerator2). In order to estimate the production yield of ^{99}Mo and the byproduct radioisotopes, we irradiated 24.6 and 46.4 MeV alpha particles onto stacked ^{nat}Zr targets at a cyclotron facility (NIRS-930), National Institutes for Quantum and Radiological Science and Technology, Japan. The stack targets were composed of natural zirconium foils (0.005 mmt) and natural titanium foils (0.005 mmt) which acted as a beam monitor. The total target thickness was thicker than the range of projectile alpha particles to measure the beam current on the targets. After irradiation, gamma-rays from each foil were measured with a HPGe detector. The production rates of radionuclides as well as ^{99}Mo in ^{nat}Zr samples are determined by a gamma-ray spectroscopy. The excitation function was deduced from the production rates of radionuclides by taking into account the projectile energies on each ^{nat}Zr foil degraded in the stacked target. In this workshop, we will present these experimental data, in comparison with other experimental data and calculations.

Acknowledgments

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Production of medical radioisotopes using electron linear accelerator

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Keywords: Electron linear accelerator, Cu-67, Ga-68, Rh-105, Lu-177, and Re-188

For a stable supply of Mo-99 that is indispensable in nuclear medicine, production of Mo-99 by using accelerators has been investigated in Japan. We also have examined production of Mo-99 by Mo-100(γ,n) and/or Mo-nat(γ,n) reactions using bremsstrahlung photons generated by the electron linear accelerator in Institute for Integrated Radiation and Nuclear Science, Kyoto University (KURNS-Linac) [1]. Since production of the other radioisotopes for medical use using KURNS-Linac has been investigated recently, its concept and activity of each radioisotope produced using the linac will be presented. The medical radioisotopes interest in this work are Cu-67, Ga-68, Rh-105, Lu-177, and Re-188, which are able to be produced by Zn-nat(γ,p), Ge-nat(γ,2n)&electron capture, Pd-nat(γ,p), Hf-nat(γ,p), Os-nat(γ,p) and/or Os-nat(γ,pn) reactions, respectively, using bremsstrahlung photons. And then, Rh-105 and Lu-177 also can be produced by Ru-nat(n,γ) and Yb-nat(n,γ) reactions and β^- decay, respectively, using neutron that is available in Kyoto university research reactor (KUR). The activities of these two radioisotopes produced using the linac will be compared with those using KUR.

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Realization of metallic Ti-48 enriched targets for the PASTA project

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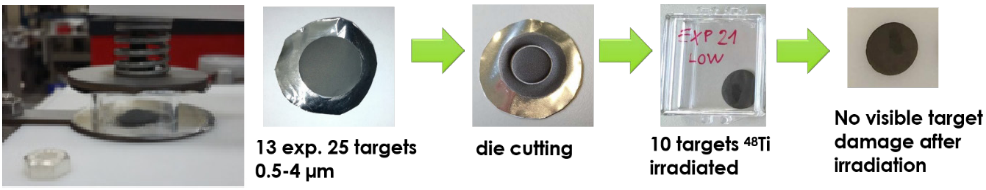
Keywords: scandium-47, production of radionuclides, targetry, enriched material, HIVIPP method

In the framework PASTA project (Production with Accelerator of Sc-47 for Theranostic Applications) at INFN-LNL (Padova, Italy), the realization of thin metallic targets composed by enriched and expensive material is a crucial issue. In general, target preparation is a key step for the success of nuclear physics experiments. In our case, the requirements to be fullfilled are thermomechanical resistance under the beam (about 100 nA of protons with maximum energy of 70 MeV), high uniformity of deposition, high efficiency (low losses of the material) and minimization of impurities. The E-PLATE (Electrostatic Powders pLating for Accelerator TargEts) project at INFN-LNL explored the High energy VIbrational Powder Plating (HIVIPP) method [1], providing the deposition with minimal losses of a number of metallic powders, including refractory metals, which are difficult to deposit by conventional methods. In this work the HIVIPP technique is applied to metallic titanium powders: the positive outcomes of the preliminary tests performed with natural titanium (^{nat}Ti, mesh 325) were followed by the deposition of enriched metallic ^{48}Ti powders. Thin and uniform deposits of ^{48}Ti on 25 µm thick aluminium supports were obtained and characterized (including SEM analysis) before the irradiation runs at the Arronax facility (Nantes, France) for the measurement of nuclear cross sections.

Considering that enriched powders shape and size are different for each particular material, the E-PLATE project aims to better understand the process and to adapt it to different types of metallic powder for future applications.



Photograph of the HIVIPP deposition system (left) and typical steps of a target preparation (right); no damage are visible after the irradiation.

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Production of radionuclides in a cyclotron for application in a PET

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Keywords: production of radionuclides, cyclotron, PET, Monte Carlo simulation, nuclear reactions

Positron Emission Tomography (PET) is a non-invasive technique used to evaluate the functioning of organs and tissues, from the administration of radiopharmaceuticals to the subject of the study. Currently radionuclides present in radiopharmaceuticals are produced in hospitals from cyclotrons, particle accelerators that produce transmutations when interacting with a target.

The present work is focused on the analysis of the nuclear reactions that can be carried out in a cyclotron for the generation of radionuclides that comply with the restrictions necessary for their medical use. These radionuclides must be positron emitters and must have a half-life as short as possible, taking into account the times of processing and administration of the radiopharmaceutical. These conditions are met for the radionuclides studied Cu-64 and Ga-68.

The methodology used is based on the modeling of a cyclotron by means of the Monte Carlo Code MCNP6 using characteristics of commercial cyclotrons with an energy for protons of 18 MeV. Liquid targets of Zn and Ni are considered in the model to obtain radioisotopes of Cu and Ga. Several simulations have been carried out using different compositions of the target. The geometry of the target is also a parameter of influence in the production of radionuclides due to the materials that interpose between the beam and the target material. This influence has been studied by performing simulations with different thicknesses in the materials of the window.

With the obtained data, the reactions produced and their efficiency in the generation of radionuclides have been analyzed. To validate the model, results have been compared with experimental data found in the literature.

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Optimization of the cyclotron production of ^{88}Zr/^{88}Y generators with a 70 MeV proton beam

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Keywords: ^{88}Zr/^{88}Y generators, cyclotron production, proton beam

Yttrium-88 is used in mixed gamma-efficiency calibration standards and also as a substitute for the therapeutic radionuclide ^{90}Y in determinations of chemical yield and labeling efficiency, as the latter radionuclide lacks suitable emissions for gamma-ray spectroscopy and imaging (c.f. [1] and references therein). At small-sized medical cyclotrons, ^{88}Y is typically produced in proton-induced reactions on targets of natural strontium, utilizing the ^{88}Sr(p,n)^{88}Y reaction [1,2]. At substantially higher energies, spallation reactions have proved useful. At Los Alamos National Laboratory, for example, ^{88}Zr/^{88}Y generator production has been based on chemically isolating the Zr induced in spent niobium target capsules [3] as a by-product from other productions. The advantage of the ^{88}Y obtained from a generator is that it is of exceptional chemical and radiochemical purity. Methods to extract the ^{88}Y from spent Nb capsules have also been established at iThemba LABS, similar to the Los Alamos strategy. In this way a useful radionuclide is obtained from waste material. While this strategy is undoubtedly sensible, there remains the question on how a dedicated, optimized production scheme will differ from this parasitic scheme, and how much in terms of yield and/or quality of the final product can be gained.

In the present study, the aim was to develop an optimized production scheme for ^{88}Zr/^{88}Y generators using natural target materials on a 70 MeV proton cyclotron. From the available nuclear data, it is shown that this can be achieved with a tandem Y/Zr target configuration. Several liquid ^{88}Zr/^{88}Y generators have recently been produced at iThemba LABS, consisting of stock solutions that contain up to 10 g of stable Zr in sulfuric acid media. The separation of the ^{88}Y from a stock solution is done with a macroporous cation exchange resin, with a very high elution efficiency, during which the bulk of the stock solution is collected almost unchanged except for the depletion of yttrium, to be kept for subsequent future elutions. It was demonstrated that the large amount of stable target Zr is not an impediment to the generator.

This "proof of principle" study included the targetry, radiochemical separation, generator production and thorough testing, investigating the shelf life of stock solutions by looking for possible slow chemical changes due to radiolysis, specific ^{88}Y activity, etc. Salient aspects of this work will be presented.

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Formation of stable and radioactive nuclides of Ga, Zn, Ni and Co during the activation of different Zn targets with protons for copper radioisotope production up to 100 MeV

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Keywords: proton beam, zinc targets, copper radioisotopes, stable and radioactive contaminants

Recently, several groups investigated the production possibility of medically relevant copper radioisotopes (^{61,64,67}Cu) using proton-induced nuclear reactions on zinc targets with different enrichment levels (c.f. [1,2]). During the activation of these targets, different amounts of other radioisotopes and/or stable nuclides are also formed (depending on the bombarding energy and irradiation time). The presence of these Ga, Zn, Ni and Co nuclides has influence both on the applicable (and useful) copper separation methods, and on the handling procedure of the radioactive waste.

Additionally, the enrichment level of those targets that are re-used many times (c.f. ^{68}Zn for ^{64,67}Cu production) could be changed due to the formation of stable Zn nuclides, produced either by the decay of different Ga radioisotopes (before the chemical separation) and/or by the secondary neutrons originating from the proton transport system. Similarly, the co-produced (or decay produced) stable ^{63}Cu and ^{65}Cu isotopes also decrease the available specific activity of the final copper products (c.f. [3]). To calculate the amount of the above stable and radioactive 'contaminants' at a known target composition and specific irradiation circumstances, reliable cross-section databases of all possible nuclear reactions, forming these isotopes, are required.

Historically, Zn+p reactions were used worldwide for large-scale radio-gallium production (^{66}Ga, ^{67}Ga, and ^{68}Ga) therefore the formation routes of these Ga radioisotopes were intensively studied in the past. As a result of these systematic investigations, reliable (and in some cases recommended) databases for cross sections and yields (both thick and thin targets) are available for these reactions up to 100 MeV.

Unfortunately, the picture is not so bright in the cases of those processes that result in Zn, Ni and Co isotopes, as well as Ga nuclides other than ^{66,67,68}Ga. The experimental cross-section databases of these reactions are either insufficient or in some energy regions still non-existent.

In this work, we aimed to prepare cross-section databases of the above reactions based on a critical analysis of the available literature data and extending them with our own measurements.

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Excitation functions for neon-induced reactions on copper up to 180 MeV

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Keywords: activation cross section, neon beam

The decommissioning of old accelerator facilities requires activation cross section data to estimate the residual activities induced in the accelerator components. But experimental data of induced activities are very scarce for low energy (lower than several tens MeV) heavy ions which were required for decommissioning of accelerator facilities such as tandem accelerator and cyclotron. We therefore irradiated 126, 189 MeV neon ions onto a Cu target to obtain experimental data of residual radioactivities for low energy heavy ions.

Irradiation experiments were performed at cyclotron facility (NIRS-930), National Institutes for Quantum and Radiological Science and Technology. The Cu targets were composed of a stack of natural Cu foils. The Cu targets were irradiated with beam intensity from 100 to 180 nA, for irradiation time from 1 to 4 hours. The beam current on the Cu targets were recorded with a current integrator, connected to a multichannel scaler to monitor the fluctuations of the neon beam.

After irradiation, radioactivities of produced nuclides on the Cu foils are determined by a HPGe gamma-ray spectrometry. The excitation functions of neon-induced reaction on the Cu foils by taking into account the projectile energy degradation in the target are estimated. In this conference, we will present these experimental cross section data, combined with calculated data.

Acknowledgments
The authors express their gratitude to the accelerator staff of NIRS-930 for generous sup-port during this experiment. This work was supported by JSPS KAKENHI Grant Number JP17K07010.

Prompt gamma activation analysis

Application of chopped beam-PGAA for short-lived isotopes

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Keywords: short-lived isotopes, delayed gamma emission, chopped-beam PGAA

We report chopped-beam PGAA collection of prompt and short-lived decay gamma-ray spectra in a single measurement. In Prompt Gamma Activation Analysis (PGAA), the decay γ rays are often obscured by the much stronger prompt gamma rays and the associated Compton scattering background. A beam chopper that cyclically blocks the neutron beam during the off cycle, eliminates the prompt γ rays, allowing measurement of very-short lived activation products with half-lives ($T_{1/2}$) less than one minute, without requiring physical transport of the sample. The neutron chopper at the PGAA instrument at NIST is a linear shutter which allows varying duty cycle (open to close ratio) with a timing resolution of 40 ms. The chopper is designed to work with neutron-gamma coincidence (prompt) and anti-coincidence (delayed).

F mass fraction at 100 mg/kg levels is difficult to determine non-destructively. Traditional neutron activation analysis (NAA), which involves irradiating samples in a reactor core with transport out for delayed counting, is impractical for F analysis because of the short $T_{1/2}$ (11 s) of ^{20}F.

Although normal PGAA can detect both prompt and delayed gamma rays, the high prompt gamma background due to Compton scattering overwhelms low levels of decay peaks, and in this case with a ratio of 1000 to 1. With the neutron beam chopper and the gamma detector acquisition in anti-coincidence mode, the decay gamma spectrum reveals the weak F peak (Fig. 1). Chopper cycle was set to 11 s on/off to match the $T_{1/2}$ of ^{20}F. Nearly 2000 chopper cycles were needed for F mass fraction at the 100 mg/kg level. Quantitative analyses have been performed by measuring prepared F standards in the same protocol. F concentrations from 100 mg/kg to 1000 mg/kg in PE matrix were determined, with uncertainty from 25 % (100 mg/kg, 18 h count time) to 5 % (1000 mg/kg, 6 h count time).

We demonstrated that the decay spectra, with lower noise baselines and fewer gamma-ray lines, are valuable for samples producing complex gamma-ray spectra, potentially lowering detection limits and increasing selectivity for some elements. Further development will continue with placement of a second detector at a closer distance, optimizing chopper duty cycle, and acquiring time-stamped list-mode data for off-line analysis.

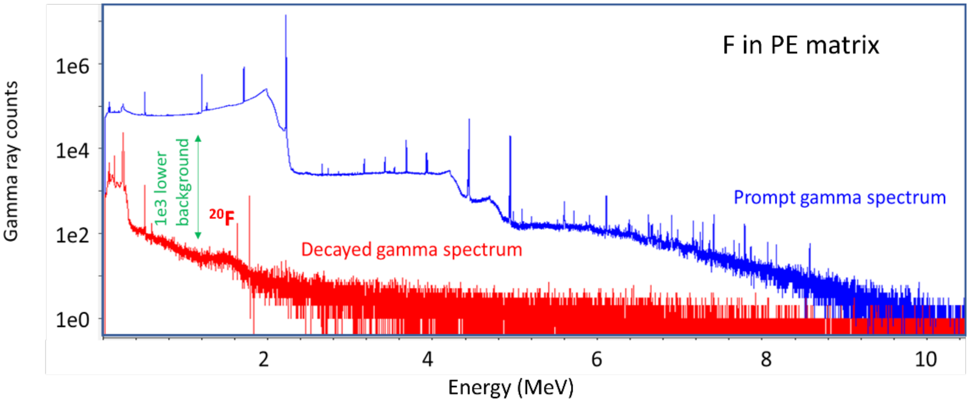

Fig. 1. An example of the chopped-beam PGAA application: F in polyethylene. Spectrum was acquired with the chopper cycle set to 11 s on/off to match the $T_{1/2}$ of ^{20}F, for nearly 2000 chopper cycles.

The PGAA potential for compositional ancient glass analysis – the case of late Roman and Byzantine glasses

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Presented by Boglárka Maróti

Keywords: PGAA, Budapest Research Reactor, Roman glass, Byzantine glass

Compositional analyses were performed on glass samples found in archaeological excavations from Dobroudja at the border of Black Sea. The samples were shards of late Roman glass (III-V Centuries AD) and fragments of colored Byzantine bracelets (X-XI Centuries). The analyses were performed by PGAA (Prompt Gamma Activation Analysis) at Budapest Research Reactor. From PGAA, the concentration of the major components, i.e. Na, Mg, Al, Si, K, Ca, Mn and Fe can be determined. Detection of Na and B are of special importance, because they are difficult to identify with X-ray based methods

For Roman glass samples (all transparent, only few with a pale greenish aspect) we focused on sodium, magnesium, aluminum, chlorine, potassium, calcium, manganese, antimony, boron concentration – characteristic for the antique recipes. For Byzantine samples (colored – blue, black, green, brown – fragments) we focused on sodium, potassium, calcium and on colorants agents as metallic oxides (iron, cobalt, copper, manganese, lead, tin). A discussion about the evolution of recipes in Balkan Peninsula during the First Millenium is presented.

