



# (Project Number: 945301)

## **DELIVERABLE D4.3**

## HoT in NF manuals for practical tasks

Lead Beneficiary: JSI

Due date: 30/09/2022

Released on: 10/11/2022

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Start date of n	roject:	01/10/2020	Duration: <b>36 Months</b>				

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ouration: **36 Months** 

VERSION: 1.3

Project co-funded by the European Commission under the Euratom Research and Training Programme on Nuclear Energy within the Horizon 2020 Programme					
	Dissemination Level				
PU	2U Public X				
RE	Restricted to a group specified by the Beneficiaries of the A-CINCH project				
СО	Confidential, only for Beneficiaries of the A-CINCH project				

A-CINCH – Deliverable 4.3 Page 2 / 55



#### Version control table

Version	Date of issue	Author(s)	Brief description of changes made	
number				
1.0	26/10/2022	Marko Štrok	Draft	
1.1	10/11/2022	Mojmír Němec	WP lead revision	
1.2	16/11/2022	Jana Peroutková	MST check	
1.3	16/11/2022 Mojmír Němec		Coordinator's approval	

#### **Project information**

Project full title:	Augmented Cooperation in Education and Training in			
	Nuclear and Radiochemistry			
Acronym:	A-CINCH			
Funding scheme:	Coordination and Support Action			
ECGA number:	945301			
Programme and call	H2020 EURATOM, NFRP-2019-2020			
Coordinator:	Mojmír Němec			
EC Project Officer:	Kateřina Ptáčková			
Start date – End date:	01/10/2020 – 30/09/2023 i.e. 36 months			
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*"This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945301."* 



## **EXECUTIVE SUMMARY**

Nuclear forensics (NF) is one of the most publicly recognized fields in applied nuclear and radiochemistry, at least after release of radioactive material by e.g. accidents. Furthermore, it is a tool covering a broad scope of sciences (e.g. chemistry, physics, biology, socials, etc.) on the analysis side and many others on the side of evidence evaluation in e.g. crime investigations. Therefore, development of a hands-on training (HoT) course to cover broad areas of interest in NF is of great importance. Within the A-CINCH project we want to develop a blended learning HoT, which will comprise e-learning part hosted on the CINCH Moodle platform and presence phase with practical tasks, which will be prepared and hosted by LUH, JSI and CTU.

This deliverable contains manuals for these practical tasks for HoT in NF:

- 1. Extraction, characterization and (SIMS-) analysis of hot particles from the CEZ (LUH)
- 2. Rapid detection of radiosilver (LUH)
- 3. Determination of U isotope ratios by MC-ICP-MS (JSI)
- 4. Alpha spectrometry of uranium isotopes (JSI)
- 5. AMS determination of U-236 isotopic ratio (CTU).

Detailed manuals for each practical task are presented in next chapters.



PAR	T 1: MANUALS FOR PRACTICAL TASKS DEVELOPED BY LUH	1
1	RAPID DETECTION OF RADIOSILVER	2
1.	1 INTRODUCTION	2
1.2	2 THEORETICAL BACKGROUND	
	1.2.1 Production of radiosilver	3
	1.2.2 Decay of radio silver	4
1	1.2.3 Autodeposition of radiosilver	5
1	3 EXPERIMENTAL	
	1.3.1 EXECUTION 1.3.2 Analysis and interpretation	
1.4	4 LITERATURE	
2 CEZ	EXTRACTION, CHARACTERIZATION AND (SIMS-) ANALYSIS OF HOT PARTICLES FRO	)M THE
2	1 INTRODUCTION	Q
2.2	2 RELEASE FROM HOT PARTICLES	9
2.3	3 EFFECT ON THE HUMAN BODY	9
2.4	4 MICROSCALE CHARACTERIZATION - ALSO IN THE CONTEXT OF DISPOSAL RESEARCH	10
2.5	5 PARTICLE ANALYSIS AT IRS: PHYSICAL METHODS	10
2.0	6 PRACTICE TASKS	10
PAR	T 2: MANUALS FOR PRACTICAL TASKS DEVELOPED BY JSI	
1	INTRODUCTION	
2	DETERMINATION OF U ISOTOPE RATIOS BY MC-ICP-MS	
2.	1 APPARATUS, REAGENTS AND MATERIALS	
2.2	2 SAMPLE ASHING	
2.3	3 ACID DIGESTION	
2.4	4 SEPARATION OF URANIUM ON UTEVA COLUMN	
2.	6 MEASUREMENTS OF U ISOTOPE RATIOS ON MC-ICP-MS	23 24
3	ALPHA SPECTROMETRY OF URANIUM ISOTOPES	
3.	1 APPARATUS, REAGENTS AND MATERIALS	
3.2	2 WATER SAMPLING AND PRE-TREATMENT	
3.3	3 TAKING WATER ALIQUOT AND ADDITION OF U-232 TRACER	
3.4	4 SAMPLE PRE-CONCENTRATION	
3 3.1	5 SEPARATION OF URANIUM ON UTEVA COLUMIN	
3.	7 MEASUREMENTS WITH ALPHA SPECTROMETRY	
PAR	T 3. MANUALS FOR PRACTICAL TASKS DEVELOPED BY CTU	35
1	INTRODUCTION	36
1 2	ΠΤΑΘΕΟΟΤΙΟΙ ΝΕΤΕΡΜΙΝΑΤΙΩΝ ΩΕ <sup>236</sup> Ι Ι/ <sup>238</sup> ΙΙ ΡΑΤΙΩ ΙΝ ΤΑΡ WATED WITH AMS	
4 CEN	DETERMINATION OF U/ URATION TAF WATER WITH AWS	······································
GEN		
APP	endia: de lekmination of 2000/2000 katio in tap watek with ams by CTU	



# PART 1: MANUALS FOR PRACTICAL TASKS DEVELOPED BY LUH



## **1** RAPID DETECTION OF RADIOSILVER

## 1.1 Introduction

Nuclear forensics first emerged as a scientific discipline in the early 1990s. During this time, an increasing number of illegal radiological and nuclear materials were seized at borders and their origin had to be clarified. The aim of nuclear forensics is therefore to identify and characterize nuclear material in order to be able to determine its origin, original use and distribution path. Therefore, nuclear forensics is an interdisciplinary science, because the various analytical methods are based on many sub-disciplines such as chemistry, physics, materials science or even biology. Radiometric measurements, which often require complex chemical sample preparation, are part of the repertoire of a nuclear forensic scientist, just as classical analytical methods such as imaging, mass spectrometry or X-ray analysis. Afterwards, the interpretation of the data collected requires extensive knowledge of commercial and military uses of nuclear materials and their production processes.

Since the 1990s, nuclear forensic techniques and databases have evolved and the scope of applications has expanded. In today's world, not only seized materials are subjected to nuclear forensics, but also by examining environmental samples, scientists can evaluate accidents at nuclear facilities if the place of accident is inaccessible or can attribute releases of radioactivity into the environment to a specific source, which wanted to be covered up by the originator. Nuclear forensics thus contributes to the non-proliferation of nuclear material and controls the proper and civilian use of such material.

In the present hands-on training, different methods and application areas of nuclear forensics will be examined in more detail in four experiments. Since nuclear forensics is an interdisciplinary science, the experiments will take place at three different CINCH partners, even though all partners operate radiochemical laboratories, each institute has its own area of expertise and specialized equipment. The experiment on the rapid detection of radio silver deals with the formation of the nuclides <sup>110m</sup>Ag and <sup>108m</sup>Ag in a nuclear power plant, how they can be detected rapidly in the event of an accidental release, and what conclusions can thus be drawn about the accident scenario.

The development and execution of the hands-on training was funded by the Euratom research and training programme H2020 945 301.



## 1.2 Theoretical background

## 1.2.1 Production of radiosilver

Radioactive silver is produced in nuclear power plants through nuclear reactions of stable silver, which occurs in reactors as pure metal or in alloys. Fig. 1 shows an extract from the Karlsruhe Nuclide Chart, which highlights the two stable isotopes <sup>107</sup>Ag and <sup>109</sup>Ag and the relative long-lived radioisotopes <sup>108m</sup>Ag and <sup>110m</sup>Ag. Due to their half-lives of  $T_{1/2}$ (<sup>108m</sup>Ag) = 438 y and  $T_{1/2}$ (<sup>110m</sup>Ag) = 250 d, these two isotopes are of particular radiological and nuclear forensic interest.



Figure 1: Extract from Karlsruhe Nuclide Chart. <sup>[1]</sup>

The dominant reactions for the formation of radiosilver are accordingly:

$$^{107}\text{Ag} \xrightarrow{(n,y)} {}^{108\text{m}}\text{Ag}$$
 (1)

$$^{109}\text{Ag} \xrightarrow{(n,y)} ^{110m}\text{Ag}$$
 (2)

In addition to neutron capture reactions of the stable silver isotopes, <sup>108m</sup>Ag and <sup>110m</sup>Ag can be formed by secondary neutron activation of fission products, but these reactions are of minor magnitude. For the production of radio silver, high and continuous neutron fluxes are required. The ratio of <sup>108m</sup>Ag/<sup>110m</sup>Ag depends, for instance, on the type of reactor and the operation time, because silver is used in different components, which experience a different neutron flux during the operation. In boiling water reactors (BWR), for example, the closure head seals of the basic tubing of the reactor pressure vessel are made of high-purity silver. In pressurized water reactors (PWR), on the other hand, silver even occurs in main components such as the alloy of the control rods. Another source of stable silver are impurities in nuclear fuel, but this is a much smaller source in relative terms.

Monitoring of radiosilver in the event of an accident can therefore help to assess the extent of the damage inside the reactor. If a particular fingerprint of radiosilver can be detected in the plume of a damaged PWR it must be assumed that there has been relevant damage to the control rods in the reactor and that these are restricted in their function. Information on the condition of the reactor core in the case of an accident provides important indications for further action and potential hazards during the upcoming containment and cleanup operations.

Gamma spectrometry is the first choice for detecting traces of radiosilver. However, in the event of a reactor accident, there is usually also a considerable release of radioactive cesium and iodine, which causes the  $\gamma$ -lines of radiosilver to be superimposed in the spectrum. This makes a separation from the radiosilver mandatory prior to the measurement.



A-CINCH – Deliverable 4.3 Page 4 / 55

### 1.2.2 Decay of radio silver

Both silver isotopes <sup>108m</sup>Ag and <sup>110m</sup>Ag have complex decay schemes, which are shown simplified in Fig. 2 and 3. In contrast to most other excited nuclei, they relax only with a relatively low probability by internal transition (IT) to the respective ground state. With the highest probability <sup>108m</sup>Ag transforms into <sup>108</sup>Pd by electron capture (EC) (*P* (<sup>108m</sup>Ag<sub>EC</sub>) = 90.9%) and emits three gamma rays with 723, 614 and 434 keV. The decay of the ground state <sup>108</sup>Ag via electron capture and subsequent  $\beta^+$ -decay to <sup>108</sup>Pd or  $\beta^-$ -decay to <sup>108</sup>Cd adds two more, less dominant gamma lines to the <sup>108</sup>Ag spectrum.



Figure 2: Simplified decay scheme of <sup>108m</sup>Ag. <sup>[2]</sup>



Figure 3: Simplified decay scheme of <sup>110m</sup>Ag. <sup>[2]</sup>



The dominant decay of <sup>110m</sup>Ag is a  $\beta^-$ -decay ( $P(^{110m}Ag_{\beta}^-) = 98.64\%$ ) to <sup>110</sup>Cd accompanied by a cascade of gamma rays with 446, 706, 763, 937, 1384, 884 and 657 keV. The ground state <sup>110</sup>Ag decays via electron capture to <sup>110</sup>Pd or a  $\beta^-$ -decay to <sup>110</sup>Cd. However, these transitions do not add any additional *y*-lines to the <sup>110</sup>Ag spectrum.

