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ABSTRACTS

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ORAL PRESENTATIONS

ABSTRACT 1

SPECIATION ANALYSIS OF ULTRA-LOW LEVEL IODINE-129 IN THE ENVIRONMENT AND ITS APPLICATION AS ENVIRONMENTAL AND OCEANOGRAPHIC TRACER

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Iodine-129 in the present environment is mainly originated from the human nuclear activities such as nuclear weapons tests, discharges from nuclear fuel reprocessing plants and nuclear accidents. Iodine is a high conservative element in the ocean; it has high volatility, active chemical property and sensitive redox. With these features and the long half-life (15.7 My), ¹²⁹I is an ideal environmental tracer for investigation of the geochemical cycle of stable iodine, dispersion of radioactive substances of gaseous and particular forms in the ecosystem (atmosphere, hydrosphere, biosphere and geosphere), water mass interaction and circulation in the seas. Meanwhile, it can be also used for reconstruction of level and distribution of the short-lived ¹³¹I released from the nuclear accidents (e.g. Chernobyl and Fukushima accidents). Although relative large amount of ¹²⁹I (more than 7000 kg) has been released to the environment, the concentration of ¹²⁹I in normal environmental samples is still very low (< 0.1 μBq/g solid samples and < 0.1 μBq/g /L in water sample, and < 0.1 μBq/m³ in air samples). This requires an effective radiochemical separation and highly sensitive method for its determination, especially for its speciation analysis.

In the past years, a series of analytical methods have been established for the determination of ultra-low level of ¹²⁹I (down 1 nBq or 1×10⁻¹⁶ g) in various environmental samples, including soil, sediment, rocks, vegetation, animal tissues, air, water (rain, lake and ground water, seawater)¹⁻⁴. Combustion and alkaline fusion/ashing combined with solvent extraction and precipitation were applied for releasing iodine from the sample matrix and separation of iodine from other element. The separated iodine was finally prepared as AgI precipitate and MgI₂ for measurement. A sensitive accelerator mass spectrometry (AMS) method was established for the measurement of ultra-low level ¹²⁹I in microgram level iodine samples. Meanwhile, a number of methods for speciation analysis of ¹²⁹I in air, water, soil and sediment were also established⁵⁻⁸. Particle associated, gaseous organic and gaseous inorganic iodine were separated from air using a sequential air sampler, and the trapped iodine in different species were separated using combustion, solvent extraction and precipitation for AMS measurement of ¹²⁹I in three species. Iodine in iodide, iodate in water sample was separated using different methods, such anion exchange chromatography, selective oxidation using NaClO followed by solvent extraction and selective precipitation of AgI-AgCl for inorganic species of iodine in fresh and seawater samples, respectively. An oxidation decomposition method was developed for release iodine from organic substance in the water and leachate of soil and sediment followed by solvent extraction and precipitation for determination of organic associated ¹²⁹I⁹. A sequential extraction method was applied for separation of different fractions of iodine followed by chromatographic method for speciation analysis of ¹²⁹I in aerosol, soil and sediment samples. This

presentation aims to summarize all these methods to give a comprehensive overview of speciation analysis of ^{129}I in the environment.

With the developed method, a number of environmental investigations using ^{129}I as tracer have been carried out ¹⁰⁻¹³. This work presents some of these works such as: (1) circulation of water masses in the Antarctic and Arctic; (2) interaction of water masses in the East China Sea; (3) long distance dispersion of air pollution in China traced by ^{129}I in precipitation; (4) source and dispersion pathway of air pollution in the Antarctic traced by ^{129}I ; (5) Level, distribution, sources of ^{129}I in overall China and its implementation in the radioactive contamination in China; (6) releases, level and dispersion of ^{129}I in the Fukushima accident.

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ABSTRACT 2

TESTS OF NUCLEAR JET ENGINES AS A NEW SOURCE OF RADIOACTIVITY IN THE ENVIRONMENT

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Russia announced that they successfully conducted test of nuclear jet engines in autumn of 2017 [1]. Although the construction details of tested nuclear jet engine remains unknown the general concept of such construction is well known since 1950s . The principle is that in place of combustion chamber of any kind of jet engine (turbo jet, ram jet, turbo fan...) the heat is generated by radioactive decay instead of combustion of liquid chemical fuel. There are two possible sources of radioactive heat: the very active radioisotope source (like in Radioactive Thermoelectric Generator, RTG) or nuclear reactor [2]. In case of RTG-like source isolated isotope source, for example Pu-238, Cm-244, Sr-90/Y-90 or Ru-106/Rh-106 can be use. The available generated power is a product of radioactive source activity and mean energy of a single decay of given isotope. On the other hand the power needed for propulsion of a plane is product of thrust of engine and speed of plane. Since the announcement was about jet engine for propulsion of cruise missile the speed is about 200 m/s and thrust about 4.5 kN. This gives energy on level close to 1 MW. Simple calculation reveals that required activity is on the order of magnitude of an EBq (10^{18} Bq). The exact value depends on energy available in decay. It means that to drive a cruise missile the activity of the level of released during Chernobyl accident has to be on board of this small plane. It is likely, that mysterious air contamination with Ru-106/Rh-106, observed in beginning of October 2017 all around Europe was a results of such tests. Since release was estimated to be on level of 1/10 of PBq [3], it means that less than one pro mille of on-board activity was released. This seems to be a result of diffusive process inside fuel element in very high temperature of it during flight. The nuclear reactor used in jet engine will also release in diffusive processes volatile fission and activation products, since due to restriction in weights of flying objects it is very unlikely that construction will have separate intermediate cooling circuits. The conducting of tests of nuclear jest engines in open air is a new challenge for radioactivity monitoring systems in many countries. In case of nuclear reactor released radionuclides are close to that released from nuclear explosion of from nuclear power plant during accidents. Perhaps more activation products of metals used in jet engine technologies will be observed but the main composition will still remain close to what all air monitoring systems are prepared to. However, the use of RTG –like radioisotopes is a new situation for which many countries and international organizations are not prepared at all. For example, if such test would be conducted not with nuclide emitting gamma radiation (like Ru-106/Rh-106) but with pure alpha emitter like for instance Po-210 or Cm-242 – who and how fast will notice any traces in air? The other important question is activity released during possible crash, which might happen during test flight.

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ABSTRACT 3

LOCALIZATION, EXTRACTION AND NONDESTRUCTIVE ANALYSIS OF HOT PARTICLES FROM ENVIRONMENTAL SAMPLES

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Introduction

During the accident in the Chernobyl nuclear power plant, high amounts of radionuclides have been released into the environment. Besides volatile elements like iodine and cesium, heavy actinides and highly radioactive fragments of nuclear fuel, so-called hot particles, have been deposited in the area around the reactor. The size of these particles varied from the range of nanoparticles up to macroscopic fragments. Depending on their location, size and chemical composition, hot particles have undergone different grades of weather-induced degradation. Investigation of these effects and especially the differences in weathering of radioactive isotopes in various chemical matrices is vital for the understanding of long-term mobility of long-lived radionuclides from such sources. An element of special interest in this regard is plutonium. Due to its medium-range half-life, it will dominate the radiotoxicity of reactor material that has been released into the environment or stored in a high-level waste repository after the decay of short-lived radionuclides. In addition, the solution chemistry of plutonium is highly complex and it can be very mobile in form of colloids or pseudo-colloids. To predict the mobility of plutonium – and other radionuclides originating from particles – a strong database is necessary. By investigation of the aforementioned hot particles and the contained radionuclides from the surrounding of the Chernobyl nuclear power plant, such data can be acquired. For the comparison of data on each single particle, every particle has to be isolated and analyzed in a nondestructive way.

Localization and extraction can be realized by α -track analysis and scanning electron microscopy (SEM) paired with a micromanipulator¹. Nondestructive analysis of isotopic compositions for trace concentrations of radionuclides however, is a challenging task. At the Institute for Radioecology and Radiation Protection (IRS) in Hannover, Germany, a commercial time of flight secondary ion mass spectrometer (TOF-SIMS) has been coupled with a laser system for resonant laser ionization of target elements, which is capable of just that. Since the method is non-destructive, beamline, dissolution and leaching experiments can still be carried out on the same particles.

Sample preparation

After sieving of soil and sediment samples from several areas within the Chernobyl vicinity, the size fraction with the highest activity is separated and dried. Hot spots are located using a small window Geiger counter and α -track analysis in combination with optical microscopy. These hot spots are fixed to double-sided carbon tape and imaged using the backscattered electron (BSE) detector of a SEM. Images taken in BSE mode give a materials contrast, highlighting areas of heavier elements,



Figure 1: SEM image of a hot particle from the Chernobyl cooling pond fixed to a tungsten tip. Green: BSE image; Red: SE image.

such as hot particles with a high concentration of uranium and plutonium. Using a built-in micromanipulator, identified hot particles are fixed to a thin tungsten tip (fig. 1), which is then mounted onto a sample holder to be analyzed in the TOF-SIMS system.

Experimental setup

In the TOF-SIMS, a focused and pulsed bismuth ion beam scans the sample surface. The impact of the ion pulses leads to sputtering of small fractions of the surface and partial ionization of the sputtered material. Consequently, a cloud of atoms, molecules and ions expands into the vacuum after each pulse. After a short delay, ions are extracted and accelerated by electric fields, to follow a flight path through the TOF, to be separated by their m/z ratio. In scanning the beam over the sample surface, a lateral resolution of down to 70 nm can be achieved, with every pixel containing a full mass spectrum. This way, mappings of selected m/z ratios can be created.

With a clean surface of a well-defined sample, this method would already be capable of identifying the chemical composition of a surface and isotopic ratios of main components. However, with an environmental sample consisting mainly of uranium, the nondestructive determination of trace element isotopic ratios becomes a challenge is impossible due to isobaric interferences and high background.

To overcome this issue, the sputtered secondary ions (SI) are suppressed and instead, the sputtered

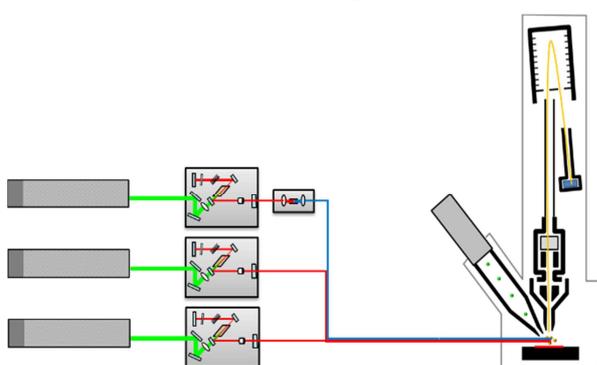


Figure 2: Combination of resonant laser ionization system (left) and TOF-SIMS (right).

neutrals (SN) are addressed, which take up as much as 99 % of the sputtered material. For the SI suppression, an electric field is applied immediately after the sputter pulse. The shell electrons of the SNs in the remaining cloud are then resonantly excited by up to three lasers, which are tuned to transition energies of a specific element. This way, atoms of the selected element are resonantly ionized in at least two steps, which results in very high element selectivity and ionization efficiency while completely suppressing background signal and maintaining the spatial and mass resolution of SIMS.

Results

A number of particles has been extracted and isolated from soil samples from the red forest and sediment from the Chernobyl cooling pond. An analysis of uranium isotopic ratios is available via standard SIMS. By applying the resonant laser ionization to the sputtered atoms, a nondestructive analysis of the isotopic ratios of trace elements becomes possible, with suppression of isobaric interferences (like ^{241}Am and ^{241}Pu) over several orders of magnitude. This method has previously been demonstrated on samples of mixed oxide fuels and natural mineral samples^{2,3}. Here, we will present results from measurements on hot particles from the Chernobyl exclusion zone for several important radionuclides.

Acknowledgments

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ABSTRACT 4

RADIOCHEMICAL ANALYSIS OF U, AM, NP AND PU ISOTOPES IN SEDIMENTS FROM A CHAIN OF FRESHWATER SYSTEMS (SWITZERLAND)

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Abstract

Anthropogenic radionuclides have been introduced to the environment by nuclear weapon tests, accidents in nuclear power plants such as Chernobyl (1986) and Fukushima (2011), transport accidents and accidental or authorised discharges from nuclear facilities. The River Aare, one of the major rivers in Switzerland, connects three lakes (Brienzen, Thun, Biel) and the reservoir in Klingnau, before feeding the River Rhine. Authorised discharges of radionuclides into the River Aare from the nuclear power plants of Mühleberg and Beznau and the nuclear facility Paul Scherrer Institute are reported every year. Sediment cores from lakes up- and downstream the discharge sites, from the Klingnau reservoir and the River Rhine have been collected. The sediment cores were split longitudinally and sliced into 1 cm layers. The sediment samples were freeze-dried, packed into plastic containers and then measured by gamma spectrometry in order to determine the total and supported Pb-210 as well as Cs-137 activities. This information was used to date the sediment layers by the Pb-210 age-dating methods constrained by Cs-time markers. After the gamma analysis, the sediment samples were ashed and dissolved by a fusion digestion technique. U, Pu, Np and Am were sequentially separated by extraction chromatography methods. Isotope ratios of U and Np-237 were analysed by sector field ICP-MS (single and multi-collector) and Am-241 was analysed by alpha spectrometry.

All Cs-137 profiles showed the impact of the Chernobyl accident and the nuclear weapon tests and their exponential decreases due to the wash out of the catchment areas. The Cs-137 profiles collected at positions downstream the discharge areas showed additional inputs, probably from the nuclear facilities.

Due to the high sensitivity of the ICP-MS, Pu could be analysed in all sediment layers. All Pu profiles showed the impact of the nuclear weapon tests and the exponential decrease due to the wash out of the catchment area. The Pu isotope ratios were measured very precisely, so that even different atomic bomb test series could be distinguished. Furthermore, an additional Pu possibly from discharges could be identified. The resulting change of isotopic ratio of Pu-240/Pu-239 could be explained.

In nuclear forensics, the Am-241/Pu-241 activity ratio is used for determining the age of the Pu contamination, assuming the initial amount of Am-241 in the sample to be zero. Due to the high sensitivity of today's mass spectrometer, Pu-241 can be determined in the sediment samples from the time of the nuclear weapon tests. The measurements demonstrated the applicability of the Am-241/Pu-241 age dating method for determining the origin and age of a Pu contamination.

ABSTRACT 5

SURVEY OF URANIUM ENTRAPMENT IN THE SWISS MOLASSE BASIN

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Exceptionally high natural Uranium (U) concentrations in ground and surface waters were found in the western part of the Swiss Molasse Basin. More than 50 public fountains were analyzed for their radionuclide content, revealing that increased ^{238}U concentrations frequently occur at the interface between the Lower Freshwater Molasse and the Upper Marine Molasse that bear U-rich fossils. Two springs at the northern slope of Mont Vully (20 km northwest of Berne, Switzerland) exhibit the highest concentrations in ^{238}U and were thus monitored for almost 2 years in order to screen seasonal variations. In addition, the arable land north of Mont Vully was surveyed by gamma dose rate measurements in order to locate possible U accumulations underground. Recording the dose rate was accomplished with a 2"x2" NaI detector combined with GPS, carried gridwise across the field. In comparison with the normal natural radiation of about 80 nSv/h, several hot spots with more than 150 nSv/h were located above ancient pathways of creeks, formerly draining Mont Vully. In order to verify the assumption that the enhanced gamma dose rate is owed to an underground U accumulation, 5 shallow sediment drill cores were taken and analyzed for their U content. The sediment cores can essentially be divided into three parts: i) an upper soil with common U concentrations of about 30 Bq/kg ^{238}U , ii) an U-rich peat horizon with concentrations of up to 500 Bq/kg ^{238}U , and iii) an impermeable clay unit that acts as an aquitard with again minor ^{238}U concentrations. Radiocarbon dating of the U-rich peat horizon reveals ages between 2000 and 5000 years. This suggests that wetlands were formed after the last glaciation due to inflowing stream water onto the impermeable clay layer. The contained dissolved U was precipitated due to reducing conditions in the wetlands and an entrapment for U was generated. Installation of drainage pipes and capturing incoming streams in the last century led to dehydration of the wetlands, making them suitable for agriculture. The subsequent change in redox conditions made the accumulated U solvable again. Incoming oxygen-rich rainwater then leaches the accumulation, resulting in increased U concentrations of drainage water.

In order to discover further possible U entrapments in the Swiss Molasse Basin, aeroradiometry of a wider zone at Mont Vully was accomplished with the help of a helicopter equipped with 4 NaI detectors. The surveyed area exceeds 75 km², reaching from Mont Vully in the South to Jolimont in the North. Jolimont is composed of the same geological units as Mont Vully, so that with a high probability, similar U accumulation processes took place there. The according results reveal increased gamma dose rates above parts of the agricultural land and green spaces. This implies that such U accumulation is not a local singularity but could have developed in a broader area in the Swiss Molasse Basin.

ABSTRACT 6

HOLDING TIMES AND PRESERVATION FOR ENVIRONMENTAL RADIOCHEMICAL SAMPLES AN EVALUATION OF ISO STANDARD GUIDELINES

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The condition of a sample taken and stored before analysis is an important aspect in analytical measurements including in the field of environmental radiochemistry. The validity of the result from the test depends heavily on the sample integrity; a sample that is not well preserved might not be a true representative of what has been sampled. For example, the radionuclides in the water sample might be adsorbed by the wall of the container during transport and storage.

This important aspect was also recognised by the Laboratory Committee of the European co-operation for Accreditation (document EA/LC(07)60). Laboratories working under ISO 17025 or ISO 15189 were recommended to apply the best available sample storage techniques. ISO 5667-3:2015 gives a full overview of best available techniques for a range of analytes in water samples and summarises both validated and tested storage and handling techniques including maximum holding, or, shelf-life times. There are however some gaps in recommendations for storage and preservation of water samples for radiochemical analyses.

This study summarises a range of shelf-life tests performed by SOCOTEC nuclear laboratory. Each test evaluated the integrity of a group of radionuclides in water samples under different storage conditions. Samples were either aqueous certified reference materials (CRM), proficiency test samples or spiked freshwater samples. Freshwater was filtered before use.

We found that Tritium was stable for a much longer period of storage than that recommended in ISO 5667-3:2015. Tritium was generally stable for up to 3 years. In one instance, the tritium concentration in a CRM sample was stable for 6 years. The tritium concentration was not affected by different storage temperature (ambient vs. cold), container type (glass vs. plastic), acidification, or the presence of head space.

The gamma emitting radionuclides ^{60}Co , ^{137}Cs , ^{226}Ra , and ^{241}Am were stable in acidified filtered freshwater (pH of 2) for up to 1½ years in plastic containers.

The actinides uranium, plutonium, americium, and curium were stable for at least 6 months in acidified filtered freshwater (pH of 2) in plastic containers. This is longer than the 2 months recommended in ISO 5667-3:2015.

We found that acidification is critical for the good preservation of most of the gamma emitting radionuclides and the actinides. If the water is not acidified, ^{241}Am concentration decreased sharply within a week. After one month of storage the ^{241}Am concentration decreased by 60% to 65%. A similar results was seen for plutonium and curium. However, ^{60}Co concentration decreased at a much slower rate over time; after 1½ year 5% to 10% was lost. Losses in radionuclides could not be recovered by acidifying the container afterwards. For some radionuclides, acidification is not as

critical. For example, the Uranium concentration was stable for at least 4 months in these unacidified samples and ^{137}Cs and ^{226}Ra stayed stable over 1½ year.

Our studies suggest that the integrity of freshwater samples can be preserved for up to 1 year when filtered and acidified for the analyses of gamma emitting radionuclides, actinides and tritium. If filtration and acidification cannot be achieved in the field, for logistic and health and safety reasons, samples should be transported as soon as possible to a suitable laboratory for filtration and acidification. For a minimum loss of the transuranium actinides, this should occur within 3 to 7 days. This period can be extended if these are not of interest. Cooling the samples during transport and interim storage is advised to prevent bacterial and algal growth as much as possible.

ABSTRACT 7

RADIUM MONITORING AT COAL FIRED POWER PLANTS

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Coal fired power plants have provided power around the world since the late 19th century. In 1882 the world's first coal fired power station was built by Edison Electric in London and coal-based power plants are still the major percentage (~40%) of global power production. The negative environmental aspects of coal-based power are also well documented. Solid waste is a major storage and disposal issue for utilities and a 2008 accident in Kingston Tennessee released 4.2 million cubic meters of fly ash into a river basin causing massive damage. This incident accelerated US regulations for active and inactive coal plants known as the "coal combustion residuals rule" or CCR (Ref.1).

The CCR addresses the storage of wastes and monitoring for chemical hazards that can aggregate in the coal cycle. The CCR Appendix IV table specifies the elements for assessment in waste streams and monitoring wells around coal plants. The regulation assigns a combined maximum concentration for Radium 226+228 as less than 0.18 Bq/l (5 pCi/l) in monitoring wells.

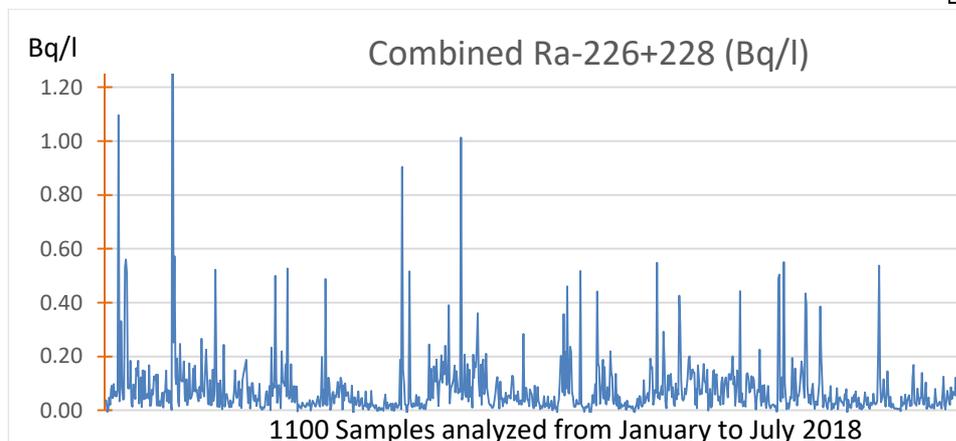
Testing for these elements was undertaken by GEL in ground water monitoring wells, and solid waste fly ash. Radium 226 was determined using a purge and trap radon emanation method using Lucas cell counting (Figure1). Ra-228 was analyzed using a traditional chemical separation followed by Eichrom DGA resin to isolate and count Ac-228 by gas flow proportional counting.

Approximately 7% of 1100 ground water samples tested through July 2018 exceeded the allowable combined radium limit. No consistent ratio between Radium 226 and 228 was observed in wells exceeding the limit but average results of 0.05 Bq/l for Ra-226 and 0.02 Bq/l for Ra-228 were recorded. Maximum observed values of 1.8 Bq/l for Ra-226 and 0.5 Bq/l for Ra-228 were observed in water samples while fly ash samples showed consistent levels of radium isotopes in the range of 0.03-0.09 Bq/g.

CCR Appendix IV Table

Assessment Monitoring

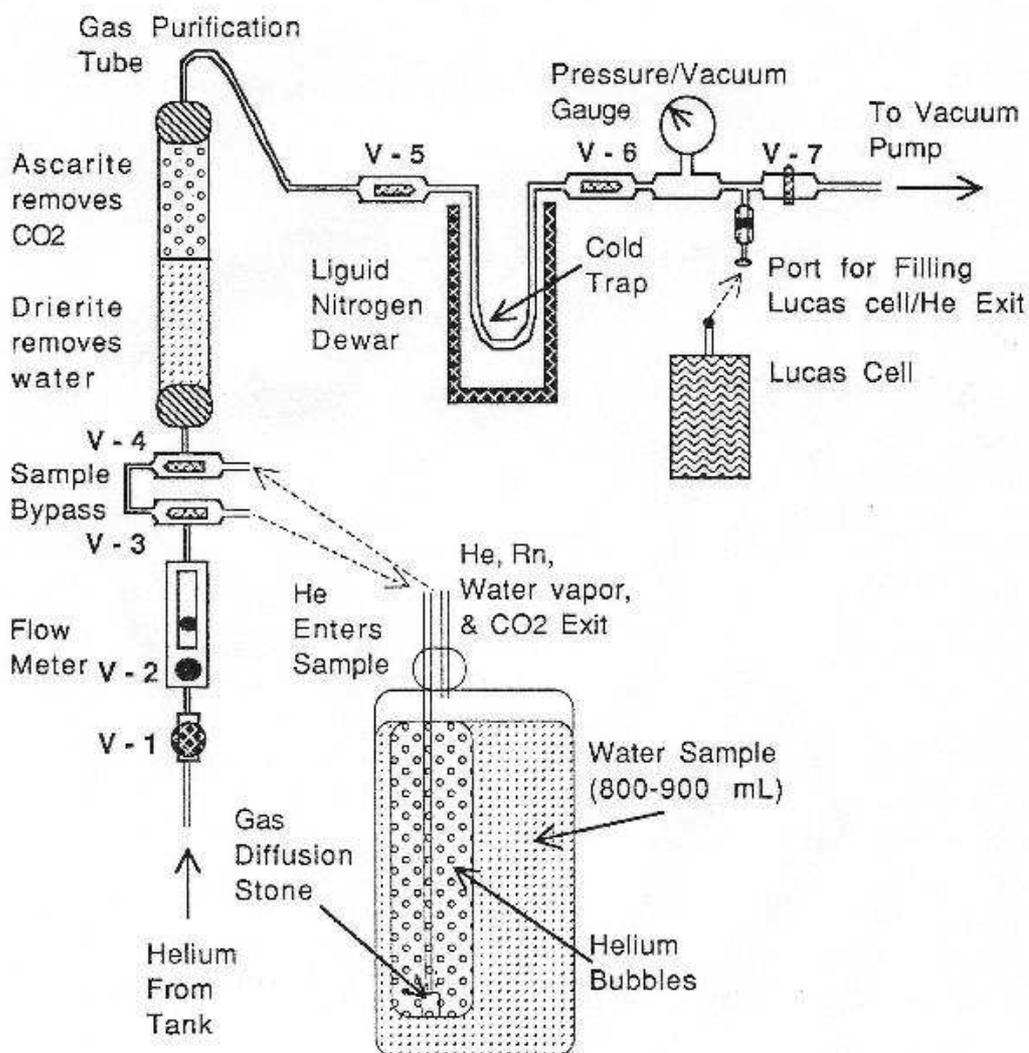
Antimony
Arsenic
Barium
Beryllium
Cadmium
Chromium
Cobalt
Lead
Lithium
Mercury
Molybdenum
Selenium
Thallium
Fluoride
Radium 226 & 228
pH (field)



The CCR regulation provided no specific method guidance but utilized the US EPA maximum contamination limits (MCL of 0.18 Bq/L combined) for drinking water. Following the drinking water guidelines, the method detection limit was 0.04 Bq/l for each radium isotope. To achieve this detection limit, sample volumes were typically 500 ml for Ra-226 and 900 ml for Ra-228 with counting times of 30 minutes for Ra-226 and 60 minutes for Ra-228.

This ongoing project illustrated the importance of careful method selection based on clear communication of data quality objectives and capacity requirements. With a lack of guidance, often the industry will default to lower detection limits than necessary. In this example, very little was known about the sample matrix until samples were being collected and results were being reported. Along the project timeline we discovered high radon and dissolved solids were contributing to false positive reporting for Ra-226 which required some added confirmatory steps to the method.

Figure 1: Ra-226 De-emanation schematic



Thanks to Dr. William Burnett for this design from Florida State University Department of Oceanography.

ABSTRACT 8

25+ YEARS OF NUCLEAR FORENSICS

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At the beginning of the 1990's, incidents of illicit trafficking of nuclear materials generated a deep concern and an unexpected new threat appeared at the horizon. For the first time law enforcement authorities were interested in nuclear material analysis, seeking support for their investigations. Apart from the need of determining the nature of the illicitly trafficked materials and their intended use, the authorities wondered about their origin. In 1992 the first nuclear forensic sample was analysed at JRC Karlsruhe. During the following three years, 21 investigations of materials seized alone in Germany were performed. Thus, effective countermeasures based on nuclear forensic capabilities had to be quickly deployed. Of course, such capabilities had to be developed first. With its range of advanced chemical and isotopic analytical techniques and methods that had been established for nuclear safeguards purposes, as well as using its expertise on nuclear materials, JRC Karlsruhe was in an excellent position to help addressing the nuclear security challenge in Europe.

A dedicated research related to nuclear forensics started at JRC Karlsruhe in 1997. The research concentrated first on signatures of uranium fuel pellets as the majority of the seizures involved them. This included e.g., analysis of trace elements as process indicators, determination of the $^{18}\text{O}/^{16}\text{O}$ isotope ratio to gather information on the location of the production site, and surface roughness characterisation in connection with grinding processes.

In parallel the development of "age" determination (i.e. the date of last chemical separation) methods for U and Pu was started in order to narrow down the number of possible production places. The age determination method for Pu was developed using multiple parent/daughter ratios by mass spectrometry and it was also demonstrated to be applicable for individual particles. In the beginning of 2000s, the work was extended to uranium.

Later, research was started on investigating potential new signatures of the origin in natural uranium and they have been tested using a comprehensive set of uranium ore concentrate (UOC) samples around the world. The studied signatures include e.g. rare earth elements (REE), anionic impurities and stable isotope ratios (e.g. Pb, Sr, S and Nd). Also the propagation of nuclear forensic signatures in various natural uranium materials has been studied lately.

Links between nuclear forensics and traditional forensics (e.g. fingerprint, DNA) was given a close consideration at JRC Karlsruhe in the preparation phase of the 2006 FIFA World Cup in Germany. The issue, how to collect and exam radioactively contaminated evidence, e.g. after a dirty bomb explosion, was raised. Together with the German Federal Criminal Police (BKA), a dedicated glove box was designed and set up, where fingerprints can be developed for radioactively contaminated items following the established protocols of the police. In later years, procedures for DNA extraction and subsequent decontamination as well as digital data retrieval have been also developed.

Today, 25 years later, the discipline of nuclear forensics has matured considerably. Besides as an emerging response measure for illicit trafficking, nuclear forensic analysis has also applied to other cases of radioactive materials being out of regulatory control, such as unauthorised disposal of radioactive waste. A number of examples and case studies will be shown to demonstrate the progress made in nuclear forensic research and methods development during these years.

ABSTRACT 9

IDENTIFYING NUCLEAR FORENSIC TOOLS FOR CLASSIFYING AND DEDUCING THE PROVENANCE OF MAGNOX URANIUM

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The scientific field of Nuclear Forensics works to identify the provenance of illicit nuclear materials by analysing the seized material for characteristic chemical or isotopic signatures and comparing these signatures to a database of reference materials¹. A total of 3068 incidents of nuclear materials outside of regulatory control were logged between 1995 and 2016 by the international Atomic Energy Authority (IAEA)². Several institutions in coordination with the IAEA have been working to characterise nuclear materials including unirradiated fuels of known origin to produce reference databases¹³.

The UK Magnox reactor fleet burned natural or low enriched uranium metal fuel rods clad with a magnesium alloy for nearly 60 years⁴⁵. Throughout the 60-year history considerable changes were made in fuel element design and composition⁶. Several other countries also built Magnox reactors, therefore it is of interest to be able to identify UK produced material and to differentiate between materials produced for different UK reactors⁶.

Here, diagnostic material characteristics with the potential to become nuclear forensic signatures have been identified within the Magnox uranium production literature. These signatures include the geometry of fuel rods, metallic structure, impurity elements, and the distribution/composition of inclusions and precipitates. Variations within these signatures could be used to deduce the production age of the material, the reactor the material was produced for or whether the material fits the specification for UK Magnox uranium. However, care must be taken to ensure the homogeneity of identified signatures within a single fuel rod.

The Magnox production literature has proved to be a useful information source, it was identified that several UK reactors had a unique fuel rod length/diameter combination and that fuel rod geometry could be used to identify an individual reactor as seen in Figure 1. In addition, quality control datasets have been used to confirm step increases in additive concentration (such as aluminium) reported in the literature.

Magnox uranium material samples have been analysed and the results of Secondary Electron (SE) microscopy, Back Scatter Electron (BSE) imaging, Energy Dispersive Spectroscopy (EDS), Electron Probe Micro Analysis (EPMA) and Electron Back Scatter Diffraction (EBSD) used to test the radial variation in potential diagnostic signatures within a single fuel rod are presented here.