Design of the explosion-proof detection integrated system based on PGNAA technology

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Keywords: explosion-proof, PGNAA, system optimization, Signal-to-Noise Ratio (SNR), explosive detection

Public security is always the focus of people's attention. How to detect the explosive in the luggage effectively, as well as prevent the hazards and panic caused by explosion in public, is an urgent problem to be solved[1-2]. Hence, the Explosion-Proof Detection integrated System (EPDS) based on PGNAA technique is investigated in the research. With the D-T neutron generator and BGO detector as the core components, the hardware modules in EPDS, including explosion-proof layer, reflection layer, etc., are modeled and optimized based on SNR evaluation method in MCNP simulation (Fig.1), finally improving the measurement performance of EPDS. Moreover, the device was modeled and tested in ANSYS software, and the result of stress test indicated the good explosion-proof performance of EPDS.

Based on the optimized model in MCNP simulation, the EPDS system was established (Fig.2) for identifying the simulated samples. C, H, O, N are chosen for spectra analysis, and the peaks are calculated by fitting method. Though the explosives have the similar elementary composition or morphology to ordinary goods, with the analysis results of simulated samples, it indicated that the explosives could be indentified based on the element ratio analysis within 300s live time(fig.3), showing the good identification performance of EPDS. In addition, the Graphical User Interface(GUI) was designed for matching with EPDS system(Fig.4), finally making a convience for explosive detection.

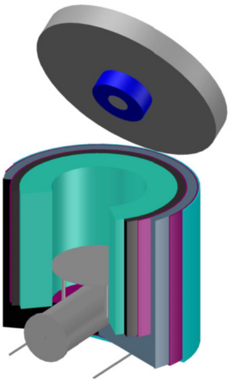


Fig.1 Sectional axonometric drawing of EPDS

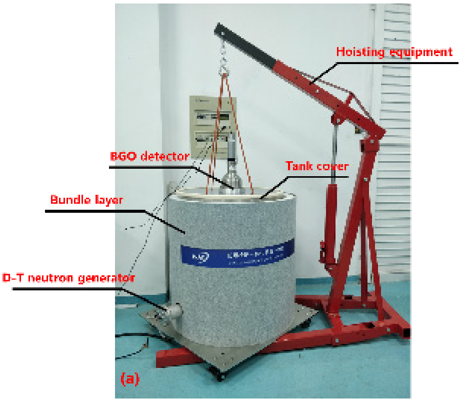


Fig.2 Experimental device of EPDS

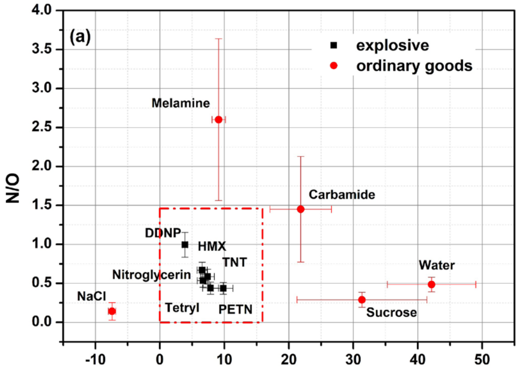
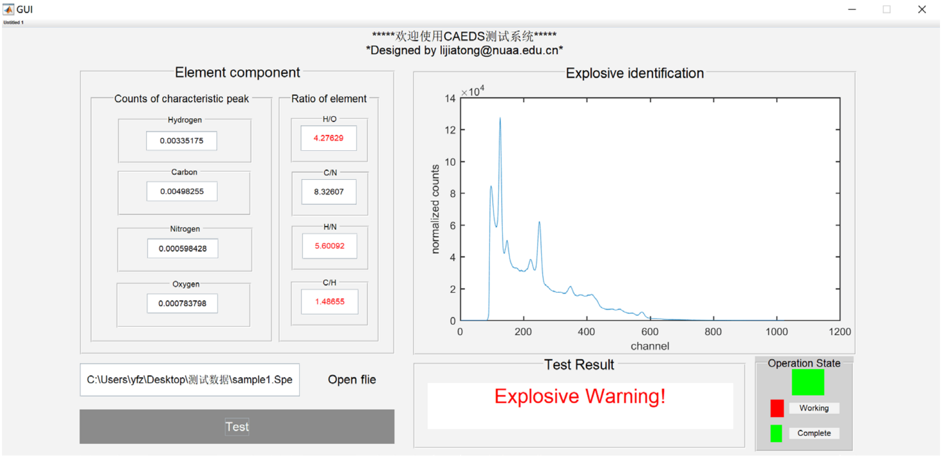


Fig.3 Identification of samples based on element ratio



*****欢迎使用CAEDS测试系统*****
Designed by lijiatong@nuaa.edu.cn

Element component

Counts of characteristic peak

Hydrogen: 0.00335175
Carbon: 0.00498255
Nitrogen: 0.000598428
Oxygen: 0.000783798

Ratio of element

H/O: 4.27629
C/N: 8.32607
H/N: 5.60092
C/H: 1.48655

C:\Users\yfz\Desktop\测试数据\sample1.Spe

Test Result: Explosive Warning!

Fig.4 Graphical User Interface of EPDS

Acknowledgments

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Radioecology and environmental radioactivity

Developing the detector efficiency determination procedure of well-type HPGe detector for low activity and small amount environmental samples such as attic dust

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Keywords: gamma-spectrometry, efficiency, heavy industry, Salgótarján

Determination of the efficiency of well-type HPGe detector for small amount environmental sample (<20g) is the subject of radiation detection studies. Since gamma-spectrometry is a good method for determining the radioactive element content of samples with small amount and environmental samples. Additionally, compared to the ICP-MS, gamma-spectrometry is cheaper, does not need complex sample preparation and it is non-destructive.

Heavy industry areas are the source of atmospheric pollution all around the world. Attic dust (from undisturbed attics) has particularly small amount and low activity, however they can be used for radioactive pollution evaluation of the industrial areas (Cizdziel Et Al., 1998). Salgótarján is one of the biggest heavy industrial areas in Hungary. The city and its environment were polluted by several sources such as coal mining, the local coal fired power plant (it worked between 1860 and 1980), iron and steel works, glass factory etc. The waste of the industrial activities (coal and steel slag, ash, sludge) was released into the environment without any regulation and heaped in the city (at Inászó, Kucord-hill, Pintértelep, Salakhegyi street). These waste dumps (e.g. the slag dumps of the Kucord-hill, the ash dumps of Pintértelep) are located within the city limits and can be enriched in radionuclides, such as U, Th, Ra and ^{40}K. The slag was widely used as a building material (slag brick, or slag concrete) and as landfilling material in parks, playgrounds and kindergartens. This is a potential risk for the human health because the material of the waste dumps can be mobilized as a result of natural processes. Due to the long-term coal mining and industrial activity, Salgótarján is a suitable place to carry out detailed urban geochemical studies on attic dust (collected from churches, kindergartens, family houses, block houses) samples.

The ^{238}U, ^{235}U(?), ^{232}Th, ^{226}Ra, ^{137}Cs and ^{40}K content of the collected attic dust samples were measured by a well-type HPGe detector in a low-background chamber. The aim of this study was to develop the full energy peak efficiency determination procedure of this well-type HPGe detector for these low activity and small amount environmental attic dust samples. To achieve this goal, we compared the results of the Monte Carlo simulation with experimental data using standard radionuclides with standardized activity A (Bq) and with a calibration standard.

Acknowledgments

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Study of the absorption and translocation of the herbicide in plants and soil using radiocarbon

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Keywords: herbicide, C-14, microcosm

Sulfonylurea derivatives is a class of chemical compounds including herbicides of a new generation demonstrating high biological activity and a consumption rate which is by one or two orders of magnitude lower as compared to the traditionally used chemicals. Sulfonylureas are the compounds with the common structure R_1-SO_2NHCONH-R_2, where R_1 is an aromatic radical or other ones, and R_2 is a substituted pyrimidine or s-triazine residue. The Ecological Risk Assessment (ERA) evaluates the potential risks to plants and animals due to the use of the herbicide rimsulfuron, including risks to rare, threatened, and endangered (RTE) plant and animal species. Information from this ERA will be used to prepare EIS.

In this connection, the aim of the present study has been to reveal the mechanisms of the impact of a herbicide belonging to the pyrimidine-sulfonylurea class, rimsulfuron, on plants in simulation experiments.

Experiments were performed with 14C-rimsulfuron to trace the molecule distribution in soil layers as well as in different parts of plants and mineralization. The experiments were made with the following treatments in triplicate: microcosms without plants as controls and microcosms with plants. The experiments allowed one to compare the behavior of rimsulfuron in the presence and absence of plants under the laboratory conditions. Two-week seedlings of *Zea mays* L., 1753 were used in the experiment. Each microcosm was sprayed with the obtained mixture (either the plants or the soil in the case of the absence of plants were treated). The treatment was carried out carefully to minimize the amount of the mixture getting onto the walls of the system. The introduced reactivity per each microcosm amounted to ~ 95 kBq.

Our results show that in the system with plants a great part of radioactivity is observed in the leaves (~41 %) while in the system without them it is observed mainly in the soil, which is due to the experimental conditions.

The physiology of the corn leaves did not undergo any significant changes, while the estimated ^{14}C content was likely to be present only at the surface or on the top layer of leaf lamina epidermis.

This assumption was confirmed by the results obtained using autoradiography.

As is seen from the results obtained, the larger amount of radiocarbon is located in the part of the leaf which is the closest to the stem (the lighter area in the figure) with some inclusions in the other parts of the leaf.

In these studies, the herbicide used hardly affected the development of corn seedlings.

Acknowledgments
The work was performed as part of the fundamental research

Quantification of radium in environmental samples: Cationic extraction and ICP-MS analysis

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Keywords: radium, environmental samples, ICP-MS/MS

Radium is a radioelement of interest since it is ubiquitous in the environment due to its high mobility in water [1]. Therefore, its monitoring in drinking water is recommended by the World Health Organization with a limitation at 1 Bq L^{-1} for ^{226}Ra, Ra isotope with the longest half-life (1600 y) [2]. Some regulations also recommend to screen water samples for ^{228}Ra, a decay product from ^{232}Th decay series, which has a shorter half-life of 5.75 y [3]. Despite all these recommendations for water analyses, there are actually no guidelines for Ra in food or environmental samples. This lack of regulation is due, in part, to a lack of reliable data regarding radium content in these matrices. The development of a robust method for radium quantification (^{226}Ra and/or ^{228}Ra) from more complex matrices than water could facilitate the quantification of Ra and help regulators to elaborate suitable guidelines.

In this study, the method proposed by St-Amant *et al.* [4] based on ionic chromatography was modified to rapidly quantify ^{226}Ra and ^{228}Ra by inorganic mass spectrometry in a broad variety of matrices at environmental levels. The sample volume loaded on the cationic resin AG50Wx8 was varied to achieve the highest possible adsorption without any significant loss of retention for radium. The pH and volume for the elution steps were optimized to obtain the highest pre-concentration factor and compatibility with plasma-based instruments and to minimize the presence of interferences. Finally, inductively coupled plasma mass spectrometry (ICP-MS) instrumental conditions were optimized for the quantification of radium. An instrumental detection limit of 0.53 pg L^{-1} in ^{226}Ra and 0.47 pg L^{-1} in ^{228}Ra were achieved. When combined with the cationic separation procedure for interference removal, the overall method detection limit decreases to 10 fg L^{-1} in less than 2 hours. [5]

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Comparison study of ancient burnt rice found at Thailand archaeological sites

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Keywords: ancient burnt rice, SEM-EDS, Micro-beam XRF, IR spectroscopy

Rice is the main foodstuff for about half of the world's population, especially in Asia. In Thailand, it is the essence of life. Archaeological evidence which based on the paddy rice revealed that rice has been planted in northeastern area of Thailand more than 5,000 years ago. The burnt rice grains were found in various archaeological sites in Thailand which related with the religious ceremony and the home prosperity. In this work, the ancient burnt rice from Nakorn Nayok (Ban Dong Lakon), Suphan Buri (U-Thong) and Prachin Buri (Sri Mohosot) was elementally analyzed using micro-beam XRF based on synchrotron radiation. FE SEM-EDS was carried out to characterize the structure and composition. IR spectroscopy was also used to study the chemical composition and bio-molecular structure. The grains were oblique in shape with a rough surface. It was found that major elements contained C, Si, Ca and Al. Other trace elements such as Ti, Mn, Fe, Cu and Zn were also detected. The IR spectra gave some information about the presence of molecular bonds.

Acknowledgments

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Measuring radon and thoron concentration in groundwater sources

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Keywords: radon, thoron, detector, hydrogeology

Measuring the radon and thoron concentration of the groundwater sources of the Buda Thermal Karst System helps us to better understand its path and velocity in the ground, the temporal variability of concentrations, so thus the hydrogeological convections, the mixture of groundwater and meteoric water, and the mineral environment that causes anomalous radiation (120 Bq/l – 600 Bq/l).

To be able to measure the concentration of radioactive isotopes in water, we used RAD7 connected to bubbling water bottles to use the radon and thoron concentration in the bubbles as a proxy. Although this debubbling method has been widely used in international studies, but the Hungarian application is rather unique. The measurements happened on site at the Diana-Hygieia Thermal Spring in 2018 and 2019.

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Radiological assessment on the terrestrial non-human biota in Turkey using ERICA tool

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Keywords: dose rate, natural radioactivity, soil, animal, plant

This paper presents the environmental radiological impact in the terrestrial ecosystem across Turkey by ERICA Tool [1]. Activity concentrations of naturally occurring radionuclides ^{226}Ra, ^{232}Th and ^{40}K, and artificial radionuclide ^{137}Cs in soils were compiled from literature [2]. The average activity concentrations in the seven regions, Aegean, Black Sea, Central Anatolia, Eastern Anatolia, Marmara, and Southeastern Anatolia, in Turkey, were calculated from compiled data. According to the average values, the highest natural activity levels were determined in Central Anatolia, and the highest ^{137}Cs activity level was determined in Black Sea. The average soil activities were used as input to ERICA Tool, operating in a Tier 2 assessment mode using the default parameter setting. ERICA Tool estimates activity concentrations, external dose rate, internal dose rate, total dose rate and total dose rate per organism and risk quotient for reference organisms (amphibian, annelid, arthropod, bird, flying insects, lichens & bryophytes, mammal-large, mammal-small, mollusc, reptile, shrub, and tree).

The results showed that the expected risk value is less than unity and total dose rate per organism is less than the default screening dose rate value,10 μGy h^{-1} for all organisms. Among the organisms, the highest total dose rate and risk quotient is estimated for lichen & bryophytes, shrub, and grasses & herbs in Central Anatolia, respectively. ^{226}Ra is the main contributor radionuclide to the total dose rate, from 83.4 % to 98.8 %. The results of this work may be used as a basis for further studies considering Turkey's first nuclear power plant, Akkuyu NPP, is under construction in Mersin province situated in Mediterranean region and planned to be in operation by the end of 2023.

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Complex study of the radiation and environmental situation on the territory of the water basin of the water reservoir Tasotkel

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Keywords: transboundary rivers, natural radionuclides, toxic elements

The following radiation-hazardous objects (RHO) are located on the territory of Kyrgyzstan and the basins of the rivers bordering with Kazakhstan: the polymetals and thorium deposit “Ak-Tyuz”, the uranium deposit “Kamyshanovskoye”, the largest mining complex for uranium processing “Kara-Balta”. It is known that the tailing-pools of the plants “Ak-Tyuz” and “Kara-Balta” contain a large amount of natural radionuclides (NR) and toxic elements (TE). In addition, the intensive agricultural activities are carried out in this area using the NRs-containing mineral fertilizers. This situation creates a great probability for contamination with NRs and TEs of the entire irrigation system and the transfer of these contaminants to the territory of Kazakhstan with the waters of the transboundary rivers Shu, Shor-Koo, Aksu, Karabalta and Toktas.