However, as mentioned above, the  $\gamma$ -lines of radiosilver are superimposed in the spectrum by other nuclides that are released in larger quantities. Tab. 1 shows the most abundant  $\gamma$ -lines of radiosilver and which radionuclides interfering with them. For this reason, a method was developed that allows silver to be reliably separated from other radionuclides and subsequently measured with minimum time and laboratory effort.<sup>[3]</sup>

Table 1: Interferences caused by other nuclides emitted in case of an accident for radiosilver measurements<sup>[3]</sup>

Radiosilver y-energy [keV]	Major interfering radionuclides, y-energy [keV] (emission			
(emission probability)	probability)			
<sup>108m</sup> Ag: 434 (90.5%)	<sup>137</sup> Cs Compton continuum (Edge: 478)			
<sup>108m</sup> Ag: 614 (89.8%)	<sup>214</sup> Bi: 609 (46.3%); <sup>134</sup> Cs: 604 (97.6%)			
<sup>110m</sup> Ag: 658 (95.6%)	<sup>60</sup> Co Compton continuum (Edge: 922, 1074), <sup>137</sup> Cs: 661 (85.1%)			
<sup>108m</sup> Ag: 723 (90.8%)	<sup>131</sup> I: 723 (1.8%)			
<sup>110m</sup> Ag: 885 (75.0%)	<sup>60</sup> Co Compton continuum (Edge: 922, 1074)			
<sup>110m</sup> Ag: 937 (35.0%)	<sup>214</sup> Bi: 935 (3.2%); <sup>60</sup> Co Compton continuum (Edge: 1074)			

## **1.2.3** Autodeposition of radiosilver

The separation of silver from other interfering radionuclides is achieved by performing an autodeposition reaction. An autodeposition is an electrochemical reaction that occurs when a non-noble metal target is placed in an electrolyte solution of a more noble metal. No external voltage needs to be applied for the reduction of the more noble metal, but the deposition reaction on the base metal sheet takes place voluntarily due to the electrochemical potentials.



Figure 4: Schematic illustration of an autodeposition of silver on a copper strip.

In the present experiment, a copper plate serves as the oxidizing agent and the experiment takes place in ammoniacal solution. Equations (3) + (4) show the corresponding reduction and oxidation reactions and their standard potential  $E^0$ . This results in the total reaction (5):

Reduction:  $Ag(NH_3)_2^+ + e^- \rightarrow Ag\downarrow + 2NH_3$   $E^0 = +0.373 V$  (3)

A-CINCH – Deliverable Page 6 / 55	2 4.3	CINC	
Oxidation:	$Cu + 4NH_3 \rightarrow Cu(NH_3)_4{}^{2+} + 2e^{-}$	$E^0 = -0.050 \text{ V}$	(4)
Redox reaction:	$2[Ag(NH_3)_2]^+ + Cu \rightarrow Cu(NH_3)_4^{2+} + 2Ag\downarrow$	$\Delta E^0 = +0.696 \text{ V}$	(5)

However, since radiosilver is usually present only in trace amounts in the solution, stable silver has to be added to the solution as a carrier. Side reactions of Ag are suppressed with tartrate ( $C_4H_6O_6^{2-}$ ).



## **1.3 Experimental**

## 1.3.1 Execution

The aim of the experiment is to identify the water samples that contain radioactive silver. X samples are to be examined, X of them are contaminated. The contaminated samples come from the Chernobyl cooling ponds and were taken in June 2022.

## Activation solution

Solve 1 g of ammonium sulphate ( $(NH_4)_2SO_4$ ) and 1 g of potassium sodium tartrate tetrahydrate ( $KNaC_4H_4 \cdot 4H_2O$ ) in 49 ml H<sub>2</sub>O and 1 ml 30% NH<sub>3</sub> solution.

## Activation of Cu plate

Remove superficial CuO from the Cu surface by immersion the sheet into the activation solution and stir for 3 min.

## <u>Autodeposition</u>

Spike 20 ml of the sample with stable Ag so that a concentration of  $c(Ag_{stable}) = 1 \text{ mg/l}$  is obtained. Use AgNO<sub>3</sub> ( $M(AgNO_3) = 169.87 \text{ g/mol}$ ; M(Ag) = 107.87 u) for this purpose. Add the spiked solution slowly to the activation solution and stir for 3 h. Cleaning of Cu plate

After 3 h rinse the Cu plate with water and ethanol and dry at 60 °C. <u>Measurement</u>

Measure the sample for 60 min on a HPGe detector.

## 1.3.2 Analysis and interpretation

<u>Task 1</u>

Identify the sample from the cooling ponds from Chernobyl.

<u>Task 2</u>

Assign the lines in the spectrum to the  $\gamma$ -rays of the Ag isotopes. Why are some lines missing?



## 1.4 Literature

- [1] Nucleonica GmbH, "Karlsruhe Nuclide Chart Online," can be found under https://www.nucleonica.com/Application/KNCOPlus.aspx, **2022**.
- [2] L. Ferreux, M.-C. Lépy, M.-M. Bé, H. Isnard, V. Lourenço, *Applied Radiation and Isotopes* **2014**, *87*, 101–106.
- [3] A. Weller, D. Zok, S. Reinhard, S. K. Woche, G. Guggenberger, G. Steinhauser, *Anal. Chem.* **2020**, *92*, 5249–5257.



## 2 EXTRACTION, CHARACTERIZATION AND (SIMS-) ANALYSIS OF HOT PARTICLES FROM THE CEZ

## 2.1 Introduction

Radioactive particles have been released into the environment through various scenarios at different locations. These scenarios include, among others, nuclear weapons tests and reactor accidents (UNSCEAR, 1993). This course is concerned with nuclear fuel particles (so-called "hot particles") from the vicinity of the Chernobyl nuclear reactor accident. These particles were released into the nearby environment during the explosion and fire that lasted several days (Grishanin, 2010) (Bobovnikova, et al., 1991). However, smallest particles were also distributed all over Europe (Pöllänen, et al., 1997) (Schubert, et al., 1987) (Devell, et al., 1986). Hot particles consist of the original nuclear fuel and include uranium, plutonium, fission and breeding products (Kashparov, et al., 2019) (Walther, et al., 2013) (Kalmykov, et al., 2011). Particular attention is paid to americium, as the fraction in the particles increases due to the decay of plutonium. Cesium is also an important nuclide, as it is easily soluble and thus mobile. It can leach from the particles and thus become accessible to plants and animals (Kashparov, et al., 2020) (Salbu, et al., 2018).

## 2.2 Release from hot particles

Hot particles weather due to various environmental factors such as rain, UV radiation, or long time in water, like the particles from the reactor cooling pond. Knowing this dissolution behavior and the extent of nuclide release from these particles is important (Kashparov, et al., 2020). If the particles are released by, for example, the drying of the cooling pond, or if storms or forest fires occur that resuspend the particles, contamination of other areas may occur and the hot particles would no longer be a localized problem. Thus, these radioactive particles pose an ongoing threat to humans and the environment.

Hot Particles exist not only in the CEZ (Chernobyl Exclusion Zone), but also in other regions of the world. Accidents also happened in some other nuclear power plants. For example, there was an explosion in Dounreay (Scotland) and even today fuel particles can be found on the beach (Dennis, et al., 2007) (Byrnes, et al., 2020). Furthermore, not only nuclear accidents are the cause of particles, but also, for example, nuclear weapons explosions or, for example, in the accident of the bomber in Palomares, which was equipped with nuclear weapons, particles containing uranium and plutonium entered the environment (Lind, et al., 2006). Furthermore, ammunition with depleted uranium was used in the second Gulf War, so that particles containing uranium were also distributed in the environment (Salbu, et al., 2003).

## **2.3** Effect on the human body

In addition to the risk of soluble radionuclides entering the soil and being absorbed by plants, which would add them to the food cycle, there is also the risk of direct ingestion or inhalation of the particles. If the particles are absorbed into the body by ingestion, the direct uptake of cesium is less than with dissolved cesium, but there is still a risk that a particle will become lodged in the stomach/intestine, leading to a high local dose. Much greater is the danger that can be posed by inhaled particles. Firstly, the lung tissue receives a considerable local dose, especially if the particles



contain alpha emitters. Secondly, due to the possible long residence time in the human body, there is a risk that the particle will slowly dissolve in the body fluids, releasing, among other things, cesium (Yoschenko, et al., 2009).

## 2.4 Microscale characterization - also in the context of disposal research

Accurate characterization at the micrometer scale can also be useful in the context of spent nuclear fuel disposal. Local effects can be studied. In addition, accurate measurements with low total activity can be performed on the smallest fragments of spent nuclear fuel, thus greatly simplifying handling. The results provide information on the corrosion and leaching behavior of spent nuclear fuel and thus help to answer relevant safety questions in final disposal. In addition, these particles are aged under authentic conditions in the reactor and the environment. Fission gases or other fission and breeder products produced in the reactor may cause the properties of used fuel to differ from those of unused fuel (Forsyth, et al., 1992). The pores found in sintered uranium dioxide fuel rods may increase as a result, leading to an increase in surface area and where the particles may lose stability (Rest, et al., 2019) (Kashparov, et al., 2000).

## 2.5 Particle analysis at IRS: physical methods

In order to analyze the dissolution behavior of the particles in more detail, various methods have already been carried out. For this purpose, the particles were first glued individually onto tungsten needles in order to be able to examine them individually and without a background. (Paper has been submitted.)

EDX measurements are first performed on the particles to obtain information on a rough elemental composition. From the mapping of the EDX signal, the element distribution on the surface of the particles can be determined. This allows irregularities in, for example, zirconium distribution to be detected. Surface contaminations by e.g. iron or sulfur can also be detected. These could also have an influence on the stability and dissolution behavior of the particles. Gamma spectrometric investigations can be used to determine the proportions and activities of <sup>137</sup>Cs, <sup>241</sup>Am and, in some cases, <sup>154</sup>Eu. These are fission and breeding products that are particularly relevant in the environment.

Other analytical methods at IRS include SIMS and rL-SNMS. These can be used to determine isotope ratios of various elements. In particular, uranium and plutonium isotopes are considered, since the burnup of particles can be determined from their isotopic ratios (Raiwa, et al., 2022). Due to the slightly inhomogeneous neutron fluxes within the reactor, each particle has a slightly different burnup. This can also provide conclusions about the formation of the particles and the operation of the reactor.

## 2.6 Practice tasks

We have to start with material, in which we expect particles to be in. In our case it will be sieved soil (< 63 micron) from Kopachi, a region in the nearer vicinity of the Chernobyl NPP.

We have to do a process called 'flotation', where we use the heavy density of nuclear fuel in order to distinguish between the hot particles we actually want and the many other particles soil is



containing.

We use a poly tungsten solution (polytungstate  $Na_6[H_2W_{12}O_{40} \text{ solution})$  with a density of around 3 g.cm<sup>-3</sup>. The particles are way denser at or higher than 9 g.cm<sup>-3</sup> and sink to the bottom of the solution. We enhance this process by using a centrifuge.

At first, we have to add our material to the polytungstate solution (a). Just like Laura is doing it in the video (click)

In order to get everything mixed, we use an ultra-sonic bath. This should get rid of any clumps too (b).