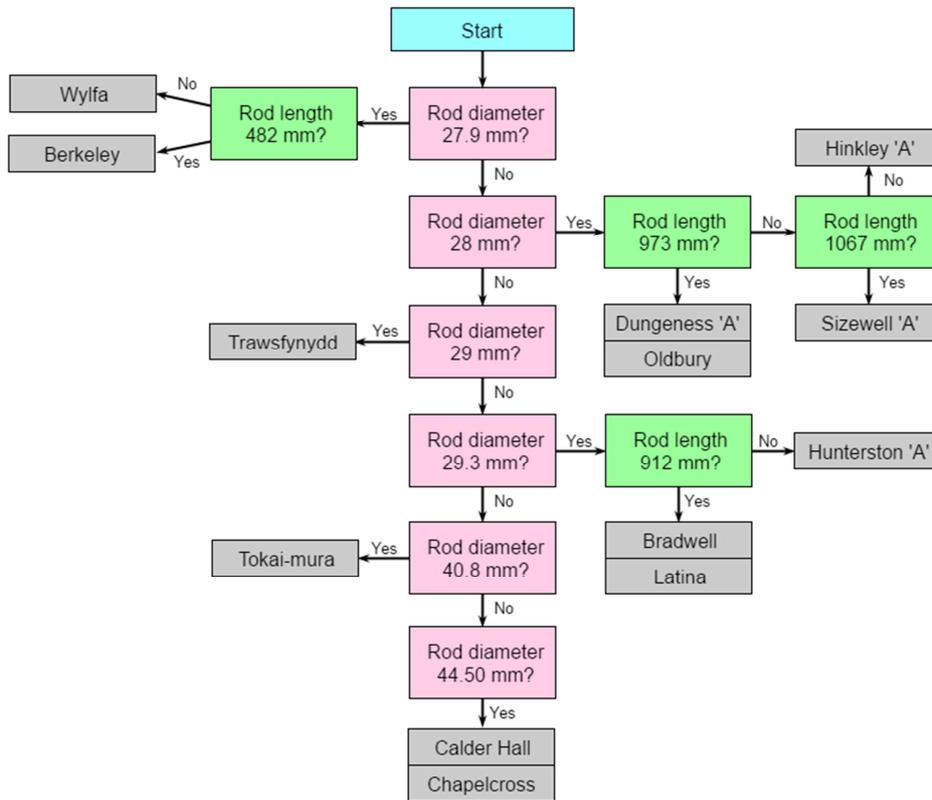


Figure 1. Flow chart to discriminate between different Magnox reactors based on fuel rod diameter and length.

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ABSTRACT 10

FUTURE FOR/OF NUCLEAR FORENSICS (RADIOCHEMISTRY)

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Nuclear Forensics is dependent on many skill areas, of which one is radiochemistry. It is very difficult to justify the dedication of major resources, both facility and staff, to be full time deployed to Nuclear Forensics. Radiochemistry, in its broadest sense, covers a wide area sample preparation, radiochemical analysis, radio metrology and a wide variety of other measurement techniques including mass spectrometry, and a large number of other measurement techniques.

It is 'accepted' that the total skill pool of trained and knowledgeable staff is declining. How is this to be managed to ensure the skills are passed on to future generations.

One method frequently raised is the use of 'Knowledge Management' – however it is rarely detailed what this means and how it is to be achieved. It can be claimed that there are many articles in the literature on radiochemistry which can be used as the basis for knowledge transfer, but how many of them provide sufficient detail to allow the basics of radiochemistry to be followed in a laboratory for a beginner? What may seem obvious to the author and the group around him now may not be obvious to those that follow, especially if there has been a gap and none of the previous generation are available to conduct schooling. How can this everyday practical knowledge be passed on, or kept in accessible useful form for when it is required?

ABSTRACT 11

DEVELOPMENT OF RAPID METHODOLOGIES FOR URANIUM AGE DATING

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The measured model age is an important signature to constrain the production history of an unknown nuclear material. The aim of this work was to validate a rapid, robust quantification scheme for bulk uranium materials, amenable to multiple detection platforms. This work describes a combination of stacked columns, vacuum assisted separations, automation and a suite of analysis techniques to determine the ages of uranium materials and CRMs of known production history. The methodology allows for the determination of $^{234}\text{U}/^{230}\text{Th}$ and $^{235}\text{U}/^{231}\text{Pa}$ atom ratios via a novel approach, starting with a three resin column separation to allow high throughput and rapid turnaround. The materials analysed have concordant ages with known production histories, leading to the potential for expanding this work to additional chronometers, and the approach offers nuclear forensic practitioners an additional, advantageous separation methodology in the analysis of bulk uranium materials.

ABSTRACT 12

RAPID SEPARATION OF AMERICIUM FROM FISSION PRODUCTS USING LN AND TEVA RESIN

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Separation of trivalent americium from lanthanides is challenging due to chemically similar behaviour. The weight distribution coefficients (Dw) for the adsorption of americium, lanthanum, cerium and neodymium on Triskem LN resin between 0.10M and 0.30M nitric acid were measured and subsequently used to formulate a column based separation using a nitric acid gradient; this method was evaluated using a sample of fresh fission products spiked with ²⁴¹Am. The combination of two fractions from the gradient attained an americium recovery of 80% with 0.5% lanthanum, 4% niobium and 1.2% neodymium; near 100% recovery of americium was possible by combining three fractions although with higher impurity levels or neodymium (25%) and niobium (7%)

An americium separation method was reported by Berne using TEVA resin with thiocyanate. The weight distribution coefficients (Dw) for the adsorption of americium on TEVA at various concentration of ammonium thiocyanate (NH₄SCN) in water, formic and hydrochloride acid were determined; the strongest adsorption of americium was found in 2M NH₄SCN (Dw 1.5x10²). Column studies were performed using a fresh fission product sample spiked with ²⁴¹Am and an americium recovery close to 100% was obtained with impurities of 0.1% niobium, 6% tellurium, 0.03% zirconium. By combining the two separation methods a rapid and complete separation of americium from virtually all fission products can be achieved with near 100% recovery.

ABSTRACT 13

RECENT DEVELOPMENTS IN RADIOANALYTICAL METHODS AT THE SAVANNAH RIVER LABORATORY-CHALLENGES AND SUCCESSES

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An important function of our laboratory is the development of new rapid radioanalytical methods in support of emergency response to radiological emergencies such as an improvised nuclear device (IND), radiological dispersive device (RDD) or nuclear accident. In addition, there has been a drive to reduce costs, shorten turnaround times and improve quality for routine lab measurements. If a radiological event occurs, there will be an urgent need for quick analyses of urban matrices materials to support decision-making, dose mitigation and environmental clean-up. Since an incident involving a RDD or IND would likely occur in an urban or metropolitan area, it is very important to employ swift, robust analytical methods that can be effectively applied to urban matrices. These types of sample matrices include soil, concrete, brick, asphalt, limestone, marble, granite and steel, which are challenging solid materials that must be effectively digested so that the analytes can be collected, purified and measured quickly. Because there may be refractory particles present in these sample matrices, the analytical methods must utilize robust sample digestion methods. The radiochemical methods need to efficiently remove radiological interferences, so that high quality, defensible measurements can be made. Rapid extraction chromatography techniques can be used to quickly purify actinide elements, ^{89}Sr , ^{90}Sr , ^{210}Po and ^{226}Ra so that these radioisotopes can be quantified with reliability. In the Savannah River Laboratory, progress has been made over the last 15 years regarding many different sample matrix types. This includes environmental samples (including urban matrices), bioassay samples, and food matrices. Radiochemical separations technology advances over recent years have been made in sample digestion and dissolution, removal of interferences and rapid purification using novel combinations of highly selective extraction chromatography resins.

Hauer describes scenarios whereby terrorists detonate a 10 kiloton (kt) nuclear device and makes persuasively the case that the United States in many ways is not prepared to respond effectively to this type of devastating event. [1] Planning for radiological incidents is complex and presents unique challenges, including management of the physical and psychosocial effects of radiation exposure. Radiological events have the capacity to trigger great anxiety and fear, creating widespread panic. [2, 3] In another study conducted by Redliner and Levin, there was a clear consensus among participants that no American city or region, even with abundant state and federal government and military support, has sufficient health care infrastructure and resources to handle the anticipated injuries and illness from the detonation of a 10-kiloton nuclear device. [4] Following a detonation event, it is critical to know as soon as possible what type of device was detonated and its impact. It is extremely important to know the scope of the radionuclide contamination and radiation exposure that results. While much of our work has focused on measuring actinides and Sr-89,90, there is also a real concern about natural decay chain isotopes such as ^{226}Ra and ^{210}Po . The defensibility of results is very important to not only protect those affected by the blast or accident, but also to maintain the public trust. The use of rugged, reliable methods to ensure high quality measurements and to maintain the public confidence is therefore essential.

This talk will discuss recent improvements developed in the Savannah River Environmental Laboratory, noting some challenges and key successes. There are some fundamental aspects of any new method that need to be considered. For example, what are the measurement quality objectives required? Detection limits for assessing dose and those for meeting decommissioning release limits, for example, will likely be very different. For radiometric counting methods, the sample aliquots and count times utilized may be very different. Some sample types may need more rugged dissolution or better removal of extremely high levels of interferences. Are refractory particles present? Are the interference levels higher than usual? All these factors need to be considered. An openness to employing the latest fast analytical techniques and a blend of old and new techniques may also offer certain advantages. Knowledge of both analytical chemistry and radiochemistry, and how to couple key aspects of each, can offer an advantage in the method development process. A clear willingness to think outside the box is advised, while avoiding making changes simply for the sake of change. Recognizing that certain analytical approaches, principles or techniques successful in one area can be applied for different sample types or for different analytes, with appropriate modifications, is also helpful. An openness to embarking in a new direction is important when an obstacle cannot be overcome, as is persevering through seemingly insurmountable difficulties and problems when success may be just around the corner. A collective world effort, continuing to push the science of radioanalytical chemistry forward through logic, creativity, perseverance and innovation is essential. I'm excited to see what that the future will bring and encourage each of you to contribute to the shape of that new horizon.

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ABSTRACT 14

CHARACTERISATION OF URANIUM AND EUROPIUM SPECIES BY TIME RESOLVED LASER FLUORESCENCE AND RAMAN SPECTROSCOPY

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Corrosion of spent nuclear fuel (SNF) typically proceeds from the development of ultra-thin films on the altered surface of the fuel, through colloidal particulates to aqueous solutions¹⁻³. The physical persistence and chemical composition of these species is largely dependent on the surrounding solution, which can either enhance dissolution rates or promote the formation of passivating surfaces⁴. Wherever feasible, theoretical prediction of leaching rates and the range of potential corrosion products formed needs to be verified by direct experimentation.

Characterisation of each state is challenging; X-ray diffraction (XRD) analysis is largely limited to crystalline phases whereas analysis of aqueous speciation products are masked by intense water features with, for example infra-red (IR) spectroscopy. This is not the case with time-resolved laser fluorescence spectroscopy (TRLFS) and Raman spectroscopy as both of these techniques can be used to characterise amorphous solids, colloids and aqueous solutions. Chemical composition data can be obtained from non-time-resolved fluorescence and multiple laser Raman spectra whereas TRLFS is used to extract fluorescence decay lifetimes. A spectral database is being compiled based on type uranium mineral specimens from national reference collections and europium-bearing compounds⁵, the latter as a surrogate of the trivalent actinides.

Experiments were performed on Eu(III) acetate ($\text{Eu}(\text{CH}_3\text{CO}_2)_3$), chloride (EuCl_3), nitrate ($\text{Eu}(\text{NO}_3)_3$) and oxide (Eu_2O_3) using fluorescence spectroscopy and a four laser Raman spectroscopy system. The fluorescence results reveal key features linked to hypersensitive fluorescence excitation and emission transitions and confirmation of crystal structure with respect to XRD results, which indicate that the Eu_2O_3 sample was mixed phase. Chemical composition was obtained from Raman spectra each collected using a 457, 532, 633 or 785 nm laser. Not all features could be observed with any one laser, highlighting the requirement for a multi-laser system. Characterisation of representative uranium (IV) and (VI) species is described together with a protocol for real-time, *in situ* tracking of uranium phase evolution.

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ABSTRACT 15

DEVELOPMENT OF AN OPTIMISED PROCEDURE FOR MEASUREMENT OF ^{99}Tc IN AQUEOUS SAMPLES BY ICP-MS/MS

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Technetium-99 is a long-lived ($t_{1/2} = 2 \times 10^5$ years), high yield fission product (fission yield 6.06%) with high environmental mobility and complex redox chemistry, making accurate measurement important for nuclear decommissioning and long term environmental monitoring. Major inputs of ^{99}Tc into the environment include aqueous discharges from reprocessing facilities at Sellafield (UK) and La Hague (France), atmospheric weapons test fallout, and the nuclear accidents at Chernobyl and Fukushima. Decay via pure beta emission means ^{99}Tc is well suited to detection by liquid scintillation counting (LSC), whilst the long half-life has also led to extensive measurement by mass spectrometry, most commonly inductively coupled plasma mass spectrometry (ICP-MS).

Rapid and accurate measurement of ^{99}Tc by ICP-MS requires complete separation of isobaric ^{99}Ru , polyatomic $^{98}\text{Mo}^1\text{H}$ and tailing from ^{98}Mo , which is usually achieved by chemical separation prior to sample introduction. To date, there has been limited investigation into instrument-based separation of interferences, which could potentially reduce the procedural time by reducing or even eliminating the requirement for chemical separation. Tandem ICP-MS/MS equipped with a collision/reaction cell positioned between two quadrupole mass filters has been proven to effectively measure a range of radionuclides, including ^{90}Sr , ^{93}Zr , ^{151}Sm , $^{135/137}\text{Cs}$ and ^{226}Ra . This study investigates the capabilities of ICP-MS/MS for measurement of ^{99}Tc in aqueous waste samples.

When operating with two quadrupole mass filters, tailing from ^{98}Mo was not detected until the concentration exceeded 1 $\mu\text{g/g}$, which is higher than in any of the samples under study. Collision (He) and reaction (O_2 and NH_3) gases were investigated for interference removal capability. The use of He was only effective for removal of $^{98}\text{Mo}^1\text{H}$, and not ^{99}Ru , and there was limited formation of Tc cell products when operating with NH_3 . However, both $^{99}\text{Tc}^{16}\text{O}$ and $^{99}\text{Tc}^{16}\text{O}_2$ were formed when operating with O_2 . When ^{99}Tc was measured as $^{99}\text{TcO}_2$ at $m/z=131$, $^{98}\text{Mo}^1\text{H}$ was converted to non-interfering $^{98}\text{Mo}^{16}\text{O}_2$, and formation of $^{99}\text{Ru}^{16}\text{O}_2$ was limited. The background at $m/z=131$ from ^{131}Xe (present as an impurity in the Ar plasma gas) was removed via a charge-transfer reaction with O_2 , resulting in a low instrument background. Customised tuning of the cell (gas flow rate, residence time and ion energy in the cell) had a significant impact on ^{99}Tc sensitivity and ^{99}Ru decontamination.

For low-Ru containing samples, direct measurement of ^{99}Tc in aqueous samples was achievable without chemical separation, with an instrument detection limit of 3.0×10^{-4} Bq/g . For high salinity samples, online aerosol dilution offered enabled samples with a total dissolved solid content of up to 2.5 % to be introduced, compared to 0.25 % without aerosol dilution. For Ru-contaminated samples, results are presented for characterisation of recently developed TK201 (Triskem International) extraction chromatography resin, focusing on the behaviour of Tc , Ru and Mo . The performance of the resin is compared to commonly used TEVA resin (Triskem International), focusing on the suitability of the resin as a separation step prior to ICP-MS/MS measurement.

ABSTRACT 16

SEQUENTIAL SEPARATION OF ULTRA-TRACE ACTINIDES AND LANTHANIDES WITH AN ANION-EXCHANGE COLUMN

*Yutaka MIYAMOTO**, *Kenichiro YASUDA*

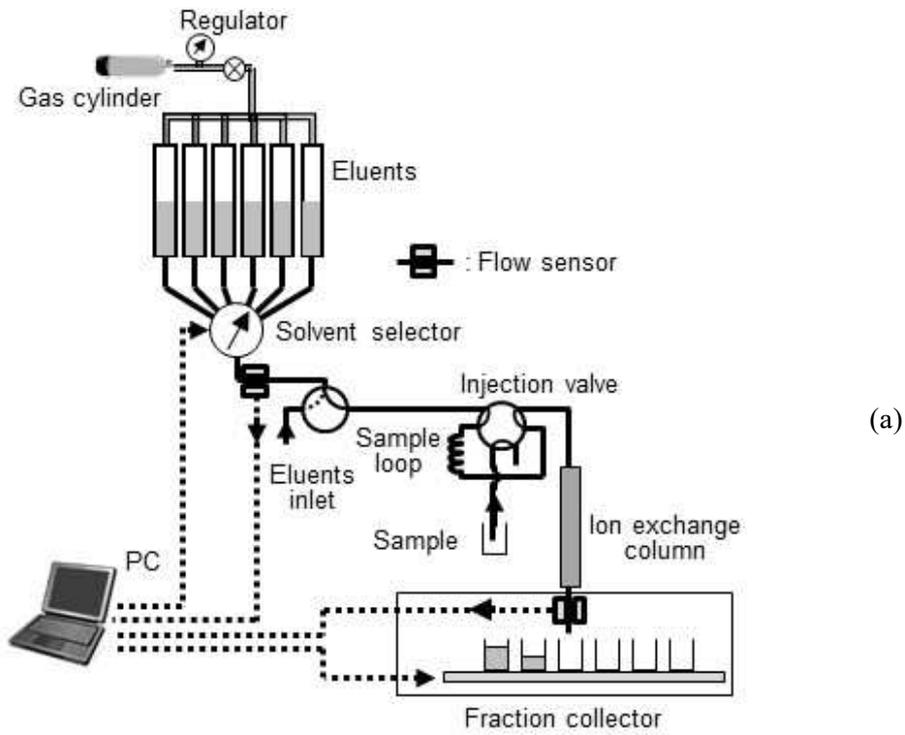
Japan Atomic Energy Agency (JAEA)

Plutonium and americium belong to anthropogenic elements, and these ultra-trace elements are detected from environmental samples. Origin of these elements come from the nuclear bomb tests and the accidental release from nuclear power plants. Isotope ratio and elemental abundance of these actinides provide information on the source term and the elapsed time^{[1],[2]}. Uranium and thorium in environmental samples also play a key role to investigate origin of the sample, dating of mineral formation, and history on mineralization. In most environmental samples, trace actinides are contained with major elements including Na, K, and Fe. The ultra-trace elements of interest have to be separated from these matrix elements to measure accurate isotope ratio and abundance. Chemical separation of ultra-trace Am from large amounts of lanthanides in a sample is very effective in accurately measurement of Am abundance. Customized extraction chromatographic columns and/or schematic chemical separations are commonly used to achieve this aim, because these elements have the similar chemical properties. These separation techniques are effective, but special columns, complex procedure, and/or specific reagents should be prepared. In the case of schematic separation, it is time-consuming, and it often needs technical skill for chemical separation.

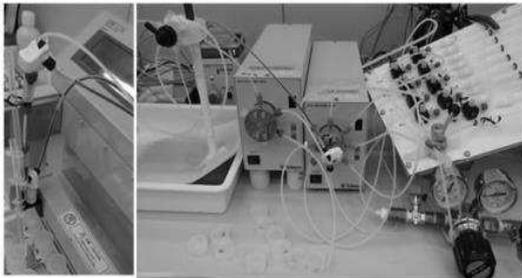
A technique of sequential separation for Pu, U, Th, Pb, and lanthanides by using an anion-exchange column and mixed acids media, including highly pure HCl, HNO₃, acetic acid, and HF was developed in our previous works^{[3],[4]}. The elements of interest were sequentially and perfectly separated by using an automatic system, CASSUAL (Fig. 1) within 5 hours. In this work, Am was included in the target elements, and sequential separation of Am, Th, U, Pu, and lanthanides from other elements by using a small anion-exchange column has been developed.

Americium was completely separated from lanthanides without any special chelate reagents by changing the component ratios of highly pure acids including acetic acid, hydrochloric acid, and nitric acid. This simple technique has excellent ability to separate actinides from the matrix elements including lanthanides. The detailed experimental results and optimized separation conditions will be shown in this presentation.

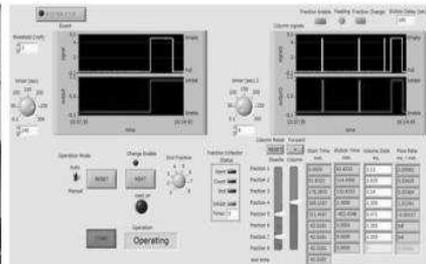
This work was supported by financial aids (JSPS KAKENHI) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan (Scientific Research (C): Grand No. 22550143, 25340078, 16K00592).



(b)



(c)



ABSTRACT 17

TRLIF AND TRLIC LASER SPECTROSCOPY AND DETECTION OF ACTINIDES/LANTHANIDES IN SOLUTIONS

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This work is devoted to applications of the time-resolved laser-induced luminescence (TRLIF) spectroscopy and time-resolved laser-induced chemiluminescence (TRLIC) spectroscopy for detection of lanthanides and actinides. Pu, Np, and some U compounds do not produce direct luminescence in solutions, but when excited by laser radiation, they can induce chemiluminescence¹⁻⁴ of chemiluminogen (luminol in our experiments). It is shown that multi-photon scheme of chemiluminescence excitation makes chemiluminescence (TRLIC) not only a highly sensitive but also a highly selective tool for the detection of lanthanides/actinides.

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

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ABSTRACT 18

DEVELOPMENTS IN AUTORADIOGRAPHY MEASUREMENTS FOR DD&R APPLICATIONS

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The localization, and the characterization, of surface contamination by radioactive substances are two recurring necessities of the dismantling process. Firstly, the estimation of the nature and the activity of the contamination is a mandatory step of the initial state characterization of any nuclear installation. Secondly, during the dismantling process, there is a strong need for wastes characterization in order to adapt the final repository accordingly. For long range radiations, such as gamma rays, various detection systems and cameras are available on the market and can be used in dismantling facilities for such purposes. However, there is currently no industrial device capable of measuring and localizing precisely the contamination of short range radiations both for beta emitters (such as ³H, ¹⁴C...) and alpha emitters (such as ²⁴¹Am, ²³⁸U, ²³⁹Pu...).

Since 2010, a CEA laboratory has been studying the applicability of autoradiography measurements for dismantling applications. Mainly developed in biology with radioactive tracers, this method is able to provide accurate imaging of radioactivity on a surface of different matrices. Very promising results have been obtained in various dismantling facilities using Phosphor film^[1, 2, 3] but the autoradiography method requires more developments in order to become a viable industrial solution for dismantling application.

First, we will report the results previously obtained with autoradiography Phosphor films in dismantling applications. We will discuss the strengths, but also the limitations, of the current solution and the improvement required for dismantling purpose. Subsequently, we will present the new generation of autoradiography detector which is currently developed by the MAUD (a national research project) collaboration. This project, supported by the French waste management agency Andra, is aiming at developing an industrial autoradiography solution adapted to dismantling applications. The First results are very promising and have led to the submission of a patent.

We would like to express our gratitude to Andra and CEA for the financial support.

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ABSTRACT 19

THERMODYNAMIC STUDY OF THE COMPLEXATION OF TRI- AND TETRAVALENT ACTINIDES AT ULTRA-TRACE SCALE WITH DEFEROXAMINE B

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Human activities in the civilian and military nuclear fields are responsible for the actual or potential release of actinides into the environment. Most metal ions are transported in natural waters chiefly in complexed form and the complexation with the organic ligands in the environment can stabilize the actinides in solution and enhance their transport through the environment up to the food chain. In order to guarantee the safety of radioactive waste storage sites and to develop contaminated soil remediation processes, it is necessary to have fundamental data on the interactions between actinides and organic ligands likely to be present in the environment or model molecules having same type of functional groups¹.

In this work, we are interested in the speciation of An(III) and An(IV) in the presence of deferoxamine B (Figure 1), a bacterial siderophore with hydroxamic functions². But due to the rarity and handling constraints of An(III) such as ²⁴¹Am, ²⁴⁴Cm and ²⁴⁹Cf, we present a preliminary study with europium at the ultra-trace scale ($C_{Eu} < 10^{-10}$ mol/L) in the form of ¹⁵²Eu isotope in order to define the appropriate operating conditions for the further study of radionuclides of interest. The technique used is liquid-liquid extraction: under our experimental conditions, the distribution coefficient of europium (D) is deduced from the measurement of each phase by γ spectrometry. At constant temperature and ionic strength, the variations of D as a function of the concentration of extractant, ligand and acidity make it possible to obtain information on the composition of the species involved in the equilibria as well as the formation constant³. The obtained stability constant of the complex Eu(H₃DFB) was found to be in very good agreement with the data from the literature⁴. In the future, this protocol is going to be applied to study the complexation of ²⁴¹Am, ²⁴⁴Cm and ²⁴⁹Cf with deferoxamine B and further with other siderophores. Meanwhile, the speciation of An(IV) like ²²⁷Th(IV) in the presence of deferoxamine B is also studied by liquid-liquid extraction. However, since An(IV) is very sensitive to pH and is likely to form colloid, polymer and precipitation in the aqueous solution, we are attempting to optimize the protocol for the determination of the stability constant between ²²⁷Th(IV) and deferoxamine B and for the further application to the study of the complexation of Pu(IV) with other strong organic ligands.

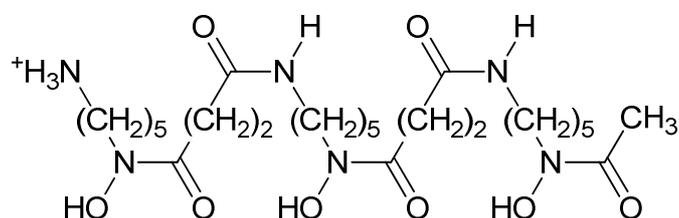


Figure 1 Deferoxamine B

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ABSTRACT 20

TOWARDS INCREASED COOPERATION AND COORDINATION OF R&I ACTIVITIES FOR DECOMMISSIONING

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CEA (French Alternative Energies and Atomic Energy Commission) is both the operator of important nuclear facilities all over the nuclear cycle, in charge of major new built or D&D projects and a R&D group with dynamic policy of technology transfer. The position of CEA in D&D is unique because of the number and the wide diversity of facilities under decommissioning, with some high level of contamination.

Innovative solutions are thus being developed in 6 main axes to protect the operators, to minimize the overall costs and the volumes of waste:

- Investigations in the facilities
- Radiological measurement of waste
- Robotics, laser cutting devices, virtual reality to simulate and choose the best way to operate,
- Decontamination of soils and structures
- Waste treatment and conditioning
- Methods and Information Technology (IT) Tools for project and waste management

CEA developed tools for its own D&D projects when they didn't exist yet on the market: robots, tele-operated equipment, cutting process and software for validation and optimization of intervention scenarios.

Concerning decommissioning and environmental remediation (D&ER), there appears to be a general consensus:

- Significant redundancy exists in current R&D programmes for D&ER being undertaken in different countries, though often no basis for industrial competition exists, e.g. on methods for treatment of exotic waste or for conditioning of intermediate and high activity waste;
- Project managers are often reluctant to use innovative technologies and need confidence from pilot operations with successful results to minimize project risks;
- Individual countries are finding it increasingly difficult to justify expenditure on developments that can require up to 10 years to complete; and
- Many possibilities exist to promote exchanges of information and lessons learnt but, beyond these, there is an **urgent need to promote and organize at multinational level, the co-financing of R&D developments by actors with common objectives.**

As a forerunner to the establishment of a framework for collaboration on R&D activities related to D&ER, it is proposed firstly to undertake a study to provide the following outputs:

- A mapping of the needs of D&ER projects, R&D programmes, human resources and platforms currently available;
- Identification of candidate topics for international financial collaboration, identification of actors involved with current sources of funding and rough business plans and schedules;
- Choice of financial and organizational model after benchmarking in other fields; and
- Proposal for an implementation schedule for projects that may begin immediately with varying timeframes for implementation, with the main focus being on projects taking place over the next 5-10 years.

ABSTRACT 21

RADIATION FABRICATION OF PRUSSIAN BLUE/POROUS NANOCOMPOSITES FOR RADIOACTIVE CS⁺ REMOVAL

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The radioactive cesium ion (Cs⁺) is one of main components in radioactive wastewater from nuclear industry, which is very harmful to environment and humans^[1]. Prussian blue (PB) has special lattice structures and can efficiently exchange its potassium ions with Cs⁺. PB and its analogues have been explored to selective removal of Cs⁺ from radioactive wastewater^[2,3]. In order to increase the contact area and improve the adsorption ability, PB is usually used in the form of very fine powder or nanoparticles, which makes it difficult to be completely separated from solution by traditional filtration or centrifugation. So, PB functionalized composites such as PB/Fe₃O₄/GO, PB/magnetite/sepiolite, copper hexacyano-ferrate/porous silica have been widely studied^[4,5]. γ -ray has high energy and can also trigger many chemical reactions *via* direct or indirect routes in solution, solid or gas, which has been considered as a green technology to process traditional materials or synthesize new materials^[6]. Compared with the traditional chemical methods, γ -radiation fabrication of nanoparticles onto porous materials will have the following advantages: 1) γ -ray has strong penetration ability, which can keep reactions uniform and realize in-situ synthesis of well-dispersed nanoparticles in porous structures; 2) Reactions are carried out in aqueous solution without excess chemicals, which can keep the purity of reaction system and reduce environmental pollution; 3) Reactions take place at room temperature under ambient pressure, which can reduce the damage to materials and avoid the release of toxic chemicals. Herein, Prussian blue/ porous adsorption materials were proposed and fabricated *via* a simple, green and in-situ γ -radiation route. The fabrication strategy of PB/natural porous adsorption materials and mechanism are shown in Fig. 1. Their morphology, structures, adsorption properties and synthesis mechanism were examined and discussed in detail.

The as prepared samples have internal porous structures with well-dispersed PB nanoparticles (60-100 nm) on the surface of skeleton. The particle size and shape of PB are affected by the concentration of reactant. Small molecule stabilizers also play important roles in the formation of well-dispersed PB nanoparticles. The XRD patterns show that the obtained adsorption materials have several new diffraction peaks at around 17.5°, 24.8°, 35.4°, 39.7°, 43.8°, 51.0°, 54.2° and 57.4°, which correspond to the (200), (220), (400), (420), (422), (440), (600) and (620) plates of face-centered-cubic lattice Prussian blue (JCPDS 73-0687). The FT-IR results show that a strong peak at around 2080 cm⁻¹ appears in as prepared samples, which is the typical signal of PB (the stretching vibration of C≡N). Langmuir and Freundlich adsorption isotherm models are employed to fit the adsorption experimental data (Fig.2). The results reveal that Langmuir model (R²=0.998-0.999) fits the experimental data better than the Freundlich model (R²=0.965-0.984), which indicates that the adsorption sites were homogenous, equally accessible to the adsorbate and monolayer sorption. According to the results from Langmuir model, the maximal Cs⁺ adsorption capacities of as prepared samples are 34.9 mg g⁻¹, 49.2 mg g⁻¹ and 68.6 mg g⁻¹, separately.

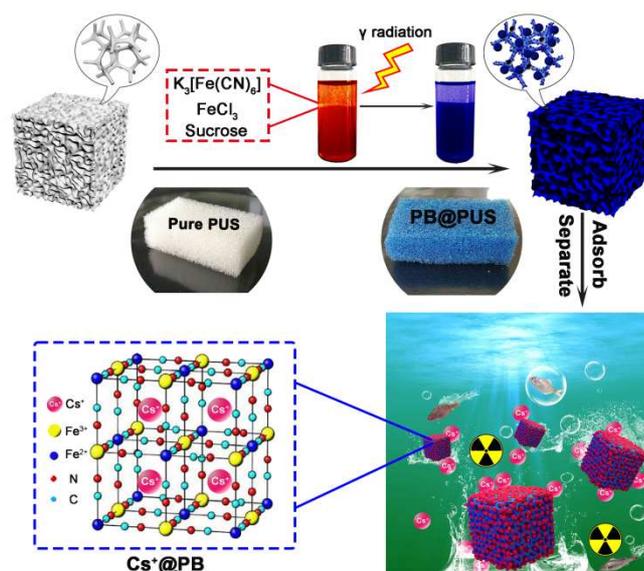


Fig. 1 Radiation fabrication strategy of PB/ porous adsorption materials for Cs⁺ removal

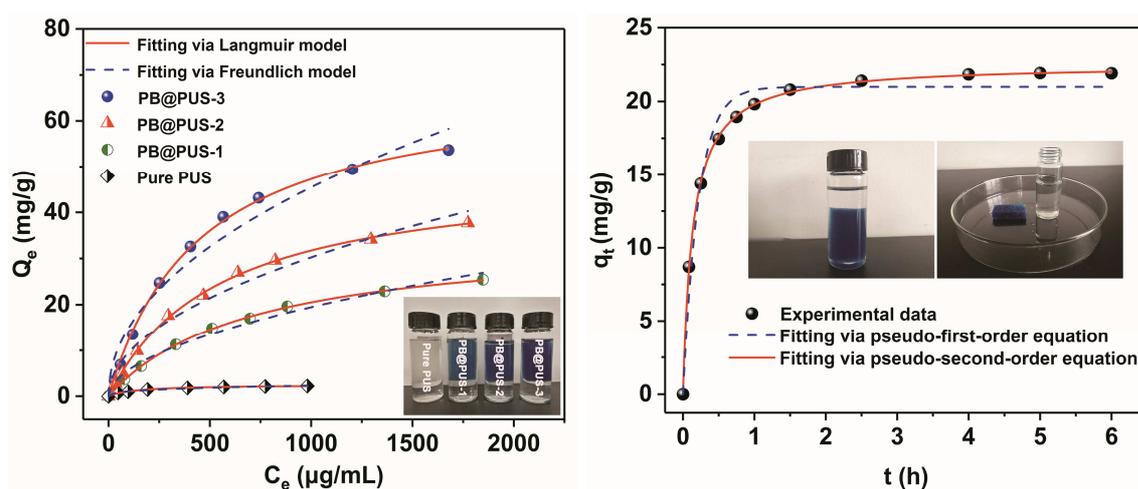


Fig. 2 Adsorption capacities of samples under different Cs⁺ concentrations (Left) and different contact time (Right).