Radiation survey and sampling of the environmental objects (soil, sediment and water) were performed in accordance with the provided scheme. It has been established that the values of the equivalent dose rate (EDR) in the surveyed area are in the range of (0.08-0.19) μSvh^{-1}. Radionuclide and elemental composition of the collected environmental objects samples was determined by the methods IGS, XRF, NAA and MS-ICP. According to XRF data, the high content (relative to world average) of the TEs (As, Mo, Pb, Th, U) was revealed at many TPs and CPs in soil and bottom sediments. According to IGS on ^{226}Ra, ^{228}Ac and^{40}K-specific activity in these objects, the absorbed dose rate (ADR) values at all TPs and CPs were calculated (in accordance with the UNSCEAR 2000 recommendations). It was established that the average ADR value (80 $nGyh^{-1}$) in the entire surveyed area exceeds the world average value of this indicator (60 $nGyh^{-1}$) by 33%. MS-ICP data showed that the waters of all studied water sources are characterized by the increased concentration of the following TEs: As, B, Li, Mo and, especially, U (up to 60 $\mu g\ L^{-1}$), for which MAC_{WHO}=30 μgL^{-1}.

The obtained results indicate that the territory of the water basin of water reservoir “Tasotkel” is contaminated with NRs and TEs, inflowing from Kyrgyzstan with the waters of the transboundary rivers. It is required to perform the studies for search of the sources and identification of the mechanisms of these rivers contamination on the territory of Kyrgyzstan.

Scheme of radiation survey and sampling of the environmental objects on the territory of the water basin of the water reservoir Tasotkel

Isotope geochemical survey of the chamber fields of the Bátaapáti National Radioactive Waste Repository

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Keywords: isotope geochemistry, stable isotope, radiocarbon

In the area of the chamber fields of the Bátaapáti National Radioactive Waste Repository (NRWR), there are tapping drills (packers) in the side walls, which are divided into several separate zones to take samples (multi-packers). With the isotope-geochemical analysis of the water samples from the multi-packers, more accurate image can be obtained about the water flow and the drainage conditions of the chamber field. This makes possible on the one hand the nature of the drainage of the cracks and the forecast of the refill of the repository after its abandonment and on the other, it can be analysed whether in the vicinity of the repository, there is water with a composition impairing the condition or the life time of the tunnel support.

In this research, principally the test series of 2011 were broadened, which included the analysis of only two multi-packers (Bp2 and Bp3) and provided only spatially limited information. The further analyses performed few years later helped the monitoring of the long-term changes. The tritium, the stable isotope, the radiocarbon and the noble gas data were good indicators for the changes in the aquifer. Although the size of the depression decreased due to the decrease of the water exploitation, the decrease of the hydraulic potential has still not stopped everywhere in the vicinity of the tunnel system.

The most comprehensive results are available for the Bp2 and the Bp3 drills. On the basis of these results it can be stated that the water of these packers became a bit younger during the analysed period.

Determination of the background activity of Be7, K40, Sr90, I131, Cs-134, Cs-137, Pu-238, Pu-239 and Pu-240 in Austria

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Keywords: radiochemical analysis, Pu-239/240, Pu-238, Sr-90, alpha spectrometry, gamma spectrometry

In late September 2017 an emission of Ru-106 was detected at several locations across Europe. Based on that incident the question emerged if in addition to Ru-106, Sr- and Pu-isotopes were emitted as well. As the actual activity concentration corresponding to the background values of these isotopes were only known for certain sample matrices at that time, the aim of our project was to determine these values for additional sample types. Sr90, Pu238, Pu239/240 and the gamma-emitting nuclides Be7, K40, I131, Cs134 and Cs137 were determined in order to ensure heightened levels of anthropogenic isotopes in the environment are discovered quickly. Within the scope of this project surface water samples were taken from the river Morava[1] as well as snow samples from Carinthia[2]. In addition, precipitation[1] and air filter samples[1] from Vienna were used. All samples were analysed in the laboratories of the Austrian Agency for Health and Food Safety.

First the activity concentration of each sample was determined by gamma spectrometry. Whereas all liquid samples were evaporated to dryness and measured to achieve a good lower limit of detection. Afterwards the radiochemical analysis of the different matrices took place starting with the ashing procedure and the oxidative acid digestion using concentrated HNO_3. Then the Pu and Sr isotopes were separated by ion-exchange chromatography and extraction chromatography. In the end, the Pu-fraction was concentrated by micro precipitation and quantified by alpha spectroscopy. The Sr activity was determined by liquid scintillation counting. In order to verify the chemical recovery of the analytes a Pu242 tracer and a Sr86/Sr88 tracer were added and determined by ICP-MS (yield about 90% for Sr) and alpha spectroscopy (yield about 70% for Pu).

All measurement values for the different sample matrices were just above or below the limit of detection. Therefore, the analytical results of this project may be used as a reliable data set for the natural background in Austria.

[1] Samples of the official environmental monitoring program of Austria according to the EURATOM Treaty and the Austrian Radiation Protection Act.

[2] Samples collected from defined sampling points that will be collected during an emergency situation.

Behavior of radiocaesium in forest catchments contaminated by the Fukushima Dai-ichi Nuclear Power Station accident

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Keywords: radiocaesium, behavior, stream water, forest catchment

A huge amount of radionuclides such as radiocaesium and radiostrontium were dispersed and deposited on the territorial area of Fukushima Prefecture, Japan, after the accident at the TEPCO Fukushima Daiichi Nuclear Power Station (FDNPS) on March 2011. Since Fukushima prefecture is covered by 70% of forest area, it is important to clear the distribution, behavior and runoff process of radiocaesium in this area. In this study, we collected stream water from two type of forest catchments (the difference of air does rate) and river water in mainstream within evacuation zone in vicinity of the FDNPS from December 2017 to January 2019, and assessed the distribution, biogeochemical behavior and fluxes of dissolved radiocaesium in these areas. Activity concentrations of dissolved ^{137}Cs in stream water collected in Takase River (mainstream: ~1 μSv h^{-1}), Saruta River (~4 μSv h^{-1}), and Maeda River (~2 μSv h^{-1}) ranged from 10.3 to 37.2 mBq L^{-1}, 44.3 to 322.9 mBq L^{-1} and 8.6 to 29.8 mBq L^{-1}, respectively. These results indicate that the activity concentration of dissolved radiocaesium is depended on the air does rate around catchment area in the river. Also, activity concentration of dissolved radiocaesium collected in Takase River and Maeda River related to water temperature. This result suggests that influential source of dissolved radiocaesium in these two rivers are desorption from litter. However, activity concentration of dissolved radiocaesium in Saruta River unrelated to water temperature. The relationship between activity concentration of dissolved radiocaesium and total concentration of sodium (Na^+) and potassium (K^+) showed positive correlation. From these results, it is inferred that some part of radiocaesium in Saruta River is likely bonded to an exchangeable fraction of particles, which is easy to leach into the water caused by ion exchange.

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Study of phosphate sorption of soils by radioactive tracer method

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

Phosphate fertilizers are widely applied in modern agriculture. The phosphate supplies, however, are rather limited, so the economical application of phosphate fertilizers is essential. Phosphate anions react with the different soil components, different interfacial and chemical reaction occur, a part of them sorb phosphate very tightly. The ratio of the sorbed phosphate species can be studied by heterogeneous isotope exchange, the portion of utilized by plants can be determined in this way. Unfortunately, the models applied in the literature for the treatment of heterogeneous isotope exchange base on incorrect principles.

The ratio of these species on some Hungarian soil types was studied by radioactive tracer method using ^{32}P isotope as phosphate ion. The effect of soil type, phosphate quantity, incubation time and plant growing was studied. The ratio of weakly sorbed phosphate can be studied by heterogeneous isotope exchange; the quantity of water soluble/weakly sorbed phosphate as well as the transport rate of phosphate in a steady state between the soil and soil solution was determined. The evaluation was made by a correct thermodynamic and mathematical model for the evaluation of the heterogeneous isotope exchange.

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Measurement of NORM in geologic and building materials by the double counting - gamma spectrometry

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Keywords: NORM, building materials, gamma spectrometry, double counting

Double counting – gamma spectrometry (DC-GS) was devised to determine the activity concentrations of naturally occurring radioactive materials (NORM) in geologic and building materials. The main radioactive nuclides in NORM for building materials are ^{226}Ra, ^{232}Th and ^{40}K. These radionuclides are a source of gamma emitting products, which will contribute to the external radiation dose. ^{226}Ra is the parent nuclide of radon (^{222}Rn), which will contributes to the internal radiation dose as well. For the determination of ^{226}Ra in natural samples using general gamma spectrometry (GGS), the samples must be stored at least 20 days for radioequilibration between ^{226}Ra and its progenies. Sometimes for radiation dosimetry, the activity concentration of radium(^{226}Ra) and the exhalation of radon (^{222}Rn) in some building materials, such as fly ash for cement and concrete, granite piece for interior materials, and gypsum for plaster board must be measured in short time. So far, the activity concentrations of NORM in some geologic and building materials by GGS could be determined and evaluated more than 20 days after sealing the counting bottles.

In DC-GS, the samples were measured 2 times using gamma spectrometry in 3 to 7 days after sealing the counting bottles. The activity concentrations of ^{226}Ra as well as ^{232}Th, ^{40}K in natural samples can be determined within a week by using the DC-GS. The activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K determined by DC-GS were compared with those determined by GGS and that results agree within a 95 % confidence level. The DC-GS method can also be recommended for use in evaluation radon exhalation from geologic and building materials.

Natural radionuclides and toxic elements in the border areas of rivers flowing into Kazakhstan from Kyrgyzstan

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Keywords: transboundary rivers, natural radionuclides, toxic elements

General situation on the territory of Kyrgyzstan in the basins of transboundary rivers, flowing into Kazakhstan, is characterized by many factors (availability of radiation-hazardous facilities, intensive agricultural activities with the use of mineral fertilizers, compact and densely interconnected irrigation system) creating a high probability for contamination of the entire irrigation system with natural radionuclides (NR) and toxic elements (TE) and the transfer of these contaminants to the territory of Kazakhstan with the water of these rivers.

This paper provides the results of radiation survey and the study of radionuclide and elemental composition of the environmental objects (water, soil and bottom sediments), sampled directly near the border with Kyrgyzstan in the main transboundary rivers (Shu, Aksu, Aspara, Talas), in many small rivers (Shor-Koo, Karabalta, Toktas, Sargau, Oirandy, Kaiyndysay, etc.) and in the Big Shu Channel. The equivalent dose rate (EDR) values were measured at each control point (CP) during the field works. It was established that EDR values are within 0.10-0.30 μSvh^{-1}. The analysis of the collected samples was performed by IGS, XRF, NAA, MS-ICP and radiochemical analysis. According to IGS data for^{226}Ra, ^{228}Ac (^{232}Th) and^{40}Kspecific activity in the samples of soil and bottom sediments, the absorbed-doserate (ADR) values were calculated (in accordance with the recommendations of UNSCEAR 2000) at all CPs. It was established that the ADR values are within 75-160 nGyh^{-1}, that is, notable (and even significantly) exceed its world average value (60 nGyh^{-1}). Based on XRF and NAA data for coastal soil and bottom sediments, the heightened content (relative to the world average "clarke" value) of As, Mo, Pb, Th, U, Zn and all rare-earth elements were revealed at many CPs. The highest concentration of some of these elements wasidentified in the coastal soil of the river Kichi-Kemin, μgg^{-1} (the "clarke" value according to A.P. Vinogradov is provided in brackets): Mo-11.2(2), Pb-175(6), Th-41(6), La-78(27), Ce-157(53), Nd-60(25). MS-ICP data showed that the waters of all studied water sources are characterized by a high concentration of the following TEs: As, B, Li, Mo, especially U (up to 100μgL^{-1}), for which MAC_{WHO}=30 μgL^{-1}. Based on radiochemical analysis with α-spectrometry termination, new data on the isotopic composition of (^{234}U, ^{238}U) uranium was obtained for the studied water samples. The values of specific activity ratio (A) of these isotopes were calculated. It was established that the calculated values of their ratios ($A_{U\text{-}234} \times A^{-1}_{U\text{-}238}$) mainly vary in the interval of 1.13-1.70. The lowest values of this indicator were established for the water of the rivers Shor-Koo and Oirandy, which indicates a significant proportion of the technogenic component of uranium available in them [1].

On the basis of the obtained results, the most probable sources and the mechanisms of contaminationof the transboundary rivers on the territory of Kyrgyzstan have been discussed.

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Radiogenic diversity of West Arctic tundra

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Keywords: radioactive contamination, lichens, mosses, Western Arctic

The research concerned state of radioactive characteristics of lichens and mosses coming from coastal zones of Southwestern Greenland, Canadian Arctic and Alaska. Over 100 samples were collected from 14 positions during two scientific expedition in 2012 and 2013. There were examined 13 species of lichens and 8 species of mosses. Application of radiochemical procedures as well as nuclear spectrometry methods allowed to calculate activity concentration of following artificial and natural radionuclides: ^{90}Sr, $^{134,\ 137}$Cs, $^{230,\ 232}$Th, $^{234,\ 238}$U, $^{238,\ 239+240}$Pu and ^{241}Am. However, the most relevant step was to establish typical isotopic ratios such as: ^{134}Cs/^{137}Cs, ^{137}Cs/^{90}Sr, ^{238}Pu/$^{239+240}$Pu, ^{241}Am/$^{239+240}$Pu, $^{239+240}$Pu/^{137}Cs, $^{239+240}$Pu/^{90}Sr, ^{230}Th/^{232}Th, ^{234}U/^{238}U and ^{232}Th/^{238}U. Additionally, for 60 samples there were made measurements on ICP MS in order to determine of ^{240}Pu/^{239}Pu mass ratios. Therefore, a relatively large data set was obtained, which was then used to make a radiological assessment of the studied area.

Firstly, it was stated the contamination of research material caused by anthropogenic radionuclides was relatively low, reaching the maximum values at: 78.7 ± 4.0 Bq/kg for ^{90}Sr, 25.3 ± 5.4 Bq/kg for ^{134}Cs, 293 ± 27 Bq/kg in case of ^{137}Cs, 7.46 ± 0.33 Bq/kg for $^{239+240}$Pu, 0.268 ± 0.019 Bq/kg for ^{238}Pu and 2.95 ± 0.19 Bq/kg of ^{241}Am. The natural radioisotopes of thorium and uranium were found in whole examined region and the highest values of activity concentration were as follows: 15.33 ± 0.53 Bq/kg for $^{230\mathrm{Th}}$, 25.1 ± 1.2 Bq/kg in case of ^{232}Th, 22.5 ± 3.3 Bq/kg for ^{234}U and 21.5 ± 2.1 Bq/kg for ^{238}U. The analysis of isotopic ratios revealed dominant contribution of global fallout + SNAP 9A on the presence of plutonium isotopes and ^{241}Am in Western Arctic tundra. The determination of radiocesium and radiostrontium origin turned out to be much more complicated. Nevertheless, in-depth investigations made it possible to establish some regional characteristics for considered radioisotopes. Because the traces of ^{134}Cs were observed and the Fukushima fallout signature was found in research material from Alaska, this releases of radioactivity seemed to be the major sources of radiocesium there. Results obtained from Canadian Arctic showed the nuclear weapon tests was the main sources of ^{137}Cs and ^{90}Sr in northwestern part of the region, but the additional sources was manifested in northeastern part which may be related with Cosmos 954 catastrophe. In Greenland, the origin of ^{137}C was evidently related to the coexistence of global and Chernobyl fallout, while the occurrence of ^{90}Sr was caused only by the first one. Besides, there were noticed several cases of leaching of strontium and cesium. The natural radioactivity results analysis allowed to observe the uranium/thorium content was higher in Canadian Arctic than in Greenland. Moreover, dry deposition seemed to be the dominant sources of uranium in Canadian Arctic, whereas it was appeared marigenic origin of these isotopes in Greenland. Generally, the TENORM existence was not detected in research material. The main conclusion of the radioaccumulation properties studies was the mosses have comprised larger reservoir of each examined type of nuclide. It was possible to classification obtained isotope content disproportions between lichens and mosses in following order: ^{90}Sr << ^{137}Cs, ^{230,232}Th, ^{241}Am < ^{234,238}U, $^{239+240}$Pu. On the basis of comparison this project's results with those coming from second half of 20th century, it was possible to establish the loss process of accumulated radionuclides with time was much more effective in case of lichens than mosses.