We have to centrifuge the solution. The denser part will sink to the bottom, and the other, not interesting lighter rest will float (c).

Liquid nitrogen is used to decant the lighter fraction. The frozen, heavier bottom part will stay in the vessel and can be poured out later (d).



The obtained fraction can be filtered and the solid remains on the filter paper is what we are now after:

A-CINCH – Deliverable 4.3 Page 12 / 55







#### We now have to localize the particles even further.

If our starting soil contained any particles, they should be on the filter paper now. In order to find them on the paper, we use a Geiger counter with a small window, just like Laura does in this video (click)

If material with higher count rate is found, it needs to be separated as much as possible. We do that by carefully scraping it of the filter paper, and then iteratively divide the material in two 'piles', look for our activity, divide the material....

Until we have as little material as possible left. This will be transferred on adhesive carbon tape on aluminum stubs.

How it should look vs how it should not. You can guess.



We also have an asphalt drill core from the market place in Pripyat, the town nearest to the NPP. Here the whole sample preparation is a little easier. We just scrape material of the top. The separation in to 'piles' is done just the same.

The aluminum stubs can now be analyzed in the scanning electron microscope (SEM).

# The search for the micrometer-sized particles would certainly be almost impossible without scanning electron microscope (SEM).

With the SEM, not only can surface structures in the sub-micrometer range, but also to draw conclusions about the composition of the sample. For this purpose, the backscattered electrons, or resulting X-rays are analyzed. The following section deals with how this important tool works.

The heart of the SEM is the incandescent cathode, which, similar to an incandescent lamp, consists of a tungsten wire. When a current flows through the cathode, electrons are thermionically emitted and accelerated by a high voltage of up to 30 kV. During the acceleration the beam is expanded and refocused several times by different magnetic optics before they are rastered over the sample in a highly focused manner. This steering is done by strong electric fields. When this thinly focused beam hits the sample the sample, various secondary effects are triggered, which will be highlighted



individually in the next section. At the IRS, a SEM of the model xI30 from RemX is used, which is equipped with three detectors, each for a different secondary effect.

#### Secondary electrons - SE mode

Secondary electrons (SE) are the electrons released by the primary electrons of the cathode from the atomic shells of the upper layers of the sample material. Since the depth of origin is only a few nanometers, a surface image can be generated here. These electrons have an energy of up to 50 eV and can therefore not penetrate from deeper layers to the detector. The secondary electrons, which are detected, have different angles and distances and are partially shielded in the height profile of the sample. This produces a signal from which a topography contrast can be generated in the image can be generated.

#### Back-scattering-electrons - BSE mode

Back scattered electrons are electrons of the primary electron beam, which are scattered back in the sample with approximately scattered. These energies are significantly higher compared to the SE, which is why they can also be detected from deeper sample layers. The probability of backscattering is higher at high electron densities, which are found in particular in elements with a high atomic number. In the signal image, material appears bright, while material with a lower atomic number remains dark. A topography contrast is not visible in this measuring mode, but it is possible to search for particles, since the contrast between uranium with 82 electrons and the carbon of the tape with 12 and the carbon of the tape (on which the sample is transferred into the SEM) with twelve is particularly high.

#### **Energy dispersive x-ray spectroscopy**

Characteristic X-rays are produced when a primary electron ionizes an atom, i.e. an electron is released from the shell. If an electron from a higher energy level moves in energy level, the difference in the binding energies is released in the form of a characteristic X-ray photon, which is measured by the detector. Here, Energy Dispersive X-ray spectroscopy (EDX) is used to determine the energy of the photons and to assign it to the emitting elements. If particles with a high BSE signal are found, they are first measured with EDX in order to exclude that it is other material with high electron density, such as tungsten, is involved. Also, for subsequent analyses of the particles, such as mappings, where EDX is used, this methodology is very important.

### We have to scan the whole sample part for part in to find the hot particles.

Keep an eye out for this picture:





This is a picture from the BSE mode. In the bottom right corner. Can you see it?

More BSE -> higher density. Could be uranium. We have to do EDX to make sure that it isn't just iron or another dense material.

If it is actually uranium, we can go on to the next stage of the process.

#### **Extracting the particle**

We want to get it onto a tungsten needle, which we are producing in house.

We have a very fine micromanipulator in our SEM, which can maneuver our needle very precisely. It looks like this:



You can see here, how we will extract the particle. The view on the SEM picture looks something like this:





Here we actually reextracted a particle from another needle, because the connection to the glue was not strong enough on the first one.

The actual process will be explained in detail in the lab, as it is very specific. You just have to do or see it yourself, to get an idea of it.

If everything works like we want it to, we can take the needle out of the SEM and put it into the in house made needle holder. Congratulations, you now have a particle on a needle!



**ToF-SIMS** measurements

The particles are now ready for ToF-SIMS measurements. With these we want to measure the composition of the particles. In particular the lateral composition of the first three atomic layers on scales below 100 nanometers. The usual measurement procedure only removes the smallest portions of the of the sample surface and is thus considered to be quasi-nondestructive.





The top layers of the sample are removed with the primary beam. Partially the particles are ionized and can thus be 'sucked off' by the extractor and accelerated into the ToF analyzer.

Using the time of flight of the respective particle to the detector, the ratio of mass and charge (m/z) can be determined.

For our Hands-on Training, the resulting mass spectrum is the most important result, even if the method can do much more, such as spatially resolved signal evaluation and also depth profiles can be offered. The ratio of uranium-236 to uranium-238 is used to infer the burnup of the particles, the length of time they have been exposed to the neutron flux in the reactor.

In addition, there is the possibility to extend the setup to include resonant laser - secondary-neutral particle mass spectrometry (rL-SNMS), in which selected neutral particles are excited with a laser system to analyze certain elements and suppress others. For example, plutonium can be measured, although it is isobarically masked by uranium.

$$B = \frac{\rho_{238}}{\rho_{236}} \frac{1}{4180}^{-\frac{1}{0,817}}$$

This is the approximate formula we use for the burnup.  $\rho$  are the counts for each isotope.



# PART 2: MANUALS FOR PRACTICAL TASKS DEVELOPED BY JSI



## **1** INTRODUCTION

Uranium was discovered as a chemical element in pitchblende specimen. Its chemical composition is largely uraninite –  $UO_2$ , but due to oxidation it contains also  $U_3O_8$ . It is named after the planet Uranus, which is the Greek deity of the Heavens. Uranium compounds have been used as colorants since Roman times for ceramics and glasses. In 1896 Henry Becquerel discovered that uranium emits penetrating rays. In 1939 Hahn and Strassman discovered nuclear fission.

Uranium is a naturally occurring element, found in rocks, soils and natural waters. The earth's crust contains 3 - 4 parts per million of uranium. About 200 minerals contain uranium as an essential component. Deposits, being of economic value, can occur in igneous, metamorphic and sedimentary environments.

Uranium occurs in highly immobile reduced state U(IV), more soluble and mobile U(VI) state and rarely in U(V) state. Salts of many oxidation states of uranium are water-soluble. The most common ionic forms are  $U^{3+}$ ,  $U^{4+}$ , the unstable  $UO^{2+}$  and  $UO_2^{2+}$ . Uranium occurs in solution in four oxidation states, +III to +VI, with +IV and + VI being the most stable ones. Uranium +V and +VI hydrolize and form uranyl species  $UO^{2+}$ , which is unstable, and  $UO_2^{2+}$ .

Uranium forms strong complexes with ligands that contain free electron pairs. The most important uranium complexes in natural waters are formed with carbonate, in acidic waters also with sulphate, phosphate and fluoride ions. Uranium forms numerous complexes with organic molecules; the most notable example is tributylphosphate, which forms complexes with U(IV) and U(VI), but not with U(III) and U(V).

There are three naturally occurring uranium isotopes: <sup>234</sup>U, <sup>235</sup>U and <sup>238</sup>U. Besides those three isotopes, there are three artificial isotopes: <sup>232</sup>U, <sup>233</sup>U and <sup>236</sup>U. The middle one, <sup>233</sup>U is a fissile isotope of uranium that is bred from <sup>232</sup>Th as part of the thorium fuel cycle. In the reactor, <sup>232</sup>Th is transmuted into the fissile artificial <sup>233</sup>U. The third one, <sup>236</sup>U is formed by capture of one neutron by <sup>235</sup>U atom. And the first one with the shortest half-life, <sup>232</sup>U is formed when <sup>233</sup>U atom captures one neutron, followed by emission of two neutrons.

Enriched uranium is a type of uranium in which the content of <sup>235</sup>U has been increased through the process of isotope separation. Natural uranium contains about 99% of <sup>238</sup>U isotope, with <sup>235</sup>U only constituting about 0.7% of its mass.

Depleted uranium is uranium with a lower content of the fissile isotope  $^{235}$ U than in natural uranium. It contains 0.3% of  $^{235}$ U or less.

Uranium is both chemically and radiologically toxic substance. The main effect associated with its exposure is kidney toxicity caused by breathing air containing uranium dusts or by eating substances containing uranium. Intake of about 100 mg of uranium can cause acute kidney failure and death; intake of about 30 mg can cause damage; at lower intake levels, the kidney repairs itself.

The radiation hazard from uranium occurs when its compounds are ingested or inhaled, as the main damage is induced by  $\alpha$  particles that have little penetrating ability. The primary radiation health effect of concern is increased probability of the exposed individual to develop cancer during the lifetime.

Uranium can be determined by numerous analytical methods, depending on its expected concentration range, matrix, required measurement uncertainty, availability of particular method, etc.



The available methods include chemical techniques such as volumetric and gravimetric determination for higher concentration ranges, spectrometric techniques and nuclear techniques.

In many applications, it is important to know not only the uranium content but also concentrations of its particular isotopes. In such instances, isotope-specific techniques such as mass spectrometric or nuclear methods should be applied. This is also of great importance in forensic studies where uranium isotopic composition can tell us more about its sources, and processing.

In the next chapters two methods on how to determine uranium isotopes in different samples are presented. One method is mass spectrometric and utilizes multicolector inductively coupled plasma mass spectrometry (MC-ICP-MS) and the other is radiometric where alpha-particle spectrometry is used.



## **2** DETERMINATION OF U ISOTOPE RATIOS BY MC-ICP-MS

To acquire highly accurate results on uranium isotope ratios, mass spectrometric methods are utilized. Here is presented determination of uranium isotope ratios by MC-ICP-MS. Advantage of MC-ICP-MS to single collector ICP-MS is that uranium isotopes are measured simultaneously on multiple detectors, which significantly increases accuracy of the results. This is of crucial importance for forensic studies as small deviations in uranium isotopic composition can be detected accurately. Next chapters are describing details about using such method, which requires appropriate sample pre-treatment, separation of uranium from interfering matrix elements, determination of uranium concentration in the sample by ICP-MS and determination of uranium isotopic ratios by MC-ICP-MS.

## 2.1 Apparatus, reagents and materials

- 1. furnace
- 2. ceramic crucible
- 3. tweezers
- 4. fume hood
- 5. 250mL glass beakers
- 6. concentrated HNO<sub>3</sub>
- 7. H<sub>2</sub>O<sub>2</sub>, 30 %
- 8. Pasteur plastic pipettes
- 9. hot plate
- 10. 0.45µm size syringe filter
- 11. 10mL plastic syringe
- 12. 50mL plastic centrifuge tube
- 13. ultrasonic bath
- 14. 2mL plastic columns
- 15. column rack
- 16. UTEVA Resin, 100-150 μm
- 17. deionized water
- 18. 3M HNO3
- 19. 6M HNO3
- 20. 9M HCl
- 21. 5M HCl / 0.05M oxalic acid
- 22. 1M HCl
- 23. 2% HNO<sub>3</sub>
- 24. 10 mL plastic vials
- 25. U standard solution (U ICP-MS standard)



- 26. Adjustable volumetric pipettes
- 27. Pipette tips
- 28. ICP-MS (Agilent 8800)
- 29. MC-ICP-MS (Plasma II, Nu Instruments)
- 30. natural U standard solution with known isotopic composition (IRMM-184)

## 2.2 Sample ashing

Swipe sample contain clean cotton tissue, which we remove from the sample by ashing.