The kinetic parameters for Cs adsorption were obtained through fitting the experimental data with pseudo-first-order and pseudo-second-order model (Fig.2). The results reveal that the pseudo-second-order model ($R^2=0.997$) fits the experimental data better than pseudo-first-order model ($R^2=0.976$). Therefore, the rate-limiting step may be chemical adsorption including ions exchange between Cs^+ and PB/ porous adsorbents. The as prepared adsorbents exhibit good adsorption properties for Cs^+ , which can be used to efficiently treat radioactive wastewater. This production method is simple, efficient and green, which can be applied to prepare other similar porous adsorbents.

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ABSTRACT 22

PREPARING FOR SITE INVESTIGATIONS

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Deep geological disposal is internationally recognised as the preferred approach for the long-term management of higher activity radioactive waste. This is also the preferred approach within the UK, which is committed to delivering a Geological Disposal Facility in collaboration with a willing community. The siting process aims to engage with a range of communities to provide information, before conducting initial desk-based investigations to determine whether any of the willing communities have potentially suitable sites. RWM then hopes to select willing communities to begin more detailed site characterisation to further assess their suitability to host a Geological Disposal Facility.

Site characterisation will include a range of geological and scientific investigations, including the drilling of deep boreholes and investigating the interaction of radionuclides with samples of the resultant cores in extracted groundwater. This will provide more information on how radionuclides would behave in the host rock and contribute to site-specific understanding of long-term radionuclide migration.

This project takes cores of both higher strength rock and lower strength sedimentary rock and aims to determine their sorption and diffusion properties with respect to a range of radionuclides which are expected to display a variety of behaviours (U, Tc, Cl, HTO, Cs, Pb, C-14 as acetate). This allows the techniques and expertise which will be required to characterise a site to be developed. The project will also provide the opportunity to identify and address challenges and understand where recent advancements in understanding and technology could be of use, developing confidence in RWM's ability to undertake appropriate site characterisation.

ABSTRACT 23

CHARACTERISATION OF FIR1 TRIGA MARK II RESEARCH REACTOR - A COMBINATION OF MODELLING AND EXPERIMENTAL

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FiR1 TRIGA Mark II type research reactor in greater Helsinki area is the first nuclear reactor in Finland. After its commission in 1962, it served in training of nuclear energy and technology professionals for over 50 years until its final shutdown in 2015. The early operations included intensive neutron beam research, activation analyses and isotope production. In the 1990s, a Boron Neutron Capture Therapy (BNCT) treatment facility was constructed to the reactor and over 200 cancer patients were treated. In comparison to nuclear power plant decommissioning, the amount of activated materials from FiR1 will be much smaller in volume and activity whereas the variety of materials will be much larger, especially due to the BNCT station. Therefore, characterisation of variety of activated materials is needed for safe and cost-efficient dismantling planning and execution.

The characterisation of FiR1 relies on modelling and experimental efforts, which feed input to each other and therefore reinforce the overall characterisation process. One of the main aims of characterisation is the formation of scaling factors. Scaling factors are material and reactor specific and they are used in calculation of radionuclide vectors and total activities in decommissioning waste packages. More specifically, scaling factors are formed by linking gamma radionuclides with alpha/beta radionuclides, which are often referred as difficult to measure (DTM) radionuclides¹. Analysis of DTM radionuclides often requires lengthy radiochemical separations and purifications, whereas gamma radionuclides can be determined using non-destructive gamma spectrometric analysis. Therefore, it is beneficial to form scaling factors in pre-dismantling phase in order to analyse only gamma radionuclides and calculate DTM radionuclides during the dismantling phase.

The initial modelling of the FiR1 was carried out in three steps. The first step consisted of collecting input data on reactor geometry, operating history and chemical compositions of structural materials. The second step consisted of calculation of neutron fluxes using a 3D reactor model built with Monte Carlo code MCNP. The third step included combination of data on fluxes with operating history using point kinetic code ORIGEN-S. The modelling results including component level radionuclide inventory and activation results are presented in a VTT research report². In these results, conservative assumptions were used for missing data on detailed chemical compositions of the materials and partly missing operational data. Especially in house analytical capabilities, namely HR-ICP-MS and ICP-OES, were needed to validate the data, because activating nuclides are typically minor impurities in materials. The results were also compared with available data on other decommissioned research reactors.

The experimental characterisation aims at verification of the radionuclide inventory, adjustment of the model and formation of scaling factors for DTM. Up to date, radiochemical separation methods have been tested for ³H, ¹⁴C, ³⁶Cl, ⁵⁵Fe and ⁶³Ni analysis in graphite, lead, aluminium, steel, and spent ion exchange resin. Low and very low level samples have been analysed in order to gain confidence in the separation method but higher activity samples are needed for the calculation of reliable scaling factors.

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ABSTRACT 24

DEVELOPMENT OF A CHEMISTRY DEGREE LOCAL TO SELLAFIELD

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This presentation will describe the process involved in the generation of a new chemistry degree to meet the requirements of the Sellafield site.

The Sellafield site will experience a significant loss of skills and experience over the next few years; at the same time reprocessing will end and the business will focus on decommissioning and remediation. It is recognised that a more flexible, agile workforce is required and the application of knowledge-based skills will be enhanced if a greater proportion of the workforce are educated to degree level. Given the lack of part-time chemistry degree courses in the UK, and the traveling time involved for SL personnel, it was felt that a local degree provision was required. The degree course should be available to new degree apprentices and to the existing employees wishing to up-skill.

Local education and apprentice providers (Lakes College, University of Cumbria and Gen 2) were engaged regarding the provision of a three year Foundation Degree in West Cumbria (Lakes College) followed up by two year BSC top-up at the University of Cumbria at Carlisle. A degree apprenticeship scheme was available and this meant that education funding could be accessed from the Apprenticeship Levy. Thus all new degree students were “badged” as apprentices.

The development of the degree course involved SL and other local employers. Analytical Services representatives contributed to the development of the curriculum to ensure that the content met SL (and NNL) requirements and to ensure that the degree was complimentary to the apprenticeship schemes. It is intended that the degree and associated apprenticeship schemes will achieve RSC accreditation.

The delivery of a degree apprenticeship scheme has made the apprentice programme extremely competitive and the standard of applicant is improving year on year. Whereas previously, all chemistry apprentices were recruited by Analytical Services, other parts of the SL business are now recruiting chemistry degree apprentices.

The development of the top-up degree has also provided opportunities for experienced SL and NNL people to deliver lectures at the University of Cumbria. This is great for Continued Professional Development and contributes to the retention of knowledge within the business.

ABSTRACT 25

ANALYTICAL SERVICES TECHNICAL DEVELOPMENT PROCESS

Darren Lee

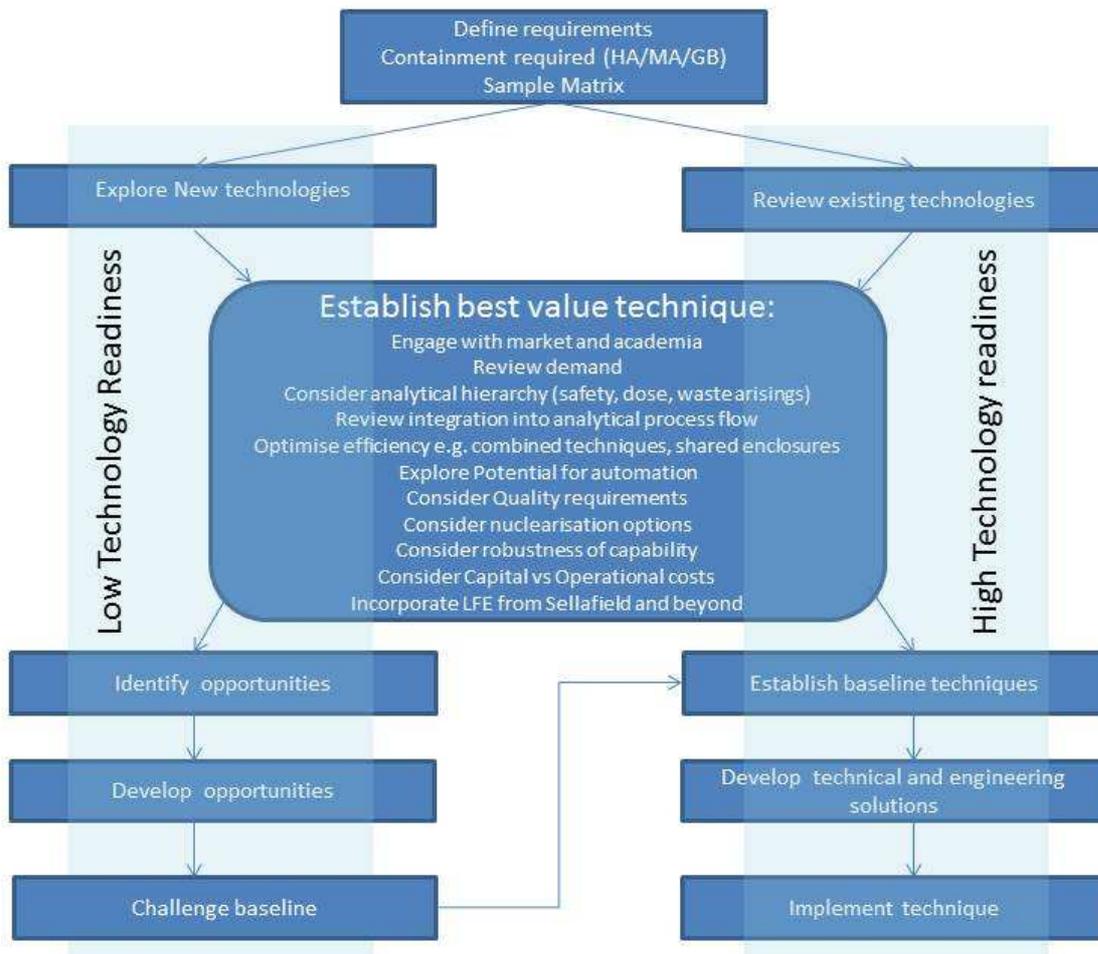
National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG UK

Analytical Services, Sellafield, has supported the Sellafield site for over 60 years, delivering the vast majority of the analysis within the same laboratory. However, the condition and age of the current facility and the imminent end of reprocessing operations has presented new opportunities and challenges in areas such as waste management, decommissioning, remediation and effluent management. Considerable effort has been made to engage these customers and establish the site baseline demand for the next 20 years.

A strategic review of the delivery options concluded that the current laboratory was not suitable and a new strategy was required to support the analytical demand associated with maintenance of the site safety and environmental envelopes. A decision was made to transfer the analysis of challenging highly active and plutonium active samples to the National Nuclear Laboratory, who will perform this work in a re-fitted NNL Central Laboratory. The current assumption is that analysis of lower activity samples will be let to the supply chain by competitive tender.

A new Analytical Services Programme has been established to manage the transition of the work from Analytical Services, Sellafield to the NNL and supply chain. This programme will manage all aspects of the transition including governance, ongoing operations during modification to the facilities and the development of equipment and methods. SL and the NNL are collaborating to ensure that the availability of operational and technical expertise is maintained throughout the transition of the work and that the resource is up-skilled to meet the complex challenges of future decommissioning work. Work is also ongoing to establish a mechanism for moving employees from SL to the NNL.

The refurbishment of NNLCL is expected to cost around £300M and will be delivered by the Replacement Analytical Project (RAP). Within the RAP project group there is a technical development team with members from SL Analytical Services, NNL and engineering. A key role of the development team is to identify and develop opportunities for new or improved methods of analysis, examples of which will be described. The provision of technical development work and the supply of instrumentation (and the required “nuclearisation”) represent a real opportunity for the manufacturing supply chain. The presentation will explain the process (see schematic below) and illustrate with appropriate examples.



ABSTRACT 26

HOW SPECIATION STUDIES CAN SUPPORT THE DEVELOPMENT OF CHEMICAL AND RADIOCHEMICAL METHODS FOR THE CHARACTERIZATION OF RADIOACTIVE WASTE

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The French National Radioactive Waste Management Agency (ANDRA) requires chemical and radiochemical characterizations of radioactive waste to guarantee the safety of the disposal facilities^{1,2}. Laboratories dedicated to the analysis of nuclear waste, such as LASE laboratory (located at CEA Saclay in France), must have accurate chemical and radiochemical protocols valid for all the various matrices encountered (sludges, muds, metals or concretes). Since the decommissioning and dismantling of nuclear sites are in growth, it is of prime interest for laboratories to develop robust and selective methods^{3,4} while taking into account of European REACH regulation. The aim of this work is to demonstrate how speciation studies can help in the optimization of chemical and radiochemical characterizations of nuclear waste.

Among the chemical measurements to be performed¹, the determination of complexing agents, such as polyhydroxycarboxylic acids, is required since those molecules favour the migration of radionuclides and toxic metals in the environment and represent a risk for the safety of waste repositories. EDTA and DTPA (respectively ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid) are the two chelating compounds that have to be identified in priority. Due to their use in decontamination processes, they are present in effluents such as sludges resulting from the distillation of radioactive liquid effluents. Owing to the complexity of the sludge composition, the technique of HPLC-ESI-MS (High-Performance Liquid Chromatography-ElectroSpray Ionisation tandem Mass Spectrometry) has been selected for the quantification of the target compounds³ using ion-pair chromatography for the separation step and metal-complexes with EDTA and DTPA for the MS-detection step. The speciation modelling revealed that the target compounds are present in solution as several complexes with metals (see Figure 1) and that a sample treatment has to be applied prior to HPLC-ESI-MS analysis. The presentation will show how speciation studies gave a support for the choice of the appropriate conditions for EDTA and DTPA quantification. As an example, this approach can be extended to other chelating agents such as NTA and TTHA (respectively nitrilotriacetic acid and triethylenetetramine-N,N,N',N'',N''',N''''-hexaacetic acid).

In regards to the radiochemical characterizations, ANDRA imposes a detailed inventory for 143 radionuclides stored in the repository site devoted to the Low and Intermediate Level short-lived Waste². Among this long list, Fe-55 has to be determined since it is a major contributor to the radioactivity of nuclear waste in the first years of storage. The LASE laboratory has adapted the NF M60-322 standard for the measurement of this radionuclide⁵. The radiochemical method relies on an anion exchange chromatography step in HCl medium, followed by an ammonium hydroxide precipitation step and finally a solvent extraction step based on cupferron and chloroform. The protocol is highly selective towards the elimination of interfering analytes (such as Co-60 and Ni-63) but it must evolve because of the restriction use of chloroform and harmful reagents through the European REACH regulation. The presentation will demonstrate how speciation modelling

contributed to the evolution of the radiochemical Fe-55 procedure. In particular, it was inferred that cobalt can co-precipitate with iron in ammonia medium depending on the cobalt concentration in the sample (see Figure 2). Consequently, a supplementary separation step has to be implemented to remove entirely cobalt. The extraction solvent step was finally replaced by an extraction chromatography step using TRU[®] resin to achieve a highly selective method. This approach can be extended to the characterization of other key radionuclides such as Sr-90 in nuclear waste.

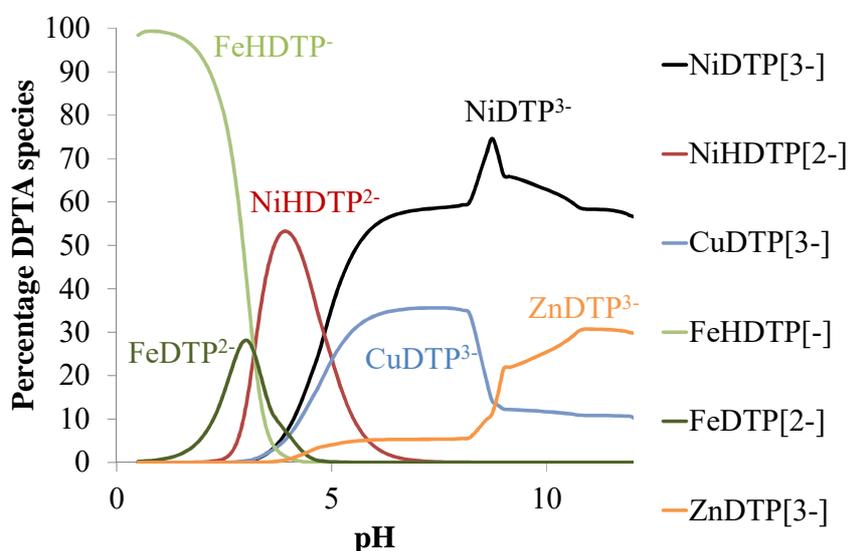


Figure 1: Speciation diagram of DTPA in a radioactive sludge.

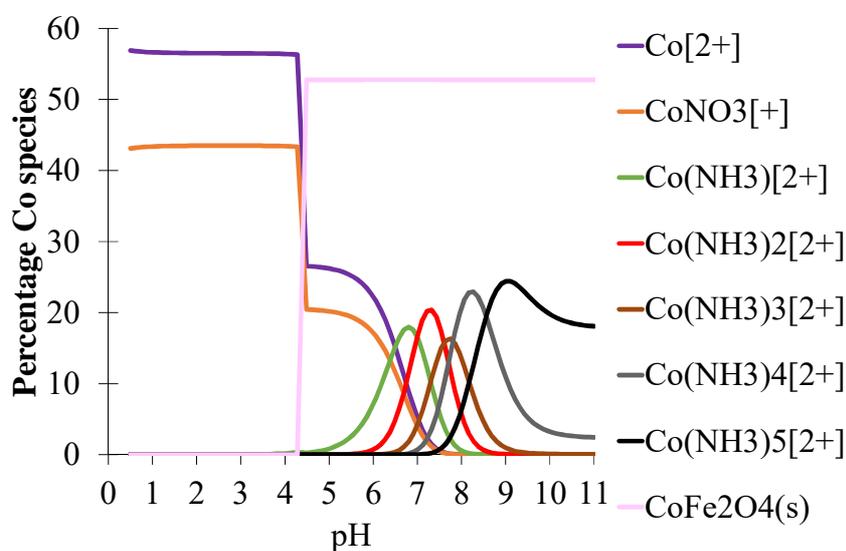


Figure 2: Speciation diagram of Co in an activated steel sample after acid digestion and addition of ammonium hydroxide.

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ABSTRACT 27

DETERMINATION OF NATURAL RADIOACTIVITY IN IRON AND STEEL MATERIALS

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It has been known since the 1990s that two natural radioisotopes from the uranium-238 (²³⁸U) decay series, polonium-210 (²¹⁰Po) and lead-210 (²¹⁰Pb), originally present in trace amounts in raw materials, are volatilised and concentrate in the form of dusts during iron ore sintering. In the UK, most of the dust generated during this process is collected by means of electrostatic precipitators and recycled back into the production system using conveyor belts. Nevertheless, a small proportion passes into the atmosphere via stack emissions and some fugitive dusts can also escape into the workplace during maintenance operations.

Tata Steel UK Ltd, a major European steel making company, has developed and validated in-house radioanalytical methods for the measurement of ²¹⁰Po and ²¹⁰Pb in a wide range of iron-making materials including raw feedstock, waste dusts, occupational and emission filter samples. The data gathered have enabled a better understanding of the fate of ²¹⁰Po and ²¹⁰Pb throughout the integrated steel making route, providing essential information to support environmental permits for discharges to the atmosphere and for confirming that chronic exposure to these two natural radioisotopes does not lead to significant radiological doses to the workforce.

Additionally, since the implementation of the BSS Directive 2013/59 Euratom and the Construction Products Regulation (CPR), there is a need for the European steel industry to characterise the levels of radium-226 (²²⁶Ra), thorium-232 (²³²Th) and potassium-40 (⁴⁰K) in slag materials and confirm those materials do not pose a significant risk of internal and external exposure to radiation when reused or recycled in building materials.

This paper highlights the technical challenges encountered when measuring those natural radioisotopes in various iron-making materials, including the difficulty of validating radioanalytical methods in the absence of suitable certified reference materials.

ABSTRACT 28

INTER LABORATORY COMPARISON EXERCISE TO DETERMINE THE RADIONUCLIDE COMPARISON OF THREE MIXED BIOTA SAMPLES

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Issues surrounding the shortage of appropriate reference materials have long been discussed as the requirement to analyse a wide range of α , β and γ emitting radionuclides in diverse sample matrices increases, particularly with the acceleration of decommissioning activities. It is an essential requirement to the underpinning of public and environmental safety in a highly regulated sector that any analysis is conducted to a suitable level of quality, often demonstrated by the accreditation of the methods to ISO 17025. To develop and validate radiochemical methods, and demonstrate ongoing competency, reference materials are used, the shortage presenting laboratories with a challenge.

The UK's Analyst Informal Working Group (AIWG) conducted a review to determine the member laboratories reference material requirements. It concluded that more solid materials were required which included a more diverse range of sample types and radionuclide composition. To address this shortage the review found that it was preferable to have a greater number of materials with a lower level of precision, e.g. method uncertainties which reflected the levels obtained during routine analysis, rather than fewer which were fully validated with higher precision. The Group took the pragmatic approach of sourcing previously analysed materials and organised an Intercomparison Exercise to determine the activity concentrations of alpha, beta and gamma emitters (^3H , ^{14}C , ^{60}Co , ^{90}Sr , ^{99}Tc , ^{137}Cs , ^{238}Pu , $^{239+240}\text{Pu}$, ^{241}Pu , ^{241}Am) in three mixed biota, environmental level materials. Three materials (molluscs, winkles and crustacea) were analysed by eleven UK and two overseas laboratories, using a range of techniques; gamma spectrometry, liquid scintillation counting, alpha spectrometry and ICP-MS. The results were evaluated in terms of levels of precision, sensitivity and limits of detection comparing techniques and intra-laboratory performance. The exercise demonstrated the value of inter laboratory comparisons as a means of addressing the shortage of reference materials and suitability for demonstrating the validity of radiochemical methods.

ABSTRACT 29

FATE OF RADIUM ON DISCHARGE OF PRODUCED WATER TO THE MARINE ENVIRONMENT

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Naturally occurring radionuclides including isotopes of radium (^{226}Ra and ^{228}Ra) are present at elevated concentrations in effluent or “produced water” from oil and gas production¹. Understanding the speciation and fate of radium from authorised operational discharges from the offshore oil and gas industry into the marine environment is important in predicting the fate of ^{226}Ra in these systems to further assess its environmental impact. Scavenging mechanisms such as adsorption, precipitation and dispersion are key processes affecting the mobility and fate of radium and formation of inorganic micro-particulate radiostrontobarite (RaBaSrSO_4) via the mechanism of co-precipitation is thought to be a significant pathway controlling ^{226}Ra solubility in these systems.

In the current work, we explore the behaviour of radium in experimental systems where synthetic produced water was mixed with synthetic seawater under laboratory conditions. Experiments showed that a significant proportion of radium co-precipitates with barium during mixing (up to 48% in 1 hour). Additionally, we also confirmed that barite precipitation occurred during mixing of seawater and produced waters from plant operations and that this precipitate was very similar in character to the synthetic water experiments. Finally, we extend these observations to a real study site where produced waters are discharged nearshore. Here, the radium concentration in sediments was assessed using gamma spectrometry. Radium was present in selected field samples at concentrations above natural background values, but within International Atomic Energy Agency (IAEA) activity thresholds³. On select sediments, heavy liquid extractions were used to separate barite particles from the marine sediments. The sediment derived barite particles were then characterised using SEM and autoradiography and there was a positive correlation between the concentration of Ba and ^{226}Ra activity in the particle samples confirming the radiostrontobarite fate pathway. Overall we were able to fully characterise formation of the precipitate (RaBaSrSO_4) in experimental systems and validate these observations with field study samples to inform environmental safety assessments for marine discharges.

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ABSTRACT 30

MICRO-FOCUS X-RAY ABSORPTION SPECTROSCOPY INVESTIGATION OF URANIUM ATTENUATION BY ARSENIC AT AN ABANDONED URANIUM MINE

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The UK's most important uranium-producing mine, South Terras, is located in Cornwall (SW England, Figure 1), which operated between 1873 and 1930. The primary ore is pitchblende (primarily UO_2 and U_3O_8) and secondary ores include torbernite ($\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$) and autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$). In the 57 year period of operation before closure, South Terras produced a total of 736 tonnes of uranium. The discovery of radium, in 1911, focused mining operations on the uranium spoil heaps at the site, which were investigated by Marie Curie and produced radium used in cosmetics (Figure 2). The tailings were reworked to extract radium through BaSO_4 recovery methods.

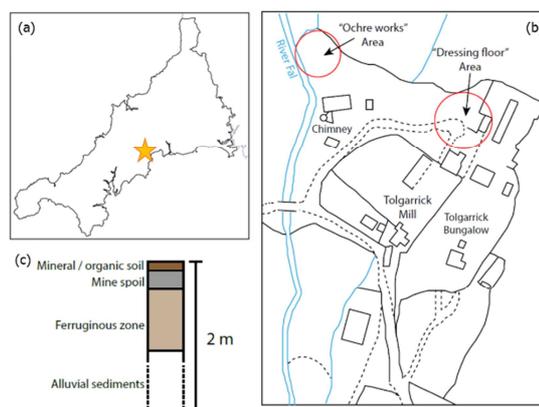


Figure 1 The South Terras site (a) located within the south west UK; (b) showing the mining buildings, river and the two sampling locations; and (c) the stratigraphic column at South Terras.¹

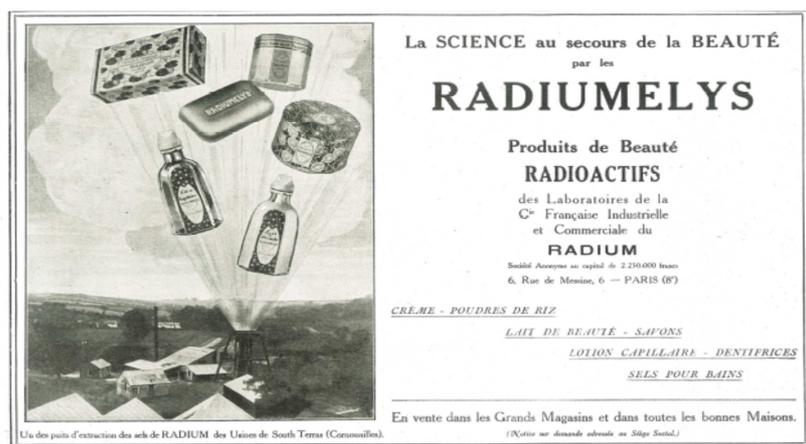


Figure 2 Newspaper advertisement (source unknown, ca. 1920) for “Radiumelys” beauty products containing radium sourced from the South Terras mine in Cornwall

South Terras has been considered to be a “natural laboratory” for the environmental degradation and behaviour of naturally occurring radionuclides. Previous investigations have attempted to elucidate the degradation process of uranium ores and subsequent transport of uranium from the spoil heaps into the River Fal. To accurately predict the U(VI) transport processes with reactive transport models,

we have undertaken a detailed mineralogical analysis of soils from the South Terras site to elucidate the mechanisms of uranium degradation and migration in the 86 years since abandonment.¹ Soils were sampled from the surface (0 – 2 cm) and near-surface (25 cm) in two distinct areas of ore chemical processing activities (Figure 1). Bulk soil analysis revealed the presence of high concentrations of uranium (<1690 ppm), arsenic (1830 ppm) and beryllium (~250 ppm), suggesting pedogenic weathering of the granitic country rock contributes to the mechanisms of uranium ore degradation.

Micro-focus XRF analysis indicated the association of uranium with arsenic, phosphate and copper; μ -XRD data confirmed the presence of the uranyl-arsenate minerals metazeunerite ($\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$) and metatorbernite ($\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) to be ubiquitous (Figure 3). Our data are consistent with the solid solution of these two so-called “uranyl-mica” minerals [$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_{2-x}(\text{PO}_4)_x \cdot 8\text{H}_2\text{O}$], not previously observed at uranium-contaminated sites. Crystallites of uranyl-mica minerals were observed to coat particles of jarosite and muscovite, suggesting that the mobility of uranium from the degraded ores at South Terras is attenuated by co-precipitation with arsenic and phosphate, which has not previously been considered at this site. This research has revealed the presence of important phases not previously considered in uranium speciation models of the site, which may influence the long-term release of uranium from the soils. The study contributes to the management of legacy uranium contamination at sites with a complex industrial history.

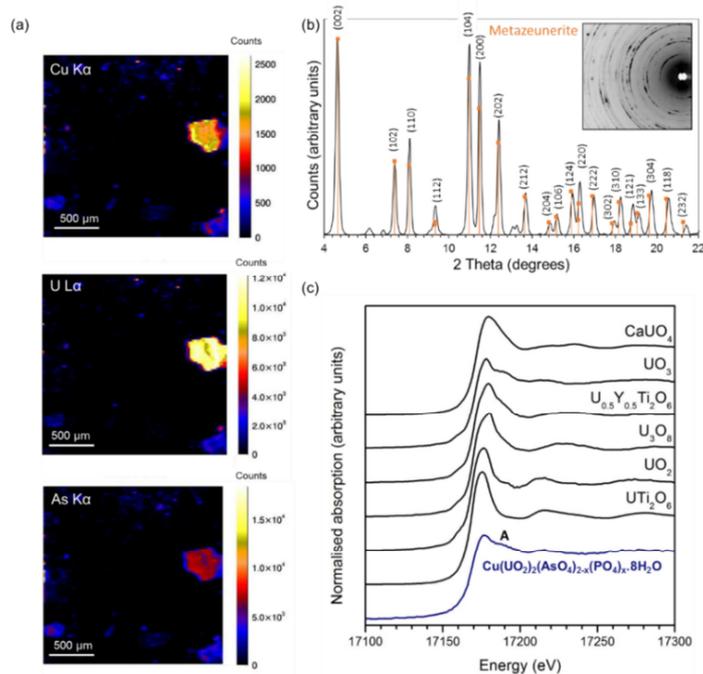


Figure 3 Analysis of particles from 25 cm at the Dressing Floor (DF) location using (a) μ -XRF mapping; (b) μ -XRD analysis; and (c) μ -XANES spectra taken at the U L_{III} edge.¹

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ABSTRACT 31

USE OF DGT FOR THE DETERMINATION OF PLUTONIUM BIOAVAILABILITY IN AQUATIC ENVIRONMENT

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Introduction

DGT is a passive method of sampling which uses diffusion of free and labile metal cations from the sampled water medium through a thin film of PAM gel. A binding phase (*e.g.* Chelex resin), also enclosed in a gel, captures and accumulates the diffusing species. The total amount of metal cations measured in the resin is proportional to the flux across the diffusive gel and the exposure time.¹ The interest of the method resides mostly in the measurement of specific species of metal cations that can freely diffused through the gel, or dissolved organic matter (DOM)-metal complex that can dissociate during the diffusion time through the gel. In this respect, DGT is a method that can gain access to dynamic aquatic species, which epitomize species available for bio-uptake from aquatic organism such as aquatic plants or benthic fauna. The method has been applied in numerous studies of heavy metals contamination but its application for determining radionuclides bioavailability is scarce and almost non-existent for actinides.

In this work, we used the DGT technique and Fick's diffusion laws to reveal several features of Pu behaviour in fresh waters environment. In particular, kinetic (k_{diss}) of the DOM-Pu complex dissociation was determined using DGT of different gel thickness and Pu spiked solution with humic acid (HA) extracted from an organic soil or FA extracted from an organic spring. In addition, we used homemade large DGT device and Pu determination by AMS to determine the bioavailable fraction of Pu in a mineral and an organic river of the Swiss Jura Mountains.

Results

Results show that the DGT technique is well suited to the study of the Pu-DOM interactions in aquatic environment. The presence of DOM of the humic acid type at a concentration in water of 15 ppm considerably hinder the diffusion of the Pu species through complex formation (Fig. 1).²

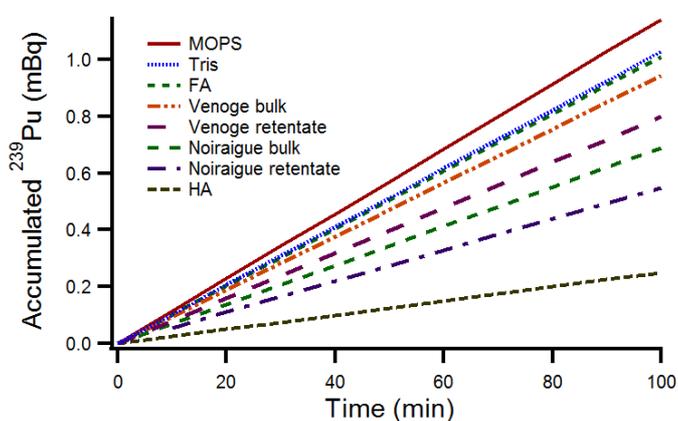


Figure 1. **Pu diffusion through gel.** ²³⁹Pu flux through PAM gel in chemically different environments theoretically calculated for D determined in this work, 0.39 mm diffusive gel thickness and $C_0=100 \text{ mBq mL}^{-1}$. From top to bottom: MOPS, Tris, FA, Venoge bulk, Venoge retentate, Noiraigue Bied bulk, Noiraigue Bied retentate, HA.