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Radiation-induced reactions of ketoacids in aqueous solution and their possible role in chemical evolution studies

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Keywords: ketoacids, gamma radiation, chemical evolution

Chemical evolution is the process through which simple compounds generate organic compounds essential for the development of life. The study of chemical evolution provides insights into the steps that preceded the appearance of life. A critical factor in chemical evolution is related to the chemical stability of the molecules formed by abiotic processes. The stability of organic compounds is an important factor in the evaluation of plausible scenarios for the formation of organic molecules in the primitive Earth. In this context, we studied the steady-state γ-radiolysis of ketoacids of astrobiological importance in aqueous solutions at high irradiation doses. The acids under study were α-ketoglutaric and pyruvic acids. We carried out the irradiation in a ^{60}Co gamma source (Gammabeam 650 PT), with doses up to 280 kGy, For the analysis, we used various spectroscopic and chromatographic analytical methods. The gamma irradiation of α-ketoglutaric acid formed appreciable amounts of succinic acid, succinic acid dimer, whereas pyruvic acid formed its dimeric product.

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Radioactivity of sodium-22 and sodium-24 produced in low-activation concrete used for the accelerator tunnel in J-PARC

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Keywords: low-activation concrete, sodium-22, sodium-24, proton accelerator, neutron

In high-energy proton accelerator facilities, secondary neutrons are produced by nuclear reactions at beam loss points. These neutrons produce radionuclides in accelerator components, room air, and concrete materials constituting the tunnel walls, floors, and ceilings. In general, sodium is one of the major elements in concrete materials. It becomes a parent nuclide producing ^{24}Na ($T_{1/2}$: 15 h) and ^{22}Na ($T_{1/2}$: 2.6 y); ^{24}Na is produced by the thermal neutron capture (n, γ) reaction, whereas ^{22}Na is produced by the fast neutron (n, 2n) reaction. Sodium-24 is the most dominant radionuclide involved in γ-ray exposures on radiation workers immediately beyond the beam stop, and ^{22}Na must be addressed from the perspective of decommissioning of accelerator facilities. To solve such problems, ”low-activation concrete”, which has low Na content, was developed for reducing ^{24}Na and ^{22}Na production.[1,2]

The Japan Proton Accelerator Research Complex (J-PARC)[3] is a large research facility using world-class high-intensity proton beams (design value; 3 GeV: 1 MW, 30 GeV: 750 kW); hence, extremely intense neutrons are produced at beam loss points. At the areas around beam-loss points, low-activation concrete was adopted in the facility-design stage of J-PARC, to reduce ^{24}Na and ^{22}Na production.

To study the production process of radioactivity in concrete, test concrete samples for radioactivity measurements were installed at twelve locations in concrete walls in the J-PARC facility. This work focused on the differences in the radioactivity produced in ordinary and low-activation concrete, and the differences were studied using radioactivity measurement and calculation methods.

The radioactive concentrations of ^{22}Na were measured using a high-purity Ge detector and were compared at two locations (depth: 30-95 mm) where ordinary concrete (Na: 1.3%) and low-activation concrete (Na: 0.035%) were used, respectively. For these locations, the dominant beam loss corresponded to the same proton energy of 400 MeV, and the fast-neutron fluences were estimated to be similar. The radioactive concentrations of ^{22}Na were determined, using radioactivity measurements, to be 2.9×10^{-2} Bq/g in ordinary concrete and 6.2×10^{-3} Bq/g in low-activation concrete. The effect of reducing ^{22}Na by adopting low-activation concrete was certified for the first time in this work, using practical radioactivity measurements of concrete at high-energy accelerator facilities.

The radioactive concentrations of ^{24}Na were estimated by Monte Carlo simulations. It was demonstrated that the concentrations of ^{24}Na decrease drastically (~1/40) when low-activation concrete is adopted.

Detailed discussion on the production process of ^{24}Na and ^{22}Na, considering the analyzed elemental compositions of the concrete materials, is also presented.

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Estimation of inital ^{129}I/^{127}I ratio for groundwater dating – case study for coastal zone in Japanese island

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Keywords: ^{129}I/^{127}I, ^{14}C, inital ratio of ^{129}I/^{127}I, AMS, groundwater

Iodine-129 (half-life: 15.7 Ma) is one of the most promising tracer for very old groundwater dating. ^{129}I is going to be popular dating method for groundwater flow and cycling of deep organic material. It will contribute that CO_2 storage and high-level radioactive waste disposal. However, ^{129}I ages are normally very old compared to other methods (e.g. ^{14}C, ^{36}Cl, ^{4}He). The currently measured value of 1.5×10^{-12} has been used as the initial ratio of iodine. Researchers have used this isotope to determine the age of groundwater based on an initial ^{129}I/^{127}I ratio of 1.5×10^{-12}. However, we found that the age of groundwater in coastal zone did not coincide with the accepted sedimentation age by using the traditional initial ^{129}I/^{127}I ratio of 1.5×10^{-12} (Mahara et al., 2013).

Therefore, we investigated ^{129}I/^{127}I ratios in groundwater samples which are ^{14}C detectable to improve our estimate of the initial ratio. The grouondwaters were collected at coastal zone in Japanese island. Iodine in grouondwater samples were purified to AgI, and then the ^{129}I/^{127}I ratios were measured by AMS. The ^{14}C in grouondwater ranged from 1.0 pMC to 79 pMC. The ^{129}I/^{127}I ratio in the groundwater is of the order of 10^{-13} in the order of magunitude. The ^{129}I/^{127}I in groundwater ranged from 2×10^{-14} to 6×10^{-13}, and the average was 1.8. Our data indicated that the initial ^{129}I/^{127}I ratio of 1.5×10^{-12} for groundwater in coastal zone is an order of magnitude too large.

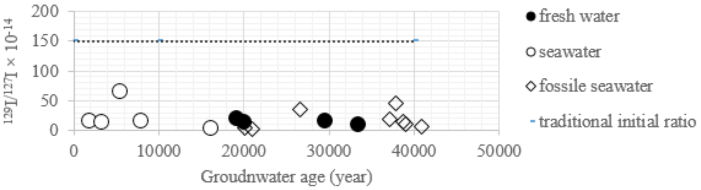

Figure. Comparsion beteween ^{129}I/^{127}I raio and ^{14}C in groundwater at coastal zone in Japanese island.

Acknowledgments

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Distribution of radionuclides in the aquatic system of a former uranium mine crater

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Keywords: uranium mines, natural radionuclides, freshwater, bioaccumulation, concentration factors

The former uranium mine of Mortórios, Portugal, was exploited as an open pit until the late 70s of past century. Once abandoned, the deep crater was flooded and became a permanent lake, a feature that is common to other old uranium mines in Portugal, some of them planned for remediation and others for preservation [1]. As a large number of legacy radium and uranium mine sites do exist in the country, a periodic radiological surveillance of sites and of the regions is performed [2,3]. In the Mine of Mortórios an aquatic community with micro plankton, macroinvertebrates, aquatic plants, and introduced fish (carps) stabilized over the years. Recently the activity concentrations were determined in the water, bottom sediment, and aquatic biota. Uranium and radium concentrations in water varied with depth probably in relationship with the dissolved oxygen in water. Concentrations of uranium, thorium, radium (^{226}Ra), lead (^{210}Pb) and polonium (^{210}Po) are reported for several living organisms. High concentrations of radionuclides especially those of uranium were determined in micro plankton living in the water surface layer. The soft sediment accumulated on the bottom of the crater indicated removal of radionuclides from the water column by settling biogenic particles. In biota, generally radionuclide concentrations were the highest in fish suggesting uptake from water and food chain transfer of radionuclides. In fish, muscle radionuclide concentrations ranked in the order Po>Pb>Ra>U, evidencing accumulation of all these radionuclides compared to activity concentrations in water. The highest concentrations were detected in internal organs such as liver and gonads. In fish liver ^{210}Po attained 560 ±23 Bq/kg (wet weight) with a Po/Pb ratio of 102 while in fish muscle ^{210}Po was 61±2 Bq/kg (wet weigth) with a Po/Pb ratio of 36. Radionuclide concentration factors of uranium and uranium daughters under these natural conditions are calculated to enrich the current data base for freshwater organisms.

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Uranium and plutonium determination in soil and sediments samples by fusion

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Keywords: uranium, plutonium, soil, sediment, fusion

The determination of the main isotopes of uranium (^{238}U, ^{235}U, ^{234}U) and plutonium ($^{239+240}$Pu, ^{238}Pu) in soils and sediments is of great interest in studies of environmental radiological surveillance, in emergency situations due to nuclear or radiological accidents, or malevolent acts with radionuclides dispersion, and in studies of geological dating, among others. However, soils and sediments are complex matrices to be analyzed by radiochemical separation, being the complete dissolution of the sample the critical step of the procedure.

In this study, conventional leaching methods (open-vessel digestion) and complete dissolution methods (fusion) were performed for soil and sediment samples pretreatment. Open-vessel digestion was perfomed with HNO_3/HCl/H_2O_2 acids, and two fusion digestion methods with borate fluxes [1] and sodium hydroxide flux [2] were tested. Borates fusion employed lithium metaborate and lithium tetraborate (80:20) in platinum or Pt/Au (95/5%) crucibles at 1000 ºC; and alkaline fusion employed sodium hydroxide in zirconium crucibles at 600ºC. After dissolution and concentration steps, UTEVA chromatographic extraction resins were employed to sequentially isolate uranium and plutonium isotopes. Finally, electrodeposition was employed to prepare the sources and they were measured by alpha spectrometry.

Comparing the different pretreatment methods, results show that conventional acid digestion method can not extract all the uranium content from the matrix, so it is not convenient when total activity has to be determined. Moreover, when refractory oxides are present in the sample, fusion dissolution methods are more suitable to dissolve completely the sample, despite their greater complexity. Finally, borate fusion was selected and validated with a reference material and intercomparison samples, since it is simpler than the NaOH fusion and less steps were needed to analyze higher amounts of sample (from 1 to 5 grams).

The final method was also tested for uranium and plutonium analyses of marine sediments from the Cantabrian Coast of Spain. Vertical distribution of plutonium isotopes in the cores analyzed were used for geological dating of the Anthropocene sedimentary record [3]. Results show activities between 0.10 - 1.49 Bq/kg for $^{239+240}$Pu, and up to 0.08 Bq/kg for ^{238}Pu; and for uranium isotopes, between 34 and 66 Bq/kg for ^{238}U and ^{234}U in secular equilibrium (average ratio ^{234}U/^{238}U of 0.98), and 1 - 2,5 Bq/kg for ^{235}U.

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Doses for critical group members as a result of VVR-S nuclear research reactor decommissioning

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Keywords: dose, critical group, radioactive effluents, decommissioning

The study presents the potential doses received by the critical group members as a result of the radioactive effluents release in VVR-S nuclear research reactor decommissioning process. The gaseous effluents resulted from activated and contaminated components cutting as well as from demolition of the concrete structures. The liquids are from the primary circuit and nuclear spent fuel pools emptying also from the reactor components dismantling and workers and equipment decontamination. In order to comply with dose constraints assigned by the regulatory body for public members in the decommissioning practice the derived emission limits (DELs) (the maximum admissible value for the activity concentration of the radionuclide) [1, 2] are established for the effluents released using the transport model in the environment (see Figure 1). The maximum annual effective doses were calculated taking into account a dose constraint of 50 µSv/ year for critical group members, considering that the weighted average equivalent dose is lower than the dose limit for each person. Dose rate estimation is done according to the age, weight, metabolism and nutrition habits of an individual. The released activities for gaseous effluents were much lower than those for liquid, thus from 50 µSv/year dose constraint, 10 µSv/year were assigned for gaseous and 40 µSv/year for liquid for dose calculation. The activities for gaseous effluents in 2014 [1], 2015 and 2016 were much lower than the derived emission limits (DELs) and the dose constraints of 10 µSv/year was fully accomplished. The most restrictive values were for the adults. On the contrary, for the liquid effluents the activities are systematically higher than the DELs. The effective dose constraint of 40 µSv/year for critical group is not accomplished and the effluents must be treated as liquid wastes. The most restrictive values were for the adults.

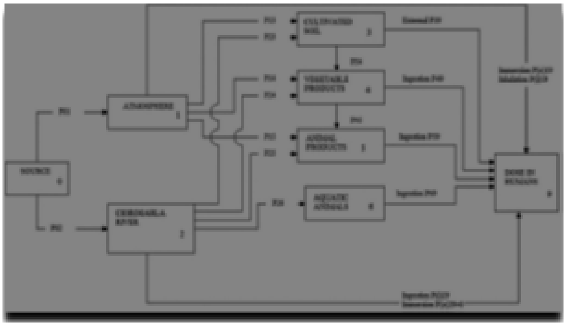

Figure 1: The transport model in the environment [2]

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Activity concentration of cesium ^{137}Cs in the ecosystem of anthropogenic dam lake in Poland, 32 years after the Chernobyl accident

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Keywords: gamma spectrometry, cesium-137, radioisotope migration, lake ecosystem, radioactive contamination

The aim of the study was to examine the migration and accumulation of ^{137}Cs in the different components of the dam lake ecosystem. A selected lake is located within so-called cesium anomaly – the area of Poland, where the post-Chernobyl radiocesium fallout was the highest. We collected surface lake sediments, lake sediment profiles and plankton samples, as well as soil and organic samples (mosses, fungi, etc.) from the lake's catchment. The ^{137}Cs concentration in the samples was measured using a gamma spectrometer with low-background, high purity germanium (HPGe) detector. We examined the lithology and pH of the collected sediment samples in order to study the correlation between these factors and radiocesium concentrations. Furthermore, the lake sediment samples were separated into different fractions and then we checked whether the ^{137}Cs activity depends on sediment granulation. Elemental analysis (C, H, N and S content) was also carried out what was used to compare the content of organic matter with the activity of cesium in the samples. The activity of ^{137}Cs in the sediment profile samples with a high content of clay fraction and organic matter was in the range of 49±11 to 88±12 mBq g^{-1}, whereas in the samples with a higher content of sandy fraction and low content of organic matter was from 2.1±0.5 to 7.2±1.8 mBq g^{-1}. A similar relationship occurred in the case of surface lake sediment samples, where the ^{137}Cs activity ranged from 1.7±0.3 to 83±11 mBq g^{-1}. These results were also used to examine the surface and the vertical distribution of cesium ^{137}Cs concentration in the sediments of the studied reservoir. Furthermore, we measured also the activity of ^{137}Cs in soil samples, where it varied from 34±4 mBq g^{-1} in the mineral layer (fluvioglacial sand) to 672±81 mBq g^{-1} in the surface organic layer. Biological samples were characterized by relatively high concentration of cesium ^{137}Cs. The highest ^{137}Cs activity was found in fungi, e.g. in *Boletus edulis* was 17 410±2104 mBq g^{-1}, while in *Boletus subtomentosus* was 4 336±523 mBq g^{-1}. Lower ^{137}Cs activities were measured in spruce (*Picea abies*) needles (from 331±40 to 452±56 mBq g^{-1}), mosses (*Polytrichum commune*; 315±39 mBq g^{-1}) and European blueberry (*Vaccinium myrtillus*; 396±48 mBq g^{-1}). These preliminary results suggest significant special differences in cesium distribution and its bioaccumulation in selected components of the food chain.

Acknowledgments

This research was funded by the Polish Academy of Sciences, Institute of Geological Sciences from the internal project *'Bioaccumulation and biomagnification of cesium $_{137}$Cs in the ecosystem of the Turawskie Lake'* and from the project for young scientist *'Determination of the degree of cesium $_{137}$Cs pollution of individual components of the Koronowskie Lake ecosystem after the Chernobyl nuclear power plant accident'*.

Experimental investigation of colloid diffusion in crystalline rock using SEM/EDS technique

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Keywords: apparent diffusion coefficient (Da), colloids, crystalline rock, SEM/EDS

Colloids present high sorption for many solutes and are considered potential contaminant carriers in geological environments. Experimental quantitative data are required for an adequate description of colloid-mediated transport within natural media. In this paper, the line scan function of SEM/EDS was firstly applied to study colloid diffusion by depth profile in crystalline rock and the measured apparent diffusion coefficients (Da) ranged from 10^{-16}~10^{-17} m^2/sec for 20 nm gold colloids. This technique can be applied to the prediction of colloid-facilitated radionuclide transport through water-saturated fractured porous rock for safety assessment of geological disposal for high-level radioactive waste (HLW).