- 1. Put swipe sample in ceramic crucible and put in a high temperature furnace for ashing, to remove organic matter from the swipe sample.
- 2. Set the oven temperature to 650 °C and ash the sample for 24 h. Raise temperature incrementally to prevent ignition of the sample.
- 3. Next day put sample out from the oven and leave it to cool down. Sample is now ready for wet acid digestion.

## 2.3 Acid digestion

- 1. Transfer sample from ceramic crucible to glass beaker with 10 mL of concentrated  $HNO_3$  and put it on the hot plate.
- 2. When the sample is warm, add 1 mL of  $H_2O_2$  for better digestion and wait until it evaporates to dryness.
- 3. Then add another 5 mL of concentrated HNO $_3$  and 1 mL of H $_2O_2$  and again evaporate until dryness.
- 4. Leave the sample to cool down.
- 5. Dissolve it with 5 mL of 3M HNO<sub>3</sub>. Place it in ultrasonic bath to speed up dissolution.
- 6. Filter sample through  $0.45\mu m$  pore size filter into 50mL centrifuge tube to remove any undigested residue from the sample.

## 2.4 Separation of uranium on UTEVA column

- 1. To reduce procedural blank, soak UTEVA resin in 6M HNO<sub>3</sub> and leave it overnight.
- 2. Next day, pack 2 mL of the resin in plastic column and place 250mL beaker under the column.
- 3. Wash the resin with 10 mL of deionized water, to rinse soaking solution.
- 4. Condition resin with addition of 10 mL of 3M HNO<sub>3</sub>. Once this solution pass through, the column is conditioned and ready to be used for separations.
- 5. Pour the sample from chapter 2.3, point 6 on the column.
- 6. When the sample pass through, rinse the beaker with 5 mL of 3M HNO<sub>3</sub> in total and transfer the solution on the column. It is more efficient to rinse it more times with smaller volume.
- 7. Add additional 20 mL of 3M HNO<sub>3</sub> on the column. With this we remove interferences not retained by UTEVA in 3M HNO<sub>3</sub>.



- 8. Once the solution pass through, convert UTEVA column to HCl media by adding 2 mL of 9M HCl.
- 9. When this pass through, elute Th by adding 20 mL of 5M HCl / 0.05M oxalic acid.
- 10. Discard all eluents collected until now.
- 11. Place clean glass beaker for collection of eluted uranium.
- 12. Elute uranium by addition of 15 mL of 1M HCl.
- 13. Place glass beaker with uranium eluate on hot plate and leave it to evaporate until dryness.
- 14. When dry, add 1 mL of concentrated  $HNO_3$  and few drops of  $H_2O_2$  to destroy organic residues from the resin and again evaporate until dryness.
- 15. Repeat step 14 two more times.
- 16. Leave the sample to cool down.
- 17. Add 3 mL of 2% HNO<sub>3</sub> and place sample in ultrasonic bath to speed up dissolution.
- 18. Transfer sample to 10mL vial.
- 19. Rinse the beaker with 2% HNO<sub>3</sub> to reach in total 10 mL in the vial. Now, the sample is ready for the measurements.

## 2.5 Uranium measurements with ICP-MS

Before we start with U sample measurements, we need to prepare calibration curve. We will prepare 9 different U concentrations to cover range from 0 to 500 ng/mL:

- 1. First pipet 5 mL of U ICP-MS standard solution with concentration 1000 ng/mL and dilute it to 10 mL with 2 % HNO<sub>3</sub> to get solution with 500 ng/mL of U.
- 2. Then pipet 2.5 mL of 1000 ng/mL U solution and dilute it to 10 mL with 2% HNO $_3$  to get 250 ng/mL U solution.
- 3. Pipet 1 mL of 1000 ng/mL U solution and dilute it to 10 mL with 2% HNO $_3$  to get 100 ng/mL U solution.
- 4. Next pipet 0.5 mL of 1000 ng/mL U solution and dilute it to 10 mL with 2% HNO<sub>3</sub> to get 50 ng/mL U solution.
- 5. To get 10 ng/mL U solution, pipet 1 mL of previously prepared 100 ng/mL U solution and dilute it to 10 mL with 2% HNO<sub>3</sub>.
- 6. Then, pipet 0.5 mL of 100 ng/mL prepared U solution and dilute it to 10 mL 2% HNO $_3$  to get 5 ng/mL U solution.
- 7. Next, pipet 1 mL of previously prepared 10 ng/mL U solution and dilute it to 10 mL with 2% HNO<sub>3</sub> to get 1 ng/mL U solution.
- 8. Then, pipet 0.5 mL of 10 ng/mL prepared U solution and dilute it to 10 mL with 2%  $HNO_3$  to get 0.5 ng/mL U solution.
- 9. For 0 ng/mL U solution, add 10 mL of 2% HNO<sub>3</sub> to the vial.



10. If expected U concentration in samples is out of calibration range 0 to 500 ng/mL, dilute them with 2 % HNO<sub>3</sub> that expected U concentration is in the calibration range. Now we are ready to start U sample concentration measurements.

Then we are ready to start with ICP-MS measurements:

- 11. Manually switch on the plasma chiller.
- 12. Then, visually check the position of lenses, cones, torch and nebulizer.
- 13. Inspect tubing and secure tubes for the sample and for the waste in the proper position on the peristaltic pump.
- 14. Check if the waste container is empty and if there is enough rinse and acid solutions in the containers.
- 15. Start the plasma on the mass spectrometry software and follow the warm-up procedure.
- 16. After warm-up, select appropriate U measurement protocol and perform the instrument tuning.
- 17. Prepare a sample list sequence by first adding block of rinses, then calibration curve standard solutions, additional block of rinses, U samples and at the end again some rinses for washing the instrument.
- 18. Then place calibration curve standards and U samples on the autosampler. Be careful that the position on sample list sequence matches the real position of samples on autosampler.
- 19. Start the measurement. On a computer program, we can follow how the results are being acquired.
- 20. Once the measurement is completed, the results are automatically processed and U concentrations in our sample are presented in the excel table.
- 21. Stop the plasma on the software, release tubes at the peristaltic pump and turn off the water chiller.

## 2.6 Measurements of U isotope ratios on MC-ICP-MS

Switching on MC-ICP-MS:

- 1. Set up glassware and cones for dry plasma. To access the cones and torch, press the button to open the hood.
- 2. On the instrument software click on the Retract button. The torch box will move back, to get access to the sampling and skimmer cones.
- 3. Place the skimmer cone with a special tool into its position, carefully, not to damage the tip of the cone.
- 4. Now place a graphite sealing gasket and after that the sampling cone.
- 5. Set back the torch box to its original position to set up a torch, by clicking on the Set button on the computer.
- 6. Place the torch to its position with the help of clamps, attach the two gas supply fittings and restraint it with the torch clamp.



- 7. Visually check the position of the torch and when you are satisfied with the position, close the hood.
- 8. Manually switch on the plasma chiller, the RF generator, Ar gas supply for desolvator and the desolvator.
- 9. Then click on Start button in the Plasma Control window to initiate the plasma start-up. This procedure goes through the start-up sequence automatically.
- 10. Once the plasma is lit, it is recommended to wait at least 1 h for instrument to warm up before starting the optimization process.



#### Tuning of MC-ICP-MS:

- 11. Adjust U concentration in natural U standard solution with known isotopic composition with 2 % HNO<sub>3</sub> to a concentration of 5 ng/mL.
- 12. After the instrument is warmed up, start with the tuning procedure. Place the prepared U standard solution on the autosampler and start with aspiration.
- 13. At the beginning, set quad values to the correct element. Go to Setup, click on Quad values, select U in the periodic table, and click on Use to confirm it.
- 14. Open the Magnet scans window to find the beam. Select the collector on which you want to scan over the peak of the most abundant U isotope.
- 15. Then you set a mass scan region to observe this peak by clicking on edit scan and entering appropriate masses. At the end, save new values.
- 16. Set the magnet to the center of the peak, by stopping the magnet scan and moving the cursor to the center of the peak with the right mouse click. Click on a Set magnet and the magnet is now set at this fixed position.
- 17. Next is to optimize the torch position. The aim is to establish the position at which the maximum beam intensity can be observed. Move the torch Back/Forward, In/Out, and Up/Down and monitor the signal intensity. Set the torch to its optimum position for maximum intensity.
- 18. To stabilize and increase the beam intensity, adjust the nebulizer pressure and flowrate of sweep gas on desolvator.
- 19. To tune cones, first, second, and transfer lenses, go to the Deflectors and High Voltages window on software and select the High Voltage tab. Adjust HV values either up or down until the maximum beam intensity is achieved.
- 20. When the HV parameters are tuned, change to the Source tab and tune the Source voltages and the Transfer voltages. Each lens setting is adjusted until maximum beam intensity has been achieved.
- 21. The instrument is now tuned to maximum beam intensity.
- 22. When the tuning of the parameters is complete, go back to the Magnet Scans window and click on Restore Range. The magnet will start scanning between the Start and Stop Scan values.
- 23. Go to the Deflector and High Voltages window and select Quads.
- 24. Firstly, adjust Quad 1 value, by changing the Quad 1 voltage up and down to achieve a symmetric peak shape with steep increase from both sides and a top as flat as possible.
- 25. Now align all the U peaks in the selected collector buckets. Scan over the peaks and adjust the scale that all peaks are displayed with similar heights by clicking on the Autoscale button.
- 26. To bring them aligned, adjust the Quad 2 Value, which affects the dispersion. Once the Quad 2 value has been adjusted, the Quad 1 value has to be re-optimized by regulating the Linked Quads values. You are finished when you set peaks to the optimized value to achieve the best possible alignment.



Sample measurement by MC-ICP-MS:

- 27. Adjust U concentration in sample solution to appropriate dilution factor with 2 % HNO<sub>3</sub> for the U isotope measurement by MC-ICP-MS. U sample solution needs to be in the same concentration as U standard solution.
- 28. Place U sample solution and U standard solution on the autosampler.
- 29. Then go to Analysis and open New Method. Here select collectors on which you tuned your measured element. Click on Next and write down the appropriate mass for the most abundant isotope, where the center of the peak is and press Enter. Double click on the most abundant isotope to perform the peak center routine. Then you define the integration time for measuring the zero value and for sample measurement, Measurement per block, Number of blocks, and Magnet delay time. You can use numbers from a routine U method that was written by manufacturers. Click on the Save button and save the file.
- 30. Now create a file with the same name, using the NICE editor for the calculation of U isotope ratios from the measured data. Go to Utilities and open NICE Editor. Here we can write an analysis program for your measurements and where data can be manipulated to subtract zeros from all data acquired, perform mass bias correction and set up ratios or outputs. Save your File and then Compile your Project.
- 31. In the end, go to Analysis and open the Automatic sequence. Here select, write or check your sample Position Type, Position, Sample Name, Analysis Method, and Wash time.
- 32. Write your sequence for U measurement in proper order. First, you need to measure U standard solution, next U sample solution and the end again U standard solution. Start the measurement by pressing play.
- 33. On a computer program, you can follow how the measurement is being acquired.
- 34. Once the measurement is finished, the results are automatically processed as specified in file created in NICE editor and are presented in the excel table.
- 35. Switch off the instrument by pressing the STOP button in the Plasma Control window.
- 36. Manually turn off Ar gas supply for desolvator and the desolvator, the RF generator and the plasma chiller.