In addition, experiments using different diffusive gel thicknesses allow the determination of the kinetic parameter of the Pu-DOM interaction. Results show that Pu, in contradiction with previous beliefs, acts as other metal cations such as Fe^{3+} or Co^{2+} , with dissociation constant of the range $k_{\text{diss}}=7.510^{-3} \text{ s}^{-1}$ and a complex lability (ξ) around 0.4 in aquatic environment.³

Finally we applied the DGT technique to the determination of Pu in water of two springs from the Swiss Jura Mountains, one mineral ($[\text{DOM}] < 1 \text{ ppm}$) and one organic ($[\text{DOM}]= 15 \text{ ppm}$). Results show that the Pu concentration measured by DGT perfectly matches the Pu concentration measured in the bulk water of the mineral spring water. To the opposite, the Pu concentration measured by DGT in the organic water spring was about two thirds of the bulk concentration, because of competition of FA for Pu binding, hindering diffusion.⁴

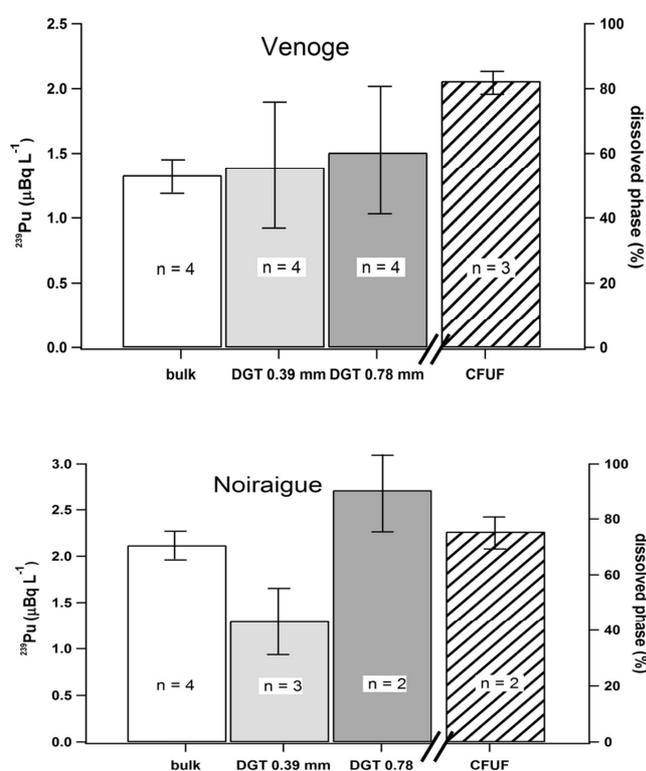


Fig.2 **Determination of Pu as bioavailable species.** Total ^{239}Pu measured in the bulk water during deployment of DGTs, concentrations of free and labile ^{239}Pu species measured with DGTs (left scale) and percentage of ^{239}Pu in the dissolved phase measured by CFUF (right scale) in the Venoge waters (top) and Noiraigue waters (bottom). Results are the average of n measurements and uncertainties are the sum of the absolute uncertainty of each measurement divided by n .

Conclusions

We hypothesise that the wide range of concentration factors listed in the literature for aquatic environment subsists because the radionuclide bulk concentration does not represent the true bioavailable fraction of metal cations, which is available for bio-uptake. We suggest using DGT concentration instead of bulk concentration to determine radioactive concentration ratios (CR) in aquatic ecosystems.

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ABSTRACT 32

NEW PROPOSALS BASED ON PLASTIC SCINTILLATORS FOR AUTOMATED, QUICK AND SIMPLE RADIONUCLIDE ACTIVITY DETERMINATION

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Over the next 20 years a huge number of Nuclear Power Plants all over around the world will be closed and dismantled. The process of decommissioning of these facilities will require the analysis of vast number of samples in order to determine which samples are radioactive and need a specific management and which are non-radioactive and can be treated as conventional waste. Moreover, in some of the active it will be necessary to go deeper and to determine the specific content of the different radionuclides. In addition, environmental monitoring or decommissioning tasks will also require of large a large number of analysis data to prevent non-desired contaminations.

In this potential scenario, it would be convenient the development of simple, cheap, fast and reliable analytical methods that could provide response to such analytical need. The current analytical approaches, in spite of being precise, accurate and validated, are not capable to manage such an amount of analysis taking into account the appropriate balance between quality of the results and resources involved, especially cost and time.

The achievement of this goal is very complex especially for two reasons: radionuclides and samples. For the former, alpha and beta emitting have a short path in the medium before to be stopped, thus their detection requires a close contact between the detector material and radionuclide. For the second, the variability of samples in terms of physical state (solid or liquid), chemical composition of the medium (acidic, organic...) and radiochemical composition makes almost impossible to define a single approximation valid for all situations.

The use plastic scintillators can contribute to overcome some of these drawbacks since they can be produced in different shapes and formats that could be adapted for the purpose of the analysis. In the present work three different formats of PS (i.e. PSresins, PSfoils, PSkits) has been adapted for the quick and fast analysis of radioactivity and preliminary results obtained show the potentiality of the three different analytical approximations based on these PS:

- Selective automated analysis radionuclides using PSresins
- Screening analysis of alpha and beta radionuclides in solid surfaces with PSfoils
- Fast analysis of liquids with selective PSkits

PSresins are a plastic scintillation microsphere coated with a selective extractant for a certain radionuclide. The use of PSresin in a SPE cartridge permits not only a simplification of the analytical methodology, since the separation and the analysis is done using the same support and no elution step is required, but also a reduction on the reagents needed and waste produced. A step forward in the improvement on the laboratory productivity is the automation of the separation process using an automated separation device. In the Modular Automated Separation System (MASS) designed by our group where samples could be treated automatically using the same procedure (including the vacuum chamber) but substituting the laboratory technician by a robotic system. The MASS has been tested for the analysis of ⁹⁹Tc in river and water samples using a PSresin designed for this purpose. Results obtained for manual separation and automated separation are equivalent in terms of detection

efficiency (85%) and deviation in the quantification of water samples of 10Bq/L equivalent to those obtained in the “in person” treatment.

automated analysis using PSresins



PSfoils



PSkits



The second approach under study is based on adhesive PSfoils. PSfoils of few hundred of micrometers of thickness have been prepared by the evaporation method. After the treatment of the surface of the PSfoils with an adhesive the PSfoils have been applied to surfaces (a laboratory table), contaminated with beta ($^{90}\text{Sr}/^{90}\text{Y}$) and alpha emitters (^{241}Am). To perform the measurements the foil applied to the surface is stick to another foil included in a 20mL vial and measured in a LS counter. Detection efficiencies for $^{90}\text{Sr}/^{90}\text{Y}$ and ^{241}Am are 181(4)% and 101(4)% respectively with 15% of misclassification when pulse shape analysis was performed. Once applied to the solid surface extraction capacity of PSfoils was 40(10)% for $^{90}\text{Sr}/^{90}\text{Y}$ and 9(4)% for ^{241}Am . This values could be improved to 83(18) and 26(7) respectively by the use of 3 PSfoils.

The last approximation under evaluation was focused on the fast and selective analysis of ^{99}Tc in liquid samples using PSkits. In this approach PS is directly prepared on a 20 mL vial though a polymerization process. The polymer prepared includes a cross-linker in order to provide more robustness to the PS in presence or high acid or organic samples. Then, a selective extractant is added to the surface of the PS to provide selectivity to the final PSkit. In this approach, the sample is just added to the vial, shaken, the solution is removed and the radionuclide attached to the surface is measured. First results obtained in the optimization of the PSkit preparation are: 42(11)% of detection efficiency for ^{99}Tc and 20(7)% of extraction.

As a conclusion, the three proposals based on PS, in spite of their early stage of development, could be considered as promising tools for the fast and simple analysis of radioactivity.

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ABSTRACT 33

DEVELOPMENT OF AN IMPROVED RAPID METHODOLOGY FOR THE ANALYSIS OF TRITIUM AND CARBON-14 IN SOLID DECOMMISSIONING WASTES

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Optimisation and validation of a novel furnace-based system and associated methodology for the determination of H-3 and C-14 in decommissioning wastes is presented. The method has been evaluated in terms of sample boat loading technique, sample loading temperature, length of heating programme and trapping system. The optimised procedure utilises direct loading of the sample into the furnace at a sample zone temperature of 600 °C, before heating to 900 °C, significantly reducing combustion times. Both H-3 and C-14 are collected in 8 mL of trapping solution directly in a scintillation vial. Co-trapping of the analytes and dual label liquid scintillation counting have been demonstrated to be effective. A reduced combustion time of 150 minutes and the ability for direct addition of scintillation cocktail to the trapping solution have led to a significant reduction in analysis time and improvement in measurement sensitivity. Validation of the procedure has been performed using a range of spiked matrices relevant to nuclear site decommissioning, reference materials and operationally-exposed materials. The potential for deployment of the system within fume cupboards or gloveboxes and within a mobile laboratory facility have also been considered.

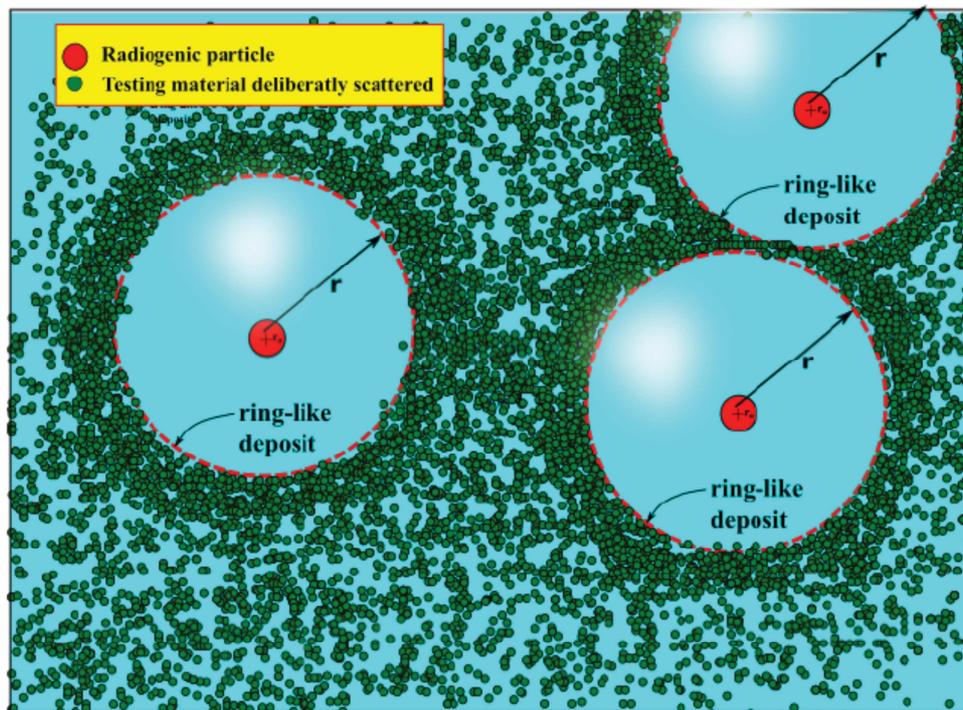
ABSTRACT 34

INDUCED RING-LIKE DEPOSITS AROUND SUSPENDED RADIOACTIVE PARTICLES BY MARANGONI STRESS AND ITS POSSIBLE USE AS DETECTION TECHNIQUE

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Marangoni self-induced stress and its significance with regard suspended radioactive particles is discussed. It is theoretically shown that due to the induced Marangoni stress around radiative particles suspended in liquids, bodies of microscopically-visible size suspended in the liquid will be propelled away from the radiogenic particle due to the thermocapillary motion induced by the heat decay of the radiogenic particle. The formation of such a hypothetical ring can be potentially important as a new technique for detection of radiogenic particles suspended in liquids. Utilizing a simplified geometrical and physical model, an analytical expression for the radius of the ring developed by the thermocapillary motion surrounding the radiogenic particle as function of several parameters was derived. It was found that the thermocapillary radius of the ring is proportional to the radioactivity of the radiogenic particle and therefore semi empirical relations between radius and activity could be employed as visual technique for detection. Additional R&D is required in order to experimentally test the theoretical predictions, feasibility and reliability of the proposed phenomena as detection technique.



POSTER PRESENTATIONS

ABSTRACT 35

PREPARATION OF PINE NEEDLE AND MILK REFERENCE MATERIALS FOR THE LABS INTERCOMPARISON RADIOCHEMICAL ANALYSIS

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Following accidental radiation release by nuclear power plants is known to have potential hazardous effects on public health, not only in the surrounding areas but also hundreds or even thousands of kilometers away. Based on the organizing of nationwide monitoring and assessment of radionuclides contamination in food and drinking water following the Fukushima Dai-ichi nuclear accident. We prepare the reference material for the routine tasks of the radioanalytical laboratories intercomparison and measured results quality control.

The sample of pine needles were selected in Changping protected natural forest at the same age located in the north of Beijing, China. After water cleaned, dried at 70 °C, jet milled and blended at about 63 µm. Spiked with ⁹⁰Sr diluted solution and blended uniformly, liquid nitrogen fixed, then freeze-dried directly for one week. Finally it was completely blended again, 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. The batch experiments for the stability and uniformity performed by the Di-(2-ethylhexyl) phosphate (HDEHP) extraction chromatography separation, yttrium-90 precipitated and counting. The minimum sample amount for the measurement is about 8 gram under the satisfaction uncertainty. This material was also used as a test material for the interlaboratory comparison exercise national-wide in China, for the determination of ⁹⁰Sr. The main two methods for ⁹⁰Sr measurement of HDEHP column separation with ⁹⁰Y counting, the Sr-spec crown ether (also lab prepared crown ether on teflon powder) separation with liquid scintillation counter. The relative uncertainty of the recommended value is 3.1% of 32.3 Bq/kg ⁹⁰Sr in pine needle powder, the certificate RM number is GBW 04329.

The sample of skim milk was collected in Hohhot China. It was spiked with strontium 90 and cesium 137, mixed by V-shaped blender for homogeneity. A unit of the sample consists of approximately 100 gram of skim milk powder.

A description of the material preparation, uncertainty analysis and the results of the interlaboratory comparison will be presented and discussed.

The authors acknowledge financial support by the Chinese Ministry of Science and Technology (Grant No. 2014FY211000).

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ABSTRACT 36

RADIOCHEMICAL ANALYSIS OF BIOLOGICAL SHIELDING OF VVER-440 REACTOR FOR DEEP GEOLOGICAL REPOSITORY

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The decommissioning of nuclear facilities is connected with a great quantity of radioactive waste. The biological shielding of reactor vessel is an example of very heavy and voluminous part of NPP decommissioning waste. It is mainly composed of concrete which is long term exposed to gamma and neutron radiation. The values of specific activities of long term nuclides produced from the activation are calculated⁽¹⁾: $^{14}\text{C} \sim 10^5$ Bq/kg, $^{36}\text{Cl} \sim 10^2$ Bq/kg and $^{41}\text{Ca} \sim 10^6$ Bq/kg.

ÚJV Řež a. s. owns one concrete block of biological shielding from NPP Greifswald's fifth reactor. This reactor was the same type VVER-440 as it is in NPP Dukovany. It is taken the advantage of experimental gamma analysis and destructive analysis of hard to detect nuclides (^{14}C , ^{36}Cl and ^{41}Ca) in this work. The aim of this work is to compare experimental values with calculated ones.

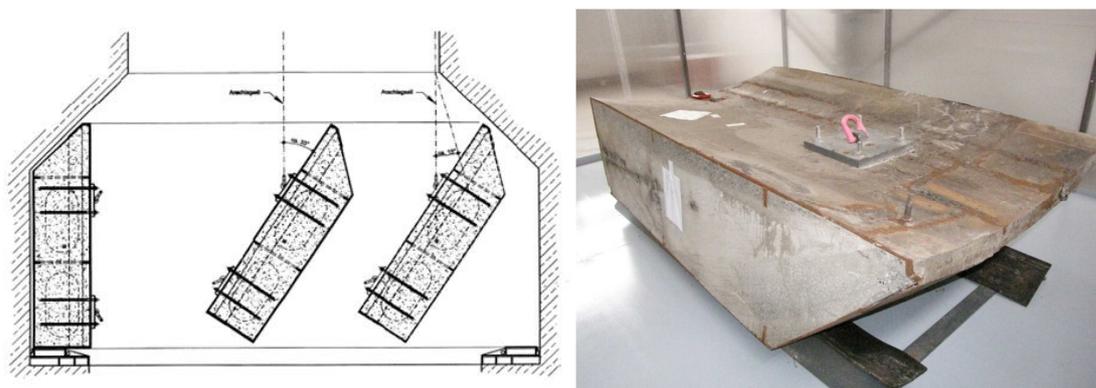


Figure 1: Biological shielding of the VVER 440 type reactor (NPP Greifswald, 5th block)

The samples from the concrete block were taken with a special care to prevent release of volatile nuclides. Sampling was performed in 7 distances from 50 mm to 750 mm from the edge closer to the reactor. These 7 samples were analysed by Central analytical laboratory in ÚJV Řež, a. s. First of all, the high-resolution gamma spectrometry measurements were done using HPGe detector. Nuclides ^{60}Co , ^{152}Eu and ^{154}Eu were identified in the samples. After gamma measurement, samples were decomposed by alkaline leaching. Content of ^{14}C , ^{36}Cl and ^{41}Ca was analysed from the leachate.

^{14}C was separated by precipitation from the leachate with solution of BaCl_2 . The precipitate was mixed with scintillation cocktail QuickSafe and measured with LSC Quantulus 1220. ^{36}Cl was separated by extraction chromatography using Cl -resin produced by Eichrome. Small part of the eluate was used to calculate the yield of separation on ICP-MS and the rest was mixed with scintillation cocktail UltimaGold LLT and measured with LSC. Evaluation of ^{41}Ca was quite problematic. There was high content of calcium in the concrete so we were not able to prepare thin layer sample for X-ray measurement. We tried to modify our procedure, but there was no improvement. Then we tried another separation procedure published by Xiaolin Hou⁽⁵⁾, which was

perfect for this purpose. Finally, after separation the sample was mixed with scintillation cocktail Gold Star LT² and measured with LSC too.



Figure 2: Sampling of the biological shield (a) and results summary of the radiochemical analyses (b)

Obtained results were compared with theoretical values computed by Monte Carlo simulations. The comparison showed quite large differences between experimental and theoretical values. One of the possible explanations is that the differences came from approximations made in theoretical MCNP model based on available inadequate chemical and elemental/isotopic composition of analysed concrete, where missing elements had to be taken from the literature for similar only (not the same) concrete^(2,3,4). Especially the content of elements like Eu, N, C and Cl⁽⁴⁾ is crucial to know likewise the content of hydrogen which moderates the neutron flux. The results from this work could be taken as a recommendation to have enough experimental values for MCNP models preparation and verification.

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ABSTRACT 37

ON THE WAY TO A STANDARD METHOD FOR TECHNETIUM-99 DETERMINATION IN RADIOACTIVE WASTE

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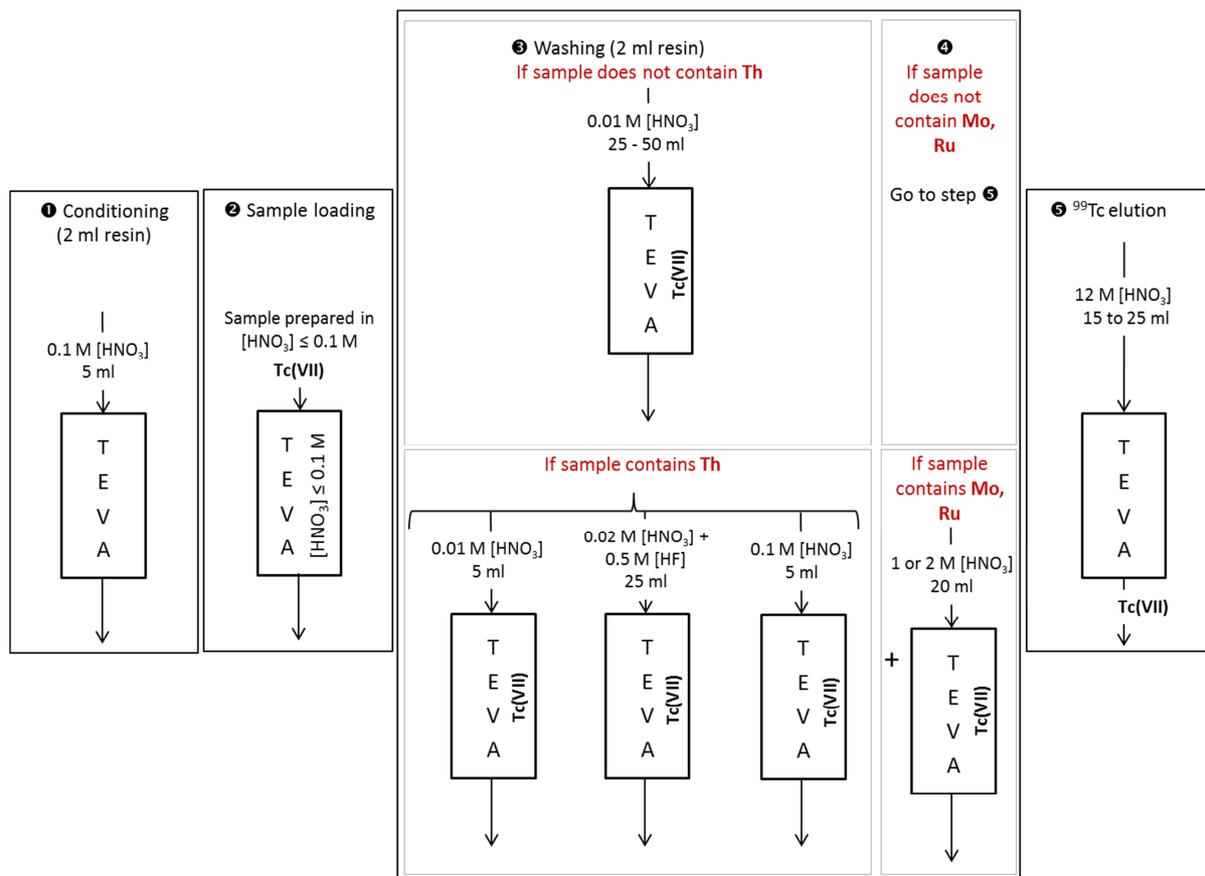
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In collaboration with members of the Working Group “radionuclides analysis in waste” (WG14 - CETAMA)

In the context of radioactive waste management, a detailed radionuclide inventory has to be compiled. In France, the National Radioactive Waste Management Agency (ANDRA) specifies radiochemical criteria for 143 radionuclides stored in the repository site devoted to the Low and Intermediate Level short-lived Waste¹. Among this long list¹, Tc-99 has to be declared as soon as its activity concentration is over 0.01 Bq/g and its maximum acceptance limit has been fixed to 44000 Bq/g. Tc-99 can be produced by thermal neutron fission of U-235 obtained according to a relatively high thermal fission yield of 6 %. It can also be generated from neutron activation of Mo. With a half-life of 214000 years, Tc-99 is a major contributor to the radioactivity of nuclear waste at long term. Furthermore, due to its high mobility in the environment as pertechnetate anion, it is crucial to characterize Tc-99. As a beta emitter, Tc-99 has to be isolated from the interfering radionuclides through a radiochemical procedure prior to any measurement. Tc-99 is widely measured by liquid scintillation counting but it can also be quantified with a greater sensitivity by ICP-MS owing to its high half-life. Many literature works² deal with the radiochemical characterization of Tc-99 in environmental samples. There is a guide standard³ for the determination of Tc-99 in soil and a standard project⁴ is currently being finalized for water samples. However, no radiochemical standard or common method has been published for the measurement of Tc-99 in radioactive waste. Since the decommissioning and dismantling of nuclear sites are in growth, it is of prime interest to set up a standard for the accurate quantification of Tc-99 in radwaste.

In the framework of CETAMA commission⁵, a working group dedicated to Tc-99 has been created in 2015. Nine French laboratories have participated to the establishment of a radiochemical procedure suitable for all the various matrices encountered in radwaste samples (sludges, muds, metals or concretes). The aim of this work is to detail the different steps which led to the publication of a common radiochemical procedure to characterize Tc-99 in radwaste (see Figure 1).



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ABSTRACT 38

PRODUCTION AND PURIFICATION OF TERBIUM ISOTOPES FOR APPLICATIONS IN NUCLEAR MEDICINE

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Four terbium isotopes (¹⁴⁹Tb, ¹⁵²Tb, ¹⁵⁵Tb and ¹⁶¹Tb) have been identified as promising isotopes for use in therapeutic, diagnostic or theranostic nuclear medicine. Terbium-161 can be produced in gigabecquerel quantities by neutron irradiation of a ¹⁶⁰Gd target followed by its subsequent beta decay¹. The other terbium isotopes are mainly produced at the CERN-MEDICIS facility by proton-induced spallation of a tantalum target followed by online mass separation and isolation of the desired radionuclides²⁻⁴. Polyatomic impurities, such as ¹³⁹Ce¹⁶O in a ¹⁵⁵Tb sample, are produced but not separated in this process, highlighting the need for further offline radiochemical separation.

Separation of terbium from cerium impurities has been studied on various extraction chromatography (TEVA, UTEVA, TK100; *Triskem International*) and ion-exchange (AG1; *Bio-Rad*) resins using stable elemental standards in nitric acid solutions. Cerium oxidation with sodium bromate (NaBrO₃) has been employed to encourage selective adsorption of the tetravalent Ce(IV) impurity over the desired Tb(III) product. The process has been optimised to provide a rapid radiochemical separation and to afford a high radiochemical yield. The quality of the achieved separations were quantified by inductively coupled plasma mass spectrometry (ICP-MS) and by HPGe gamma-spectrometry following successful trials on active samples provided by CERN.

Alternative ¹⁵⁵Tb production routes have been studied at the University of Birmingham's MC40 cyclotron. Both proton irradiation of ^{nat}Gd foil targets and alpha irradiation of ^{nat}Eu foil targets have been investigated and the results are promising. Further work on isotopically enriched targets is planned. The work described will allow isotopically pure terbium solutions to be prepared in quantities that are suitable for decay data measurements and primary standardisation, as well as in pre-clinical applications and single photon emission computerised-tomography (SPECT) studies on prepared phantoms.

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ABSTRACT 39

IMPROVING THE ACCURACY OF RADIONUCLIDE METROLOGY IN SUPPORT OF NUCLEAR DECAY DATA AND CHARACTERISATION OF NORM

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Certified reference materials (CRM) are used to ensure quality control and metrological traceability through method validation and calibration of instruments.¹ Similarity in composition between a CRM and the material being analysed is vital for the accuracy and precision of the measurement. Owing to the wide variety of sample types encountered across various industrial sectors, it is often difficult to find appropriate standards and there are currently insufficient CRM to support characterisation and remediation of many radioactive materials. One sector that suffers in particular from a lack of CRM relates to those generating Naturally Occurring Radioactive Material (NORM)², where accurate determination of the radionuclides present is vital to ensure operator safety and cost efficient waste disposal.

The first aim of this project is to develop suitable CRM for a suite of NORM materials of major importance to the UK; namely, the steel, titanium, China Clay and oil & gas industries. Recycling of industrial residues is also being considered; for example, blast furnace slag from steel production is used as a feedstock for cement. An inter-laboratory comparison exercise is being formulated to assist testing laboratories both in the UK and other European countries.

A second aim is to reassess nuclear decay data for those isotopes where the current level of uncertainty is deemed to be too high, or the original data may have been collected many decades ago and based on a very limited number of measurements.³⁻⁴ Recent advances in technology now allow for more accurate determination of the necessary information.⁵ The project is focussing on naturally occurring ²³⁸U and ²³²Th, both of which have major geochronological applications. The methodology developed for measurement of half-life values for such long-lived radionuclides involves a combination of decay counting and tandem inductively coupled plasma mass spectrometry (ICP-MS/MS), which is applicable to other natural and anthropogenic radionuclides that suffer from similar decay data limitations.

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ABSTRACT 40

THE USE OF COLUMNS OF THE ZEOLITE CLINOPTILOLITE IN THE REMEDIATION OF AQUEOUS NUCLEAR WASTE STREAMS

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Samples of the zeolite clinoptilolite, mined from Mud Hills in California, have been tested in column experiments to determine their ability to remove radioactive Cs⁺ and Sr²⁺ ions. The clinoptilolite was effective in removing both Cs⁺ and Sr²⁺ from aqueous solution. Increasing concentrations of Ca²⁺, Mg²⁺, Na⁺ and K⁺ competed with the Cs⁺ and Sr²⁺, and increased elution of Cs⁺ and Sr²⁺. Ca²⁺, Mg²⁺ and K⁺ were more effective competitors than Na⁺, with Na⁺ concentrations 1 – 2 orders of magnitude higher required to produce the same effect. For Na⁺, it was found that if the concentration was reduced, then the column performance recovered rapidly.

The Mud Hills clinoptilolite has been used in an effluent treatment plant (SIXEP) at the Sellafield nuclear reprocessing site in Cumbria (United Kingdom). There was a large variation in performance for both Cs⁺ and Sr²⁺ across the mine site. However, a subsection of the site was identified that provided material within the required specification. This material has been used to remove ^{134/137}Cs and ⁹⁰Sr successfully from effluents for 3 decades.

A coupled chemical transport model has been developed to predict the performance of the clinoptilolite. The removal of Sr²⁺ from the effluent was better than expected, considering the zeolite Si/Al framework composition. The formation of Sr-bicarbonate complex ions may be responsible.

ABSTRACT 41

PRECISION AND ACCURACY OF THE METHODOLOGY FOR THE DETERMINATION OF Pb-210 BY LSC AND Po-210 BY ALPHA SPECTROMETRY USING A SR-SPEC RESIN

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Pb-210 and Po-210 were important from the radiation protection and environmental protection point of view, due to its high toxicity. It is part of the U-238 natural series, formed by decay of the Rn-222 gas; Pb-210 has a half-life of 22.3 years and emission beta particles with 16.5 keV (80.2%) and 63.0 keV (19.8%); and Po-210 has a half-life of 138.4 days and emission alpha particle with 5.3 MeV.

The methodology for the Pb-210 and Po-210 determination is based on the purification and concentration of the radionuclides using a Sr-Spec resin from EICHRON and performed by Liquid Scintillation Counting (LSC) and Alpha Spectrometry, respectively. The sample solution was loaded onto the Sr resin column preconditioned in advance with 100 mL of 2M HCl. Lead and polonium were retained, Po-210 was stripped with 60 mL of 6M HNO₃ and Pb was eluted with 60 mL of 6M HCl. Po was spontaneously deposited on a silver disc and counted on an alpha spectrometer for 80,000 seconds. The Pb solution was evaporated three times with 5 mL portions of 65% HNO₃ and the final residue was dissolved in 10 mL of 1M HNO₃. Pb was precipitated as Pb-oxalate, which was dried and weighed to calculate the chemical recovery using the gravimetric method. The precipitate was quantitatively transferred into a liquid scintillation vial and 1 mL of 1M HNO₃ was added to dissolve the precipitate. The solution was mixed with 15 mL of Hisafe III scintillation solution. The final solution was counted on a 1220 Quantulus™ Ultra Low Level Liquid Scintillation Spectrometer for 24,000 seconds.

In this paper, evaluates the accuracy and precision of the methodology of Pb-210 by LSC and Po-210 by alpha spectrometry using a separation technique with resin Sr-Spec was performed.

ABSTRACT 42

METHOD DEVELOPMENT FOR ELECTRONIC AUTORADIOGRAPHY WITH GEOLOGICAL SAMPLES; APPLICATIONS IN NUCLEAR WASTE MANAGEMENT

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The final disposal of spent nuclear fuel will be started in 2020s in Finland in a geological repository in crystalline granitic rock at a depth of 400 meters¹. The transport properties of radionuclides from the spent nuclear fuel to the biosphere need to be carefully considered in the overall long-term safety analysis of the repository². Thus, it is necessary to study the sorption and diffusion properties of safety relevant radionuclides from laboratory scale all the way up to in-situ scale in the different barriers of the repository, for instance, the bedrock. In this study the sorption and diffusion of ¹³³Ba and ⁷⁵Se was studied in veined gneiss and pegmatitic granite obtained from the Olkiluoto site and granodiorite from the Grimsel Test Site using filmless electronic autoradiography (i.e. the BeaverTM). Diffusion was studied in rock cubes and sorption was studied on thin sections³ in the presence of groundwater simulants made to resemble the fracture groundwater in the sites.

The spatial distribution of the mineral specific ¹³³Ba activity in rock cubes and thin sections was measured with two autoradiography methods; digital autoradiography using phosphor imaging plate technique (Fuji 5100) and the BeaverTM (Figure 1), which is based on a gas detector incorporated by micromesh Parallel Ionization Multiplier (PIM)⁴. The BeaverTM allows real-time counting of charged particle emission from the analyzed surface with high sensitivity and linearity. The advantages of using BeaverTM over phosphor imaging plate autoradiography are linear response to activity and that the activity is measured directly from the sample.