Stable isotopic fingerprint of Sangyod rice

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Keywords: stable isotope, fingerprint, rice, IRMS

Sangyod rice is the geographical indication product of Phatthalung province in Thailand. Stable isotope analysis has been used to trace the origin of rice. In this work, stable isotopic fingerprint of Sangyod rice samples was investigated using isotope ratio mass spectrometry (IRMS). A total of fifty rice samples collected from ten districts in Phatthalung were analyzed for stable isotopic composition ($\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$). The range concentrations of $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$ in rice samples were –28.41 to –26.81, +3.08 to +8.31 and +23.46 to +29.46 ‰, respectively. The highest mean concentration of $\delta^{13}C$ was observed for rice samples from Tamot whereas the lowest value was found for rice sample from Si Banphot. $\delta^{15}N$ was highest in sample from Si Banphot and lowest in sample from Khao Chaison. Kong Ra showed the highest content of $\delta^{18}O$. Pak Phayun had the lowest $\delta^{18}O$. Almost Sangyod rice samples from Si Banphot can be distinguished from other cultivation areas by a scatter plot of isotopic values.

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^{210}Po in honey from northern Poland

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Keywords: honey, polonium, morphological structure of plants, industry

The results of polonium (^{210}Po) determination in different environmental honey samples collected in northern Poland are presented and discussed. The main aim of this study was determination of ^{210}Po concentration as well as calculation of annual effective dose radiation for ^{210}Po from honey consumption in honey samples collected by courtesy of beekeepers from northern Poland. Moreover, the aim of this work was the diversification of ^{210}Po sources in the analyzed honey samples, confirmation of the potential contaminants of the increased levels of natural radionuclides and morphological structure of plants, as well as indication of the usefulness of honeys as bioindicators of environmental pollution.

The analysis of obtained results indicated that ^{210}Po concentrations in honey samples from West Pomeranian, Pomeranian and Kuyavian-Pomeranian Voivodeships recorded are higher than the contents of ^{210}Po from Warmian-Masurian and Podlaskie Voivodeships. Higher ^{210}Po concentrations in analyzed honey samples were found in three voivodeships, which is connected with the development of many branches of industry (e.g. chemical industry, petrochemical and sodium industry, as well as fertilizer industry). It also seems that a type of plant from which bees have been collecting pollen or nectar may have some effect on the bioaccumulation of this radionuclide. The presented results also proved that honeydew honey contains more polonium than nectar honey.

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Acknowledgments

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Sorption of uranium from aqueous solution by TiO_2 based nanomaterial

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Keywords: uranium, nanoparticles, sorption, $TiOSO_4 \cdot H_2O$

Uranium is known as a harmful environmental pollutant Nevertheless, its range of applications is wide and extends across many industrial sectors, however, there is still the possibility of an accidental release of uranium into the environment. Therefore, there is a need for the development of new decontamination methods, such as the new promising sorbents since adsorption (along with ion exchange) is the common technique used for treating radionuclides. In this study, a new TiO_2 based nanomaterial (TSM) was prepared and tested. The structure and surface morphology of the developed material were studied by available methods (XRD, SEM, BET etc.). Sorption experiments with uranyl cation $(UO_2)^{2+}$ were focused on studying time dependency of sorption and dependency on varying initial concentration of contaminant $(UO_2)^{2+}$. Results were obtained performing batch experiments and the sorption of uranyl cation was studied in acidic environment (pH = 3,5). Adsorption equilibrium was reached within an hour and efficient removal was achieved (98%) and fitted with Langmuir isotherm model.

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The stability of kaolinite colloids: Effect of ion strength, pH and humic substance

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Keywords: kaolinite colloids, stability, attachment efficiency

Colloids with particle sizes ranging from 1 nm to 1 µm, have quite high reactivity and mobility in aqueous and aquifer environments, and play an important role in physico-chemical processes in natural environment. Colloids associating with radionuclides released from radioactive waste repository can migrate through water conducting fractures toward biosphere, thus provide an important mechanism for radionuclides migration. However, the stable colloids may facilitate the migration of radioactive. Therefore, the knowledge on colloidal stability is essential for understanding the migration processes.

In this work, effect of colloids concentration, electrolyte concentration, pH and humic substance on aggregation kinetic of kaolinite colloids from Tianjin Kaitong Chemical Reagent Co., Ltd. (China) was investigated by using the photon correlation spectroscopy (PCS) technique. The results showed that the stability of kaolinite colloids was dependent significantly on colloidal concentrations, cations concentrations and pH values. The kaolinite colloids were more stable in low cations concentrations and high pH conditions, aggregation was getting obvious and kinetically fast when increasing either salinity or acidity. Interesingly, the stability of kaolinite colloids can be improved in the presence of humic acid and can be qualitatively described by the attachment efficiency (Fig 1). The results in present work can provide an improved understanding on environmental behavior of kaolinite colloids.

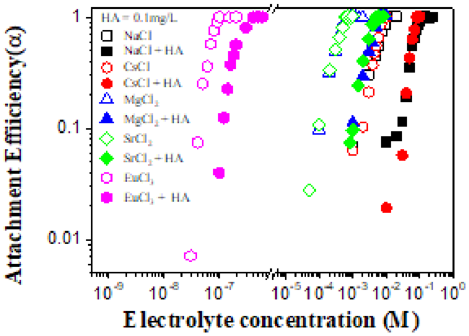

Fig 1. Attachment efficiencies of kaolinite colloids as a function of ionic strength. pH = 6.68 ± 0.05, T = 25°C.

Acknowledgments

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Attachment behavior of fission products released from neutron-irradiated UO_2 to solution aerosol

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Keywords: radioactive aerosol, fission product

Understanding the production mechanism of radioactive aerosols is important to elucidate behavior of radioactive materials released from the Fukushima Daiichi Nuclear Power Plant after the Great East Japan Earthquake in 2011. The attachment behavior of fission products to aerosol particles in a production process of radioactive aerosols has been investigated using neutron irradiated uranium in the present work. The neutron irradiation to uranium samples was performed at Kyoto University Research Reactor (KUR). Powder of uranium dioxide was encapsulated in a quartz tube under reduced pressure, and the quartz tube was inserted into a polyethylene capsule to irradiate neutrons using pneumatic transport system of KUR. The amount of UO_2 was 10 mg, and the neutron irradiation time is 30 min. The experimental setup for production of radioactive aerosol is shown in Figure 1. A part of irradiated UO_2 powder was set in another quartz tube placed in an electric furnace. Fission products produced in the irradiated UO_2 powder was released by heating. On the other hand, solution aerosol was generated by an atomizer using sodium chloride solution. Both fission products and solution aerosol particles were mixed in a cylindrical chamber to produce radioactive aerosol particles by attachment of fission products to aerosol particles. The produced radioactive aerosol particles were collected on a polycarbonate filter. The amount of fission products which attaches to aerosol particles were estimated by gamma-ray spectrometry for the filter using a Ge-detector. On the other hand, the amount of fission products released from the irradiated UO_2 powder was estimated by subtraction of gamma-ray spectra for before and after heating to the UO_2 powder. As a result, the attachment ratio to aerosol particles for fission products (^{132}Te, ^{137}Cs, ^{140}La and ^{141}Ce) was obtained.

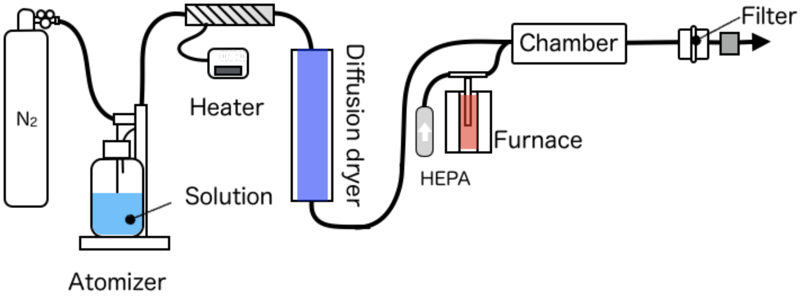

Figure 1. Experimental setup for production of radioactive aerosol using neutron irradiated UO_2.

Acknowledgments

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Synchronous dissolution of uranium, thorium and rare earths from hydrous oxide cake of monazite using hydrochloric acid

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Keywords: hydrous oxide cake, hydrochloric acid, uramium, thorium, rare earth, phosphorus

The dissolution of the hydrous oxide cake from the caustic soda-monazite reaction in hydrochloric acid was studied. The influence of the hydrocholric acid dosage, temperature, Liquid-to-solid ratio and dissolution time on dissolving rates of uranium, thorium and total rare earth were investigated. The results indicated the possibility of dissolving, synchronously, uranium, thorium and rare earths by using hydrochloric acid. The dissolution of uranium, thorium and rare earths was significantly affected by hydrochloric acid dosage. The optimum hydrochloric acid dosage is 135%, and residual acid concentration of 0.3 mol/L. Dissolving rates of uranium, thorium and rare earths in the solution were not significantly different with increasing temperature. When the liquid-to-solid ratio is 2:1, the solubility of rare earth almost reaches the limit value, and the dissolving curve of uranium, thorium and rare earth tended to flatten after 5h. The potential in the solution obtained under the above conditions fluctuates basically within the range of 560-580 mV. Iron in solution is dominated by ferric ions, which can oxidize a small amount of tetravalent uranium into soluble hexavalent uranium, no additional oxidants need to be added. The final results show that dissolving rate of uranium, thorium and total rare earths can reach 91.88% of 93.49%, 93.64% respectively under the above conditions. The hydrochloric acid dissolution test of two kinds of hydrochloric acid with different phosphorus content indicated that the content of phosphorus in hydrous oxide cake was the key factor affecting the dissolving rates of uranium, thorium and rare earths.

Radiolabeled compounds and radiopharmaceuticals

Laminin derivative peptide labelled with iodine-131 have promising therapeutic properties for a specific melanoma cells

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Keywords: melanoma, laminin, uptake, labelled peptide

Melanoma is a tumor of constantly accumulative occurrence for which novel methods of imaging and targeted therapy are generally pursued. We have developed a newly laminin class peptide that been labeled with position emitter Ga-68 or I -124 and with SPECT emitter I-131. In order to evaluate the potential relevance of positron emitter; radiolabeled short peptide of a laminin family with enhanced melanoma targeting capacity, the uptake of ^{68}Ga/^{124}I-peptide were investigated in SK-MEL 28 melanoma cell line. Also the same peptide was labelled with ^{131}I to be tested as therapeutic approach.

The peptide was radioiodinated using direct electrophilic method were used with High RCY as determined by high performance liquid chromatography (HPLC) system and Thin Layer Chromatography (TLC) that been used for quality control purposes. The radiochemical purity were > 99.00% (n=5).

Due to its easy handling and quite high uptake by melanoma cells, we expect that this peptide could be successfully used in routine application for melanoma imaging or eventual radiotherapy suggesting great potential for noninvasive clinical evaluation of suspected metastatic melanoma. Labelling technique, purification metods and in vitro studies will be presented.

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Pre-clinical studies of the radiopharmaceutical for radiation therapy of metastatic spinal tumors

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Keywords: radiopharmaceutical, Samarium-153, kyphoplasty, radionuclide vertebroplasty, polymethyl methacrylate, pharmacokinetics, pre-clinical studies, bone cement, malignant tumors

The pre-clinical studies of the functional suitability of a new radiopharmaceutical preparation intended for radionuclide verterboplasty were performed. The radiopharmaceutical represents two-component formulation and consists of powder-like polymer of methyl methacrylate with barium sulphate and benzoyl peroxide serving as polymerization initiator, and liquid monomer of methyl methacrylate with incorporated N,N-Dimethyl-p-toluidine and radionuclide Samarium-153.

In experiments in laboratory animals it was shown that in 6 hours after filling of a bone defect the proportion of hold-up radiopharmaceutical was 99.89% on the average. After 72 hours the preparation remained at the injection site for almost 100%; the preparation uptake in non-target organs and tissues was at background values level that clearly indicates the complete fixation of the radiopharmaceutical in the bone cement.

The condition of the animals treated with the radiopharmaceutical varied from almost complete failure to the equivalent use of both limbs. This indicates not only the decrease of pain severity, but also the stabilization of the bone structure with impaired integrity. In the group of untreated animals the impaired function did not recover, and the autopsy showed spontaneous fractures of tibia in the area of the bone defect.

In vitro studies showed a slowdown in the formation of monolayer of mammary adenocarcinoma cells in the culture flasks, and their death on the 2nd day after incubation start in the presence of the radiopharmaceutical. The studies results indicate the functional suitability of the developed radiopharmaceutical.

The efficient preparation of radiolabeled aromatic amino acids via Cu-mediated radiofluorination of Ni-complexes

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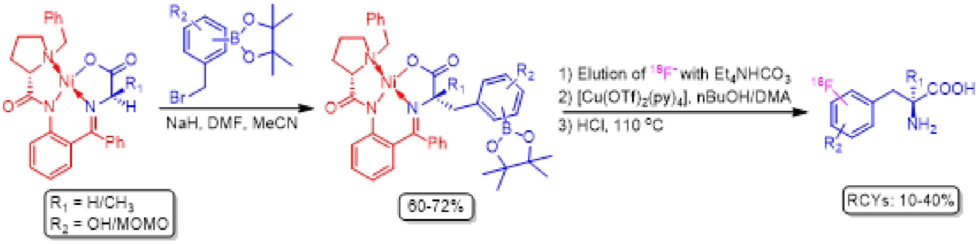
Keywords: aromatic amino acids tracers, Cu-mediated radiofluorination, PET, Ni-complexes

The aim of this work was to develop a versatile procedure for the preparation of ^{18}F-labeled aromatic amino acids (AAA) via alcohol-enhanced Cu-mediated radiofluorination using Ni-BPX auxiliaries as easily-removable dual-protecting group functionalities. Additionally, the use Ni-BPA-Ala complexes was investigated in order to access synthetically challenging α-Me-AAA tracers. Furthermore, the implementation of the radiosynthetic methods into automated modules was carried out in order to facilitate the production of these AAA tracers for biological evaluation.

The Bpin-substituted precursors of radiofluorinated AAAs and α-Me AAAs were prepared by alkylation of (*S*)-Ni-BPB-Gly and (*S*)-Ni-BPA-(*RS*)-Ala with the corresponding Bpin-substituted benzyl bromides. Radiolabeling was carried out according to the protocol for alcohol-enhanced Cu-mediated radiofluorination as follows: [1] [^{18}F]F$^-$ was loaded onto a QMA-cartridge which was subsequently washed with MeOH; [^{18}F]F$^-$ was eluted with Et_4NHCO_3, solvent was evaporated, the residue was taken up in to a solution of $Cu(py)_4(OTf)_2$ and precursor in DMF/*n*BuOH (2:1), and the reaction mixture was stirred under air at 110 °C for 10 min. The evaporation of the DMA/*n*BuOH was followed by deprotection using 12 m HCl at 110 °C for 15 min. Finally, the desired tracers were isolated by semi-preparative HPLC.

The appropriate BPin-substituted Ni-BPX-AAA complexes were prepared from commercially available materials in 10-72% yield over 1-4 steps. Radiolabeled Ni complexes containing 2-4-[^{18}F]FPhe, 2-4-αMe-[^{18}F]FPhe, 6-[^{18}F]FMT, αMe-6-[^{18}F]FMT, 4-[^{18}F]FTrp and 2-[^{18}F]FTyr residues were synthesized in RCCs of 50-95%. The purified tracers were isolated in n.d.c RCYs of 15–40% and in excellent radiochemical and enantiomeric purity. Radiosyntheses of 3-[^{18}F]FPhe, 4-[^{18}F]FPhe and 4-[^{18}F]FTrp were implemented to an automated module furnishing tracers in n.d.c RCYs of 10%, 15% and 17%, respectively, within 75–80 min.

Alcohol-enhanced Cu-mediated radiofluorination of BPin substituted Ni-BPX-AAA complexes is a simple, yet powerful method for the fast production of structurally diverse radiolabeled AAAs and α-methyl substituted AAAs. The attractiveness of the procedure is highlighted by the accessibility of radiolabeling precursors, high RCYs and easy implementation into an automated module.



Scheme 1) Facile preparation of radiolabeled AAAs using Ni-BPX complexes.