## **3 ALPHA SPECTROMETRY OF URANIUM ISOTOPES**

Alpha particle spectrometry is method, which allows us to determine uranium isotopes in different samples. It detects alpha particles emitted during decay of uranium isotopes. It can be used for various samples but it requires laborious sample pre-treatment, which normally involves either pre-concentration or digestion of samples, then separation of uranium from other interfering radionuclides, preparation of counting source and measurement using alpha particle spectrometry system, which is equipped with passivated planar implanted silicon (PIPS) semiconductor detectors. In the following chapters, procedure for determination of uranium isotopes in water is presented in detail.

## 3.1 Apparatus, reagents and materials

- 1. fume hood
- 2. 5L sampling container
- 3. filtration unit
- 4. 0.45 μm filter
- 5. source of vacuum (water pump or vacuum pump)
- 6. concentrated HNO<sub>3</sub>
- 7. pH indicator paper
- 8. deionized water
- 9. 1L glass beaker
- 10. stirring and heating block
- 11. magnetic stirrer
- 12. working solution of <sup>232</sup>U tracer, 0.3 Bq/mL
- 13. 1L volumetric cylinder
- 14. 0.1 1mL volumetric pipette
- 15. plastic Pasteur pipettes
- 16. analytical balance
- 17. precise balance
- 18. Fe<sup>3+</sup> solution, 5 mg/mL
- 19. NH4OH (25 %)
- 20. 50mL centrifuge tube
- 21. Centrifuge
- 22. 3M HNO3 / 1M AI(NO)3
- 23. ultrasonic bath
- 24. 2mL plastic columns, BIORAD
- 25. column rack



- 26. UTEVA Resin, 100-150 μm
- 27. 3 M HNO<sub>3</sub>
- 28. Nd<sup>3+</sup>, 0.5 mg/mL
- 29. TiCl<sub>3</sub>, 15%
- 30. concentrated HF
- 31. 0.1mL volumetric pipette
- 32. ice bath
- 33. polysulfone membrane filter disc (0.1 µm)
- 34. NdF<sub>3</sub> substrate, 10  $\mu$ g/mL
- 35. 0.58M HF
- 36. Al disc
- 37. glue with water-based solvent
- 38. heating lamp
- 39. plastic container for storage of prepared counting source
- 40. alpha spectrometry system with PIPS detectors

## 3.2 Water sampling and pre-treatment

Sampling of water is the first step, which you will take once you will conduct any analysis of radionuclides in water. Depending on your problem, you might sample rainwater, river water, seawater, ground water, pore water, tap water, bottled water or other kind of waters.

First thing, which you have to consider when sampling water is that your sampling is representative to your problem or to what you want to answer. For instance, if you are interested in monthly precipitation, you should sample for the whole month, but if you are interested in one rain event, sampling for longer period could spoil your sample.

In general, we are dividing sampling on discrete events that means we take sample one time in short period of the time or continuous over longer period of the time. Sometimes we are interested also in sub-sampling of continuous sampling. This means that we take some of the sample in pre-defined time intervals during continuous sampling for separate analysis.

Depending of your sampling strategy, you might have different sampling equipment for continuous sampling, or just collect sample in your container for discrete sampling.

Independently of the sampling strategy, you need to assure that you collect the sample in clean container. For most of the time we are using HDPE containers, but other types of material like glass of teflon might be also in use. For new containers it is usually sufficient to rinse them three times with deionized water. To ensure that the containers are not contaminated it is the best to fill them up with deionised water of milli Q quality with no radionuclide of interest present and then to analyse this water as regular samples. If we found out contamination, we might try to acid-clean the containers using HCl or HNO<sub>3</sub> or if this does not help we might try to using containers from another producer or batch.



Once we are sure that our containers are clean, we are ready to go to collect the sample. In our case the sample will be tap water from our laboratory:

- 1. First open the tap and wait for some time that some water passes through. If you are sampling tap water on the field, we have to assure that we are sampling from the tap, which is regularly in use in order that we get representative sample.
- 2. Fill up the container to the top and then close it tightly. Collect enough sample for all planned analyses.

First step after sampling is sample filtration. Even if it looks like that our sample is transparent with no suspended solids, often we are surprized on the amount of undissolved solids in it once we filter it. Therefore, filtration step is very important. For some applications we may not want to filter our sample, for instance if we want to determine dose from drinking water since usually nobody filter drinking water through 0.45  $\mu$ m pore size filter before drinking it.

But we have to be careful with this because undissolved solids might cause problems during different analysis steps. Sample is filtered following these steps:

- 1. Connect sample collecting flask with filter support with frit where we will place the filter and filtration funnel, which is attached to the filter support.
- 2. Place polysulfone filter with 0.45  $\mu$ m pore size on the filter support.
- 3. Wet the filter with deionized water and then attach filtration funnel.
- 4. Connect receiving flask to source of vacuum and apply vacuum to the filtration system.
- 5. Check for leaks of the filtration system.
- 6. Pour the sample on the filtration funnel and wait that it is filtered.
- 7. Repeat step 6 until you fill up the collecting flask with filtered sample.
- 8. Detach filtering flask from the vacuum line and transfer filtered sample to clean HDPE container.
- 9. Repeat steps 6.-8. to filter all sample.
- 10. Acidify sample with adding 3 mL of conc. HNO3 per litre of sample.
- 11. After acid addition, cap the sample and shake it thoroughly.
- 12. Check pH of the sample with pH indicator paper.
- 13. If pH is not 1-2, repeat steps 10-12.
- 14. Store sample for next steps.

## 3.3 Taking water aliquot and addition of U-232 tracer

- 1. Shake water sample, which is filtered and acidified.
- 2. Take 0.9 L of the sample with volumetric cylinder.
- 3. Then transfer the sample to the beaker with inserted magnetic stirrer.
- 4. Start stirring of sample with magnetic stirrer.
- 5. Next add 0.1 mL of U-232 working solution as a tracer and equilibrate it with the sample by stirring it for couple of hours. Tracer is needed in order to trace chemical recovery of our



procedure. The added activity of the tracer should be similar to the activity of uranium expected in the sample.

## 3.4 Sample pre-concentration

- 1. Heat the sample to 40-50 °C in order to speed up precipitation.
- 2. To change pH of the sample from acidic to alkaline, add ammonia solution. The amount added depend on the initial sample acidity. Start with adding 4 mL and wait that this addition is mixed with sample.
- 3. Then check pH with pH indicator paper. The pH should be 10-11. If it is not, repeat step 2.
- 4. Once pH is alkaline, add 1 mL of Fe<sup>3+</sup> solution. Iron hydroxide precipitate starts to form.
- 5. Continue to stir and heat the sample for 1h, then switch off the heating and stir for another 3h. This will allow sufficient time for co-precipitation of radionuclides on iron hydroxide.
- 6. Remove stirring magnet, cover the sample and leave it overnight to settle precipitate to the bottom.
- 7. Next day decant overlying solution and discard it either by water pump or by decantation.
- 8. Transfer precipitate with the solution in the centrifuge tube.
- 9. Rinse the beaker three times with deionized water.
- 10. Centrifuge it for 5 min at 3000 rpm to be able to remove remaining solution.
- 11. After centrifugation decant the solution.
- 12. Add more deionized water to wash the precipitate and change pH to neutral.
- 13. Repeat centrifugation.
- 14. Check if the pH of the solution above the precipitate is neutral. If it is not, repeat from step 12.
- 15. Once the pH is neutral, decant the solution and proceed with the next step.
- 16. Dissolve precipitate by adding 10 mL of 3M HNO<sub>3</sub> / 1M Al(NO)<sub>3</sub>.
- 17. After addition shake the sample and place it in ultrasonic bath to speed up dissolution.
- 18. After end you should get clear solution ready for further analysis steps.

## 3.5 Separation of uranium on UTEVA column

- 1. Pack 2 mL of the UTEVA resin in plastic column and place 250mL beaker under the column.
- 2. Condition resin with addition of 10 mL of 3M HNO<sub>3</sub>. Once this solution pass through, the column is conditioned and ready to be used for separations.
- 3. Pour the sample from chapter 3.4, point 18 on the column.
- 4. When the sample pass through, rinse the beaker with 5 mL of 3M HNO<sub>3</sub> in total and transfer the solution on the column. It is more efficient to rinse it more times with smaller volume.
- 5. Add additional 20 mL of 3M  $HNO_3$  on the column. With this we remove interferences not retained by UTEVA in 3M  $HNO_3$ .



- 6. Once the solution pass through, convert UTEVA column to HCl media by adding 2 mL of 9M HCl.
- 7. When this pass through, elute Th by adding 20 mL of 5M HCl / 0.05M oxalic acid.
- 8. Discard all eluents collected until now.
- 9. Place clean glass beaker for collection of eluted uranium.
- 10. Elute uranium by addition of 15 mL of 1M HCl.

## **3.6** Preparation of counting source

- 1. Add 0.1 mL of 0.5 mg/mL of Nd<sup>3+</sup> solution to uranium eluate and stir the sample.
- 2. Add 1 mL of 15 % of TiCl $_3$  to reduce uranium and stir the sample. You should observe the color changed to violet.
- 3. Finally, you add source of F to precipitate  $NdF_3$  by adding 1 mL of concentrated HF acid and stir the sample.
- 4. To enhance precipitation, put the sample in ice bath for 30 min.
- 5. Assemble filtration unit for filtration of micro-coprecipitate and attach it to source of vacuum (water pump or vacuum pump).
- 6. Wet filter support part with deionized water, place  $0.1\mu m$  filter on it and attach filtration funnel.
- 7. Test for leakage between filtration funnel and filter support part by adding deionized water and applying vacuum.
- 8. Add 10 mL of  $NdF_3$  substrate. Add it on the walls of the filtration funnel and not directly on the filter that we don't disturb precipitate on the filter.
- 9. Take uranium sample, which is micro-co-precipitated with NdF<sub>3</sub> from the ice bath. Place it for 1 min in ultrasonic bath to destroy possible large precipitate aggregates and to detach precipitate from the walls of the centrifuge tube.
- 10. Pour the sample on the walls of the filtration funnel and wait until solution passes through the filter.
- 11. Rinse centrifuge tube with 2 mL of 0.58M HF and put it for 1 min in ultrasonic bath prior pouring on the filter. Repeat this step one more time.
- 12. Repeat step 11 twice but instead of 2 mL of 0.58M HF add 2 mL of deionized water.
- 13. Finally, add 10 mL of deionized water to rinse the funnel and wash the filter.
- 14. Then remove filtration funnel and place the filter with tweezers close to heating lamp for drying.
- 15. Write down sample ID on one side of the clean Al disc.
- 16. On the other side put thin layer of water-solvent based glue to prevent dissolution of the filter, which is from organic material.
- 17. Finally, gently place filter on Al disc and glue it by letting it dry under heating lamp.