The diffusion coefficients of ¹³³Ba were determined with electronic autoradiography from diffusion profiles and with gamma spectrometry from the activity decrease in the solution. Additionally, the mineral specific distribution coefficients of ⁷⁵Se and ¹³³Ba were determined with the BeaverTM measurements from thin sections and gamma spectrometry. The BeaverTM has proved to be an efficient method for quantifying mineral specific and heterogeneous sorption of sorbing radionuclides on granitic rock (Figure 2). In addition, sorption experiments on thin sections provide a way to upscale distribution coefficients from crushed to intact rock. The diffusion and sorption data obtained in this study will be utilized in the heterogeneous diffusion modelling as well as in the interpretation of results from the in-situ diffusion experiments.

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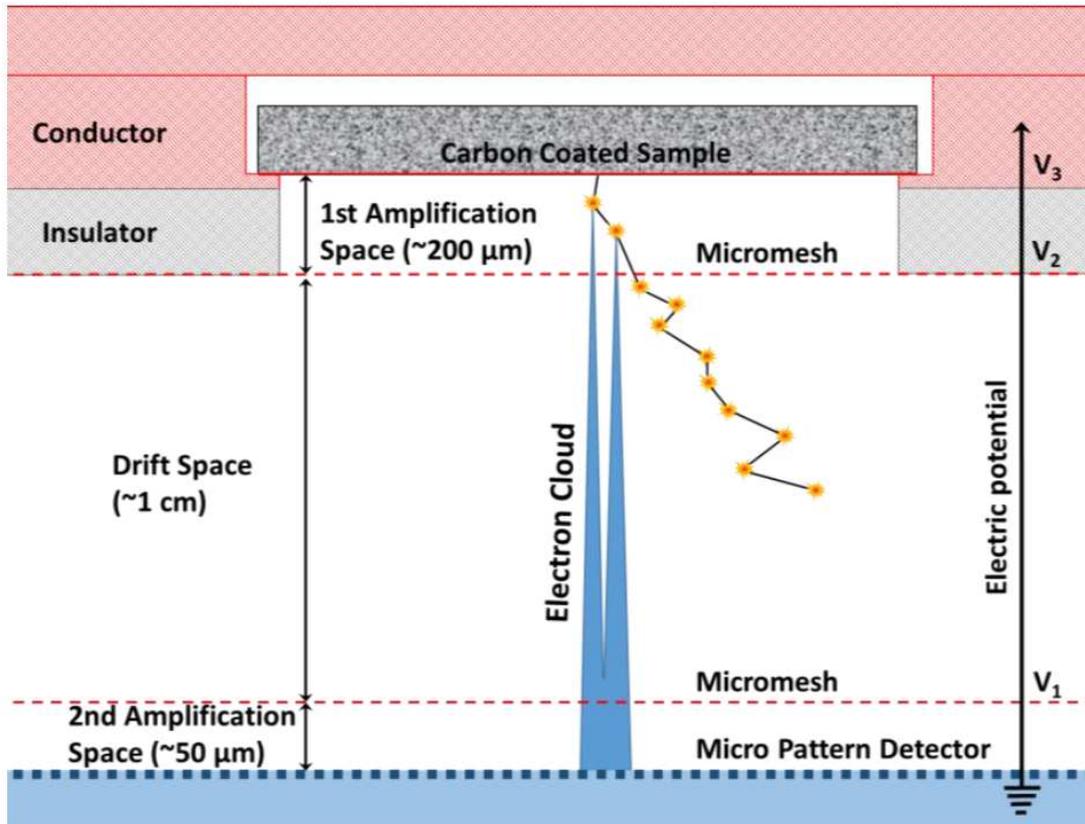


Figure 1. A schematic image of the BeaverTM where the primary electrons created during ionization by emitted electrons are multiplied in the amplification spaces. The resulting electron cloud is then localized on a micro pattern detector⁵.

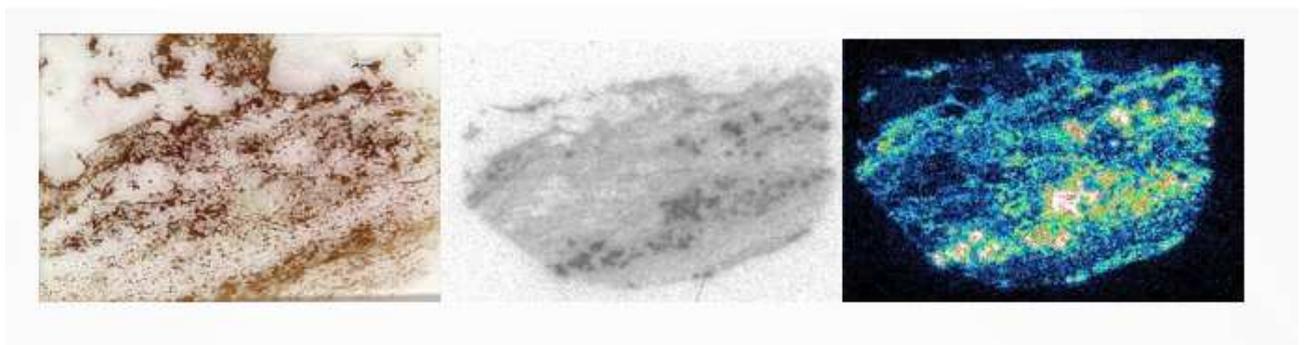


Figure 2. The scanned thin section (left), digital autoradiograph (middle) and electronic autoradiograph with BeaverTM (right) of veined gneiss

ABSTRACT 43

ASSESSMENT OF Sr-90, Cs-137, NATURAL RADIONUCLIDES AND METALS IN MARINE FISH SPECIES CONSUMED IN THE CITY OF SÃO PAULO - BRAZIL

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The study of artificial radionuclides dispersion into the environment is very important to control the nuclear waste discharges, nuclear accidents and nuclear weapons testing. The accident in Fukushima Daiichi Nuclear Power Plant on 11 March 2011, released several radionuclides in the marine environment by aerial deposition and liquid discharge, with various level of radioactivity. The ^{90}Sr and ^{137}Cs were two of the elements released into the environment, ^{90}Sr is estimated that its atmospheric releases ranged from $3.3 \cdot 10^{-3}$ to 0.14 PBq, and ^{137}Cs is estimated that its atmospheric releases ranged from 7 to 20 PBq. The ^{90}Sr and ^{137}Cs are produced by nuclear fission with a physical half-life of 28.79 years and 30.15 years, respectively. The natural radionuclides (^{210}Pb , ^{226}Ra and ^{228}Ra) were determined to check the reference values. The concentrations of metals were determined to compare with the values of the maximum limits of the regulation.

The aim of this study is to quantify the concentration of the ^{90}Sr , ^{137}Cs , natural radionuclides and metals in the muscles of marine fish species most consumed in São Paulo city. The species and scientific names of the fishes analyzed were bluefish (*pomatomus saltatrix*), croaker (*micropogonias furnieri*), hake (*merluccius merluccius*), Smooth-hounds nei (*Mustelus spp.*), sardine (*sardinella brasiliensis*) and mullet (*Mugil brasiliensis*). The determination of ^{90}Sr by liquid scintillation counting (LSC) measurement was performed using a 1220 Quantulus™ Ultra Low Level Liquid Scintillation Spectrometer. The ^{137}Cs and natural radionuclides were measured by gamma spectrometry, using an HPGe detector. The metals concentration was determined by instrumental neutron activation analysis (INAA).

The results obtained in this study can be used to ensure the quality of the fish consumed in the São Paulo city.

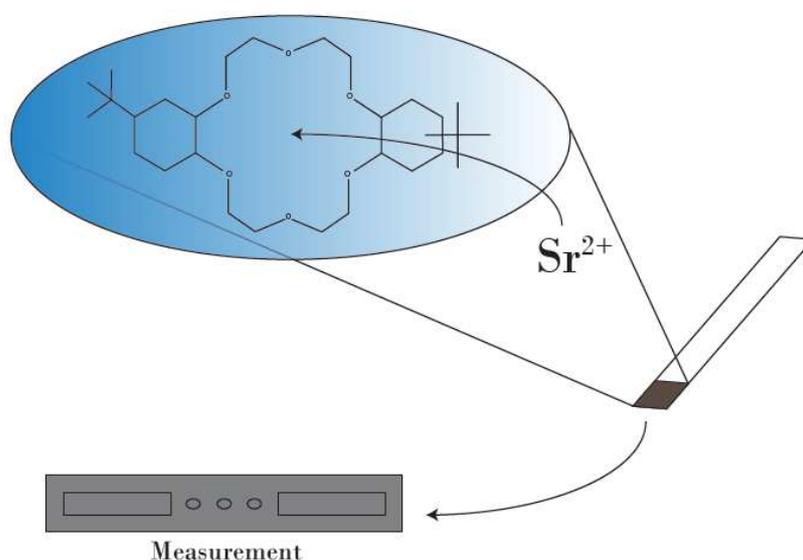
ABSTRACT 44

SCREENING OF STRONTIUM-90 IN AQUEOUS SAMPLES USING TEST-STICK TECHNOLOGY

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Nuclear site decommissioning is underpinned by robust radioanalytical waste characterisation. The UK and European nuclear industries are therefore investing in research into next generation characterisation technologies to meet the increasing demands for efficient waste characterisation. Screening of nuclear decommissioning wastes for non-gamma emitting radionuclides has often relied on time-consuming radiochemical analysis by expert laboratories remote from the decommissioning site. This need to use off-site laboratories partly reflects the volume of characterisation work required to achieve desired site end-states. Dispatching samples to off-site laboratories introduces a significant overhead linked to Health Physics and Transport requirements and solutions that can reduce this can be attractive. There are significant advantages to developing a rapid screening approach that can be deployed on site for the initial identification and quantification of radionuclides, permitting more time and cost-effective screening of wastes.



Developing rapid on-site technologies for screening difficult-to-measure radionuclides could contribute to accelerated characterisation. Test-stick technology aims to characterise significant DTM radionuclides such as ⁹⁰Sr and additionally be readily deployable by non-specialists. Interest in ⁹⁰Sr is derived from the fact that it has been identified as one of the major radionuclide contaminants in nuclear decommissioning partly due to its high fission yield. The ability to quantify the levels of ⁹⁰Sr in nuclear waste including groundwater using an on-site technique is an attractive option for a financially and time demanding process such as nuclear decommissioning. This project compares the sorption capabilities and selectivity of two commercially available resins via batch-uptake

experiments. These cationic exchange resins are then implemented into a test-stick format and applied in further batch-experiments to determine the kinetics and sorption isotherms of both. This includes employing both resin-type test-sticks in groundwater and acid leachate samples to give comparative and representative performance information of both. These experimental data will identify the most suitable resins to be used for test-stick technology for field deployment and meeting the above requirements in providing rapid characterisation of ^{90}Sr in nuclear waste. By doing so, this project will look to offer the first step to achieving a novel analytical technology for the robust, efficient and cost-effective characterisation on radioactive wastes.

ABSTRACT 45

PILOT STUDY FOR DETERMINING ^{55}Fe , ^{63}Ni AND ^{59}Ni FROM NUCLEAR REACTOR PRESSURE VESSEL STEEL IN FINLAND

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Increasing efforts towards nuclear reactor decommissioning have created a demand for radioanalytical methods adapted for nuclear reactor materials and low/medium level nuclear waste. A pilot project was launched in Finland, for surveying the needs and capabilities in analysis of difficult to measure radionuclides in different decommissioning waste materials.

In Finland, the most common and therefore important materials are steel, concrete and spent ion exchange resins.

BWR and VVER types of irradiated pressure vessel steel were studied for determining activity concentrations of ^{55}Fe , ^{63}Ni and ^{59}Ni . A preliminary comparison was performed between two separation methods for simultaneous determination of Ni and Fe from steel.

Both radiochemical separation methods started with dissolving the steel samples in concentrated HNO_3 and HCl , also Ni- and Co-carriers were added to the samples. Fe and Ni were separated from each other and sample matrix by anion exchange. Ni fraction from anion exchange was purified either with DMG (dimethylglyoxime) precipitation, or separation by extraction chromatography, Ni-resin. The beta particles of ^{55}Fe and ^{63}Ni were detected with liquid scintillation counting, Quantulus 1220 LSC, and x-rays of ^{59}Ni by x-ray fluorescence spectroscopy from the purified sample fractions. The concentrations of stable Fe and Ni were determined by MP-AES, for calculating fractions of Fe and Ni lost during radioanalytical separation procedure.

The determined activity concentrations of ^{55}Fe , ^{63}Ni and ^{59}Ni in steels will be used for determination of scaling factors and assessing validity of mathematical models. By combining radioanalytical results with mathematical modelling, the radionuclide distribution and activation level of the reactor materials can be estimated in a broader scope.

The results from the project will be presented and discussed in the presentation.

ABSTRACT 46

STUDY INTO THE USE OF GLOW DISCHARGE MASS SPECTROMETRY FOR PLUTONIUM IMPURITY ANALYSIS

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Glow-Discharge Mass Spectrometry (GDMS) is an analytical tool that could be valuable to Analytical services for the analysis of solid materials. Currently it is something of a niche analytical technique used mainly in the semi-conductor industry for low-level impurity analysis (sub-ppm) and depth-profile studies, though it is also used for soil analysis.

Sellafield's current analytical process for elemental impurity analysis of plutonium oxide requires gramme quantity sample dissolution and generates both aqueous and solvent plutonium contaminated wastes. Disposal routes for these are complex and expensive, and may not be available in future. GDMS is practically non-destructive so is very attractive for nuclear applications. A study has been launched to ascertain whether or not GDMS can meet customer quality requirements.

Successful development of the GDMS for impurity analysis of plutonium oxides promises the following benefits:

- Analysis on solid samples with minimal pre-treatment required
- Waste production from the analytical process will be solid and hence easier to manage
- The amount of sample required for analysis is small (10's of milligrams)
- Capability to measure the full periodic table (H to Pu) in a single analysis
- Potential to use for isotopic analysis
- Potential for minimal calibration using standard Relative Sensitivity Factors (RSFs)
- Potential to analyse carbon, halides and nitrogen which is also required on this material
- Significant potential infrastructure and capital cost saving if GDMS can replace multiple techniques
- Capability could be expanded to analyse sludges/other solid matrices

If the studies into GDMS are successful and demonstrate that this technique is suitable for elemental impurity analysis then it will be included in the new analytical facility due to be installed within the National Nuclear Laboratory's Central Lab.

ABSTRACT 47

STUDY INTO THE USE OF A COMBINED FURNACE UNIT IN RADIOACTIVE ANALYTICAL CELLS

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A furnace unit for analysis of radioactive samples has previously been miniaturised for operation in a vented enclosure. This poster will describe work being performed to expand the functionality of a furnace unit and enable operations within an analytical cell.

It is proposed that the following analysis be performed in-cell using a single unit:

1. Loss on Heating
2. Total Solids
3. Total Inorganic and Organic Carbon (TIC/TOC) analysis
4. Isolation of tritium (^3H) and radiocarbon (^{14}C)
5. Isolation of radioiodine (^{129}I)

It is not expected that all five processes be performed simultaneously but that the unit is capable of delivering any of the five functions at one time. The analysis/ preparation will be performed on a variety of matrices e.g. solid, liquid or mixed phase and the temperature profiles will vary with the analytical requirement.

Measuring these species outside of a cell is not possible; significant sample preparation is required to reduce the size or activity of samples and this inevitably reduces the accuracy and precision of the analysis, and results in a loss of volatile species. Hence the successful development of this unit is important to meet customer demand and to support the operating philosophy of analytical cells in the modified NNL Central Lab.

The furnace unit is being developed for installation into two types of shielded cell facility; one with some 'hands on' operations and another with no 'hands on' operations. The poster will outline the steps required to modify the equipment and procedures for use with remote manipulators, while confirming that quality analytical data can still be achieved after modification.

ABSTRACT 48

STUDY INTO THE USE OF A HIGH RESOLUTION GAMMA SPECTROMETRY IN HIGHLY RADIOACTIVE CELLS.

Craig Johnston

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The replacement Analytical Project at Sellafield is building a brand new suite of cells to perform analysis on Medium Active samples (defined at Sellafield as those samples with a contact dose rate of 10 - 100mSv/hr). It is envisaged that all of these samples will be analysed by High Resolution Gamma Spectrometry. The poster will discuss the philosophy, optioneering and development process associated with the development of this capability.

The imminent end of reprocessing operations and the consequent reduction the number of samples where the matrix and radioactivity is well understood will have a significant impact on future analytical methodologies. Work already carried out on samples associated with remediation has demonstrated the importance of upfront gamma spectrometry in informing sample handling protocols and supporting quality control of subsequent sub-sampling and sample preparation activities. At present, Analytical Services has no in-cell gamma spectrometry capability but this is an essential element of the analytical plan for the modified NNL Central Lab.

The purpose of in-cell gamma spectrometry is summarised below:

- Analysis is non-destructive and can be performed before the sample is opened
- Delivers an initial check that activity levels are appropriate for MA cell containment
- Informs sample management protocols e.g. ensures appropriate dilutions for work performed outside the cell
- Establishes baseline fingerprint to improve quality control of sub-sampling and analytical protocols
- Allows correction of final result for the presence of volatile gamma emitting species.

It is anticipated that initial gamma spectrometry will become part of the sample registration process for all samples and that source-less calibration protocols will be employed to accommodate variable sample sizes and matrices whilst minimising the use of in-cell sources.

ABSTRACT 49

^{210}Pb DEPTH-AGE-RELATIONS COMPARED TO “IMPRINTS” OF NUCLEAR DISCHARGES IN SEDIMENTS OF A CHAIN OF FRESHWATER SYSTEMS

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Bottom sediments from several water systems (Lake Biel, Klingnau Reservoir, old river branch near Augst) along the Rivers Aare (Switzerland) and Rhine (Germany, Switzerland) were taken and analyzed by gamma-spectrometry (Weingarten) and ICP-MS (Spiez) with respect to the fallouts from the NWT and from Chernobyl as well as to radioactive discharges from NPPs. The NPP Mühleberg and Beznau are situated upstream Lake Biel and Klingnau Reservoir, respectively. The aim of this project is to understand the fate of radionuclides in a chain of freshwater systems.

When the official discharges from the NPPs Mühleberg and Beznau are convolved with a Gaussian function and the fallouts from Chernobyl and from the NWT are described by a sum of two exponential functions convolved with a Gaussian function the distribution of ^{137}Cs in sediments over time is described already reasonably.

A simple compartment model incorporating all relevant radionuclides calculates isotope-ratios in a low temperature nuclear U-reactor, using the thermal n-flux with corresponding absorption and fission cross-sections and -yields as well as the epi-thermal n-flux with corresponding n-resonance-integrals and radioactive decay. This leads to model-descriptions of e.g. the vertical distributions of $^{240}\text{Pu}/^{239}\text{Pu}$, $^{137}\text{Cs}/^{239}\text{Pu}$ or $^{137}\text{Cs}/^{241}\text{Am}$. The model was calibrated with measurements and calculations for different burn-up of a fuel rod from a nuclear power plant (Kirchner and Schäfer, 1985, ISBN 3-923290-31-4) which allows simple nuclear forensics.

The Pu-240 and the Pu-240/Pu239 spectra of River Rhine sediments shown in Fig. 1 are compatible with a Pu-discharge from NPP Beznau in 1971 after a rather low burn-up. Vertical distributions of ^{137}Cs and the ratios $^{137}\text{Cs}/^{239}\text{Pu}$ and $^{137}\text{Cs}/^{241}\text{Am}$ will be shown for the three water systems. Fits to the ratios are again compatible with first discharges into the Klingnau reservoir with a rather low burn-up, later discharges with larger burn-up. Depth-age-relations and sedimentation rates were calculated according to the ^{210}Pb CRS- and piecewise CRS-methods. The latter one is constrained by the Chernobyl- and the NWT-peaks in 1986 and 1963. The recognized NPP-discharges are added for comparison and they fit quite well into the depth-age relation.

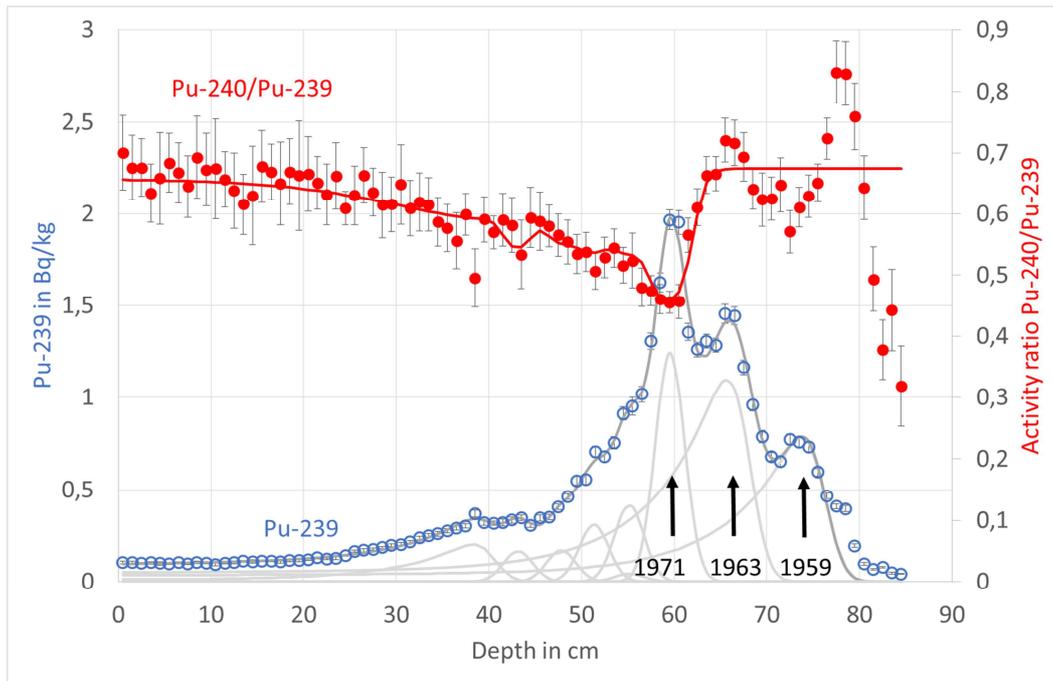


Fig. 1: Vertical distribution of ^{239}Pu activity concentration and number ratio $^{240}\text{Pu}/^{239}\text{Pu}$ in a sediment from the old river branch near Augst. Dots: measured values, lines: model description.

This study has led to a deeper understanding on the fate of radioactivity discharged into a chain of lakes and reservoirs connected by a river (here Aare and Rhine) and has given some insight into the discharges of the NPPs Mühleberg and Beznau which leave their specific signature a rather long way down the river system.

See also the talk “Radiochemical analysis of U, Am, Np and Pu isotopes in sediments from a chain of freshwater systems (Switzerland)” by S. Röllin.

ABSTRACT 50

AUTOMATED RADIOCHEMICAL SEPARATIONS USING A NiV SEPARATOR

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The NiV Separation System (developed jointly by NNL and Microlab Devices Limited) performs automatic radiometric separations to isolate specific radionuclides from the species interfering with detection and measurement. The instrument fits into a standard fumehood and replaces current wet chemistry and ion exchange separation techniques.

A single system can perform numerous types of radiochemical separations dependent on the software and the cartridge used. The chemistry is performed within a disposable cartridge with up to 4 separations per cartridge.

Sellafield will shortly be installing a NiV separator for Sr-90 separations and it is envisioned that this technology will be used in the new re-fitted NNL analytical facility where its flexibility is key to the efficient support of Medium Active and Highly Active analytical operations. Sellafield Limited and NNL have confidence that this instrument will offer a number of advantages over the current manual separation techniques:

- Reduced liquid and solid waste
- Reduced chemical handling and hazard
- Reduced radiation dose to operators
- Significant reduction in operational time
- Scope for human error and inter-operator variability is removed leading to improved analytical reproducibility
- Reduced training requirements; very simple interface
- Reduced infrastructure and footprint requirements (one instrument in a single enclosure can be used for multiple separation protocols e.g. Sr, Pu, Am/Cm etc.)
- One cartridge and two cartridge system available (4 or 8 simultaneous analyses)
- Two cartridge system fits into a standard fumehood enclosure
- No operational efficiency losses from performing analysis in small batches – SL has a customer that requires daily Sr90 analysis on quick turnaround
- Chemistry is performed within cartridges so there is minimal cross contamination potential
- Significant capital and operational cost savings
- Potential to use in-situ if detection techniques are available.

ABSTRACT 51

MONITORING OF CAESIUM-137 IN SURFACE SEAWATER AND SEAFOOD IN BOTH THE IRISH AND NORTH SEAS: RECENT TRENDS AND OBSERVATIONS

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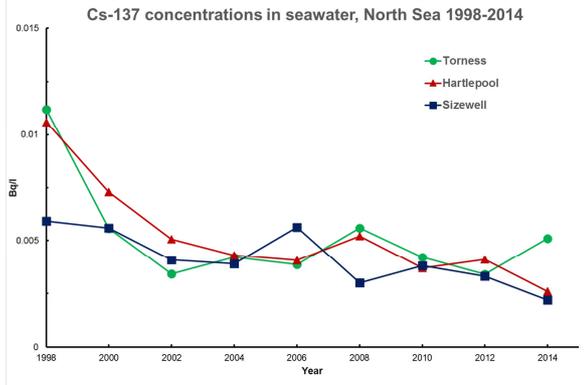
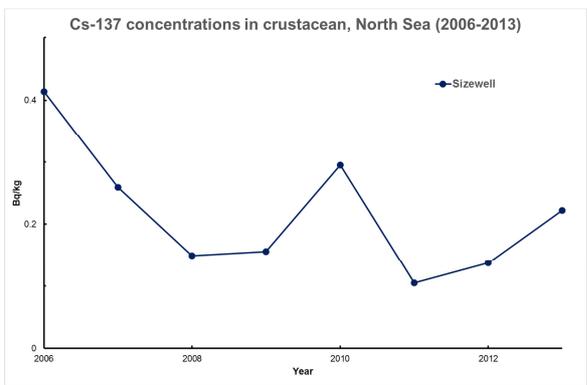
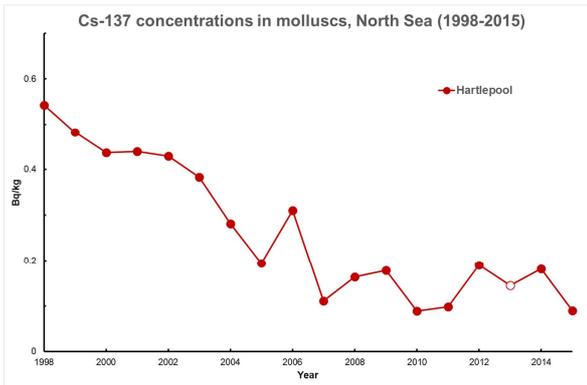
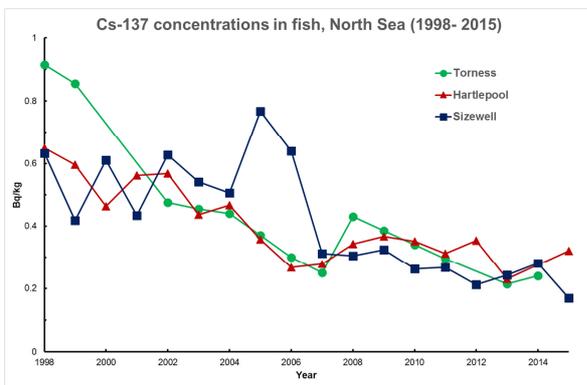
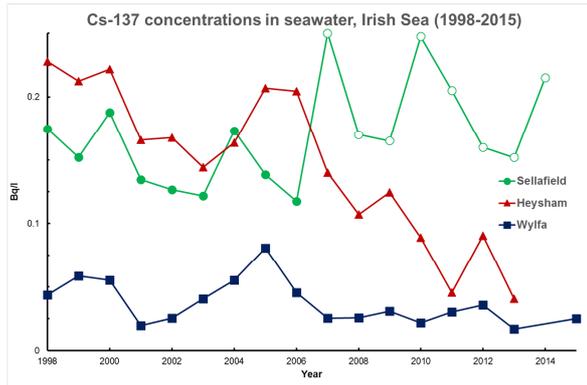
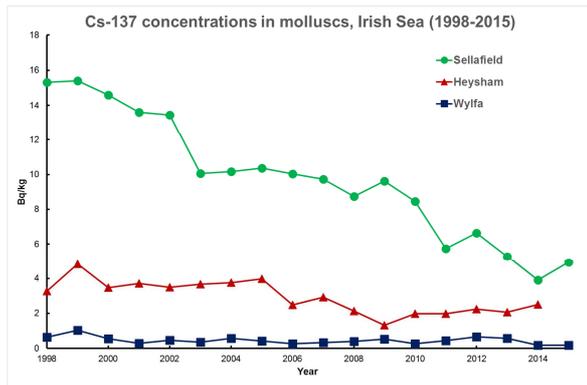
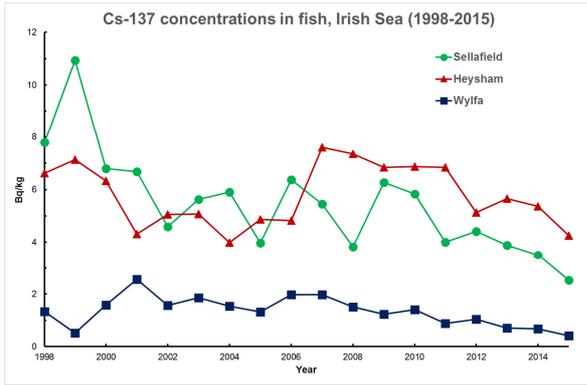
** Presenting author*

The objective of the OSPAR Commission's Radioactive Substances Strategy is to prevent pollution of the OSPAR maritime area (North East Atlantic) from ionising radiation through progressive and substantial reductions of discharges, emissions and losses of radioactive substances. The UK Governments are committed to preventing pollution of the marine environment. The continuation of UK annual surveillance programmes to determine the distribution of radionuclides in the food and the environment is maintained year on year. Selected results of monitoring at UK nuclear licensed sites and in adjacent coastal seas contribute to the data collected by the OSPAR Commission. The information provided in this paper is taken from data submitted by the UK (since 1998) to the OSPAR Commission for the purpose of evaluating the extent to which the Radioactive Substances Strategy is being met (by the year 2020). Data are also published annually in the Radioactivity in Food and the Environment Report (RIFE) report series by the UK.

The objective of this paper is to provide selected concentrations of caesium-137 in the Irish and North Sea coastal waters and seafood, and to assess the impact upon the surrounding environment. These data give a clearer and broader picture of caesium-137 trends in the environment which are not obvious from the annually submitted or published technical reports. The data have been summarised, at a variety of sampling locations, to produce a review of trends and observations over time, from 1998 - 2015.

Generally, caesium-137 concentrations, in each of the OSPAR indicators (by sample type and site locations), have declined in both the Irish and North Sea environments over the years. This overall trend reflects the reduced discharges (that have included deploying improved BAT) at Sellafield over the period.

The overall decreases in both winkles and lobsters (Irish Sea) were ~ a factor of 4, these trends are generally consistent with the overall decline in Sellafield discharges (also ~ a factor of 4). Caesium-137 concentrations in North Sea seafood and seawater samples (including annual averages of activity) were significantly lower than those observed in the corresponding species in the Irish Sea.



ABSTRACT 52

RETROSPECTIVE MEASUREMENT OF U-236 IN HUMAN LUNGS

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Human lung ashes were collected in Vienna, Austria, during the early sixties of the last century in order to determine short-lived fission products from the nuclear test explosions by gamma-spectrometry¹. Later on in part of these samples also plutonium was determined by alpha-spectrometry².

Last year we started to investigate some of the remaining samples with regard to ²³⁶U (half-life 2.3·10⁷ years) which is produced via ²³⁸U(n,3n) by fast neutrons and by thermal neutron capture on ²³⁵U; the cross section for the latter reaction is about 1/6 of the ²³⁵U fission cross section.

The ash-samples were dissolved in half-concentrated nitric acid, a certain amount of ²³³U was added as a spike and uranium was then separated by anion exchange (UTEVA) and co-precipitated with Fe(OH)₃. After calcination the samples were measured by accelerator mass spectrometry (AMS) at the VERA laboratory. The derived ²³⁶U/²³⁸U isotopic values were in the range of 10⁻⁸, as expected for global-fallout samples, corresponding to 10⁷ atoms ²³⁶U per g of lung-ash. Although the values for individual samples from the same year scatter rather strongly, the calculated mean values clearly display the well-known bomb-peak. The new results will be discussed in connection with the old published data as well as with unpublished ¹³⁷Cs data.

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ABSTRACT 53

THE CONCENTRATION FACTORS OF MARINE ORGANISMS AND THE DISTRIBUTION COEFFICIENTS OF SEDIMENT

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The concentrations factor of 14 heavy metals in marine organisms at the neighbouring sea of Korea were measured and investigated, respectively. The 359 seawater samples, 332 fish samples, 20 Cephalopods and 22 Crustaceans, 15 Molluscs, 38 Macroalgae were measured the concentrations of heavy metals. The concentration factors (CFs) in 314, 22 sampling locations were analyzed in concentration of seawater and marine organisms, and in that of seawater and sediment, respectively.