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Separation, speciation

Pillararene-based phosphine oxides: extractants with potential application for uranium extraction

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Keywords: pillararene, phosphine oxide, uranium, solvent extraction

Pillar[n]arenes (P[n]As) have received growing attention in recent years due to their unique pillar-like structures and verstile host-guest properties [1]. Among the various applications, utilizing P[n]As as macrocyclic ligands to separate ions and molecules arouses broad interests of researchers[2]. Allowing for the importance of uranium in nuclear industry and its limited storage on earth, it is imperative to recover uranium from spent nuclear fuel. Our group has developed a class of extractants by incorporating phosphine oxide moieties into pillar[5]arene framework (POP5As) [3]. POP5As demonstrated superior affinity towards uranium via solvent extraction over the acyclic phosphine oxides and tri-*n*-octylphosphine oxide (TOPO), and thus could efficiently separate uranium (%E_U up to 94%) from other metal ions in organic diluent as a result of the favorable preorganization effect. Radiolytic degradation studies showed that the POP5As are stable at the dose of 300 kGy using a linear electron accelerator, suggesting their potential applicability in highly radioacitve environment. Moreover, the extraction of uranium by POP5As in ionic liquid (IL) [4] was also investigated for the purpose of establishing “green” extraction process. Higher D_U and $SF_{U/M}$ values were observed as compared to POP5A-DCM systems, which could be rationalized by the unique supramolecular cation-exchange mechanism. Our work indicates the great potential of POP5As as extractants for uranium extraction.

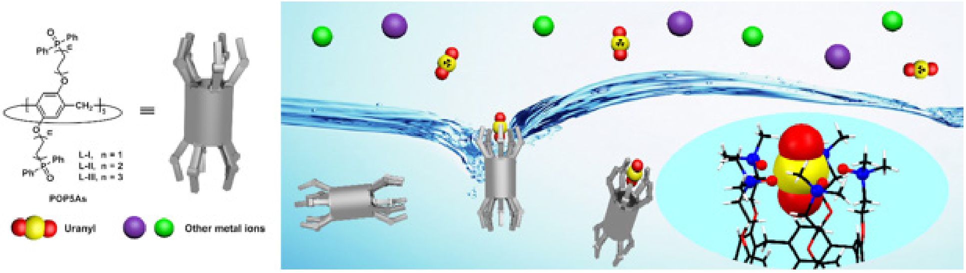

Figure 1. Chemical structures of POP5As and schematic representation of uranium extraction.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (201471105).

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Kinetic studies of cesium and strontium adsorption from aqueous solution onto potential barrier material

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Keywords: cesium, strontium, adsorption, kinetic models, diffusion coefficients

For long-term storage of high level nuclear waste in geological repositories besides natural geologic barriers human made multiple-barrier systems are used to prevent dispersion of long-lived radioactive elements in waste to the surrounding environment in a probable accidental or unexpected situation. This type of barrier systems can stop long-lived radionuclides in waste before they arrive to earth's surface even if they disperse to the environment and prevent reaching of groundwater to waste. Therefore, it is necessary to have good knowledge about probable reactions in material after interaction of radionuclides with human made barrier materials.

This experimental study was performed to determine kinetic behaviors of cesium and strontium transport through amino pyridine sulphonamide resin by using batch experiments at ambient temperature. The kinetic experimental data was properly fitted by the pseudo-first and pseudo-second-order rate equations. The transport mechanism of cesium and strontium which comprises a diffusion process from aqueous phase to amino pyridine sulphonamide resin was described by two kinetic models consisting of derived equations: the homogenous particle diffusion model (HPDM) and the shell progressive model (SPM). The effective particle diffusion coefficient D_{eff} values derived from both the HPMD and SPM equations were compared.

Acknowledgments

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Study on the treatment of wastewater from the SP-HyBRID decontamination process of a nuclear power plant

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Keywords: SP-HyBRID decontamination process, nuclear power plant, wastewater, treatment

As a representative commercial process, the HP CORD UV decontamination process using organic acid has difficulty in treating radioactive wastewater from the process, and a considerable amount of ion exchange resin wastes generates during the treatment of radioactive wastewater. To resolve these problems, KAERI has been devloping a new decontamination process using inorganic acid, SP-HyBRID decontamination process, and it was confirmed that the performance of the SP-HyBRID decontamination process was smilar to the HP CORD UV. However, it is necessary to develop an optimal wastewater treatment process for the reduction of raioactive wastes from the SP-HyBRID process. Wastewater generated from the SP-HyBRID process contains impurities such as sulfate ion (SO_4^{2-}), metal ions (M^{2+}), and hydrazine. Metal ions contains radioactive metals such as Co-60, Mn-54, and Cr-51, and it is known that hydrazine is possible to be carcinogenic to humans. Thus, the impurities must be removed to a safe level through an optimal wastewater treatment process. The ions in the wastewater can be removed by a precipitation process using $Ba(OH)_2$, and the precipitation reaction occurs through the following equation.

$SO_4^{2-} + M^{2+} + Ba(OH)_2 = BaSO_4 + M(OH)_2$

The pH in the wastewater was increased from pH 2.76 to 11.5 with increase in the additions of $Ba(OH)_2$. Hydrazine can be decomposed using H_2O_2 ($N_2H_4 + 2H_2O_2 = N_2 + 4H_2O$). In this method, the decomposition of hydrazine can depend on the pH of the waste because the chemical forms of hydrazine change with the pH. The removal of hydrazine was optimally processed at a pH of 9.0. Based on these results, the optimal wastewater treatment process was derived as an integated process which consists of 1st precipitation, hydrazine decomposition and 2nd precipitation. Firstly, the 1st precipitation is terminated at a pH of 9.0, and the decompostion of hydrazine is processed near pH 9.0. Then, the 2nd precipitation is completed at about pH 11.3. It was confirmed that the impurities in wastewater from the SP-HyBRID process can be removed to a safe level through this optimal process, and the use of ion exchange resins can be greatly decreased. This result means that it is possible to rdramatically reduce the decontamiation wastes using the optimal process when comparing with the HP CORD UV.

Acknowledgments

The authors would like to express their appreciation to the National Research Foundation of Korea (NRF) for the award of a grant funded by the Ministry of Science, ICT and Future Planning (MSIP) of the Republic of Korea, in support of the authors' work through the Nuclear Research and Development Program (NRF2017M2A8A5015144).

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CO_2 sequestration using Sr-incorporated glass for ^{14}C capture

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Keywords: CO_2, ^{14}C, carbowaste, sequestration

^{14}C is one of the most problematic waste elements coming from nuclear power plant (NPP). Since ^{14}C is long-lived radionuclides with half-life of 5730 years, it should be safely stored separately for the future generation. Moreover, due to the hazardous property of ^{14}C itself, the clearance level is very low, < 1 Bq/g, in the Republic of Korea. For example, ^{12}C consisting of living organism like human could be substituted by ^{14}C, and this could make serious problem for the human being.

There are several different carbowastes containing ^{14}C such as spent activated carbon, spent resin, and irradiated graphite etc. Among those, spent activated carbon has occupied significant amount of carbowates. Each NPP generates dozens of spent activated carbon every year. Since it causes significantly demanding disposal cost issue, it is necessary to reduce quantity of wastes. Spent activated carbon comes from HVAC (heating, ventilation, and air conditioning), and it is used for the adsorption of ^{131}I to protect radiation worker. Due to the short half-life of ^{131}I, 8 days, there is no gamma radiation remained in activated carbon. However, activated carbon is converted to ^{14}C during the adsorption of radioactive materials. Also, ^{3}H is adsorbed into the activated carbon. ^{3}H has relatively short half-life, 12 years, and easy clearance level, 100 Bq/g. Thus, ^{14}C is the major problem to remove from the carbowastes.

CO_2 sequestration using adsorbents is becoming increasingly by a number of novel materials to improve the performance. Inorganic materials are advantageous due to its high chemical and thermal stability and ease of surface functionalization. To safely treat the ^{14}C, CO_2 seqestration technique can be used. Moreover, final form of CO_2 must be considered to further solidify the product. Here, we present CO_2 sequestration using Sr-incorporated glass. This adsorbent has extremely large amount of Sr to sequestrate CO_2, and strontium carbonate as product is preferred form for solidification. The resulting Sr-glass exhibits high CO_2 capacity (>2.5 mmol CO_2/g adsorbent) in aqueous stream under mild conditions. To optimize the CO_2 capture capacity, we performed CO_2 capture with different size of powder and bulk to increase to CO_2 capacity up to 4.0 mmol CO_2/ g adsorbent. Further, the stability of Sr-glass under beta ray is also studied to understand the $^{14}CO_2$ capture.

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Tritium separation from heavy water using a membrane with deuterated manganese dioxide

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Keywords: tritium, deuterium oxide, separation, manganese dioxide

Abstract: Extraction of the tritium (T) present at low concentrations in water using conventional methods is fundamentally difficult [1-7]. In our previous reports [8,9], a membrane containing protonated manganese dioxide (MnO_2) powder that is able to selectively extract T from light water at room temperature has been studied. The extracted T was recovered as concentrated HTO for a retrievable final product. This study introduces a membrane containing deuterated MnO_2 powder to separate the T present at low concentrations (e.g., 5597 Bq/mL) in a high purity heavy water (D_2O, 99.9 %) under normal laboratory conditions at room temperature. **Fig. 1** illustrates the schematic cross section of a T extraction system using the membrane unit consisted of deuterated MnO_2 powder, graphite powder, and an electroconductive porous resin. The deuterated MnO_2 powder was prepared from $LiMn_2O_4$ powder in membrane by acid treatment of the membrane with a dilute deuterium chloride heavy aqueous solution (DCl, 0.55 M). T extraction test was performed by dispersing the membrane in test water (D_2O, 99.9 %: 80 mL) containing T under suitable pH control by adding an adequate amount of a dilute sodium deuteroxide heavy aqueous solution (NaOD, 0.55 M) to test water. A liquid scintillation counter was used for measuring the radioactive concentration of T in samples (each vol.: 1.0 mL) collected from test water. A continual decrease of the T concentration in the test water was observed as shown in **Fig. 2**.

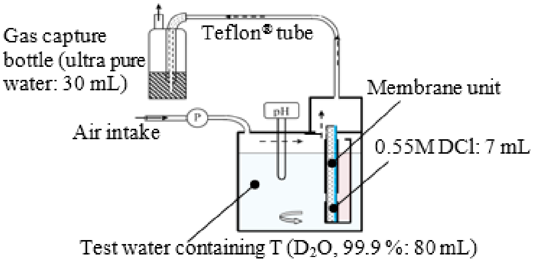

Fig. 1. Schematic cross section of T extraction system

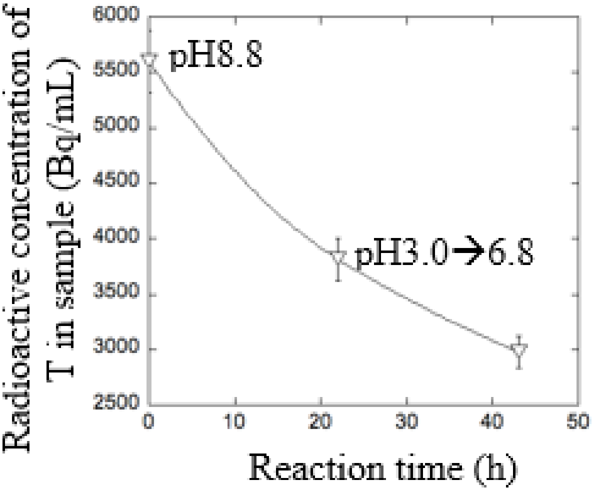

Fig. 2 Variation in the radioactive concentration using the membrane unit in a sealed container.of T in the test water (23.6~23.8°C). 44.2 % of T was removed from the test water in 43 hours.

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Complex formation of lanthanides with N-(2-hydroxyethyl) ethylenediamine-N,N',N'-triacetic acid (HEDTA) in aqueous solutions: Thermodynamic analysis and coordination model

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Keywords: HEDTA, lanthanides, thermodynamic, coordination

N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA) is a strong chelating ligand that is widely used in separation sciences of f-elements, such as rare earth refining and radiochemical analysis. There is much to be learned about the structure and composition of the coordination sphere of the complexes of HEDTA with lanthanides. The complexation of HEDTA with light lanthanides (La^{3+}, Nd^{3+} and Eu^{3+}) was studied thermodynamically and structurally in aqueous solutions in this paper. Potentiometry and microcalorimetry were used to measure the complexation constants (25-70°C) and enthalpies (25°C), respectively, at $I = 1.0$ mol·L^{-1} $NaClO_4$. Coordination modes of the complexes were investigated by optical absorption spectroscopy, luminescence spectroscopy, Raman spectroscopy, and nuclear magnetic resonance spectroscopy. The most noticeable in complex formation is the hydrolytic speciation which is present as a centrosymmetric dimer with the hydroxyl group in HEDTA deprotonated and one of carboxyl groups is shared by two adjacent cations in the dinuclear complex (Fig. 1).

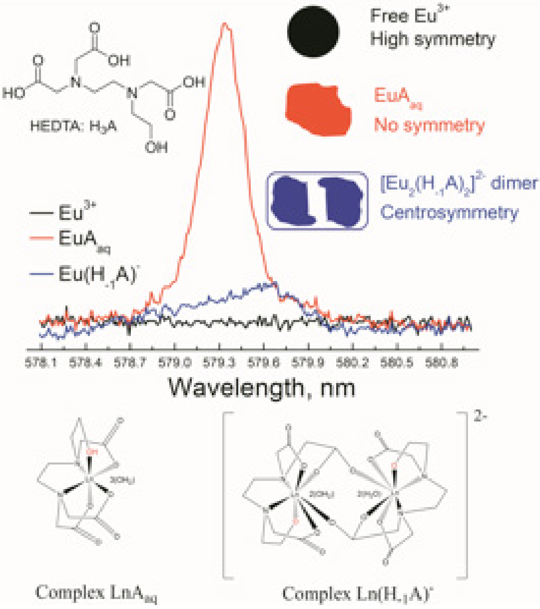

Figure 1. Coordination modes in the complexes of HEDTA with Ln (Ln = La^{3+}, Nd^{3+} and Eu^{3+}).

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Synthesis of ultralight phosphorylated carbon aerogel for efficient removal of U(VI): Batch and fixed-bed column studies

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Keywords: carbon aerogel, phosphate groups, uranium, adsorption, interaction mechanism

A novel ultra-flyweight phosphorylated carbon aerogel ($CA-PO_4$) was successfully synthesized with phosphate functionalized graphene as skeletons and CNTs as reinforcing ribs and was applied to adsorb uranyl ions from radioactive wastewater. The characterization of XPS, Raman, FT-IR and Boehm titration confirmed that on the surface of $CA-PO_4$ there were abundant phosphate group which could bond with uranyl ions selectively via surface complexation and electrostatic interaction. The maximum adsorption capacity of $CA-PO_4$ was improved from 98.0 $mg \cdot g^{-1}$ (CA) to 148.4 $mg \cdot g^{-1}$ at 298K and pH 5.5 and the U(VI) selectivity remained over 50% in the wide range of 1.0 to 5.5 and reached its maximum of 66.8% at pH 5.5. In addition, the U(VI) adsorbing on $CA-PO_4$ was proved to be a feasible, spontaneous, endothermic and monolayer chemical adsorption. And the fixed bed column experiments revealed that the external and internal diffusions was the limiting step and that the lower flow rate and higher bed height, the higher adsorptivity. Furthermore, $CA-PO_4$ exhibited excellent structural stability, satisfied regeneration and reusability after five cycles. A simple synthesis and application of $CA-PO_4$ was highlighted in this work as an efficient adsorbent for effective adsorption/recovery of uranyl ions from radioactive wastewater.

Acknowledgements
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Prussian blue based nano-composites for radiocesium pre-concentration from seawater

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Keywords: Cs, Prussian blue nano-composites, seawater, Baltic Sea

A wide range of treatment methodologies have been proposed to treat wastewater or pre-concentrate Cs from environmental waters, however, adsorption is one of the promising techniques for these purposes due to its simple design, high efficiency, low-cost, etc. The most specific adsorbents suitable for seawater samples were reported to be based on ammonium molybdophosphate (AMP) and Prussian blue (PB).After the accident in Fukushima, there is an increased interest in developing effective and selective methods for removing Cs+ ions from highly polluted waters and seawater.