18. After approximately 30 min, place it in plastic container for storage until measurement by alpha spectrometry.



## 3.7 Measurements with alpha spectrometry

- 1. Select empty chamber with Idle status and select to load the sample.
- 2. Open selected chamber and place counting source on the counting shelf. For low- level radioactivity samples, measure it on the first shelf.
- 3. Once the sample is inserted, close the chamber.
- 4. Insert data about sample, select appropriate measurement protocol and start measurement.
- 5. In spectrum preview window you can follow how the spectrum is being acquired.
- 6. Once enough counts are acquired in the spectrum, terminate counting. We are usually satisfied with approximately 1000 counts in the peak in spectrum, which gives us around 3 % uncertainty, which is in the range of uncertainty of tracer.
- 7. The results are processed and presented in the report, which can be printed for further use.
- 8. Release vacuum from the chamber and unload the sample.



# PART 3: MANUALS FOR PRACTICAL TASKS DEVELOPED BY CTU



## **1** INTRODUCTION

This part is focused on measurement of <sup>236</sup>U with accelerator mass spectrometry and related sample preparation from water samples.



## 2 DETERMINATION OF <sup>236</sup>U/<sup>238</sup>U RATIO IN TAP WATER WITH AMS

Determination of <sup>236</sup>U at natural and close-to-natural concentrations is a complex task due to its abundance and specific activity. This isotope belongs together with others to the so-called fingerprint of nuclear material in nuclear forensics. On the other hands, this nuclide was introduced to nature by anthropogenic activities and plays a special role of the trace of natural processes, such as migration or other transport phenomena, namely in hydrosphere.

Measurement of this nuclide at and above natural concentration requires sufficiently sensitive method and careful sample treatment and preparation. This task aims on determination of this isotope in tap water (or any other sufficiently "clean" water) with accelerator mass spectrometry (AMS). This method is currently one of the most sensitive tools for selected nuclides.

This task should present students the AMS as an analytical method on the edge of mass spectrometry and high energy beam physics, which is using chemical and physical aspects of the nuclide to suppress possible interferents. But more important, the role of contamination in the sample preparation is highlighted in the task, which plays important role in <sup>236</sup>U analysis. Student will get knowledge and skills about uranium separation and experience about sample preparation, contamination and detection limits.

Complete manual is attached in the Appendix.



## **GENERAL CONCLUSIONS**

This deliverable was prepared by LUH, JSI and CTU. It includes manuals for practical tasks for NF HoT and is structured in three parts, each developed by one partner. Manuals for all practical tasks are described with sufficient detail to allow them to be used in the course. Therefore, general conclusion is that deliverable meets criteria and expectations of the A-CINCH project.



# APPENDIX: DETERMINATION OF <sup>236</sup>U/<sup>238</sup>U RATIO IN TAP WATER WITH AMS BY CTU



# Hands-on Training in Nuclear Forensics

Manual for practical exercise

Version: 1.0



2022



# 1 Determination of $^{236}$ U/ $^{238}$ U ratio in tap water with AMS *Abstract*

This task is dedicated to fundamentals of  $^{236}$ U determination with accelerator mass spectrometry. It consists of simple separation steps, preparation of target matrix sample, target cathode, and measurement of  $^{236}$ U/ $^{238}$ U ratio with AMS MILEA.

#### 1.1 Introduction

Uranium is the last element in periodic table present in nature in relative high content, in Earth's crust its abundance reaches 2.7 ppm in average. There are three main isotopes  $^{238}$ U (99.27 %, 4.47  $\cdot$  10<sup>9</sup> y),  $^{235}$ U  $(0.72\%, 7.04 \cdot 10^8 \text{ years})$ , and  $^{234}\text{U}(0.0055\%, 2.455 \cdot 10^5\text{y})$  – daughter of  $^{238}\text{U}$ . The first two belong among so called primordial radionuclides, which means that due to their long half-lives they have not decayed since formation of the Earth. Uranium isotopes <sup>238</sup>U and <sup>235</sup>U, together with <sup>232</sup>Th, are also mother nuclides of radioactive decay series, significant sources of natural radionuclides and radiation. There are more uranium isotopes such as <sup>236</sup>U and <sup>233</sup>U, which are now supposed to be of anthropogenic origin, because due to their shorter half-lives they already decayed during the 4.5 Gy of the Earth age. But when using ultrasensitive measurement, the story is more complex. Uranium isotope  $^{236}$ U is an alpha emitter with a half-life of 2.342  $\cdot$  10<sup>7</sup> years. It can be produced via neutron capture on nucleus <sup>235</sup>U by reaction <sup>235</sup>U(n,  $\gamma$ )<sup>236</sup>U with cross section of 99 barn for thermal neutrons, which is approximately six times lower value than 585 barn in the case of induced fission [1]. Other possible production path includes  $^{238}U(n, 3n)^{236}U$  reaction with fast neutrons, contributing significantly in the case of nuclear weapons. And the last option comes from an alpha decay of <sup>240</sup>Pu. These options show that production of <sup>236</sup>U, which has decayed since formation of Earth, is strongly dependent on neutron flux. Hence, the abundance of <sup>236</sup>U varies dramatically between natural and artificial sources. While in uncontaminated natural samples the  $^{236}$ U/U ratio ranges as low as  $10^{-10}$  to  $10^{-14}$ [2], for artificial nuclear sources such as fission reactors the situation is entirely different. The combination of isotopic enrichment with significantly higher neutron fluxes caused by chain fission reaction of <sup>235</sup>U results in relatively high yields of <sup>236</sup>U. Total mass abundance of <sup>236</sup>U in irradiated fuel produced by a standard PWR-type nuclear fission reactor with an initial <sup>235</sup>U isotopic enrichment of 3 % reaches approximately 0.4 % after a 3-years campaign [3], with a corresponding isotopic ratio  $^{236}U/^{238}U$  around 5  $\cdot$  $10^{-3}$ . According to the estimations [2], the inventory of natural <sup>236</sup>U reaches only as low as 36 kg worldwide, while its anthropogenic production exceeds the value  $10^6$  kg. As a consequence,  $^{236}$ U can be considered a predominantly anthropogenic radionuclide with a high potential for analytical applications as even the smallest emissions to the environment lead to a significant change in isotopic ratios.

Abundance of  ${}^{236}$ U and its possible sources are used as marker in nuclear forensics. High  ${}^{236}$ U/ ${}^{238}$ U isotopic ratio is a clear evidence that the sample was present in high neutron flux field or its portion was in contact with spent nuclear fuel. The widely used standard for  ${}^{236}$ U measurement with accelerator mass spectrometry (AMS), so called KkU, was prepared and validated in AMS laboratory VERA (Vienna, Austria) from uranium nitrate produced before World War II. It originates from Jáchymov (Czech Republic) uranium mines, from where also Marie Skłodowska-Curie got uranium ore for her discoveries. The ore was very rich, what probably caused relatively high neutron flux in the ore. The reference  ${}^{236}$ U/ ${}^{238}$ U value of this material is  $6.93 \cdot 10^{-11}$ . All values higher by more than one order of magnitude most probably indicate a sample of anthropogenic origin or a contaminated one.

#### 1.2 Basic principles for uranium separation

Uranium as well as other actinides tends to form complexes with oxygen-containing ligands, typically oxides, hydroxides, phosphates, and carbonates. Its behaviour is strongly influenced by several main aspects of its chemistry:



- Oxidation state. Uranium may exist in two main oxidation states U (IV) and U(VI), other as U(III) and U(V) are not stable and require special redox conditions and stabilizers to suppress disproportionation.
- Solubility. Species containing U(IV) are generally much less soluble than U(IV), which forms soluble salts with  $UO_2^{2+}$  cation.
- Complex formation. Uranium creates numerous complexes in the solution with common anions (Cl-, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>), through hydrolysis of the UO<sub>2</sub><sup>2+</sup> at higher pH, or with organic complexing ligands.

Uranium tendency to form complexes is used in various separation procedures. Some of them widely used in AMS sample treatment follow.

#### 1.2.1 Co-precipitation with non-isotopic carrier

Precipitation procedures are based on limited solubility of uranium hydrolytic products and general behaviour of trace concentrations to create colloids and follow any present solids to aggregate and adsorb on their surface. For actinoids, widely used procedure is based on co-precipitation with iron hydroxides formed by hydrolysis of iron salts (mostly FeCl<sub>3</sub>) at higher pH. The voluminous precipitate of number of iron minerals/species formed in the solution (i.e. Fe(OH)2.7Clo.3, Ferrihydrite, Goethite, Hematite, Lepidocrocite, Maghemite, and many others depending on the actual composition of the chemical system and its pH) provides large charged surface for adsorption of colloidal forms of uranium hydroxides and diuranates. In the standard procedures, masses up to several tens of milligrams per litre of this carrier are used, which is sufficient to reach 80 up to 100% yield of co-precipitated uranium. One of the drawbacks of this method is strong affinity of uranium to formation of carbonate complexes. These are highly soluble thus decreasing the co-precipitation yield of uranium – practically no uranium can be precipitated from highly carbonated water. The second disadvantage is in composition of the precipitate and the solution. Following steps aiming on concentration of uranium into several milligrams of the final products must deal with very high concentration of iron in the solutions, which negatively affects separation steps. The advantage is that practically all actinides will follow the precipitate and can be then separated and measured.

Another option to co-precipitate uranium is hydrated titanium dioxide. TiO<sub>2</sub> can be formed directly in the solution by hydrolysis of TiCl<sub>4</sub> or better by organotitanates such as titanium butoxide (TBOT, tetrabutylorthotitanate). The advantage of TBOT above TiCl<sub>4</sub> is its chemical stability, lower vapour pressure and no HCl emissions. Uranium content in organometallic chemicals is also limited, and it does not introduce any chlorides to the system. As well as in the case of iron hydroxides, actinides tend to co-precipitate with TiO<sub>2</sub>. Uranium sorption is also affected by the presence of carbonates, but in general, hydrated titanium compounds are adsorbing uranium in relatively wide pH interval, less sensitive to pH and uranium speciation, and can be performed under pH 5.5, what limits presence of carbonates. Other actinoids also follow. Another advantage is that TiO<sub>2</sub> material can be after drying directly used as a suitable target matrix for AMS. The disadvantage of such co-precipitation is that uranium may be incorporated into the created TiO<sub>2</sub> particles and become less available for following dissolution steps.

#### 1.2.2 Ion exchange of carbonate complexes

In the case of highly carbonated samples, when it is not practical to acidify whole volume and heat it up to 90°C to remove all the carbonates, another other option is to add more carbonates and completely transform all the uranium present into carbonate complexes  $[UO_2(CO_3)_{1+n}]^{2n-}$ . Negatively charged complexes can be then easily separated on an anion exchanger in the carbonate form. There are several disadvantages of such procedure, the main ones are



- Na<sub>2</sub>CO<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and NH<sub>4</sub>OH must be used and the purity of such chemical is limited and they may be source of sample contamination with uranium, which would change the measured isotopic ratio.
- Other elements in the sample will be precipitated and/or create colloidal species. Hence filtration step is crucial to avoid clogging of the column with ion exchanger. It is also not possible to get other actinoids, they will not create carbonate complexes in such extent.

The option to limit the second drawback is to use iron hydroxides to strip all the colloids and get other actinoids, too. For uranium, clear solution is then treated.

Anion exchange procedure then needs slow flows rates through the column to ensure complete uranium exchange. Washing the column can be done by acids (HCl, HNO<sub>3</sub>) depending on requirements of the next separation/concentration steps – extraction chromatography on UTEVA resin or another precipitation to the final target matrix (Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, PrF<sub>3</sub>).