The concentrations in seawater were Sr(7,030 $\mu\text{g}\cdot\text{kg}^{-1}$), Rb(106 $\mu\text{g}\cdot\text{kg}^{-1}$), Fe(13.6 $\mu\text{g}\cdot\text{kg}^{-1}$), and Cs(2.08 $\mu\text{g}\cdot\text{kg}^{-1}$), respectively. The concentrations of muscle of marine organism were Sr(56.1 $\text{mg}\cdot\text{kg}^{-1}$), Fe(23.0 $\text{mg}\cdot\text{kg}^{-1}$), Zn(9.12 $\text{mg}\cdot\text{kg}^{-1}$), Cs(5.64 $\text{mg}\cdot\text{kg}^{-1}$), and Mn(1.88 $\text{mg}\cdot\text{kg}^{-1}$), respectively.

CFs in all of organism were highest in P, Mn, Cs, Fe and lowest in Na, Sr, Rb, Mo. CFs of muscle in fishes showed strikingly high P(383,000), Mn(42,700), Cs(25,000) and Sr(3.06), respectively. Highest concentration factors of P(286,000), Cu(169,000), Mn(111,000), and Sr(10.1) were measured in molluscs, respectively. CFs of macroalgae showed P(127,000), Mn (64,800), Cs(25,500), and Sr(15.1). The results indicated that CFs of 14 heavy metals in the echinoderms, molluscs were higher than that in the fish and cephalopods except for Mo, Ba.

The concentrations of sea sediment were Fe(32,700 $\text{mg}\cdot\text{kg}^{-1}$), Mn(705 $\text{mg}\cdot\text{kg}^{-1}$), Sr(467 $\text{mg}\cdot\text{kg}^{-1}$), and Cs(0.889 $\text{mg}\cdot\text{kg}^{-1}$), respectively. The sediment distribution coefficients showed Fe (88,600,000), Mn(8,020,000), Cs(4,560), and Sr(71.2), respectively.

The mean CFs and the sediment distribution coefficients of the heavy metal were similar to the recommended value from IAEA (2004) and IAEA (2010).

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Fig. 1 Concentration factors for marine organisms and distribution coefficients for sediment

	Fish	Crustacean	Cephalopods	Molluscs	Macroalgae	Sediment
Cr	1.7E+03	6.7E+03	2.5E+03	8.6E+03	9.5E+03	1.3E+06
Mn	4.3E+04	2.3E+05	8.8E+03	1.1E+05	6.5E+04	8.0E+06
Fe	1.2E+04	5.6E+04	1.1E+04	3.8E+04	1.1E+05	8.9E+07
Co	6.7E+02	3.4E+03	5.0E+02	3.1E+03	1.4E+03	4.3E+05
Ni	2.2E+02	2.0E+03	1.8E+02	3.7E+04	5.3E+03	1.9E+05
Cu	8.4E+02	1.5E+04	7.6E+03	1.7E+05	1.6E+04	5.9E+04
Zn	4.2E+03	4.5E+03	2.5E+03	4.1E+04	1.4E+04	1.1E+05
Pb	1.8E+03	4.3E+03	4.9E+03	2.2E+04	3.8E+03	1.3E+06
Cd	5.1E+02	8.5E+03	2.1E+03	8.9E+03	2.1E+03	7.3E+03
Sr	3.1E+00	9.7E+01	4.7E-01	1.0E+01	1.5E+01	7.1E+01
Mo	1.6E+01	1.0E+02	8.7E+01	4.1E+01	9.0E+00	1.9E+02
P	3.8E+05	3.8E+05	2.2E+05	2.9E+05	1.3E+05	4.6E+04
Rb	1.5E+01	5.4E+01	1.5E+01	3.6E+01	2.6E+01	1.6E+03
Na	1.5E-01	3.9E-01	1.5E-01	3.7E-01	3.5E-01	1.3E+00

ABSTRACT 54

Γ-RAY SPECTROMETRY MEASUREMENT OF CONCRETE SAMPLES FROM NUCLEAR DECOMMISSIONING FACILITIES - VALIDATION OF THE LABSOCS EFFICIENCY CALIBRATION FOR Γ- EMITTERS AT LOW ENERGIES -

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Proper characterization and segregation of materials arising during decommissioning operations are very important factors in waste minimization. Characterization helps develop a complete understanding of the radiological characteristics of these materials in order to enable them to be segregated and to be sent for selected disposal. A number of techniques for measuring the radioactivity of materials generated in decommissioning operations are available. Failure in control procedures at any step can cause important consequences, not only in follow-up steps, but, in some cases, may result in generating waste packages which are not compliant with the waste acceptance criteria for long term storage or disposal.

γ-rays spectrometry using high-purity germanium (HPGe) detectors is a widely used laboratory technique in determining the activity of various radionuclides in the field of decommissioning of nuclear facilities. Laboratory measurements of construction materials as concrete samples from nuclear facilities are often required. The radioactivity in these materials comes from many radionuclides, primarily ^{60}Co , ^{133}Ba , ^{137}Cs , ^{152}Eu , ^{155}Eu , ^{241}Am , ^{109}Cd ...

The use of Monte Carlo simulation for the efficiency calibration in γ-ray spectrometry has become more common, but we have to consider the detailed chemical composition of the samples and the detailed characteristics of the detector (Tian Zi-Ning and all, 2014). The process of creating geometries and calibration of efficiencies by Mirion LabSOCS™ (Laboratory Sourceless Calibration Software) based on MCNP enables automatic corrections of self-attenuation effects by mathematical calculation taking into account the chemical composition if known and apparent density of solid samples. However, this method cannot be used directly to calculate the efficiencies of the samples for low energies because of the system errors. At low energies, the γ-rays self-attenuation in the material constituting the samples is not negligible and varies greatly according to the energy of the photons and the atomic number of the present elements. If these parameters are accurately obtained, we can also use Monte Carlo method through the LabSOCS software to complete the self-attenuation correction. In this work we propose three different methodologies to adjust the attenuation coefficient of the sample and to validate the calibration curve generated by LabSOCS simulation in the case where it is desired to perform measurements at energies below 200 keV, on concrete samples of unknown chemical composition.

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ABSTRACT 55

AN INVESTIGATION INTO THE EFFECT OF DECONTAMINATION AGENTS ON THE ACTINIDE SORPTION PROCESSES

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Ferric oxyhydroxide flocs are effective sorbers of radionuclides, both in the environment and also in effluent treatment processes, for example, in the Enhanced Actinide Removal Plant (EARP) at Sellafield (Cumbria, U.K.). During effluent treatment in EARP, radionuclides in nitric acid feeds containing Fe(III) are co-precipitated with ferric oxyhydroxide floc, which is removed from solution by ultrafiltration, carrying sorbed activity with it. Organic complexants have the potential to compete with sorption processes, and so increase the concentration in the solution phase. For this reason, organic complexants may be used as agents to decontaminate solid surfaces. However, their ability to compete with sorption processes has the potential to lead to a deterioration of abatement performance during effluent treatment. Therefore, there is a need to assess their impact on the process before they may be deployed. The objective of this work was to test the effects of four species (EDTA - Ethylenediaminetetraacetic acid; citrate/citric acid; oxalate/oxalic acid; formate/formic acid) on the processes in EARP using simulants of its acidic feeds.

The effects of oxalate and formate on iron hydrolysis and floc production were studied to determine whether they had the capacity to complex with the Fe^{3+} ions and so affect the ferric oxyhydroxide hydrolysis and precipitation processes (floc production). In some experiments, the acidic Fe(III)/complexant simulants were allowed to equilibrate to test whether any redox reactions took place. The effects of EDTA, citrate, oxalate and formate on Am(III) sorption were also assessed.

Potentiometric titrations were used to assess the effects of the decontamination agents on the floc production and caustic dosing processes, whilst batch experiments with ^{241}Am were used to assess their effect on americium behaviour. The results from the Am batch experiments are shown in Figure 1 as the percentage of Am remaining in solution plotted versus the time since precipitation of the floc for a system with an initial Fe(III) concentration of 100 ppm. Data are plotted for systems containing complexants, and also for a control system with no complexant present (blue line).

Formate concentrations up to 10 mM had no significant effect on the Fe (III) hydrolysis and precipitation processes for Fe(III) concentrations greater than or equal to 50 ppm. The effect on Am behaviour was also negligible under the same conditions. Therefore, it seems likely that formate concentrations less than or equal to 10 mM will not have a significant effect on the EARP process, provided that the iron concentration remains above 50 ppm. No evidence was found for the removal of formic acid by a redox process in systems where the formate was present in excess.

Unlike formate, it was found that oxalate can complex with Fe^{3+} ions under EARP simulated conditions, particularly in the slightly acidic – neutral pH region. However, there was no effect on the sorption of the Am by the ferric floc under the same conditions for iron concentrations greater than or equal to 50 ppm and oxalate concentrations up to 10 mM.

In the oxalate system, complex redox reactions took place when the solutions aged under acidic conditions, with the behaviour depending upon the ratio of iron to oxalate. In systems where the Fe was present in excess, a catalytic cycle results in the removal of the oxalate from the system, which

was associated with a temporary reduction of Fe (III) to Fe (II). It was found that exposure to visible light was a prerequisite for the cycle to operate.

For systems with an excess of oxalate, but no exposure to the air, there was partial removal of the oxalate, and the iron remained reduced. This behaviour was explained by direct reaction of intermediate hydrogen peroxide (formed as a by-product of the reaction of oxalic acid with Fe (III) in the presence of light) with oxalic acid, which prevented the completion of the catalytic cycle. When the reaction mixture is exposed to the atmosphere, dissolution of oxygen allows the catalytic cycle to be completed. The result is that an excess of oxalate over Fe (III) may be removed from the system, although the reaction is slow, requiring several weeks.

Thermodynamic speciation modelling was used to assess the effects of formate and oxalate on the precipitation and floc production processes and also Am sorption to the floc. The model was able to predict both the iron and Am behaviours in the formate and oxalate systems.

Previous work had shown that for EDTA and citrate, at iron:complexant concentration ratios of 400 ppm: 0.35 mM, there was an effect on the iron hydrolysis and precipitation processes. The experiments reported here used the same iron:ligand ratio, but with lower iron concentrations (50, 100 ppm). For citrate, there was no effect on Am sorption. However, for EDTA there was evidence that the ligand was starting to have an effect on the Am sorption, and so in that case, if the relative concentration of EDTA increased further, then there would likely be effects on the Am sorption at the same time that floc production is affected.

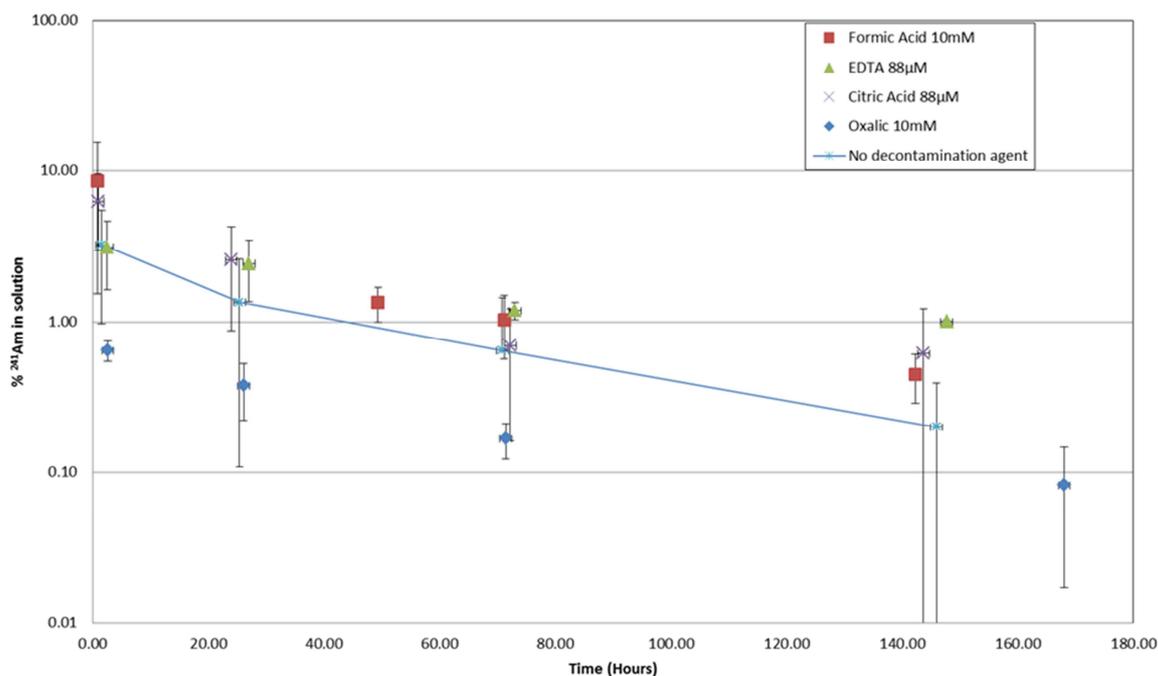


Figure 3 – ^{241}Am sorption in the presence of decontamination agents ($[\text{Fe}] = 100 \text{ ppm}$; $\text{pH} = 10$)

ABSTRACT 56

ENVIRONMENTAL IMPACT ASSESSMENT OF RADIONUCLIDES ASSOCIATED WITH NATURALLY OCCURRING RADIOACTIVE MATERIAL (NORM) AND TECHNOLOGICALLY ENHANCED NORM (TENORM) IN COAL AND COAL ASH FROM NIGERIA.

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Radionuclides concentrations in coal and associated ash post combustion can occur at levels well above background, sufficient to raise potential human and environmental health concerns associated with the release of coal dust and ash into the environment as either emission from smoke stacks, disposal to landfills, coal ash ponds, abandoned mines, spills into rivers and uptake by plants and animals. This project is focused on assessing the environmental impact of radionuclides associated with Naturally Occurring Radioactive Material (NORM) and Technologically Enhanced NORM (TENORM) in coal and coal ash from Nigeria. In addition to samples collected, the coal mines were also surveyed, and radiation maps generated. The survey was performed using a hand held Kromek Sigma Thallium-doped CsI gamma spectrometer coupled to a base unit. Samples will be dried and grinded before analysis; a portion of each coal sample will be combusted to ash in a furnace at a temperature of 1,400 degrees Celsius, the same as the average combustion temperature in coal power plants. The residual ash samples as well as the precursor coal samples are currently being analysed for radionuclides using high purity germanium (HPGe) detector, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and X-ray fluorescence (XRF). Results arising from the analysis will then be used to compute radiological doses for comparison with safe limits set by international organisations such as IAEA, UNSCEAR and ICRP. All results will be shared with the Nigerian government to help inform safety legislation for the coal mining and use in Nigeria and form the basis of an environmental radioactivity database for Nigeria's mining sector whilst building skills and awareness for a planned future nuclear energy programme.

ABSTRACT 57

MEASUREMENT OF ^{238}Pu AND $^{239+240}\text{Pu}$ IN SOIL SAMPLES AFFECTED BY FUKUSHIMA DAIICHI NUCLEAR POWER PLANT ACCIDENT USING ALPHA SPECTROMETER

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The impact of the actinides after Fukushima NPP accident on the environment is still unclear. There are reported values (1-3) that can help public to supplement general overview of the contamination level of Pu isotopes in the soil. The activity concentration of $^{239+240}\text{Pu}$ in our soil samples from Namiemachi area ranged between (13-360) mBq/kg, whereas ^{238}Pu was detectable in a few samples. This fact suggests especially global fallout as a main source of Pu isotopes in analyzed samples. Based on the activity ratio of the $^{238}\text{Pu}/^{239+240}\text{Pu}$ for Pu that equals to 0.03 as global fallout ratio [4]. We are allowed to estimate that level of the ^{238}Pu concentration, which should be closed to the detection limit for alpha spectrometry. However, additional ^{241}Am analysis may be able to clarify and update our results. The activity concentration of ^{241}Am ranged from 0.04 ± 0.01 Bq/kg to 0.34 ± 0.08 Bq/kg. The relationship between activity concentration of ^{241}Am and $^{239+240}\text{Pu}$ ($^{241}\text{Am}/^{239+240}\text{Pu}$) strongly indicated contribution of the other source than global fallout for a few samples (activity ratio higher than 0.3 [5]).

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ABSTRACT 58

ENVIRONMENTAL SAMPLE ARCHIVE IN FINLAND

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The Finnish Meteorological Institute (FMI) has an extensive archived environmental sample collection that can be utilized in research co-operation. The sample matrices include air filters, reindeer tissues, lichen, peat, vegetation and miscellaneous other environmental samples since the year 1960. Besides radioecological studies, the archived environmental samples can be used in ecotoxicological research e.g. for the determination of heavy metals. Most of the samples are from Finland but there are a small number of samples from the Arctic Ocean and Arctic Russia. The samples are available for joint research projects and graduate works utilizing these samples.

In addition to the sample archive, the FMI and University of Helsinki can contribute to sample analysis with radiochemical separation methods, gamma and alpha spectrometry, liquid scintillation counting, and ICP-MS.

ABSTRACT 59

AUTOMATED PRODUCTION OF [¹⁸F]PSMA-1007 USING 7.5-MEV CYCLOTRON: A FEASIBLE ALTERNATIVE FOR REMOTE SITES

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Abstract:

The necessity of targeting the prostate-specific membrane antigen (PSMA) with radiotracers other than the generator-based [⁶⁸Ga]PSMA, led to the production of the ¹⁸F-labelled PSMA-1007. The production of [¹⁸F]PSMA-1007 was achieved using a low energy cyclotron (7.5 MeV) and the NEPTIS mosaic-RS automated synthesis module.

Introduction:

Prostate cancer (PCa) is the most common cancer in men and it can be characterized as the second most common cancer-related cause of death.^[1-3] When detected in early stages the survival rate can reach up to 95%^[4]. Therefore, its early diagnosis is considered of uppermost importance. A plethora of positron emitting radiotracers has been developed to target PCa^[5-9]. One of them is the positron emitting gallium-68 (Ga-68) labelled prostate-specific membrane antigen (PSMA), which has proven to be highly sensitive in detecting metastatic PCa.^[7,8] However, Ga-68 is a generator-based radionuclide leading to limited production capacities. Additionally, the emerging demands on GMP radiopharmaceutical production has led to a generator shortage. As a result, a radioactive fluorinated compound that could successfully target PSMA was of great interest due to the large number of facilities with immediate access, in high activities, of GMP conforming fluorine-18 production. BG 75 Biomarker Generator (ABT Molecular Imaging; Knoxville, TN, USA) is a low energy (7.5-MeV) self-shielded, proton beam, positive-ion cyclotron^[10] intended to satisfy patient needs of 2-deoxy-[¹⁸F]fluoro-*D*-glucose (FDG) using the principle of “dose on demand” radiopharmaceutical production. This can be translated to “a cyclotron run” or “30 minutes of cyclotron bombardment” for a dose.^[11,12] The successful combination of BG75 with a third-party synthesis module, will boost the capabilities of remote sites as they will no longer be restricted to FDG and can offer additional PET examinations such as [¹⁸F]PSMA-1007.

Materials & Methods:

All chemicals, reagents, and solvents needed for the synthesis of [¹⁸F]PSMA-1007 were purchased from ABX GmbH. Irradiations were performed in the facility with the BG75 7.5 MeV proton beam, positive-ion cyclotron. Modifications were made on the system to increase the production efficiency for a low initial volume of ¹⁸F/¹⁸O H₂O.

Results:

The mean value of the radiochemical yield (decayed corrected) achieved, was $50.8 \pm 8.9\%$; with mean initial activity of 5.3 GBq. The average activity of the final product measured was 2.4 ± 0.4 GBq. Mean production time was estimated at 40 minutes; QC required an extra 25 minutes. A radiochemical purity of more than 99% was recorded. Imaging was performed 180 minutes after intravenous administration of 3.8 ± 0.5 MBq/Kg*BW [^{18}F]PSMA. The images were obtained from head to knees. Axial, sagittal and coronal PET reconstructions with and without attenuation correction were performed. After 10 successful synthesis, a total of 25 patients were able to undergo a PSMA-PET examination.

Conclusion:

Production of [^{18}F]PSMA-1007 can be achieved with an average yield (d.c.) of 50.8% using a low energy cyclotron. Since one batch of the radiotracer can be used for more than one patient, [^{18}F]PSMA-1007 can be considered as an alternative or replacement of the already existing and generator-based [^{68}Ga]PSMA.

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ABSTRACT 60

VALIDATION OF A RAPID PROCEDURE FOR THE DETERMINATION OF Sr-90, Sr-89, Am-241, Cm-244 AND PLUTONIUM ISOTOPES FOR EMERGENCY SITUATIONS

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Introduction:

Exercises for emergency situations after a nuclear incident are held in the Austrian Agency for Health and Food Safety every year. In the past the samples for these exercises were only measured by gamma spectrometry. In 2017 an exercise with radiochemical sample preparation for Sr-90, Am-241 and Plutonium isotopes was also conducted afterwards. The method used for these exercises was then modified and expanded by using a microwave muffle furnace for rapid ashing and microwave digestion. Moreover, the radionuclides Sr-89, Cm-244 and Pu-241 were added to the list of analytes. A project was conducted to establish this rapid procedure and to perform linearity and precision tests. The projects were funded by the Federal Ministry of Sustainability and Tourism.

Material and Methods:

Internal standards were added to 21 samples which included 8 soil samples 4 grass samples 4 air filter samples, 3 milk samples and 2 feeding stuff samples. Sr-Spec Resin and DGA Resin were used for the separation of the analytes. Sr-90 and Sr-89 were calculated after a Cherenkov counting followed by a Liquid Scintillation Counting (LSC). Chemical recovery was measured by Sr-86 and Sr-88 with ICP-MS. After chemical separation, Am-241 and Pu-239/240 were measured with alpha spectrometry, followed by the measurement of Pu-239 via ICP-MS and Pu-241 via LSC. Compared with the sample volume of gamma spectrometry the sample amount suitable for rapid chemical separation is very small. Therefore, one goal is to achieve a homogenized representative subsample in an adequate time frame. In this method, bigger sample amounts were firstly ashed which eases the process and enhances the quality of homogenization. However, the ashing is still a time consuming step which cannot be avoided.

Results and Discussion:

This method shall be used for the next emergency exercise. Therefore, a theoretical time table was created to analyzed 10 samples within 4 days. The results were satisfactory with the exception of Am-241 and Cm-244 calculation. The evaluation of the alpha measurements was difficult due to the tailing of the Am-241 which interfered with the Am-243 and peak broadening. The linearity of the radionuclides is independent of the matrices which were used for the analysis and lies between 0.77 for Am-241 and 0.98 for Sr-89. The precision was within the theoretical calculated 3 sigma confidence level of the activity used for the determination. In future reference materials should be taken for further validation. Furthermore, the determination of Am-241 and Cm-244 will be improved by additional separation steps-. Chemical separation steps should be speeded-up by using vacuum boxes by Triskem.

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FATE OF URANIUM IN THE SOILS AFFECTED BY FUKUSHIMA DAIICHI NUCLEAR POWER PLANT ACCIDENT

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On March 11, 2011 a massive earthquake and ensuing tsunami struck the northern coast of Honshu-island, Japan. The earthquake and subsequent tsunami severely damaged the Fukushima–Daiichi Nuclear Power Plant (FDNPP) resulting in hydrogen explosions at nuclear reactor. Although it is believed that nuclear material such as plutonium and uranium isotopes must have remained largely inside reactor, the chances of their release in environment should be considered¹. Consequently, the study of fate of radionuclides that could be present due to FDNPP accident is of great importance from the viewpoint of radioecology².

In order to understand migration behavior of U, determination of sorption-desorption characteristics in contaminated soils from exclusion zone in Okuma town has been carried out in present work. K_d (distribution coefficient) values were established using batch method with ^{238}U as a tracer. Isotope ratios of uranium were measured using TIMS to find out level of contamination. Analytical chemical separation of U from digested soils was carried out with AER (AX 1 x 8)-UTEVA resins. Characterization of different soil parameters like particle size distribution, pH, organic content, cation exchange capacity (CEC), CaCO_3 , elemental and oxide composition of soil has been determined.

Sorption K_d values varies from 400-5500 (L/Kg) for uranium. However, desorption K_d measurement will be presented during conference. This explains that soil surrounding the FDNPP has good retention capacity for actinides like U. The radioactive dis-equilibrium of $^{234}\text{U}/^{238}\text{U}$ was noticed in case of a few samples, indicating contribution of other sources in Fukushima environment than global fallout.

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ABSTRACT 62

INFLUENCE OF EXTRACTION YIELD OF ^{14}C FROM WATER SAMPLE BY DIFFERENT PARAMETERS THROUGH WET OXIDATION-ACID STRIPPING METHOD

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Background/Aim: Some organic compounds have been presented as possible ^{14}C species formed in the coolant water in nuclear power plant including ethanol, methanol and formaldehyde and so on¹, not limited in methane and CO and these compounds might influence the recovery yield of ^{14}C from water. This study aims at the establishing optimum procedure for the analysis of ^{14}C in water via modifying parameters in the wet oxidation-acid stripping system² (Figure 1). Materials and Methods: Various parameters including different concentration of organic compound in samples, oxidants ($\text{K}_2\text{S}_2\text{O}_8$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$), catalyst (AgNO_3) and repeat treatment (1~3 runs) of sample by system were investigated and ^{14}C standard source was used as tracer to determine the recovery yield of ^{14}C by liquid scintillation counting. Results: existence of different amount of organic compound in water has significantly affected on recovery yield. By contrast, increasing amount of $\text{K}_2\text{S}_2\text{O}_8$ and/or accompanying with adjuvant $(\text{NH}_4)_2\text{S}_2\text{O}_8$ seem to improve the recovery yield. However, twice sequential treatment of sample by system can almost reach 90% (Table 1) of recovery yield. Conclusion: Preliminary results demonstrate that optimum procedure of analysis of ^{14}C can be predicted in accordance with liquid matrix (concentration of organic compound) and minimum detectable activity can be achieved as 0.066 Bq/ml.

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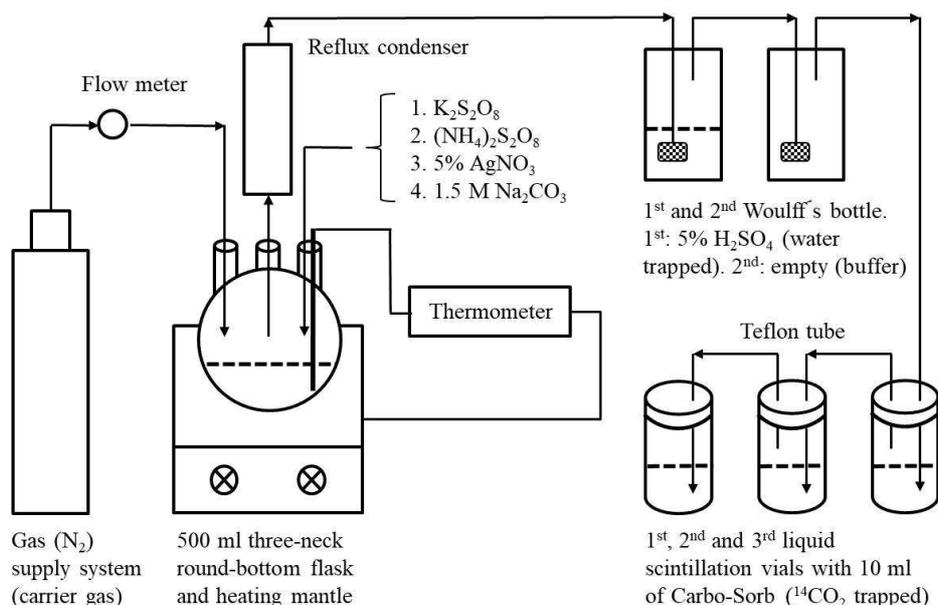


Figure 1: Schematic flowchart of the wet oxidation-acid stripping system for extracting ^{14}C from water

Table 1: Evaluation of recovery yield of ^{14}C from water with various parameters by wet oxidation-acid stripping method

No.	Amount of ^{14}C standard source (μl)	Reactant				Recovery yield (%)			
		Potassium persulfate (g)	Ammonium persulfate (g)	Silver nitrate (ml)	Sodium carbonate (ml)	RUN-1	RUN-2	RUN-3	Total
Influence factor: organic contents (^{14}C standard source's content: 1-Pentanol and 1,3-Butanediol)									
1	5	8	0	5	1	69.3	20.6	0.1	90.1
2	50	8	0	5	1	46.5	44.0	2.7	93.2
3	100	8	0	5	1	22.8	57.9	7.7	88.3
4	1000*	8	0	5	1	6.6	23.7	24.5	54.7
Influence factor: oxidant (potassium persulfate)									
5	50	4	0	5	1	18.5	54.2	10.7	83.3
6	50	8	0	5	1	46.5	44.0	2.7	93.2
7	50	12	0	5	1	50.7	37.9	1.6	90.2
Influence factor: catalyst (silver nitrate)									
8	50	8	0	0	1	13.1	56.3	8.1	77.5
9	50	8	0	5	1	46.5	44.0	2.7	93.2
10	50	8	0	10	1	32.2	55.1	5.5	92.8
Influence factor: double oxidant (potassium persulfate and ammonium persulfate)									
11	50	8	4	5	1	55.2	38.0	1.2	94.4
12	50	4	8	5	1	17.0	70.6	7.7	95.4

Note: *No.4's tracer (1000 μl) was prepared as diluted by 1 ml of 95% ethanol.

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COMPARISON OF DIFFERENT GAMMA-RAY IMAGING TECHNIQUES FOR VISUALIZATION OF THE INDUCED ACTIVITY IN ACCELERATOR MAGNETS

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We are working on the research for establishment of more reasonable decommissioning process of accelerator facilities with the aid of Japan Nuclear Regulation Authority. In this presentation, we will discuss the development of novel technique for assessment of activation.

When the decommissioning of the accelerator facility, we have to evaluate the activation of the facility, from the view point of what kind of and how much nuclides were generated. Until now, core sampling and destructive analysis was the only way to investigate the activation of the facility. Since the core sampling analysis investigates only a point, we can obtain limited information, though, a lot of labors and times are required. On the other hand, since the accident at the Fukushima Daiichi Nuclear Power Plant, the gamma-ray imaging technique was rapidly prevailed. This technique visualizes high dose sites and rapidly provides information of the activation with wide range. However, the evaluation of activation in accelerator facilities with a gamma-ray imaging technique has hardly performed. In a case of activation of accelerator facilities, ^{60}Co and ^{152}Eu which emits high energy (over 1 MeV) photons are principal nuclides, but most of current techniques aim detection of ^{137}Cs which emits 662 keV photon. Moreover, since, whole component of the facilities such as walls, floor, and ceiling, became activated and emit gamma-rays, identifying the source location is quite difficult. In our presentation, we evaluated and compared the current imaging techniques following viewpoints; 1) they can detect gamma-ray of over 1 MeV or not, 2) they can detect the location of radiation source correctly or not while gamma-rays of ^{60}Co and ^{152}Eu are coming from all direction.

We measured activated accelerator magnets with three gamma-ray imager: HGD-E1500 (Hitachi), Gamma-Catcher (Hamamatsu-photonics), and iPIX (Million Technologies Canberra). These were selected as representatives of pin-holed type, Compton scattering type, and masked type, respectively, which are currently available imaging technologies.

Comparison of visualization results of the gamma-rays emitted from the activated magnet is described in Fig.1. Left image was taken with the HGD-E1500, center image was taken with the Gamma-Catcher, and right image was taken with the iPIX. According to the gamma-ray spectrometry with CdTe semiconductor detector, ^{60}Co and ^{22}Na were detected from the magnet, and the maximum dose rate on the surface was 15 $\mu\text{Sv/h}$. HGD-E1500 and Gamma-Catcher reflected high dose area clearly in the center of the duct, but iPIX failed to visualize high dose areas. It was caused the detection crystal was too thin to detect high energy gamma-ray. In the image taken with gamma catcher, the high dose area is divided into two parts. it is suggested, since there was no shielding around the detection crystal, high energy photons reached the detection crystal directly from elsewhere (there

were strongly activated magnet at 3m on the right side). HGD-E1500 and Gamma-Catcher were installed spectrometry mode, but peaks of ^{22}Na and ^{60}Co were not confirmed in the spectrum. In addition, we will discuss the results of other magnets and possibility for applying to assessment of accelerator facilities.