The objective of this work was to synthesize Prussian blue graphene oxide based nano-sized composites using different synthesis approaches, characterize the obtained adsorbents and to study their sorption efficiency towards radiocaesium. The synthesized particle sizes estimated by Mössbauer spectrometry and XRD analyses ranged from 8.14 nm to 11.2 nm. The nano-composites were characterized using FTIR and Raman spectroscopy. In addition, morphology and the particle size of the nano-particles were investigated by SEM and TEM. The PB nano-composites showed a high sorption capacity which varied from 200 to 700 mg/g depending on a chemical composition of the sorbent.

The adsorption capacity of Cs^+ on PB nano-composites, studied at different initial CsCl concentrations in seawater solutions up to 35 ‰ at pH of 7, showed that even at high ionic competition it remained consistent.

Experiments carried out with natural seawater indicated a high efficiency of 100 % for adsorption of Cs^+ ions by PB nano-composites. The BP nano-composites were applied for ^{137}Cs pre-concentration from the Baltic Sea seawater samples. Activity concentrations were measured using gamma spectrometry and ^{134}Cs was applied as the yield tracer in the pre-concentration procedure. Activity concentration of ^{137}Cs ranged from $25 \pm 2 Bq/m^3$ to $37 \pm 3 Bq/m^3$ in seawater samples collected at the state monitoring sampling stations in the Baltic Sea.

Stereolihtographic printing of radionuclide doped resins

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Keywords: stereolithography, doping, calibration, forensics

The advent of readily available additive 3D printing has opened interesting and novel opportunies in radiological manufacturing. Methods for steroelithographic printing of novel geometries and materials were investigated using ^{198}Au doped photoreactive resin and a Form 2 printer by Formlabs. Such artifacts have potential as references for radiation detection apparatus and calibration methods. A variety of resins were tested to distinguish unique properties and the ability to distribute radionuclides homogeneously throughout the medium. Initial trials of the technology printed pellets of hard plastic with ^{198}Au activities between 134.7 Bq and 69.5 Bq with an average of 105.4 Bq and a standard deviation of 22.2 Bq. More complex structures were printed for proof of concept.

Liquid-liquid extraction of radiochemical separation for the determination of selenium in *Mentha pulegium* L. samples

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Keywords: trace element, selenium, RNAA method, *Mentha pulegium* L., human health

Selenium (Se) has been a focus of attention as an important micronutrient with its impact on human health, with there being consequences either due to excess or deficiency in intake. *Mentha pulegium* L. plant has been largely used in Algerian traditional medicine to contribute significantly to human health related to digestive ailments. Radiochemical neutron activation analysis (RNAA) is well established method for determination of a number of elements at trace level concentrations with high sensitivities. In this work, we used the RNAA by Liquid-liquid extraction method for determination of selenium content in *M. pulegium* L. The result of this study was compared with those samples from different countries. The result obtained show that, Se concentration obtained in *M. pulegium* L., is close to the minimal FAO recommendation.

Extraction and seperation of americium(III) and europium(III) with 2,6-bis(5,6-diethyl-1,2,4-triazin-3-yl) pyridine in ionic liquids

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Keywords: extraction, ionic liquids, americium(III), europium(III)

In recent years, the application of room temperature ionic liquids (RTILs), labeled as “designer solvents”, has increased enormously as can be seen from rapid rise in the number of publications in this area. However, their shaking times were several hours only, and this might be not enough to reach a stable equilibrium for the RTILs with high viscosity in the specific condition. Therefore, it is necessary to remeasure the distribution ratios and separation factors of metal ions with BTP in RTILs under an extended time scale.

In our present work, the extraction behaviors of Eu(III) and Am(III) from nitric acid medium by 2,6-bis(5,6-diethyl-1,2,4-triazin-3-yl) pyridine (C2-BTP) dissolved in different room temperature ionic liquids, *viz*. $C_n mim^+ \cdot NTf_2^-$ ($n = 2, 4, 6, 8$), were investigated at 298 K and 323 K, respectively. The distribution ratios of Am(III) and Eu(III) were measured as a functions of the extraction time and the concentration of nitric acid. It is found that the systems exhibit much slower kinetics than that in molecular diluents, and the distribution ratios for Am(III) and Eu(III) decrease with higher nitric acid concentration. The extraction mechanism is found to be cation-exchange in RTILs, which fits on well with the literature reports. Though higher temperature leads to faster kinetics in the experiment, the equilibrium time still remain over 24 h. Anyway, C2-BTP still shows a good potential application for An/Ln separation in combination with RTILs and the distribution ratios for Am(III) are significantly enhanced at higher temperature. The computational methods can theoretically provide a hint to studying the sophisticated extraction systems. It is also expected that the intermolecular interactions should be well tuned to design a novel seperation systems in the future.

Figures

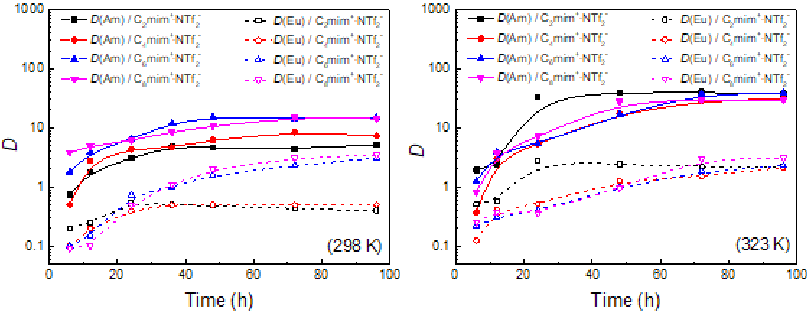

Fig. 1. Kinetics of extraction of Am(III) and Eu(III) using C2-BTP as extractant in $C_n mim^+ \cdot NTf_2^-$ (n =2, 4, 6, 8) at 298 K and 323 K; [C2-BTP] = 0.02 mol L^{-1}, [HNO_3] = 1.0 mol L^{-1}, [$NaNO_3$] = 1.0 mol L^{-1}.

Uranium sorption from pregnant solutions prepared by carbonate leaching from peat ore

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Keywords: uranium peat ore, pregnant leach solutions, ion exchange, humic substances, regeneration

Uranium-containing peat deposits are primarily considered as a source of environmental pollution, and not as a source of raw materials. The peat deposits can be objects of commercial exploitation in the case of high uranium content in the ore and the opportunity of ecosystem restoration during uranium mining.

There are two main technological schemes for the processing of peat ores: thermal destruction of enriched peat (burning or gasification), followed by sulfuric acid leaching of uranium from the obtained ash, or direct leaching of uranium from the ore. The second scheme is more prevalent, as it requires less capital and operating costs. Uranium leaching from peat ores is carried out by using of carbonate or less commonly sulfuric acid solutions. The use of sulfuric acid are limited by high consumption of the reagent and the lower degree of uranium recovery compared to the carbonate method. However, content of organic compounds in acid pregnant solutions does not exceed 50 mg L^{-1}. Carbonate solutions, on the contrary, effectively dissolve macromolecular humic substances (humic acid, fulvic acid). Ion exchange is the main method for processing of pregnant leach solutions (PLS). Uranium is extracted from carbonate PLS using anion exchange resins.The presence of humic substances in the solution leads to contamination of the ion exchanger and the fall of its sorption capacity for uranium. Therefore, special attention is paid to the choice of ion exchange resin during the designing a site for sorption processing of the PLS.

Processes of uranium sorption from the PLS by anion exchangers AMP, Tulsion A-233U, Lewatit K6367, Purolite A660/4759 were investigated in this work. The PLS was prepared by the carbonate leaching of uranium from peat ore. The content of elements (compounds) in the PLS was (mg L^{-1}): 80 U, 3860 Na_2CO_3, 218 S, 286 Mg, 180 Si, 122 Al, 31 Ca, and about 7000 humic substances (mainly in the form of sodium humates). Uranium sorption was carried out in static and dynamic modes. According to the experimental data, anion exchanger Purolite A660/4759 had best capacitive characteristics for uranium. The sorption capacity value of this resin at full saturation state was 36-40 kg m^{-3}, while capacity values of another anion exchangers were 1.5 times less.

The process of uranium desorption from saturated anion exchangers was carried out in static and dynamic modes using solutions of ammonium carbonate/bicarbonate mixture (ACBM) with concentration 100-200 g L^{-1} at a temperature 40-50 °C. The process in dynamic mode must be carried out in two stages with gradually increasing the content of ACBM in the eluent solution. The liquid and solid phase ratio 4: 1 ensures the obtaining of pregnant solution with a uranium concentration of 9 g L^{-1}. The degree of uranium recovery was 97%. The residual capacity of anion exchange resin for uranium did not exceed 1.1 kg m^{-3}. The degree of uranium precipitation during crystallization of ammonium uranyl tricarbonate from pregnant solution was 72%, the residual content of uranium in the liquid phase was 2.5 g L^{-1}.

The decrease in the sorption capacity for uranium was about 30% during long-time exploitation of ion exchanger (10 cycles of sorption-desorption). It was due to contamination of ion exchangers with humic substances. However, the decrease of ion exchange capacity can be reduced to 5% through intermediate treatment of resins with an alkaline solution of sodium chloride (10% NaCl + 2% NaOH). The use of this solution for the regeneration of ion exchangers was effective in the organization of the process in both static and dynamic modes. At the same time, completely regeneration of resin under conditions of a limited time of the technological process was not possible because of contamination with fulvic acids. The desorption of these compounds from gel anion exchangers is extremely difficult.

Preconcentration of uranium from urine on a complexing membrane

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Keywords: uranium preconcentration, urine, membrane complexation, alpha spectrometry

Membrane complexation is a successful technique which has been used in analysis of trace elements [1], as well as in radiochemistry for ^{238}U and ^{234}U analysis in water samples [2]. The present method relies on the complexation of uranium at a selective membrane which was used as a mean of preconcentration.

The preparation of the complexing membrane in its liquid form relies on the use of tetrahydrofuran, PVC as membrane matrix, dibutyl phthalate plasticiser, Aliquat-336 and calconcarboxylic acid ligand.

The membrane was stabilized at the bottom of glass labware such as beakers and crystallization dishes of different diameters and left to dry. The urine samples were afterwards added above the membranes with a simultaneous addition of a known amount of ^{232}U tracer, in order to calculate the chemical recovery. The processes were held at room temperature.

After uranium complexation the membranes wet ashed and dry ashed to remove the organic matter. Uranium isotopes were separated by interfering radionuclides via anion exchange. The source preparation performed by electrodeposition at stainless steel plates which were finally measured by alpha spectrometry via the use of PIPS detectors with an active area of 600 mm^2.

The maximum uranium recovery, of the order of 55%, was achieved on 0.25L of sample through the use of an 22cm diameter crystallization dish under continuous stirring (Fig. 1).

The FWHM of ^{232}U peak ranged from 26.9 keV to 28.9 keV after a few repetitions of the methodology. Additional experiments relative to the complexing conditions as well as the consistence of the membrane will be performed to optimize uranium recovery.

Fig. 1. Uranium membrane complexation process

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Development of a sequential analysis procedure for polonium, uranium, and thorium isotopes in urine samples

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Keywords: Sequential extraction, alpha emitting radionuclides, background survey, urine samples

Internal dosimetry of victims can be used for medical treatment as critical information in radiation emergency. Many international organizations have recommended to perform radiobioassay for the efficient medical treatment. For radiobioassay, in-vitro technique especially using excreta sample analysis method is one of the effective way. In case of the artificial radionuclides, the background radioactivity level in urine samples collected from the public is hardly measured if there were not exposure accident, while naturally occurring radionuclides have a tendency to intake through the air and foods etc. The background level in these kinds of natural contaminants should be corrected from measurement results of victims' sample, which it have been also advised by the previous research works.

Generally, alpha-emitting radionuclides such as polonium, uranium, and thorium isotopes should be extracted from raw samples by using chemical treatment due to their physical characteristics. Many laboratories have studied to enhance the efficiency of the sample preparation time, and there have been a lot of analysis procedures related to polonium, uranium, and thorium isotopes. The conventional methods only focused on single extraction technique or other types of matrix such as environmental samples. However, the pretreatment work is time-consuming, and especially urinalysis has limit on the total amount of sample due to the difficulties on sampling from victims.

In this study, the sequential analysis procedure for urine samples is developed and verified mainly focusing on Po-210, natural uranium and thorium radioisotopes. The amount of sample for analysis and counting time were estimated to meet the criteria of minimum detectable activity which was referenced from international standard. The analysis procedure was improved using sequential extraction system from one sample. The time required for sample preparation was discussed compared with other methods. The validation of analysis procedure was performed using certified reference samples provided by U.S. NIST (National Institute of Standards and Technology). The chemical recovery yield of each radionuclide was estimated to verify the effectiveness of this methods. Forty urine samples collected from participants were analyzed with the preparation method. The participants are living in local places where are not related to radiation work. Also, the measurement results were reviewed for comparison with other studies and environmental radiation level of the local cities.

Special application of radioanalytical and nuclear chemistry

Effect of gamma-ray irradiation on the electrical properties of NPT-trench gate IGBT

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Keywords: gamma-ray irradiation, NPT-trench gate IGBT, threshold voltage, switching time

Insulated gate bipolar transistors (IGBTs) have been widely used for high power switching devices due to its low forward voltage drop and high input impedance. One of such efforts is to generate lattice defects in the drift region of an IGBT so as to increase the recombination of minority carriers. Irradiation using neutrons, protons, or electrons is a possible way to generate recombination centers for minority carriers. Among various particle irradiations, fast neutron irradiation in a nuclear reactor is the most effective way to improve switching characteristics and short circuit durability of IGBTs because of its ability to produce recombination centers uniformly distributed in the devices.

The IGBTs irradiated in a nuclear reactor are exposed not only to fast neutrons, but also to thermal neutrons and gamma rays. Hence, the effects of gamma irradiation are also of concern. Gamma rays may induce damages by heating and producing recoil atoms. The effects of gamma irradiation on various metal oxide semiconductor (MOS) devices have been actively studied including IGBTs.

In this study, we evaluated the effects of gamma irradiation dose on a Non Punch-Through (NPT)-trench gate IGBT static electrical characteristics such as gate threshold voltage and switching characteristics such as turn-off and turn-on delay time.

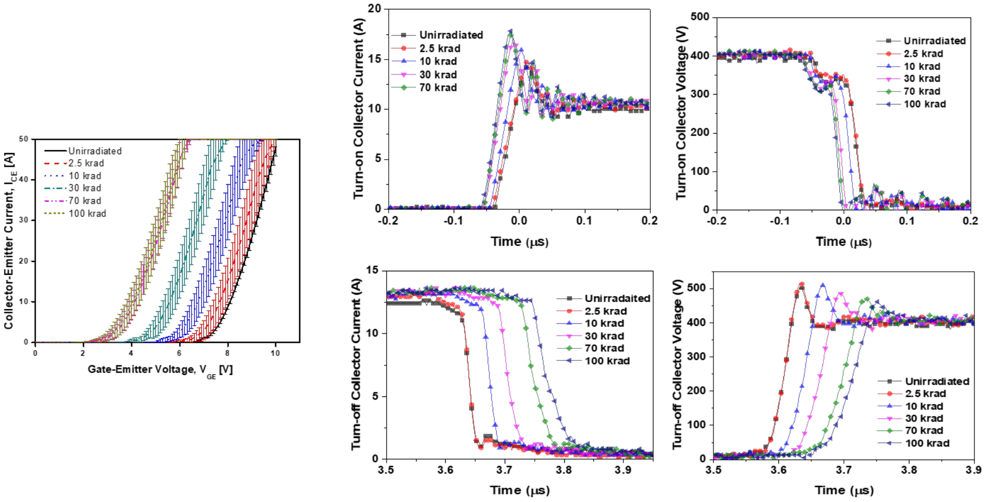

Fig 1. Threshold voltage and Wave forms of the turn-on collector (a) current, and (b) voltage, and those of the turn-off collector (c) current, and (d) voltage

Acknowledgments

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Total reflectance Xray flourescence spectrometry for the analysis of Se in human body fluids

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Keywords: TXRF, selenium, urine, diabetes

Total Reflectance Xray Fluorescence (TXRF) spectrometry is an advancement of XRF technology, that has been available commercially since the last 2 decades (fig. 1). The exciting x-ray beam after monochromatization, is made to impinge on the sample carrier at an angle below its critical angle of total (external) reflection (< 0.06°) for x-rays. The sample to be analyzed is deposited as a very thin layer at the centre of the flat specularly reflective sample carrier where it is excited by both the incident beam as well as the reflected beam. The large angle between the incident and reflected beams allows the detector to be positioned very close to the sample resulting in a large solid angle for the collection of the fluorescent x-rays. The consequence of all this is that the sensitivity of detection of the flouresced photons is greatly increased, allowing quantitative elemental analysis at the ultratrace level.