#### 1.2.3 Uranium separation on UTEVA resin

It the steps following to the above procedures, extraction chromatography (EC) is one of the options for separation of unwanted elements and interferents as well as concentrating uranium to the volume suitable for target matrix preparation. EC is often also used to mutually separate and concentrate actinides present in the precipitates. In these processes, UTEVA® (Uranium und TEtraValents Actinides) resin is mostly used for uranium separation, in combination with the resin (Tetra Valent TEVA® Actinides. trialkylammonium), TRU® resin (TRansUranium octylphenyl-N,Nelements, isobutylcarbamoylphosphine oxide) or others based on selected nuclides.

UTEVA® uses diamyl-amylphosphate (DAAP) as an extraction agent. Separation principle is coming out well from the Figure 1 showing retention of actinoid ions on the column as a function of acid concentration. In single column use, sample is loaded in 3M HNO<sub>3</sub>. Then plutonium is eluted with 2-3M HCl, and uranium



Figure 1: Retention of selected actinoids on UTEVA resin. Source: Triskem International product sheet, adapted from Eichrom, <u>https://www.triskem-international.com</u>

with 0.1 M HCl. Very often, complexants such as fluorides or oxalates are used to achieve better and sharper elution.

#### 1.3 Fundamentals of accelerator mass spectrometry measurement and operation

Accelerator mass spectrometry is analytical method using ion beam technologies for detection of ultra-trace amounts of an analyte. It can be viewed as extension of classic mass spectrometry with tandem accelerator, but the whole device and its arrangement is much more complex. As other mass spectrometric methods, AMS also aims on maximum suppression of molecular and atomic isobaric interferences to get clean signal of the measured rare nuclide. This is also the main purpose of the AMS

– measure long-lived radionuclides at very low abundancies, when radiometric methods are not suitable or even possible to use, and counting the respective atoms is the only option. Because of its



complexity and nature of the involved physical and chemical processes, it is a relative method, where samples are compared to the standards and background, and isotopic ratio of the rare nuclide to given stable, much more abundant isotope is measured. Nowadays, AMS is well adopted for measurement of <sup>10</sup>Be, <sup>14</sup>C, <sup>26</sup>Al, <sup>41</sup>Ca, <sup>129</sup>I, <sup>236</sup>U and actinides, some other nuclides can be measured at high accelerator voltages or when using special arrangements.

The device can be divided to several main parts: ion source, low energy (LE) part with mass spectrometric injector, tandem accelerator, high energy (HE) part with mass spectrometric analysis, and detector measuring the rare nuclide. These parts will be now discussed in more detail in the example of AMS MILEA (Multi Isotope Low Energy AMS), MILEA scheme is shown on the Figure 2.



**Figure 2:** MILEA and its parts: 1 – sample changer, 2 – ion source, 3 – Box lens, 5 – LE electrostatic analyser (ESA), 6 – LE injecting magnet, 7 – LE Faraday cups (FC), 8 – accelerator, 9 – quadrupole triplet, 10 – movable FC, 12 – first HE analysing magnet, 13 – HE analyser with 7 positioned FC and set of degrader foils for <sup>10</sup>Be measurement, 14 – HE ESA, 16 – movable FC, 17 – second HE magnet, 19 – gas-filled detector. 4, 11, 15, and 18 are gate valves separating respective beamline sections, which are used for protecting vacuum during service or emergency situations. (*With permission of Ionplus AG*).

#### 1.3.1 Ion source

The ion source produces negative ions by sputtering the target with sample with accelerated caesium ions in the environment of metallic caesium vapours. In more detail, the measured sample is pressed into a small cathode. Its material is selected based on nature of the samples, generally aluminium is used for oxidic samples, copper for halides, or titanium for gaseous CO<sub>2</sub>. Cathodes are shown on the Figure 3 below. In the ion source, small reservoir with metallic caesium is heated up to temperatures up to 140°C. Because of the high vacuum, metallic vapours are produced and led to the circular nozzle at the ionizer. Tantalum ionizer is heated to high temperature (orange to yellow glow, T > 1100°C), caesium is ionized and accelerated and focused towards the negatively biased cathode. These accelerated ions sputter the sample, the ions and molecules formed are interacting with the



surrounding condensed and gaseous caesium metal and are "stealing" electrons. The resulting negative ions are extracted and accelerated from the cathode as initial "dirty" ion beam.

To the MILEA ion source, sample changer with 40 positions magazine allowing measurement without interruption is attached; it can be exchanged for the new one without losing vacuum, thus the samples can be measured without interruption.



Figure 3: Copper and aluminium cathodes together with aluminium balls in plastic bag. Diameter of the hole in the cathode is 1 mm – this is the spot where the caesium beam is focused.

#### 1.3.2 Low energy part

The LE part is the first mass spectrometer aimed at selection of an ion fraction suitable for analysis. The negative ion beam from the ion source is accelerated and formed by the 90° LE electrostatic analyser (ESA) followed by the 90° LE magnet to select ions with the given m/z (mass to charge) ratio for the first part of the accelerator. The magnet contains a bouncer, the role of which is to focus the ion beam of stable or major isotopes of the given m/z ratio to Faraday cups (FC, beam current detectors) in short cycles with a micro- to milli-second frequency. The current in FCs is used to calculate the ion source efficiency and the transmittance of the AMS system. The rare isotopes are routed in their pulse to pass the whole AMS path to the detector.

#### 1.3.3 Tandem accelerator

The accelerator is based on the electrostatic principle and makes use of the change of the charge of ion current between the first and second part. The terminal positive voltage is connected to an electrode in the middle of the accelerator. The negative ion beam enters the accelerator with the ion energy of tens kV and is accelerated up to the terminal voltage. During passage through the accelerator the ion beam enters a collision cell filled with helium having an areal density (gas thickness) of a few  $\mu$ g cm<sup>-2</sup>, where negative ions lose electrons, become positively charged, and simultaneously molecular ions are destroyed. The positive ions are further accelerated away from the positive electrode towards the accelerator exit. The vacuum insulated accelerator at MILEA uses the terminal voltage tuneable up to 300 kV and takes advantage of the use of He as the stripping gas, which accomplishes a higher ionizing efficiency and a smaller ion beam scatter compared with other gases, such as Ar, O<sub>2</sub> and N<sub>2</sub>.

#### 1.3.4 High energy analysis

The accelerated ion beam then enters the next part of MILEA, which is a complex mass spectrometer of high-energy (HE) ions composed of other magnets, ESA, the necessary ion optics and FC for measurement of stable isotopes. MILEA uses a quadrupole triplet right after the accelerator to direct



ions with various masses/energies to the focal point of the first 90° HE magnet. Here, the ions with the m/z ratio of the examined rare radionuclide are selected and directed down to the beam line, while the stable isotope ions are deflected into FC for measurement of the AMS system transmittance and for normalization of the rare isotope signal. A 75 nm thick Si<sub>3</sub>N<sub>4</sub> degrader foil is inserted in the HE analyser for <sup>10</sup>Be measurement to help in resolving the <sup>10</sup>B and <sup>10</sup>Be isobars. The selected ion beam then passes another 120° ESA for filtering away the ions with unwanted energies, and finally the last 110° magnet to focus the ion beam scattered by the foil passage and to direct the beam of rare isotopes to the detector.

#### 1.3.5 Detector

MILEA uses a gas ionization detector (GID) with two collective electrodes, which is filled with isobutane. For <sup>26</sup>Al measurement, an absorption cell filled with isobutane is placed in front of the detector to remove the intense m/z ambiguity with <sup>13</sup>C<sup>+</sup> ions. An important construction innovation is the achromatic arrangement of all parts of the ion optics, which guarantees a link-up of the focus points of the individual parts of the ion optics even for various ion mass/energy ratios.

### 1.4 Experimental part

#### 1.4.1 Sample collection and uranium separation

#### 1.4.1.1 Chemicals and equipment

For sampling and uranium separation prepare:

- Plastic vessel of volume at least 25 litters (canister or barrel) with tight lid.
- Strong anion-exchanger such as DOWEX X1 (about 100 mesh). If possible in the form of suspension without bubbles. 30 mL (ideally in CO<sub>3</sub><sup>2-</sup> form)
- 50 mL column (diameter approx. 2 cm) with frit and stopcock for operations with ion exchanger
- Wide (square) column for fast carbonate sorption on anion exchanger.
- Filtration textile or frit and suitable column or funnel for filtration
- Chemical glass beakers, rods, Petri dishes, tubes
- FeCl<sub>3</sub> solution 5% (pre-WW2 or tested for <sup>236</sup>U content)
- Na<sub>2</sub>CO<sub>3</sub> analytical grade or better.
- Concentrated ammonia solution analytical grade or (better) isothermally distilled
- 1M Na<sub>2</sub>CO<sub>3</sub> solution in demineralized water with conductivity lower than 50 nS, 100 mL
- Supra pure HCl and HNO<sub>3</sub> solutions: concentrated, 3, 1 and 0.1 mol.L<sup>-1</sup>.
- Hot plate with regulated heating and magnetic stirrer
- Centrifuge, aspirator, peristaltic pump
- PTFE dishes with volumes up to 100 mL
- PTFE mixing rods, spoons etc., plastic string (nylon or similar)

#### 1.4.1.2 Sampling

Sampling is the first and one of the most important procedure. It could be directly responsible for errors in results due to contamination of the sample, or misleading analytical result. With sampling and sample conservation or during the first treatment step, chemical form of the analyte is very often changed. In case of natural (surface, sea) water samples, filtration of the sample must be included.

- 1. Wash the sampling canister with tap water several times.
- 2. Fill the canister with 25 L of tap water (up to the label)
- 3. Add 20 mL FeCl<sub>3</sub> solution, close the canister tightly.
- 4. Mix it several times by shaking the canister.



During sampling and following sample treatment uranium from other chemicals or laboratory environment can be introduced to the sample. The reason is that at the ultra-trace concentrations, no chemicals are tested for uranium content, neither for <sup>236</sup>U, and such "omnipresent" concentration could introduce relatively high <sup>236</sup>U blank. This is the reason for using suprapure or isothermally distilled acids and pressure to use as less chemicals as possible.

In any case, blank sample has to be prepared; due to time-consuming preparations and for the model purpose of this task, blanks will be usually prepared in advance. For co-precipitation with iron hydroxides, best iron possible is from pre-WWII productions, when no anthropogenic uranium was spread into environment.

#### Extension

If it is necessary to know the amount of uranium in the sample and yields of separations steps, a tracer must be added. As a tracer, uranium  $^{232}$ U or  $^{233}$ U of suitable activity can be used and must be added during or just after step 3. In the following, aliquot samples can be taken for ICP-MS and radiometric (alpha or gamma spectrometry) analyses for total uranium content and yield calculations. When  $^{233}$ U is used, AMS measurement for yield calculation can be used and, in such case, sub-limit amount of  $^{233}$ U can be used as tracer.

#### 1.4.1.3 OPTION 1: Uranium separation and concentration with iron co-precipitation

Here, the option using direct co-precipitation of uranium on iron hydroxides and cleaning on UTEVA resin is described.