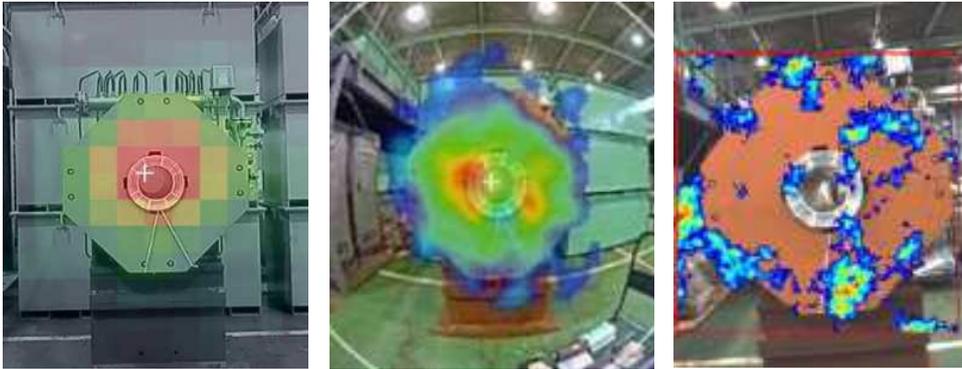


Fig.1 Comparison of visualization results of the gamma-rays emitted from the activated magnet. Left: taken with the HGD-E 1500 (pin-holed type), Center: taken with the Gamma-Catcher (Compton scattering type), Right: taken with the iPIX (masked type).

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DISTRIBUTION OF RADIONUCLIDES NEAR THE FUKUSHIMA DAI-ICHI NUCLEAR POWER STATION

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During the process of decommissioning of the Fukushima Dai-ichi Nuclear Power Station (FDNPS), various types of solid radioactive wastes, such as soil, trees, have been generated from the environment. For the safe disposal of these wastes, evaluation of inventory of radionuclides is essential. However, it was observed that inventory of radionuclides on the FDNPS site varied depending on the location of sampling ^[1], while the concentration data of the generated waste was quite limited. For this purpose, Japan Atomic Energy Agency is carrying out a project to evaluate the off-site distribution of various radionuclides deposited on the soil and trees in the environment in order to estimate the on-site distribution. In this study, the concentrations of several radionuclides in off-site topsoil were evaluated and the characteristic of spatial distribution and depth profile was discussed.

Six traces of the discharged radioactive plume, which we defined as NNW, W (divided into W-N and W-S), SW and S (divided into S-W and S-E) from a north to south direction, were clearly identified based on the off-site distribution of air dose rate measured by un-manned helicopter survey within 5 km from the FDNPS ^[2]. The soil was sampled with at 1 cm intervals up to 20 cm depth by a scraper plate at the nearest point from the FDNPS on each trace of plume in order to evaluate migration behaviours of radionuclides. Soil samples were dried at 105°C overnight followed by α -spectrometry. A concentration of Sr-90 was also measured by the online solid phase extraction coupled with inductively coupled plasma mass spectrometry (SPE-ICP-MS) ^[3, 4] following to hydrothermal leaching in 20wt% HNO₃ in a PTFE thermal degradation vessel with 0.3 g/mL of solid-liquid ratio at 200°C for an hour. The layer with the highest concentration of Cs-137 at each sampling point was subjected to measurement of concentrations of Pu-238, Pu-239+240, Am-241 and Cm-244 according to standard methods of radioactivity measurement issued by the Ministry of Education, Culture, Sports, Science and Technology ^[5, 6]. Some additional layers were also subjected to the same measurement in order to estimate the depth profile. To compare the inventory of radionuclides independent of radioactivity, the transport ratio (TR) was defined as the ratio of the concentration of a specific radionuclide to the reference radionuclide (Cs-137) both of which were normalized by the estimated content of the fuel ^[1]. Once the TR of trace amount of radionuclide which was difficult to detect was defined against easily detectable Cs-137 based on the observed off-site inventory (if it was assumed to be applicable to on-site as well), the amount of this radionuclide in any environmental wastes from on-site could be estimated from the inventory of Cs-137. It was expected to improve the efficiency of on-site activities, such as reduction of exposure.

The TRs of Sr-90 in the topsoil sampled in the NNW, W-N, SW, S-W and S-E were 8.9×10^{-5} , 9.5×10^{-4} , 3.1×10^{-4} , 3.7×10^{-4} and 1.9×10^{-4} , and those of Pu-238 were 3.4×10^{-6} , 1.5×10^{-5} , 3.3×10^{-6} , 4.8×10^{-6} and 4.9×10^{-6} , respectively. This tendency was consistent with that of observed in the previous on-site sampling [1]. Therefore, the data suggested that the estimation of on-site distribution of radionuclides inventory based on the off-site distribution was applicable. Concentration of Cs-137 drastically decreased from top of the surface to around 10 – 15 cm depth, then gradually decreased, suggesting that Cs-137 was strongly adsorbed and retarded at upper part. Surprisingly, the profile of Pu-239+240 was quite different from that of Pu-238, while it was similar to Am-241. It was considered that the behaviour of Am-241 was strongly reflected by that of Pu-241, of which Am-241 was daughter, and the deposition event of Pu-239+240 and Pu-241 was different from that of Pu-238.

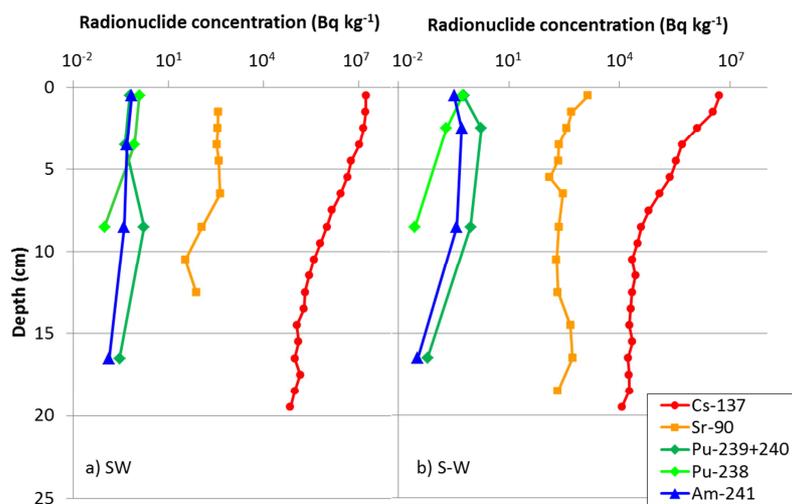


Fig.1 Depth profile of each radionuclide in the soil sampled at a) SW and b) S-W.

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ABSTRACT 65

MEASUREMENT OF Sr-90 IN HIGH MATRIX SAMPLES BY ICP-MS

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Since Sr-90 is one of the high yield and hazardous fission products, accurate and low-level detection of Sr-90 is essential for environmental samples. Especially, in case of nuclear power plant accidents, rapid and precise assessment of Sr-90 for environmental monitoring and health physics is required.

In order to evaluate the migration of radionuclides in the environment, not only Sr-90 in water but also those in soil and biological samples should be measured. A new method for rapid quantification of Sr-90 by online solid phase extraction coupled with inductively coupled plasma mass spectrometry (SPE-ICP-MS) has been developed ^[1, 2]. In this method, it is unavoidable to eliminate the interference by polyatomic ion (e.g., ArCa, Ca₂) induced by isotopes and matrices in fishes and soil. In this study, SPE-ICP-MS method was applied to the measurement of Sr-90 in fishes, and the influence of the Sr isotopes and coexisting ions such as Ca was evaluated.

Fish samples were collected off the coast of Fukushima for application to biological tissues. The dried fish samples (approximately 0.5g) were digested with 8mL conc. HNO₃ in a microwave oven at 180°C for 35min. Known quantities of Sr-90 (30 or 48 Bq/L) were spiked into digested samples and HNO₃ concentration was adjusted to 20 v/v%. In the SPE-ICP-MS measurement, recovery percentage (R%) of Sr is calculated by using intensity of split-flow line and column line. In this study, for accurate measurement of Sr, the signal intensity in the system was corrected with internal standard and the R% of Sr was calculated by comparing intensity of stable Sr through the Sr resin column and that of through split-flow line bypassing the column. In this measurement, due to high content of natural Sr in fish samples, Sr-84, which was much lower isotopic ratio than other natural isotopes such as Sr-88, Sr-86, was used as reference isotope to confirm the R%.

Results are shown in Table 1. In case of Sr-90 spiked sample without digested fish, measured value showed good agreement with the spiked amount. On the other hand, in case of the samples with digested fish, measured values were higher than the spiked amount. It is considered that the increasing of concentration occurred to the influence of the polyatomic species (e.g., ArCa and Ca₂) without passing resin. And if polyatomic interference had occurred, it would have not increased the intensity of Sr-90 but Sr-84. However, as shown in Fig.1, 10 mg/L of Ca or S in solution (equivalent concentration of Ca and S in fish) has insignificant effect on the intensity of 1 ppb of natural Sr. Therefore, some coexisting metals in the solution with digested fish seemed to increase the intensity of only Sr-90. In the future, the factors affecting the measuring of Sr-84 to calculate R% is going to investigate by using solution including high concentration matrix (K etc.).

Table.1 Measured concentrations of Sr-90 in the solution with/without digested fish.

sample (in 20 v/v% HNO ₃)	Sr-90 [Bq L ⁻¹]		measured /spiked	R%
	spiked	measured		
blank	0	ND*	-	-
Sr spiked	30	32	1.1	79
digested fish, diluted 4 times, Sr spiked	48	63	1.3	105
digested fish, diluted 2 times, Sr spiked	48	67	1.4	98

*ND: Detection limit was 4.3 Bq L⁻¹.

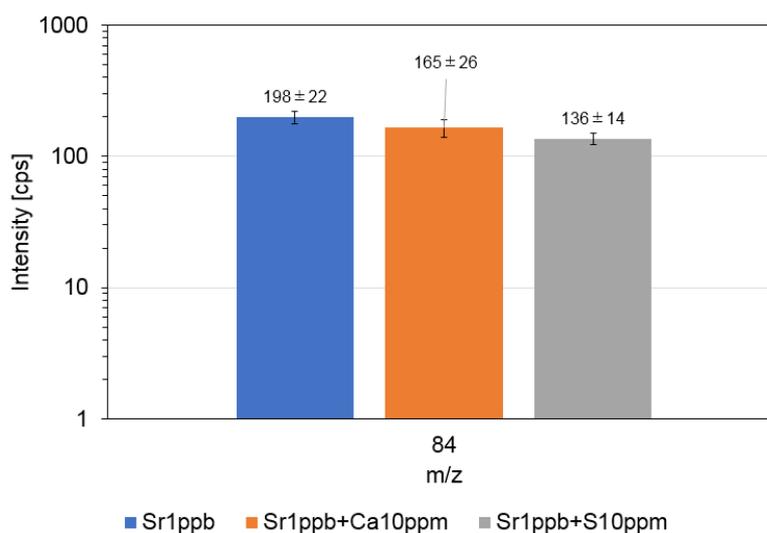


Fig.1 Intensity of stable Sr-84 measured through split-flow line.

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- [2] M. Furukawa et al., *Anal. Chem.*, 2016, **88**, 9397-9402.

ABSTRACT 66

QUANTITATIVE EVALUATION OF THE RADIOACTIVITY IN THE CONCRETE AT PET CYCLOTRON FACILITY WITH SIMPLE AND NON-DESTRUCTIVE MEASUREMENT

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Introduction

In many small medical purpose cyclotron facilities such as PET radiopharmaceuticals generator, neutrons generated with the accelerator operations activate the concrete walls, floor, and ceiling. Especially ^{152}Eu and ^{60}Co which are long-lived and high energy photons emitter are troublesome when the decommissioning of facilities. It is important to evaluate how much radioactivity in the concretes, at present destructive analysis with core boring is the only way. In this research, we tackled non-destructive analysis of neutrons generated with the accelerator operation. Thermal and epithermal neutron fluxes were determined by the activation detector method using a gold foil. The accumulated radioactivity was estimated from the information of cumulative operating conditions and neutron flux at the time. The estimated value was compared with the result from sampling method.

Measurement

a) Neutron fluence monitoring during operation

At the National Cerebral and Cardiovascular Center, Japan (NCCC), a PET-cyclotron (HM-18, Sumitomo Heavy Industries, Ltd) has been used. We used a pair of gold foils (6mm□ and 20μm in thickness) as an activation detector. One was covered by Cd plates (10mm square and 1mm in thickness), and another was not covered. In the accelerator room, we pasted these pairs on the concrete walls, floor, and the surface of accelerator, before operation of the PET-cyclotron. After operation, we teared off the pairs. The ^{198}Au activity of one gold foil was measured by Ge-detector for γ -ray spectrometry, and all of foils were pasted on a sheet and contacted with an imaging plate to measure relative activity of each foil simultaneously. The accelerator operations were carried out two facilities. The accelerators were same, HM-18. One facility was National Cerebral and Cardiovascular Center, Japan (NCCC) and another was Osaka University Hospital, Japan. We carried out two operations each facility. The operations at National Cerebral and Cardiovascular Center, Japan, one was accelerated H^- (18MeV) to make ^{18}F , the other was accelerated H^- (18MeV) to make ^{11}C . At Osaka University Hospital, Japan, two operation was performed such as ^{18}F production using H^- (18MeV) and ^{15}O production using D^+ (9MeV).

b) Concrete core samples

At NCCC, we also obtained the concrete core samples from the pasted points of gold foils. A diameter of each core was 65mm and sampling depth was about 500mm. From the surface to the bottom, a 20mm thick disk was cut at certain intervals to make a measurement samples. Each samples were powdered and measured by Ge-detector to obtain the specific activity of each nuclide.

Results

Almost all concrete samples, ^{60}Co and ^{152}Eu were detected. Maximum specific activity of ^{60}Co was 1.14×10^{-2} Bq/g, and ^{152}Eu was 3.84×10^{-2} Bq/g.

The maximum thermal neutron flux on the cyclotron surface at operation H⁻ to make ^{18}F was 3.76×10^6 particles/s/cm² and epithermal neutron flux was 1.10×10^5 particles/s/cm². The beam current was different at each operation. So when normalized with the beam current and comparing neutron flux for each operation mode, the neutron flux ratio of the production of ^{18}F , ^{11}C and ^{15}O were 15:5:9.

We got operating record including accelerated particle (its energy and beam current) and the operating time at NCCC. By using the record, neutron flux, flux ratio of accelerated particles and typical amount of Co and Eu in the concrete, we estimated specific activity in concrete samples. At the point of near the target box of cyclotron, the estimate of ^{60}Co was 1.6×10^{-2} Bq/g, and measurement result was 1.1×10^{-2} Bq/g. The estimate of ^{152}Eu was 3.2×10^{-2} Bq/g, and measurement result was 1.9×10^{-2} Bq/g.

Conclusion

The neutron flux which is attributed to the accelerator operation at the PET cyclotron and accumulated activity in the concretes could be determined non-destructively. The result of non-destructive method reproduced the result with the sampling method. We found that radioactivity in the concrete can be evaluated easily if there is information for flux ratio of operation mode and operation history.

ABSTRACT 67

ELECTRON MICROSCOPIC ANALYSIS OF THE RADIOCAESIUM MICRO PARTICLES IN LICHENS COLLECTED AROUND THE FUKUSHIMA DAI-ICHI NPP

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Mainly volatile radionuclides were released into the atmosphere by the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident [1]. The local radioactivity depositions around the FDNPP, the radioactive plume's traces, were formed depending on the released situations: the kind of reactors sources, meteorological condition, etc [2]. In order to clarify the deposition characteristics of the plume's traces, the physicochemical state of radiocaesium, dominantly distributed in the environment, is required to understand their behavior and migration. In recent years, micro particles containing radiocaesium (Cs-P) have been reported as one of the radiocaesium deposition states, although contribution of Cs bearing particulate to the total emitted radioactive caesium seems small but is unknown yet. Their physicochemical properties could be shown one of the information for exploring in reactor event at the accident. Thus, it is necessary to investigate their chemical characteristics for example, internal structure, solubility etc. However, it is difficult to collect the particles from soils normally by applying ordinal radio-environmental technique which needs lots of repeated autoradiography operation to recognize the Cs-P in collected soil particles based on their radioactivity.

We focused on lichens because they are well known organism to retain radionuclides for a long period and capture the micro particles in the air. Several Cs-Ps collected from soil was reported to coexist with heavy metals in previous researches [3], [4]. Similar type of such Cs-P was also found on lichen thalli by using electron microscope in our previous study. The Cs-P in organic tissues was expected to be easy to find in reflected electron image, but it was difficult to find the Cs-P as the lichen surface tissue is uneven, the Cs-P was considered to be hidden. In this study, we try to improve our Cs-P separation method by combining organic decomposition and using by electron microscope analyzer (EPMA).

A field investigation of lichens was carried out around the FDNPP within 4 km between January 2016 and January 2017. Focusing on the 2 plumes of 6 plumes based on our previous study, the west and south direction plumes, *Parmotrema tinctorum*, a common species within the area, growing on trunks of trees was collected.

The lichen was analyzed for 15 minutes by the autoradiography to confirm Cs-Ps were captured. Then the lichen was narrowed down to about 10 mm² sized fragment. Since lichen organic matter was thought to be an obstacle to Cs-P observation, the fragment was digested by hydrogen peroxide with reference to our previous study. The residue consisted of insoluble particles was obtained by this

digested treatment. After confirming the presence of the Cs-P in residue, it was used for analysis to detect the Cs-P. The Cs-P was found using by electron probe micro analyzer (EPMA, JXA-8530F) with automated particle analyzer system under the condition of detecting particles containing heavy elements. As a result, Cs-P per 1 digested fragment (about 10 mm² size) was found from hundreds to thousands insoluble mineral particles in one night. In case of manual observation, it took several days (around 100 particles per day) to search the Cs-P. It is shown that the Cs-P can be detected rapidly using this automated system compared to manual observation by human. In addition, the digestion of organic matter was shown to be effective treatment to exclude structural obstacles in lichen.

Applying above method, 4 or more Cs-Ps were isolated from lichen collected in each west and south plume direction site. Their particle sizes were around 2 micro meters. Some particles were inferred to be derived from the Unit 2 and/or 3 based on the comparing of their radioactivity ratios of ¹³⁴Cs and ¹³⁷Cs data and the reference calculation code [5]. These particles showed similar characteristics to our previous research particles found in lichen without digestion treatment. It also showed that the Cs-P characteristic was not different regardless of the treatment of hydrogen peroxide. There are at most 4 such Cs-P found in a single lichen sample. And each sample fragment, only 1 Cs-P detected from several thousands of mineral particles, the number is quite rare.

We suggested our method is useful in two viewpoints, (1) lichen is useful material to obtain the Cs-P with application of hydrogen peroxide decomposition, and (2) EPMA with automated particle analyzer system is also helpful to detect the Cs-P in huge amounts of mineral particles quickly. This method is expected to be helpful to grasp the chemical composition of Cs-P as first step before detailed trace elemental analysis such as transmission electron microscope (TEM) and synchrotron radiation X-ray fluorescent (SR-XRF) analysis.

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ABSTRACT 68

INTER-COMPARISON OF ANALYTICAL METHODS FOR RAPID MEASUREMENT OF ^{226}Ra IN ENVIRONMENTAL WATERS

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Environmental waters are routinely used for domestic supply, agriculture and industry. These waters contain naturally occurring radionuclides at varying concentrations depending on the local geology. The radium isotopes, ^{226}Ra and ^{228}Ra , are of particular concern due to their biological availability, relatively long half-lives and radiotoxicity^[1]. Stringent regulatory limits are in place for drinking water^[2,3], with compliance being achieved through routine monitoring. Therefore, accurate measurement of water sources is required to ensure protection of both the Public and the environment.

Superimposed on the above, several industries produce residues containing elevated levels of ^{226}Ra and/or ^{228}Ra , termed naturally occurring radioactive materials (NORM), which must be characterised prior to discharge or disposal. Regulations are in place to ensure that release of NORM into the environment does not present a significant radiological risk to workers and general population, as required by national^[4] and international standards^[3,5].

Rapid, routine chemical analysis methods are available for the majority of radionuclides considered to present a radiological risk. However, these are less routine in the case of ^{226}Ra and ^{228}Ra , particularly at low environmental levels and hence, are generally cost and time intensive.

Results are presented on an inter-comparison study, using spiked groundwaters (1 L), in order to compare direct radiometric methods (gamma and alpha spectrometry) to a recently developed and optimised ICP-MS method, highlighting each method's capabilities and potential applications (Table 1).

Measurement Technique	Procedural Time	Operator Time	Analysis Time	Samples per Day	Mean Recovery (%)	MDA (mBq)
Gamma Spectrometry (Non-destructive)	-	-	12 h	2*	-	3600 ± 500
Gamma Spectrometry (Post-precipitation)	1.5 h	30 mins	12 h	2*	97 ± 10	31 ± 4
Alpha Spectrometry	8 h	4 h	12 h	Up to 8*	88 ± 7	4.6 ± 0.3
ICP-MS	8 h	4 h	< 5 min	< 20	70 ± 30	6.5

Table 1 Evaluation of alternative measurement techniques for radium isotopes. *sample throughput limited by number of detectors available.

Direct, non-destructive analysis of the samples was achieved by gamma spectrometry. The subsequent co-precipitation step with BaSO_4 effectively removed the ^{235}U interference at 185.7 keV, whilst also

improving the counting geometry, resulting in a Minimum Detectable Activity (MDA) two orders of magnitude lower for the same count time. Sample throughput was limited to 2 per day by the count time and number of detectors available. Alpha spectrometry samples were prepared for measurement using MnO₂ pre-concentration followed by micro co-precipitation. Micro co-precipitation was limited to samples with low Ba content (<250 µg), as higher content resulted in sources with low spectral resolution. Again, sample throughput was limited by the detectors available and long count times. If more detectors were available throughput could be increased to 20 per day, at which point throughput becomes limited by sample preparation.

Direct measurement of ²²⁶Ra by ICP-MS/MS was considered as a rapid alternative to radiometric techniques^[6,7]. The instrument's collision reaction cell was optimised to allow for online removal of polyatomic interferences, whilst handling of complex matrices was achieved through use of online aerosol dilution. Direct analysis of ²²⁶Ra in samples of 10 and 100 Bq L⁻¹ provided measurement uncertainties of <30 and <10%, respectively.

In order to reach relevant limits of detection for environmental analysis, ICP-MS was combined with a suitable pre-concentration technique. The extraction chromatography resin TK100 (Triskem International)^[7,8] was characterised for ²²⁶Ra, achieving a pre-concentration factor of 100 during this study, with minimal signal suppression suggesting larger pre-concentration factors could be achieved through loading larger samples. A pre-concentration factor of 200 would allow for the measurement of ²²⁶Ra in the final samples at concentrations of ~0.5 Bq L⁻¹ with measurement uncertainties <10%. This would make ICP-MS a viable alternative to alpha spectrometry as a means of assessing drinking water quality with respect to its ²²⁶Ra content^[2,3] providing a similar sample throughput with the added benefit of simultaneously measuring other stable elements and long-lived radionuclides

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ABSTRACT 69

SIMPLIFIED DETERMINATION METHOD OF RESIDUAL SPECIFIC ACTIVITY IN ACTIVATED CONCRETE OF A PET-CYCLOTRON ROOM USING A SURVEY METER

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Introduction

Many accelerator facilities in Japan are entering the stage of considering decommissioning due to their useful life. In general, volume of concrete wall and floor of the accelerator room is very large. In decommissioning the accelerator facility, activated parts of the concrete should be separated from non-activated parts of the concrete in order to reduce the volume of the activated waste as much as possible. For efficient decommissioning, a simplified determination method of residual specific activity in the concrete wall and floor of the accelerator room is needed.

Currently, determination of the specific activity in the concrete is performed by a sampling method, which is determination of the specific activities after concrete core boring. The sampling method involves an immense amount of time and effort to determinate the specific activity. Therefore, in the previous study¹, we examined an in-situ determination method contacting a portable Ge detector with the concrete surface of a PET cyclotron room. It was found that the specific activity could be determined by the in-situ determination method using the portable Ge detector. In this study, we could be obtained an in-situ determination method using survey meter, which is much simpler than the method using the portable Ge detector.

Experimental site

The PET cyclotron room of the Medical and Pharmacological Research Center Foundation (Hakui, Ishikawa, Japan) was used as the experimental site. The entire cyclotron body and its accessories were removed from the room. Because the room was also used in the previous study¹, the distribution of the specific activity was well known. The operation period of the PET cyclotron is from 1998 to 2015. This experiment was performed in 2018.

Survey meter equipped with a small detector probe

For in-situ surface dose rate measurement using a survey meter, the detector probe has to be shielded from ambient gamma-rays by a Pb shield. The weight of the Pb shield depends on the shield size,

which depends on size of the detector probe of the survey meter. To minimize the detector probe, the CsI scintillation survey meter (T-SP2, TAC Inc.) was customized specification. Since a 1-inch CsI scintillator combined with Multi-Pixel Photon Counter (MPPC) was separated from other components, the size of the detector probe could become 4 cm × 5 cm × 3 cm.

Lead shield for the survey meter

In order to make the shield as light as possible, we examined Pb thickness dependence of shielding effect from ambient dose rate. Lead shields with a space where the detector probe of the survey meter can just enter were made with the thickness of 1 cm, 2.3 cm, 4.5 cm and 6.5 cm. As the results, it was found that more than 4.5 cm thickness of the Pb shield needs for dose rate measurement unaffected from the ambient dose rate. The weight of the 4.5-cm thick Pb shield for the customized T-SP2 was 16 kg.

Calibration curve of the specific activity from the surface dose rate

We obtained a relationship between the net dose rate measured using the customized T-SP2 and the specific activity ($^{152}\text{Eu} + ^{60}\text{Co}$) determined using the portable Ge detector on the surface of the activated concrete floor. There is a good correlation between the dose rate and specific activity. Therefore, using this relationship as a calibration curve, the specific activity can be estimated immediately from the dose rate measured by the survey meter.

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ABSTRACT 70

EXAMINATION OF NEUTRON FLUENCE MEASURING METHODS TO ESTIMATE THE ACTIVITY INDUCED BY NEUTRONS IN AN ACCELERATOR ROOM

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Introduction

During operation of accelerators, accelerated particles hit various accelerator components such as slits, monitors and beam dump and highly activate these materials and secondly neutrons also activate surroundings. Activity induced by neutrons is low but activated area is wide. Therefore, it is very important to estimate activated area of surrounding materials including building components. Evaluation of neutron fluence measurement is indispensable. In case of cyclotron, we have used gold foils as activation detectors. In case of electrostatic type accelerators, particle energy is generally low and thermal neutron fluence was also very low.

We attempted to use several methods, such as activation detectors, dosimeters and detecting radioactivity in surroundings for measuring neutrons generated by beam irradiation on a metal target at the 6MV tandem electrostatic accelerator in the University of Tsukuba and discussed these features.

Neutron flux at the surface of the concrete floor near the stainless target during 12MeV operation estimated by the above four methods was compared. The neutron flux estimated by using the gold foil was $(9.4 \pm 8.0) \times 10^2 \text{ cm}^{-2}\text{s}^{-1}$, by using the TLD was $(8.3 \pm 2.1) \times 10^2 \text{ cm}^{-2}\text{s}^{-1}$, by using CR39 was $6.5 \times 10^3 \text{ cm}^{-2}\text{s}^{-1}$, by the activity of ²⁴Na was $(1.2 \pm 0.09) \times 10^3 \text{ cm}^{-2}\text{s}^{-1}$ and by the activity of ⁵⁶Mn was $(1.3 \pm 0.08) \times 10^3 \text{ cm}^{-2}\text{s}^{-1}$. Ratio of activity in the bare gold foil to the cadmium covered foils was nearly 1, which means fast neutrons caused activating the gold foil and made the error of measurement with gold foils larger than of the measurement for cyclotrons. The detectable neutron flux of gold foils was almost $10^2 \text{ cm}^{-2}\text{s}^{-1}$ and that of TLDs was $10^0 \text{ cm}^{-2}\text{s}^{-1}$, however the TLDs could not measure at near the targets because strong gamma rays hindered measuring thermal neutrons. CR39 showed a larger value than the other measurements. Thermal neutron dose at the concrete surface was 0.6 mSv, whereas fast neutron dose was 21.9 mSv. It was suggested that fast **Methods**

Figure 1 shows a plan of the 6MV tandem electrostatic accelerator. The A3 line was used in the experiment. The target was set in a chamber in the A3 line and two kinds of metal, stainless (SUS304) as material of accelerator beam pipe or tantalum as material of faraday cup was used. The accelerator was operated in three modes. First one was 12 MeV protons, 1 mA and 2 hours on the stainless target, second one was 12 MeV protons, 1 mA and 2 hours on the tantalum target, and third one was 6 MeV protons, 1.3 mA and 2 hours on the stainless target.

To measure thermal neutrons and epithermal neutrons, sets of a pair gold foils; one is a bare and the other is a covered with cadmium sheet, were installed around the A3 line in the Experimental room. We used the thermoluminescent dosimeters (Panasonic UD813PQ4) for neutron detection. Sets of a bare TLD and a TLD covered with cadmium sheet (0.5 mm in thickness) were also installed around the A3 line, the Beam transport line and the beam pipe in the Accelerator room. The TLD has two

kinds of phosphor that is sensitive to both thermal neutrons and gamma rays, other is sensitive to only gamma rays. The difference of the sensitivity shows thermal neutron dose. CR39 plastic nuclear track detectors were also installed with the TLDs in the rooms. Radioactivity in the surrounding materials such as floor and walls were measured with a Ge detector before and after the accelerator operation. Neutron flux was estimated by using activity of ^{24}Na or ^{56}Mn .

Results and discussions

Neutrons may affect the measurement of thermal neutrons in places where the ratio of fast neutrons to thermal neutrons is large. Using a Ge detector on the concrete floor showed the flux, however it required good shields for measurement.

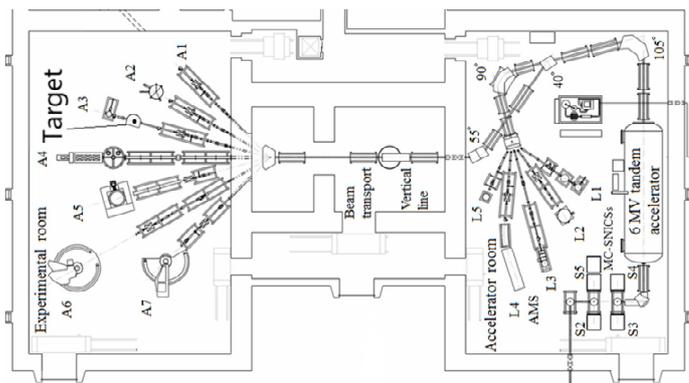


Figure 1 A plan of the 6MV tandem electrostatic accelerator in the University of Tsukuba.

ABSTRACT 71

COMPARISON BETWEEN DIRECT MEASUREMENT OF 186 KEV AND INDIRECT MEASUREMENT OF 352 KEV AND 609 KEV GAMMA RAYS FOR THE DETERMINATION OF ^{226}Ra IN STEELMAKING SLAG MATERIALS

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Since the implementation of BSS Directive 2013/59 Euratom and the Construction Products Regulation (CPR), there is a need for the UK steel industry to demonstrate that the reuse or recycling of blast furnace, basic oxygen steelmaking (BOS) or electric arc furnace (EAF) slag materials in building materials does not pose a significant risk of internal and external exposure to ionising radiation. Natural radioactivity is present in all building materials of geological origin. However, some building materials may be composed of industrial by-products or residues known to contain enhanced levels of natural isotopes, such as iron and steel slag materials. It is well known that steelmaking slag materials can slightly concentrate in radium-226 (^{226}Ra). Radium-226 is commonly measured directly or indirectly by gamma spectrometry but both analytical routes can potentially suffer either from interferences or decay disequilibrium.

The aim of this study was to assess whether steelmaking slag materials can undergo ^{226}Ra analysis by gamma spectrometry via direct measurement using its 186 keV gamma ray without the need for progeny ingrowth, which is advantageous with regard to analysis turnaround times. However, direct measurement of ^{226}Ra utilising the 186 keV emission has a major limitation due to the interference from uranium-235 (^{235}U) at 185.7 keV, with currently available gamma spectrometers lacking the energy resolution to separate the two emission peaks. This can lead to a positive bias in the measurement of ^{226}Ra in samples containing ^{235}U . The common approach to avoid this issue is to determine ^{226}Ra activities by using the information from two of its decay products, lead-214 (^{214}Pb) at 352 keV and bismuth-214 (^{214}Bi) at 609 keV, after sealing the sample for a minimum of 20 days to allow secular equilibrium with ^{226}Ra to be achieved.

Unfortunately, there are currently no certified reference materials of similar texture and chemical composition to the steelmaking slag materials of interest. For this work, the International Atomic Energy Agency (IAEA) certified reference material (CRM) phosphogypsum IAEA434 was used as a direct reference for determining ^{226}Ra in unknown samples of steelmaking slag materials sampled at several UK steel plants.

To assist with validating the results obtained by both approaches, one blast furnace slag material was sent to several laboratories across Europe as part of an inter comparison study aiming to develop CRMs for industries affected by the presence of naturally occurring radioactive materials (NORM).

ABSTRACT 72

VERTICAL DISTRIBUTION OF WATER QUALITY PARAMETERS AND RADIONUCLIDES IN PIT LAKES

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A pit lake is a former open-pit mine where precipitation and groundwater are allowed to fill up the pit until reaching the water table. The differences between pit lakes and natural lakes are a rock basin instead of sand or silt basin, steep cliff walls compared with gradual sloping banks, high concentration of ore(s) in the bedrock and being much younger. The time required to fill the pit and to reach the water table varies depending on the geography, climate and the size of the open pit and can be up to 50 years or more. This means that the final environmental impact cannot be seen until several decades after end of mining operation. The left-over heaps of rocks and gravel scattered around the open pit can still contain high concentration of ore(s), which used to be in the bedrock deprived of atmospheric oxygen and water, but now exposed to weathering. This weathering can result in leaching of elements which can contaminate the pit lake with heavy metals and NORM (Naturally Occurring Radioactive Material).