Recent discoveries in clinical medicine have linked high serum Se levels to the prevalence of diabetes. Hence in volcanic regions such as the state of Michoacan in Mexico, where Se levels in soil and water are naturally high, it is worthwhile to study the possible correlation between high Se concentrations in body fluids and the incidence of diabetes.

In this work we present the quantification of Se in urine, the human body fluid that can be collected non-invasively and which is therefore commonly used for the analysis of body Se burden. Blood and urine Se concentrations are similar. Se is present in urine in the form of organic compounds that have low thermal stability. While some Se volatilization does take place due to x-ray bombardment in the TXRF sample chamber, the sensitivity of TXRF detection is near the maximun at the Kα energy of Se, thus enabling reduced counting time. This means that urine samples can be analyzed with minimal sample preconditioning. In this work we first test Na_2SeO_4 standard solutions of various concentrations to determine the lowest detection limit for Se and the statistical figures of merit of analysis by the TXRF technique using Ga or Y as internal standard. The effect of the ionic matrix composition that simulates the matrix of urine, is tested by adding the appropriate concentrations of the major ions, Na^+, Cl^-, SO_4^{2-}, K^+, PO_4^{3-} as well as the neutral compound, urea. Finally, urine samples were analyzed after appropraite digestion. The preliminary results are presented.

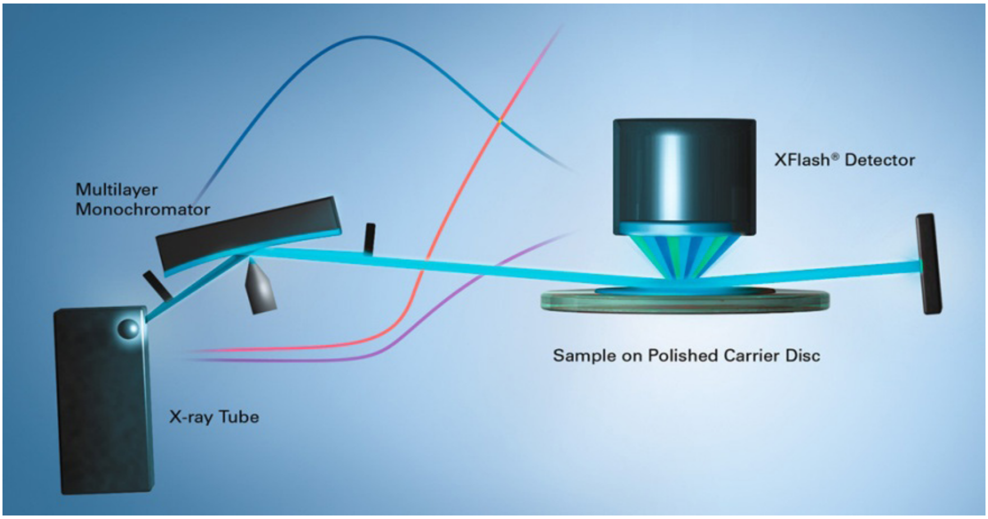

Figure 1. The Bruker S2 Picofox™ Total Reflectance X-ray Fluorescence spectrometer

The influence of iron on selenite removal using bentonite and spectroscopy studies

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Keywords: HLW, bentonite, removal efficiency

In deep geological repositories of high-level radioactive waste (HLW), selenium is one of the few radionuclides that can be transported into the biosphere and contribute to the ultimate exposure dose over the geological time scale according to a scenario analysis. Recently, we studied the influence of iron, pH and oxygen conditions on the Se(IV) removal efficiency from aqueous solutions using natural bentonite or Fe(0, II, III)-modified bentonite and discussed the possible mechanisms.

Influenced by multiple factors, Se(IV) removal using bentonite always reached a maximum value at a pH of 4 under oxic conditions and at a pH of 8 under anoxic conditions. Iron has a large influence on Se(IV) removal using bentonite because of its redox and sorption behavior. The Se(IV) removal efficiency was enhanced (> 90%) when bringing Fe into the bentonite under both conditions. Ferric selenite precipitation and green rust may contribute to the highest removal efficiency at pH 4 under aerobic conditions and at pH 8 under anaerobic conditions. A linear combination fit (LCF) of the X-ray absorption near edge structure (XANES) spectroscopy data revealed that Se(0) was the dominate selenium species under aerobic conditions; however, Fe selenide was the major species under anoxic conditions, especially at high pH values. Selenite prefers to form inner-sphere complexes with Fe(III)-oxyhydroxide. A two-step mechanism for the redox reaction between Se(IV) and Fe(0) was proposed under anaerobic conditions. Besides, Fe(II) can replace Mg(II) in montmorillonite. Overall, this study indicated that the natural and extra Fe in clays can greatly enhance the selenite removal efficiency.

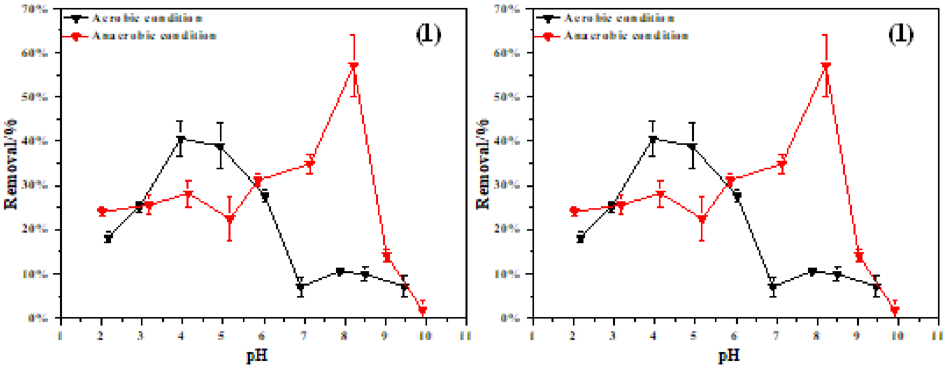

Figure 1. Removal percentage values derived from the batch experiments as a function of pH under aerobic conditions (black line) and anaerobic conditions (red line)

Analysis of historical paintings using ion beam analysis and radiocarbon dating techniques

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Keywords: PIXE, PIGE, proton beam, painting, radiocarbon dating, elemental composition

PIXE (Particle Induced X-ray Emission) and PIGE (Particle Induced Gamma-ray Emission) techniques have been used to investigate elemental composition of historical paintings. On the other hand, radiocarbon dating (^{14}C) has been utilized for specimen age determinations. The preservation of sample integrity is of the highest priority, therefore the non-destructive potential of the ion beam analysis (IBA) techniques [1] must be treated carefully. The research of proton beam affecting the colour in the painting [2] confirmed that the beam fluency represents the crucial parameter in non-destructive analyses of paintings using external beam lines. Research of various samples is being conducted at the CENTA facility [3, 4], but the effects of particle beam incident on the sample have not been investigated yet. The examined samples consisted of several canvas cuttings from the back side of historical paintings which probably originated from Slovakia. The canvas cuttings were analysed using PIXE and PIGE, keeping the beam fluency low (below 2 $\mu C/cm^2$). Several elements, e.g., Pb, Zn, Fe, Ba and Al, Na, P were observed in the PIXE and PIGE spectra, respectively. Absolute concentrations from the PIXE measurements were calculated using GUPIXWIN software. The PIGE measurements were used only for the identification of elements not visible in PIXE. Consequently, the paint was chemically separated out of canvas. After careful treatment and preparation of graphite targets, the ages of canvases were determined using radiocarbon dating technique. The aim of this study has been to evaluate the risk of potential damage of the samples and to manifest the ability of the CENTA PIXE/PIGE spectrometer of determining the elemental composition of historical paintings.

Acknowledgments

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Enhancement of radioactive Cs adsorption using Prussian blue/TiO_2 under UV irradiation

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Keywords: radioactive Cs, adsorption, Prussian blue, TiO_2, photocatalytic

After the Fukushima nuclear accident, tremendous efforts were made to treat radiocesium, radiostrontium, and other radioactive materials. Recently, nanostructured inorganic materials such as titanate, vanadate, tungsten-based material, manganese oxides, hexacyanoferrates, metal sulfides, and hydroxyapatite, have attracted great attention as adsorbents for Cs removal. Recently, we have also investigated that Prussian blue incorporated polyacrilonitrile nanofiber can rapidly adsorb the radioactive Cs and directly use without further preparation or purification.

In this study, we synthesized PB-deposited TiO_2 (PB/TiO_2) by photodeposition method and investigated the adsorption of Cs ions on PB/TiO_2. Cs ions adsorption by PB/TiO_2 was drastically enhanced under irradiated UV light conditions. No photocatalytic-enhanced adsorption of Cs ions was observed on PB/SiO_2 or under visible light irradiation. This implies that the photocatalytic reaction influences the structural state of PB. The enhancement of Cs adsorption means an increase in the capacity of Cs adsorption per unit mass of PB and results in a reduction in volume of secondary waste. These performance characteristics are important considerations in terms of cost-effectiveness. The physicochemical properties of PB/TiO_2 were measured, and the various photocatalytic reaction parameters for the adsorption of Cs ions by PB/TiO_2 were investigated. Detailed mechanisms of the photocatalytic enhanced adsorption of Cs ions by PB/TiO_2 are also discussed.

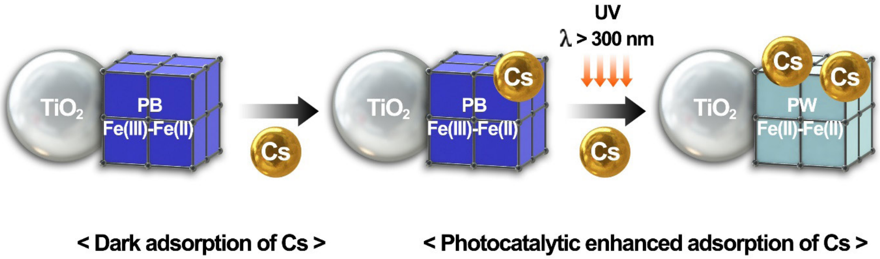

Figure 1. Schematic of dark and photocatalytic-enhanced adsorption of Cs ions by PB/TiO_2 and simple illustration of the reduction of PB by photocatalytic reaction.

Acknowledgments

This work was supported by the Basic Science Research Program, through the National Research Foundation of Korea (NRF), funded by the Ministry of Science, ICT & Future Planning (2017R1A2B4003919).

Visualization of ^{14}C-photosynthates in plants

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Keywords: real-time radioisotope imaging system, photosynthates, translocation

Photosynthesis plays an important role for plant growth. After carbon fixation, photosynthates move to tissues. To improve crop productivity, it is important to understand these physiological phenomenons. There is not enough information about the movement of the photosynthates in plants. To examine the movement of the photosynthates, it is crucial to analyze living plants. We have been developing a live imaging system (RRIS) which can visualize ions and chemial compound movement, using the commercially available radioisotopes without, nondestructively (Sugita et al. 2016). The mechanism of the system is that the radiation emitted from the plant is converted to light by a scintillator and then the light image is obtained by a CCD camera. To analyze photosynthates movement in plants, $^{14}CO_2$ was supplied from the specific tissue of the up-ground part. $^{14}CO_2$ was prepared by mixing ^{14}C labeled sodium hydrogen carbonate with lactic acid. Then the emitted $^{14}CO_2$ was introduced to a plastic bag covering the plant tissue. In addition, to visualize photosynthates distribution inside the plant, frozen samples were cut to make thin sections and the radiation emitted from the samples were detected using an Imaging Plate. As test plants, model plant; *Arabidopsis*, and crops; rice and soybean were employed for the imaging. When $^{14}CO_2$ was introduced to the *Arabidopsis* leaves, ^{14}C-photosynthate was accumulating in the tips of the main stem and the roots (Fig. 1). In a soybean plant, when $^{14}CO_2$ was supplied to the selected mature leaf, ^{14}C-photosynthate was transferred and accumulated to the younger leaves preferentially. When $^{14}CO_2$ was supplied to the younger leaves, ^{14}C-photosynthate was hardly moved. In the case of the pods, fixed $^{14}CO_2$ in the leaf was preferentially transferred to the closest pod.

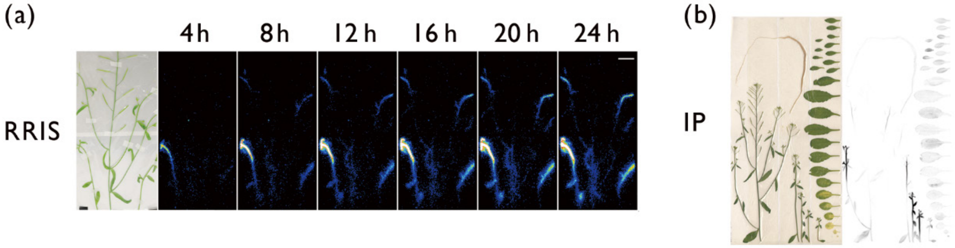

Fig. 1 ^{14}C- photosynthate movement.

(a) Sequenatial images of ^{14}C- photosynthate. $^{14}CO_2$ was supplied to leaves.

(b) ^{14}C distribution images by an Imaging Plate (IP).

Acknowledgments

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Analysis of meteorite samples using IBA and AMS techniques

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Keywords: PIXE, proton beam, meteorite, geological standards, distribution maps of elements

The non-destructive approach to the sample treatment during the analytical process is one of the crucial advantages of the PIXE (Particle Induced X-ray Emission) technique [1]. Rare and precious space and environmental samples can be analysed non-destructively in order to evaluate the concentration of individual elements presented in the specimen [2]. Three meteorite samples were recently analysed using 3 MeV protons incident in a narrow ion beam (1.5 mm diam.), namely, a fragment of Canyon Diablo Arizona meteorite (iron) [3], a cut block of Rumanová meteorite (chondrite) from Slovakia [4] and a recent fall - Ozerki meteorite (chondrite) from Russian Federation. Evaluation of the measured X-ray spectra were carried out using GUPIXWIN software. Absolute concentrations of several elements were calculated using geological standard materials. Subsequently, surface distribution maps of evaluated concentrations of elements presented in the samples were constructed.

Acknowledgments

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Sponsored abstract

Nuclear measurement solutions of gamma technical corporation

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Keywords: nuclear measurement techniques, scintillation, radiation monitoring, measuring instruments

It is my great pleasure to introduce the activity and product line of our company. GAMMA Technical Corporation was founded in 1920 and has been developing and manufacturing radiation measuring instruments for more than 50 years. Our company has always been involved in R&D of innovative technologies. Today we offer unique solutions in the field of radiation detection, measurement and identification such as portable, shielded activity measuring instruments, radiological food tester, complex building monitoring, on-board radiation reconnaissance systems and radiation portal monitors. We manufacture highly customizable intelligent scintillation probes with integrated analyser and a wide range of scintillation crystals for various radiation counting and spectrometry tasks, based on our own crystal-growing facility, including sandwich scintillators for the simultaneous measurement of different kinds of radiation. Our portfolio also includes handheld and fixed radiation measuring devices, which are designed to withstand harsh environmental conditions due to their rugged, military construction. We can provide complete instrumentation for nuclear measurement, research and education. Measuring systems, including intelligent nuclear detector(s), lead shielding, displaying and analytical software are available for a wide range of applications. GAMMA offers complex monitoring stations for both outdoor and indoor use, customized for area, building, region or countrywide scale monitoring, radioactive emission monitoring, air or water quality surveillance purposes.

Our main products in the field of nuclear measurement:

- GM tube based radiation measuring instruments,
- scintillation crystals and detectors,
- radiation portal monitors,
- radioactive particle monitoring systems,
- local and countrywide monitoring and early warning systems,
- radiation reconnaissance devices,
- radioactive emission monitoring systems,
- meteorological instruments,
- respiratory protective equipment.