- 1. To the canister, add 20 mL of concentrated ammonia solution to reach pH between 9-10. Close the lid carefully and mix it well. After mixing, check pH with pH paper, add more NH<sub>4</sub>OH if needed.
- 2. Leave it stay for 2 hours to settle.
- 3. After the precipitate is settled, carefully suck out majority of the liquid above and filter the rest. It the case when settling did not went well it is necessary to filter the whole volume with large filter to collect all the hydroxide.
- 4. Wash the filter with the minimum volume of the treated water necessary and adjust the total volume to 40 mL.
- 5. Dissolve the precipitate with stepwise additions of concentrated suprapure HNO<sub>3</sub>, mix it between additions. The resulting concentration of HNO<sub>3</sub> should be  $3 \text{ mol}.L^{-1}$ .
- 6. Wash UTEVA column (2 mL bed volume, BV) with 6 mL (3 BV) 3M HNO<sub>3</sub> (suprapure) and load the sample. In both cases leave it flow through by gravity.
- 7. Wash the column again with 2mL (1BV) 3M HNO<sub>3</sub>.
- 8. Use 5mL (2.5 BV) of 0.1M HCl (suprapure) to elute uranium, collect it in the PTFE dish.
- 9. Add 200  $\mu$ L of FeCl<sub>3</sub> solution to the eluate and mix it well.
- 10. Place the dish on the hot plate and heat it to approx. 80°C. If pure (isothermally distilled) NH4OH is available, dose it stepwise until basic vapours are coming out (approx. 500 μL). Work in fume hood and protect your eyes!
- 11. Evaporate it to dryness below the boiling temperature.
- 12. Collect the resulting precipitate and place it into the oven. Anneal it for 30 minutes at 800°C.
- 13. Collect and store the final material in closed tube.

#### 1.4.1.4 OPTION 2: Uranium separation and concentration as carbonate

There are several options how to separate uranium from the water sample. In the real sample, addition of Na<sub>2</sub>CO<sub>3</sub> to the water will result in precipitation of various colloids, which may clog the column and limit the flow-rate. Hence, time-consuming filtration is necessary and only columns with bigger



diameters and flat beds are suitable. Because the exchange kinetics is not so fast, column load must be limited, flow rate of several bed volumes per hour is recommended.

In the first step, strong anion exchanger must be converted to carbonate form. If you know the actual form, you can skip some of the steps. Usually the exchanger is in chloride of hydroxide form or in unknown one and must be unified. Let's start with the dry anion exchanger from the bottle.

- a. Take approximately 30 mL of the exchanger with graduated cylinder and weight it. Afterwards pour 100 mL demi-water into the cylinder and mix the suspension carefully but intensively.
- b. Let the exchanger settle down and quickly pour our water with unsettled pieces, dirt etc. Repeat at least twice.
- c. Pour suspension of the exchanger into Erlenmayer flask and add demi-water to have water level at least 1 cm above the suspension. Use water aspirator to decrease pressure above water level until bubbles are coming out form the exchanger.
- d. Transfer the exchanger suspension into column (approx. 2 cm in diameter with stopcock), but do not let it dry, always keep it in water. Use modified dropper if needed.
- e. Wash the column with 1M HCl solution (60 mL), slowly, max 20 drops per minute regulated by stopcock. Then wash the acid residues out with demi-water, check pH with pH paper. Wash the column with 1M NaOH (60 mL) the same way as HCl. Again wash with demi-water and check pH.
- f. Repeat previous step. The exchanger will remain in OH- form.
- g. Convert the column to the carbonate form with 75mL 1M Na<sub>2</sub>CO<sub>3</sub> solution. The solution should pass through slowly, up to 10 drops per minute. The eluate should be basic check regularly with pH paper.

Because FeCl<sub>3</sub> was added during the sampling, carbonates should be added immediately afterwards. For treating the whole volume, the exchanger in the carbonate form must be transferred into wide column suitable for higher flow rates. This is described in the following steps:

- [1] Add 100 g of Na<sub>2</sub>CO<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and leave it dissolve (alternatively prepare concentrated solution in demineralized water), close the canister tightly.
- [2] Leave it stay for 2 hours to settle.
- [3] After the precipitate is settled, carefully suck out majority of the liquid above and filter the rest. Keep the solution, which now contains uranium. In the case when settling did not went well it is necessary to filter the whole volume with large filter to remove all the hydroxides.
- [4] Pump the solution through the wide column with 30 mL of converted anion exchanger, set up flow rate about 5 BV per minute (150-200 mL per minute). Slower is better.

The other option is to let uranium carbonate complex adsorb directly onto the exchanger in the sampling vessel.

- 1) Add 100 g of Na<sub>2</sub>CO<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> to the sample and leave it dissolve (alternatively prepare concentrated solution in demineralized water), close the canister tightly and mix it well. The iron will start to precipitate, but uranium will stay in the solution.
- 2) Wash converted exchanger out from the preparation column with the minimum necessary volume of 1M Na<sub>2</sub>CO<sub>3</sub> solution (25 mL) as a suspension.
- 3) Pour the suspension directly into the canister. Leave uranium complexes to absorb for 1 hour with regular mixing/shaking of the whole volume.
- 4) After sorption, the whole volume must be filtered through the filtration textile. Colloids will mostly pass through, but the absorber is separated. Under-pressure/sucking connected after



filtration unit must be used to protect the exchanger against mechanical damage – peristaltic or vacuum pump with buffer bottle can be used to ensure higher flow rates.

After having the uranium carbonates on the exchanger, it is time to wash it out.

- 5. Collect the exchanger, transfer it into the beaker and wash it with necessary volume (approx. 30 mL) of 1M HCl. After bubbling stops, use small column to separate exchanger and solution, and wash it with 30 mL 0.1M HCl. Merge eluates in the PTFE dish.
- 6. Place the dish on a hot plate and start evaporation below the boiling point small bubbles should come out, but it should not be boiling. Pay attention to the process no aerosols and spits should be spread around. Hot plate can be replaced with infrared lamp.
- 7. After a while, when  $\frac{1}{4}$  of the solution is evaporated, add 200  $\mu$ L of the FeCl<sub>3</sub> solution, and continue with evaporation (mix it with PTFE rod if necessary).
- 8. Evaporate it to approx. 10 mL (1/4 of the initial volume) and then add 1 mL of concentrated NH4OH solution.
- 9. Concentrate the precipitate in the centre of the dish with circular motions and let it cool down to the ambient temperature.
- 10. Decant cold solution carefully and continue the evaporation. Evaporate to dryness and let hot at the plate at elevated temperature for 10 more minutes set up the temperature of the plate to 250-300°C.
- 11. Take it out and let it cool down. Transfer the precipitate with PTFE spoon to a pre-weighted clean crucible.
- 12. Place the product into the oven. Anneal it for 30 minutes at 800°C.
- 13. Weight, collect, and store the final material in closed, weighted tube.

#### Alternative 1

Instead of FeCl<sub>3</sub>, tetrabutylorthotitanate (TBOT) can be used. Start mixing the whole volume and add 5 mL of TBOT dropwise directly into fresh sample (without addition of any other chemicals, in case of highly carbonated water, acidification to pH 4 with HCl can be used. Decanting and centrifugation, or filtration of the product is needed.

#### Alternative 2

In the steps 5-8, instead of pouring ion exchanger into the canister, it may be placed into textile bag and immersed to the canister. Such solution needs longer sorption times, but simplifies exchanger separation.

#### 1.4.2 Preparation of target cathodes

In this chapter, produced powders must be pressed into the AMS aluminium cathodes. In the real procedures, blank samples have to be prepared w/o reference materials to get information about possible contamination. Here, all blanks and standards are already prepared in cathodes, only sample materials will be pressed. If possible, divide your sample into half and prepare more target cathodes, for low weights use more niobium and homogenize it with the sample carefully.

#### For all the manipulations with cathodes use gloves!

#### **Check Pneumatic Press manual for operation details!**

1. Check the weight of precipitate, or weight it again. Weight the cathode.



- 2. Mix the precipitate with niobium metal in the ratio 1:1 directly in the glass tube (check if the sample is in powder form and it is not sticking or baked on the tube walls in such case it has to be taken out, crushed with agate mortar and pestle, weighted again)
- 3. Place new, weighted cathode into the press holder, do not forget to place ZrO<sub>2</sub> ball underneath the facing part of the cathode, as it is written in the pressing manual.
- 4. Transfer the mixture to the target cathode, cathode should be full of the material. Be careful not to lose any material. When it is filled in, place there 1 aluminium ball and press it. Weight how much sample is in the cathode.

#### 1.4.3 Measurement

With the samples pressed in the cathodes, it is now time to mount them to the satellites, as the cathode holders are called. Hold the cathode in the left hand, rear opening facing up. Place there a small stainless-steel ball and press it by the spring from the satellite. Push the satellite against the cathode, until it is possible to turn the bayonet lock. With the cathodes in satellites, push them into the magazine together with ready-to-use standards and blanks. In the magazine, between the samples at least one standard and one blank should be placed.

Cover the magazine with aluminium foil and take it to the machine. Ask operator to open sample changer and follow operator's instructions how to place it in.

Operator will show you respective parts of MILEA's hardware. Together you will create database input of measurement software, summarizing all the information about your samples. After starting the measurement, you can follow measured data on the screen. At the end, you will get measurement results in the form of excel sheet. If possible, you will sputter the whole samples = all the present uranium will be measured in the form of ions.

							Transmissi	Measureme
				ULE			on	nt
Cycle	U	A [nA]	<b>B</b> [pA]	[nA]	U/A	B/A %	[%]	time [s]
24.1	0	5.18	37.6	4.24		0.7265	122.27	4.824
24.0	3	4.94	1.36	4.21	5.56E-12		117.33	52.485
23.1	0	5.15	37.2	4.21		0.7229	122.28	4.813
23.0	16	4.92	1.30	4.20	2.98E-11		117.3	52.483
22.1	0	5.11	37.0	4.18		0.7249	122.18	4.822
22.0	16	4.88	1.52	4.16	3.01E-11		117.19	52.486

#### 1.4.4 Calculation and evaluation of the results

The results will be in the form represented by following table:

In the presented case, ratios of  ${}^{236}\text{U}/{}^{238}\text{U}$  and  ${}^{235}\text{U}/{}^{238}\text{U}$  were measured. Because in this case 3 isotopes are measured, but only 2 of them can be measured in parallel, parameters of the machine are sequentially changed; durations of these cycles are then set up proportionally to the beam intensities of the respective isotopes. In the Cycle labelled 24.0 in the above table, isotope  ${}^{236}\text{U}$  was measured with 3 counts per 52.485 s,  ${}^{238}\text{U}$  beam current was 4.94 nA at the HE side and 4.21 nA at LE side before injection to the accelerator. These data give transmission of 39.11 % (117.33/3 because U<sup>3+</sup> ions are used on HE side) and  ${}^{236}\text{U}/{}^{238}\text{U} = 5.56 \cdot 10^{-12}$  (without background and standard correction). In similar way  ${}^{235}\text{U}/{}^{238}\text{U}$  was measured as 0.7265 in the cycle 24.1, where B [pA] is the beam current of  ${}^{235}\text{U}$ .

Together with operator, you will go through the data and calculate all isotopic ratios and their final values in your samples.

A-CINCH – Deliverable 4.3 Page 51 / 55



#### 1.5 Conclusions

With the final isotopic ratios, beam currents, sample weights, etc., and according the measured isotopic ratio, discuss origin of the measured uranium and the possible concentration in the water.

#### 1.6 References

- [1] NNDC NuDat 2.7 Database [online], available at <a href="https://www.nndc.bnl.gov/nudat2/">https://www.nndc.bnl.gov/nudat2/</a>
- [2] Steier P., Bichler M., Fifield L. K., et al., Natural and Anthropogenic <sup>236</sup>U in Environmental Samples, Nuclear Instruments and methods in Physics Research B, Vol. 266 (2008), 2246-2250, DOI: 10.1016/j.nimb.2008.03.002
- Benedict M., Pigford T. H., Levi H. W., Nuclear Chemical Engineering, 2<sup>nd</sup> edition (1981), McGraw-Hill, ISBN: 978-0070045316