Pit lakes in Sweden are often used by the locals for recreational purposes and in some cases as drinking water reservoirs. There is a need to characterize these pit lakes by studying the vertical distribution and seasonality of elements and NORM that might affect the environment and human health.

In spring and summer in 2015 we examined a mining site in central Sweden containing three different sized pit lakes where mining operation was conducted from the years 1870 to 1988, allowing 28 years for the water to fill up the open pits and reach a steady water table. The site contains three pit lakes (A, B and C) within a radius of 160 m with maximum depth of 60 m, 5 m and 4 m, respectively. External dose rates were measured using a scintillator probe (6150AD-b, Automess) at 1 m height in several locations around the pit lakes. Water quality parameters were measured in-situ using a multiparameter probe (MS5, Hydrolab). Samples of water from different depths, surface sediments and rocks found around the pit lake were collected. XRF and ICP-MS were used to identify major and trace elements. Sediment and rock samples were crushed and sieved to isolate the <0.5 mm fraction, for alpha spectroscopy the fraction was dissolved using hydrofluoric acid and microwave-assisted digestion. U, Th and Po were analyzed by using liquid-liquid solvent extraction with tributyl phosphate, combined with Th purification with UTEVA columns and alpha spectroscopy. Gamma spectroscopy was used to study ^{238}U and ^{232}Th decay series in sediments and rocks.

Mean external dose rate was 0.40 $\mu\text{Sv/h}$ (compared with background levels in Sweden of 0.13 $\mu\text{Sv/h}$) indicating moderate enhanced levels of NORM in the bedrock and the surroundings. Results from

XRF analysis of surface sediments for the pit lakes were similar, indicating homogenous bedrock within this area. With alpha and gamma spectroscopy, equilibrium in the ^{238}U and ^{232}Th decay chain were found both in surface sediment and in rock surrounding the pit lakes. Furthermore, elemental and radionuclide concentrations in surface sediments were in close agreement with those in rock samples.

Figure 1 shows the vertical distribution of lake A for dissolved oxygen (DO) concentration and pH in the summer and spring, and ^{238}U and ^{234}U activity concentration in the spring. A seasonal variation was found in the DO and pH, which was also seen in other water quality parameters such as specific conductance and oxidation reduction potential. This implies that chemical reactions dependent on these parameters are also likely to exhibit seasonal variations. The vertical distribution shows a stratification of the water from 30 m to 40 m depth where concentration of several elements and radionuclides were different. ^{238}U concentration increased with 50% at 35 m depth compared with the surface concentration. The vertical distribution of toxic elements is important for pit lakes used as drinking water reservoirs e.g. for the planning of the depth of the water extraction pump.

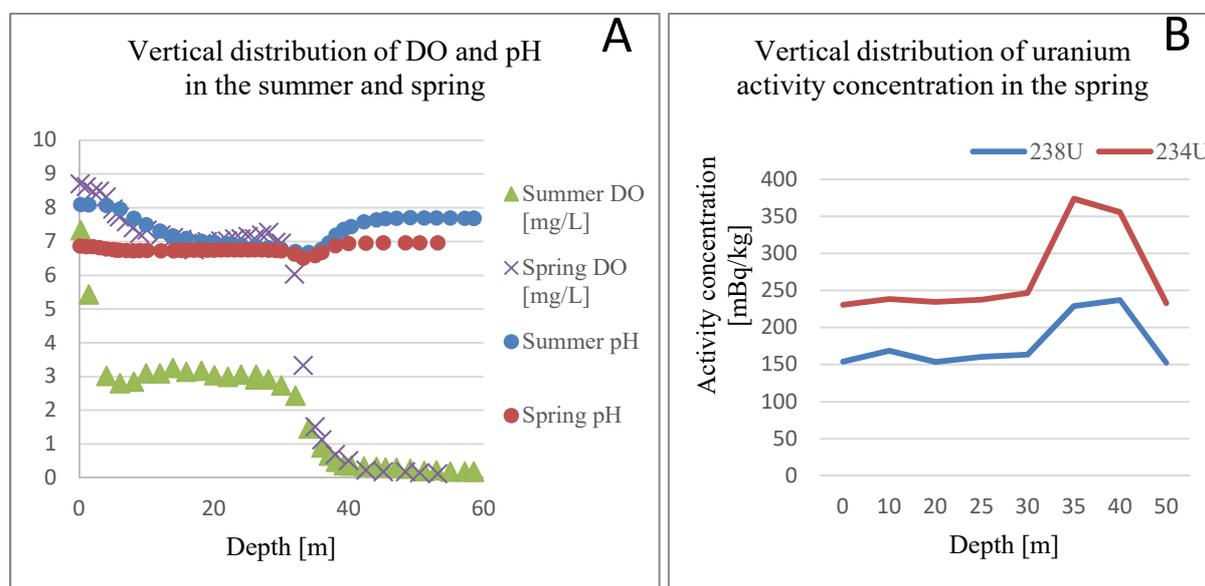


Figure 1 A) Vertical distribution of dissolved oxygen (DO) concentration and pH for lake A in the summer and spring, B) Vertical distribution of ^{238}U and ^{234}U activity concentration for lake A in the spring

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ABSTRACT 73

URANIUM ISOTOPES (^{234}U AND ^{238}U) IN CALCIUM AND MAGNESIUM SUPPLEMENTS

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The objectives of this research were to investigate the naturally occurring ^{234}U and ^{238}U in calcium and magnesium supplements, find the correlations between ^{234}U and ^{238}U concentrations in medicament and its chemical form, as well as calculate the effective radiation dose connected to analyzed supplement consumption. The analyzed Ca and Mg pharmaceuticals contained their organic or inorganic compounds; some from natural sources as shells, fish extracts, or sedimentary rocks.

Uranium is widely spread in nature, occurs in over 160 minerals, locally at high concentrations. Isotopes ^{234}U and ^{238}U occur naturally in uranium decay chain; both are alpha emitters of low radioactivity and radiotoxicity. The harmful effect of uranium results from its high chemical toxicity which is comparable to lead. The occurrence of uranium in environment can also be result of human activity – nuclear industry, combustion of fossil fuels, production and use of phosphorous fertilizers use of depleted uranium for military purposes. Next calcium and magnesium are one of the most essential elements in living organisms and their deficiencies are common, so their supplements have become extremely popular.

The highest ^{234}U and ^{238}U activity concentrations, in both Ca and Mg supplements, were found in all samples of natural origin – marine shells or sedimentary rocks. Among chemically processed supplements (during production), there was one exception, namely chelate compound, which contained high uranium concentrations as well. Similarly to previous ^{210}Po and ^{210}Pb analyses in Ca and Mg supplements, the results showed that inorganic forms of analyzed supplements were richer in ^{234}U and ^{238}U than organic.

Based on ^{234}U and ^{238}U content calculated in analyzed calcium and magnesium supplements, the effective radiation doses were estimated. Obtained data showed there is no radiological risk connected to uranium ingestion with calcium and/or magnesium supplements.

ABSTRACT 74

POLONIUM ^{210}Po , LEAD ^{210}Pb AND URANIUM (^{234}U , ^{238}U) CONTENT IN FRUITBODIES OF KING BOLETE (*BOLETUS EDULIS*) COLLECTED IN YUNNAN PROVINCE (CHINA) AND THEIR PARTICIPATION IN EFFECTIVE RADIATION DOSE

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Mushrooms typically grow in forests and fields, but almost all ecosystems will favor their growth in the correct substrate medium. They are considered as organisms that well bio-concentrate in fruitbodies certain mineral constituents absorbed by mycelium e.g. heavy metals or radiocaesium. Hence, to some degree mushrooms can be useful as indicators aiming to evaluate degree of soil pollution, while fruitbodies of edible species when loaded with heavy metals may pose a risk for consumer. This study aimed to assess potential radiotoxicity to human consumers from ^{210}Po , ^{210}Pb and uranium (^{234}U , ^{238}U) accumulated in king bolete (*Boletus edulis*) collected in Yunnan Province (southern China).

The results of ^{210}Po determination showed its highest activity was found in mushrooms samples collected near Ninger in the Puer county (53 Bq/kg dry biomass), while the highest ^{210}Pb activity was found in mushrooms taken near Jinning in Kunming county (11.4 Bq/kg dry biomass). The results of uranium measurement in analyzed mushrooms indicated the highest ^{234}U activity was determined in samples from Pudacuo, Diqing (0.98 Bq/kg dry biomass), while the highest ^{238}U activity was measured in samples from Weixi, Diqing (0.76 Bq/kg dry biomass). Moreover, the analysis of the values of $^{235}\text{U}/^{238}\text{U}$ activity ratio showed increased amount of ^{235}U in northern Yunnan.

On the basis of determined activities of analyzed radionuclides, the effective radiation doses from dried mushrooms consumption were calculated. The results indicated 1 kg of dried mushrooms would give 1.04-63.4 μSv from ^{210}Po decay and 0.70-10.0 μSv from ^{210}Pb decay. In case of uranium, 1 kg of dried mushrooms would give 9.2-48.0 nSv from ^{234}U decay and 6.7-34.3 nSv from ^{238}U decay. However, the results mean if consumers would eat the analyzed mushrooms, they should not increase significantly the total effective radiation dose from analyzed radionuclides when compared to their other sources from typical diet.

ABSTRACT 75

EXTRACTION EFFICIENCY OF ^{210}Po IN POLISH HERBAL TEAS

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Air and food are the main sources of many chemical elements, also natural and artificial radionuclides transferred to human organisms. The intensity of radioisotopes intake depends on the place of residence, local radiation quantity, diet habits and food origin. So far, during annual radiation doses evaluations in Poland, the most often consumed food products were considered. Among naturally occurring radionuclides, their potential ingestion and internal exposure, the most important seems to be ^{210}Po and its parent nuclide ^{210}Pb .

Presented are results of a study on ^{210}Po extraction efficiency in Polish herbal teas and risk to human consumer due to exposure from highly radiotoxic decay particles emitted by ^{210}Po . 12 most popular commercially available Polish herbal teas, and their infusions in tap water and filtered water, were analyzed and ^{210}Po activity concentrations were calculated.

The results in dried plants were between 2.11 ± 0.09 for milk thistle and 33.70 ± 0.42 Bq·kg⁻¹ dry wt. for cistus. The extraction efficiencies into tap water ranged from 4.93 ± 0.39 for lime to 27.40 ± 1.43 % for elderberry, while for activated carbon filtered water were between 7.55 ± 0.47 for lime and 20.32 ± 1.09 % for elderberry and there were no statistically significant differences between both extractions. There was no correlation found between ^{210}Po extraction efficiency into infusions and ^{210}Po activity concentrations in dried herbs. The effective radiation doses estimated showed that herbal teas consumption should not contribute significantly to the annual effective radiation dose in Poland.

ABSTRACT 76

ON USING 50 YEARS OF DISCHARGED RADIONUCLIDES HISTORY FROM NUCLEAR FACILITY TO UNDERSTAND COASTAL ZONE SEDIMENTATION PROCESSES ON SWEDISH COAST – PRELIMINARY RESULTS

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Radioactive releases from Swedish nuclear facilities are reported to and controlled by the Swedish Radiation Safety Authority (SSM). One of these nuclear facilities is Studsvik located in the Trosa archipelago. Fifty years of historical data on the discharges from this facility is present which give an excellent opportunity to examine behavior of artificial actinides in marine environment. The recipient bay, Tvären, has high sedimentation rate and undisturbed sediment that enables high time resolution in the sediment core. By comparing historical discharge records with levels found in the sediment, parameters controlling the mobility of the radionuclides can be gained.

Until now 23 sediment cores have been collected and multiple radioanalytical analyses and measurements are ongoing. All cores will be dated using ^{210}Pb model assuming constant flux and initial concentration. In the presented research project we intend to investigate geochemical behavior of γ -emitting nuclides: ^{60}Co , ^{134}Cs , ^{137}Cs , ^{152}Eu , ^{154}Eu ; α -emitting nuclides: ^{237}Np , $^{238,239,240}\text{Pu}$, ^{241}Am , $^{243,244}\text{Cm}$, $^{234,235,236,238}\text{U}$ and β -emitting nuclides: ^{55}Fe , ^{63}Ni , ^{90}Sr in Baltic Sea sediment cores. The preliminary results show that both ^{90}Sr and ^{60}Co measured values correspond quite well to the release data while ^{137}Cs present in sediments is mostly of Chernobyl accident origin. The obtained data for analyzed actinides show high activity concentrations for ^{238}Pu and ^{241}Am (56 ± 2 Bq/kg and 65 ± 7 Bq/kg dry mass, respectively), and extremely unique $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity ratios (between 0.2 and 1.6). $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ activity ratios suggest natural origin of uranium radioisotopes in Tvären.

ABSTRACT 77

CHARACTERIZATION OF HIGHLY ACTIVE CELLS IN PREPARATION FOR POST OPERATIONAL CLEAN OUT AT SELLAFIELD – 18139

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The Highly Active Liquor Evaporation and Storage (HALES) Plant at Sellafield receives highly active (HA) raffinate liquors from the Magnox and Thermal Oxide (THORP) Reprocessing Plants. These liquors are concentrated through evaporation into Highly Active Liquor (HAL), conditioned and stored in HALES before immobilisation in glass in the Waste Vitrification Plant (WVP). Reprocessing operations at Sellafield are nearing completion and hence these liquor feeds will soon cease. Therefore, HALES is starting its planning and preparation phases for Post Operational Clean Out (POCO) and decommissioning.

POCO is a transitional phase between operations and decommissioning and encompasses activities undertaken to remove residual inventory and activity from the facility. Key drivers for POCO include risk and hazard reduction and facilitating subsequent decommissioning activities (including potential surveillance and maintenance or care and maintenance regimes). Characterization is a critical enabler for development and implementation of effective POCO. In addition to the key drivers above characterization within HALES will be used to:

- Define the start and end points of POCO (radiological condition, inventory sources and location, configuration, etc.)
- Develop and technically underpin the wash out strategy (volumes, rates, reagent types, etc.)
- Monitor the effectiveness of POCO activities (reduction in inventory/activity, points of diminishing return, confirmation of end points for POCO)

There are a number of significant challenges that present to characterization of the HALES facilities. Perhaps the most significant of these is the radiological status of the facility. HALES is an HA facility meaning that the high dose rates limit not only the technology selection for characterization (i.e. those with a very high radiation tolerance) but also place constraints on the access and deployment for the selected technology. Additionally, parts of the facility are circa 60 years old which brings its own challenges such as poor quality construction drawings and limited operational knowledge. Finally, limited sampling capability and minimal data regarding historic operations has resulted in uncertainties that will need to be addressed in order to undertake POCO as efficiently and effectively as possible.

The solution to this challenge requires a novel and innovative approach and an example of this is the technique which is described in this paper. This is a radiometric characterization technique which

utilizes remotely deployed dosimetry to determine the activity distribution within the vessels of interest to POCO. The results to date have been extremely promising, and the ability to produce concise visual representation of these results has already begun to facilitate better informed discussions around the POCO of the facility. It is expected that in the future this technique will be applicable to other areas of Sellafield which face similar characterization challenges. This paper presents a summary of the development and implementation of the solution along with the results obtained so far.

ABSTRACT 78

DEVELOPMENT OF LSC TECHNIQUES FOR THE ON-LINE MONITORING OF ENVIRONMENTAL RADIONUCLIDES IN AIR AND WATER

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The regular monitoring of air and water samples in and around civil nuclear sites (both active and during the process of decommissioning) is of key importance, both in terms of ensuring that any possible contamination resulting from leaks or spills is detected in a timely fashion and to satisfy the regulatory and environmental demands of government bodies such as the UK Environment Agency (EA) and Office for Nuclear Regulation (ONR). Currently, the periodic manual sampling, analysis and reporting process is resource heavy in terms of both the cost and time (sometime weeks) required to obtain, analyse and collate the data arising from measurements of manually acquired samples.

Here, we present a comprehensive update on the design, development and evaluation of an innovative radioactivity monitoring system, based on LabLogic's 'WILMA', an instrument developed in conjunction originally with the US EPA¹. The system combines a low-level, liquid scintillation-based radioactivity detector and an automated fluid handling system that enables small samples (5 ml total volume) to be collected from a supply point and mixed with scintillation cocktail automatically. The mixed sample is analysed in a measurement chamber, where the radioactive count rate (gross or windowed alpha/beta) of the sample is obtained, along with an LSC spectrum, to determine the elemental origin of any possible contamination. Following automated flushing and washing cycles, the complete measurement cycle can then be repeated to give up to four analyses per hour, over periods in excess of 30 days.

This work focuses on recent system development for two key applications in the civil nuclear and environmental monitoring sectors:

1) Integration of the fluid handling and LSC modules with an automated air sampler and bubbler system for ³H and ¹⁴C analysis in air samples. The development of the WILMA platform for this application has taken the form of the integration of a ³H air sampler and bubbler for waste repository sample collection and analysis in collaboration with the National Physical Laboratory (NPL) as part of the Euramet EMPIR MetroDecom II programme², which is seeking to develop definitive measurement techniques to support the decommissioning process and characterisation of radioactive waste. As part of Work Package 4, a complete WILMA system is undergoing characterisation and metrology testing with tritium gas standards before field deployment; preliminary results from this work will be presented here.

2) We also describe an extension to the MetroDecom II Work Package 4 objectives: a comparison experiment for measurements of NORM, in particular ²²⁶Ra in high salinity matrices associated with

groundwater monitoring. Samples of ^{226}Ra at two activity concentrations in the range 0.1 to 0.2 Bq/g and 1 to 2 Bq/g and containing a mixture of seven chloride compounds³ were prepared at NPL and measured using two LSC systems: the WILMA on-line LSC system and a Hidex 300SL TDCR LSC. As well as the effect of the salinity level on the counting capability, the response using two different scintillation cocktail formulations was investigated. For a typical, high-aqueous sample cocktail, it was found that interaction between the sample chlorides and the cocktail gave rise to a transient luminescence effect over the duration of the 30 minute measurement, which would impact on the accuracy of the sample activity determination prior to disposal (Figure 1). Moving to a different, organic-based cocktail optimised to hold samples with high levels of salinity reduced the effect considerably and allowed the measurement to be started after a settling period of only four minutes.

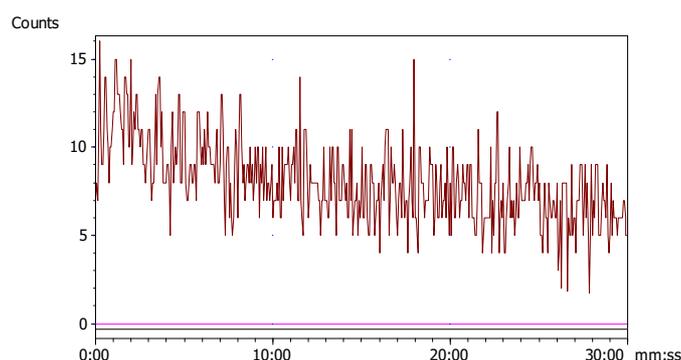


Figure 1. Transient luminescence effect of chloride and scintillation cocktail interaction during an LSC measurement

Comparison between the on- and off-line techniques yielded similar detection levels owing to the high alpha detection efficiency via the LSC method. Resulting spectra also indicated the presence of ^{226}Ra , ^{222}Rn and ^{218}Po within the samples; NaCl loadings in excess of 100 g/l resulted in the LSC spectra assuming a wider distribution across the same measurement channel range. Calculations of the lower limit of the detection⁴ for the on-line technique yielded a value of 36 Bq/l for a 30 min count time.

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ABSTRACT 79

SYNTHESIS AND CHARACTERISATION OF MODEL UO_2 FUELS DOPED WITH TRI- AND TETRA-VALENT ELEMENTS

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We here present two investigations aimed at developing synthesis methods for the production of simplified UO_2 materials, doped with tri- or tetra-valent element species, representative of (1) modern high-burn up nuclear fuels; and (2) Fukushima fuel debris material. Development of such model materials allows for detailed characterisation, at the atomic scale, of local coordination environment, defect chemistry, oxygen stoichiometry and degradation behaviour without the requirement to handle highly radioactive spent fuel materials.

Model Fukushima nuclear fuel debris material: The earthquake and the tsunami that occurred on the 11th March 2011 at the Fukushima Daiichi Nuclear Power Plant (NPP) induced a loss of coolant accident and the partial meltdown of boiling water reactor Units 1 to 3. The temperature within the reactor rose in excess of 2000°C causing melting and reaction of UO_2 pellets with the steam-oxidised zircaloy fuel cladding, forming nuclear accident fuel debris (NFD) and, where melting of other reactor components occurred (e.g. concrete, steel from the pressure vessel), corium. We present results of an investigation aimed at simulating NFD and corium, including an assessment of the distribution of simulant fission products (Ce as a surrogate for Pu and Nd to represent trivalent rare earth fission products), which is an important prerequisite to fuel debris retrieval from the Fukushima reactors, due to commence in 2021. Synthesis of materials in the $\text{U}_{1-x}\text{Zr}_x\text{O}_2$ solid solution was performed by wet and dry chemistry routes, and materials in the $\text{U}_{1-x}\text{Ln}_x\text{O}_2$ ($\text{Ln} = \text{Ce}$ and/or Nd) solid solutions were mixed with Zr metal and heated $>2000^\circ\text{C}$ by oxyfuel processing. Selected phases were further melted with concrete and steel to synthesise simulant corium materials. Analysis of each phase was performed by techniques including XRD, SEM/EDX, XPS and Raman spectroscopy.

Model high burn-up, modern UO_2 fuels: Nuclear power producers are seeking to lower the cost of generating electricity through the development and application of new fuels that are capable for being “burnt” for longer within the reactor. One of the main limitations for how long fuel can remain in the reactor is the ability of the fuel to accommodate fission products, especially fission gases like Kr, Xe, He, etc. The build-up of these gases can lead to a swelling of the fuel and to cladding failure, resulting in downtime of the reactor. The solution to this issue is to improve the UO_2 fuel by promoting the growth of larger grains and increasing the rate of diffusion of fission products to the grain boundaries during fission. This is achieved by doping UO_2 with additives; the most extensively applied are Cr_2O_3 , Al_2O_3 and a mixture of Cr_2O_3 - Al_2O_3 . The dissolution behaviour of these new fuels, as compared to UO_2 fuel, is unknown, therefore development of model doped- UO_2 materials is required to perform durability assessments.

We here describe the synthesis and characterisation of Cr, Al and Cr+Al doped-UO₂ materials, containing between 100 and 1,500 ppm of dopants. Samples were prepared by dry (oxides mixing) and wet (oxalic or nitrate precipitation) synthesis routes. Oxide powders thus obtained were pelletized and sintered at 1700°C for 8h under a reducing atmosphere. SEM images and pycnometer measurements have respectively highlighted an increase of the grain size and of the densification rates in presence of additives. XRD patterns confirmed that the fluorite structure (space group Fm $\bar{3}$ m), the characteristic crystalline structure of UO₂, was retained when the samples were doped. Further characterisations (e.g. HR-XRD and EXAFS) were performed to further determine the solubility limit of Cr and Al within the UO₂ lattice, the lattice parameter and the Cr-coordination in these materials.

ABSTRACT 80

FORENSIC SCIENCE IN A NUCLEAR SCENARIO, DNA ANALYSIS

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INTRODUCTION

DNA samples collection by law enforcement authorities is a critical forensic step in a criminal scenario (crimes, terrorism ...). When the event involves radioactive material, the exposition to radioactivity can have significant influence on the degradation of the forensic evidences, and compromise the evidentiary value of samples for criminal prosecution¹. Moreover, the collection of samples in a RN scenario may involve the risk of exposure to radiation fields and / or radioactive contamination of law enforcement authorities responsible for the task. These two considerations and the limited data published nowadays highlight the need to determine, up to what dose; the DNA of a biological material can be useful for forensic investigations².

This work shows the results obtained on the impact of the ionizing radiation field have on DNA structure and furthermore on the analysis and interpretation of irradiated DNA forensic evidence, i.e., in the integrity of the sample. On this basis a proposal of the dose thresholds for DNA degradation will be documented. Knowledge of this dose value will help the authority to evaluate strategies taking into account ALARA principle, i.e., the usefulness of the evidence collected in these circumstances and the protection of the personnel in charge of it.

EXPERIMENTAL

With this aim a set of experiments were selected irradiating forensically relevant samples at different accumulated radiation dose in the range 1 to 1000 kGy. The biological matrices selected were blood and mucous membrane cells (epithelial cells), common evidences at crime scenes.

Irradiation conditions

The irradiation was carried out in the CIEMAT ⁶⁰Co pool facility (labelled NAYADE) with a nominal activity of 423 TBq (11450 Ci). The experiments were performed in a dry atmosphere and standard conditions with exposure times ranging from minutes to several hours in order to achieve the selected accumulated doses (i.e., 10, 50, 100, 500 and 1000 kGy). Delivered doses were measured with Fricke (ferrous ammonium sulphate) dosimeters. Lower value selected (10 kGy) is based the results already published, due to values < 1 kGy level there have not effects on the DNA profiles.

DNA Analysis

The forensic analysis of samples comprises the following stages: *extraction and purification* of DNA based on Solid-Phase Extraction (SPE) with paramagnetic silica beads, *quantification* with the real-

time/quantitative PCR (fluorescence reporter probe method) system and *fragment separation and detection* by Capillary Electrophoresis (CE) (Figure 1).

Data analysis and DNA profiling was conducted using the GlobalFiler[®] PCR Amplification Kit and GeneMapper ID-X[®] expert system from Applied Biosystems. The analysis includes the study of 24 short tandem repeats (STRs) or microsatellite markers (loci), which encompass the European Standard Set (ESS)³ and CODIS (Combined DNA Index System) composite set of markers.

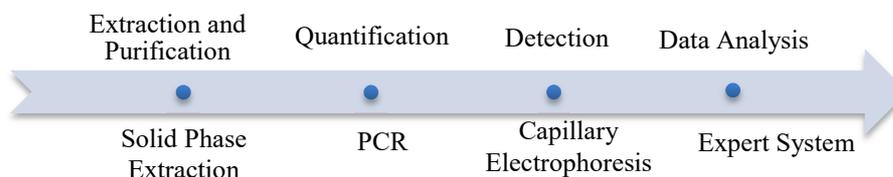


Figure 1. General scheme of DNA analysis

In present study the amount of DNA analyzed was sufficient in all cases to obtain a complete profile and to limit the variations due to low DNA concentration

RESULTS

The results of DNA profiling patterns after irradiation shows three groups depending on the number of markers identified: (a) complete, in which all markers are correct (23 markers and amelogenin), (b) partial although with the minimum number of markers required in the identification procedure (9 markers and amelogenin) and (c) no profile or partial profiles with insufficient number of markers (Figure 2).

CONCLUSIONS

Regarding the type of irradiated matrix, for blood samples no considerable effect as a result of exposure is detected until accumulated radiation dose = 1 MGy, while epithelial cells show substantial degradative changes above 50 kGy. So, in comparison to the epithelial cells DNA, the blood samples appear to be more resistant to the effects of accumulated radiation dose possibly due to nature of the blood matrix with presence of cellular proteins.

Another conclusion is that the DNA fragmentation induced by irradiation did not lead to the appearance of additional peaks in the profiles.

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Figure 2. Results representation using a heat map

ABSTRACT 81

ACHIEVING THE END STATE OF A NUCLEAR LICENSED SITE

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End State (ES) refers to the condition of a nuclear licensed site (or part thereof) following all physical decommissioning and clean-up activities required to make the site (or part thereof) available for its next use. To reach the ES, a site must be released from radioactive substances regulation (RSR). Site operators must apply to the environment agencies for agreement for a site to be released from RSR. The release of the site will only be granted when all disposals of radioactive waste have ended and the site is in a state that will ensure a satisfactory standard of protection for people and the environment. A guidance document, known as the “GRR”, on the release of nuclear sites from RSR was published in July 2018 [1]. A site specific assessment of the benefits and detriments of clean-up and radioactive waste disposal options must be carried out as a requirement of the GRR. This involves identification of potential disposal options, assessment and comparison of options with stakeholder engagement and optimization of the preferred option if any waste is to be left on site. As part of the assessment of waste disposal options, the GRR requires that operators assess potential consequences of inadvertent human intrusion into the site and aqueous releases from features on the site after the ES has been reached. Calculations of potential impacts from human intrusion and aqueous release scenarios are carried out and compared against guidance levels specified in the GRR. These assessments should also show that the consequential effects on non-human species are acceptable. Results of these assessments help identify implications of leaving radioactivity associated with particular components of the site and inform comparison of alternative end state options.

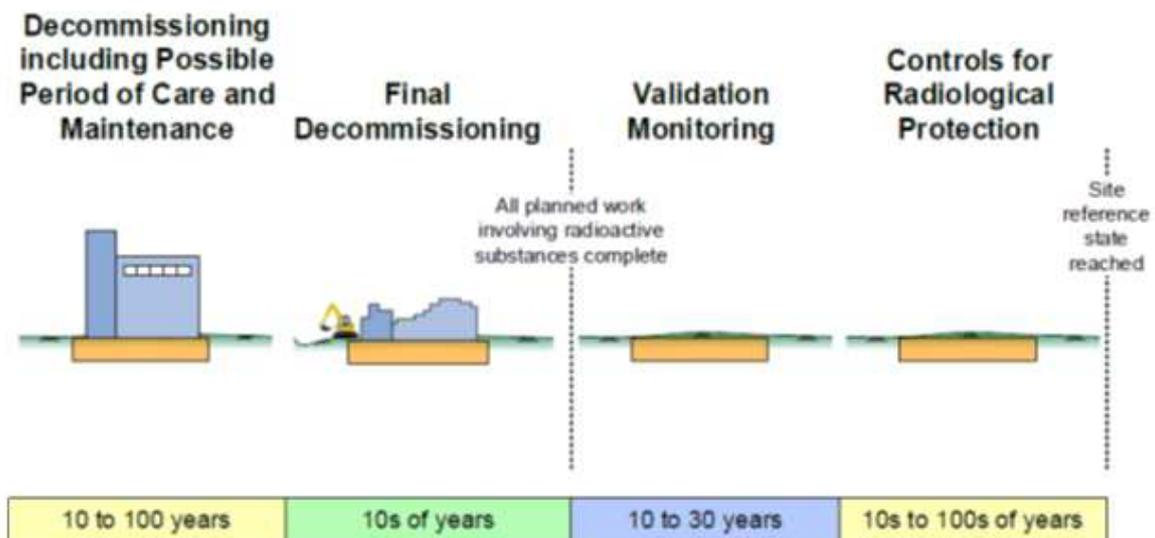


Figure 1: Timeline for a nuclear site to be released from RSTR [1]

- [1] SEPA, EA, and NRW. Management of radioactive waste from decommissioning of nuclear sites: Guidance on Requirements for Release from Radioactive Substances Regulation Version 1.0, July 2018

ADDITIONAL ORAL PRESENTATION: ERA13 Session 2, 18th September 2018

ATOM PROBE TOMOGRAPHY AS A NUCLEAR FORENSICS TOOL- ANALYSING FALL-OUT MATERIAL FROM THE FUKUSHIMA REGION OF JAPAN

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In addition to its high spatial and chemical resolution, atom probe tomography (APT) can identify divergences from the natural isotopic abundances of elements. This includes the study of relative abundances of parent-daughter nuclei to age geological material [1] or using tracer isotopes in chemical processes, such as actinide corrosion [2]. Another potential field of study is within the rapidly evolving field of nuclear forensics, where isotopic ratios can indicate the radioactive provenance of a material. Identifying a radioactive material's isotopic composition can be vital not only for national nuclear security, operational compliance but also in the remediation of sites of nuclear accidents, such as surrounding the Fukushima Daiichi Nuclear Power plant (FDNPP) in Japan.

Following the earthquake and tsunami of March 2011, cooling to the reactors on the FDNPP site was lost, resulting in an exothermic reaction of steam with the zirconium cladding in the reactors, releasing significant volumes of hydrogen gas. The ensuing building explosions distributed highly-radioactive particulate across the surrounding Fukushima Prefecture. As each reactor unit was subtly different in its design and at a different stage of the refuelling cycle, fuel material from each core has a characteristic isotopic signature. APT analysis of the isotopic ratios of fallout particulate can identify the reactor unit where each particle originated and so distinguish the edges and overlap of each explosion plume, aiding remediation and understanding of the behaviour of particulate in the plume and environment.

Particulate material ejected from FDNPP was collected from sediment at the edge of the 30 km exclusion zone. These sub-micron particles were screened using backscattered electron and energy dispersive spectroscopy detectors in a variable-pressure scanning electron microscope to identify those with a high-Z composition [3].

Using a micromanipulator, these were transferred into a focused ion beam and mounted for APT analysis. This talk will present a comparison of the signature of particles from different affected areas around FDNPP with known "core inventory" values. The work will also evaluate the implications of this material on the on-going remediation efforts, in addition to a discussion of the limits of APT in studying the isotopic ratio of actinides.

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