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Method-MS, final report 2010

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Abstract

Radiometric determination methods, such as alpha spectrometry require long counting times when low activities are to be determined. Mass spectrometric techniques as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Thermal Ionisation Mass Spectrometry (TIMS) and Accelerator Mass Spectrometry (AMS) have shown several advantages compared to traditional methods when measuring long-lived radionuclides. Mass spectrometric methods for determination of very low concentrations of elemental isotopes, and thereby isotopic ratios, have been developed using a variety of ion sources. Although primarily applied to the determination of the lighter stable element isotopes and radioactive isotopes in geological studies, the techniques can equally well be applied to the measurement of activity concentrations of long-lived low-level radionuclides in various samples using "isotope dilution" methods such as those applied in inductively coupled plasma mass spectrometry (ICP-MS).

Due to the low specific activity of long-lived radionuclides, many of these are more conveniently detected using mass spectrometric techniques. Mass spectrometry also enables the individual determination of Pu-239 and Pu-240, which cannot be obtained by alpha spectrometry. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are rapidly growing techniques for the ultra-trace analytical determination of stable and long-lived isotopes and have a wide potential within environmental science, including ecosystem tracers and radio ecological studies. Such instrumentation, of course needs good radiochemical separation, to give best performance.

The objectives of the project is to identify current needs and problems within low-level determination of long-lived radioisotopes by ICP-MS, to perform intercalibration and development and improvement of ICP-MS methods for the measurement of radionuclides and isotope ratios and to develop new methods based on modified separation chemistry applied to new auxiliary equipment.

Key words

Long lived radionuclides, ICP-MS, method developement

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By Lindis Skipperud and MKS Method partners



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Background and introduction

Radiometric determination methods, such as alpha spectrometry require long counting times when low activities are to be determined. Mass spectrometric techniques as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Thermal Ionisation Mass Spectrometry (TIMS) and Accelerator Mass Spectrometry (AMS) have shown several advantages compared to traditional methods when measuring long-lived radionuclides. Mass spectrometric methods for determination of very low concentrations of elemental isotopes, and thereby isotopic ratios, have been developed using a variety of ion sources. Although primarily applied to the determination of the lighter stable element isotopes and radioactive isotopes in geological studies, the techniques can equally well be applied to the measurement of activity concentrations of long-lived low-level radionuclides in various samples using “isotope dilution” methods such as those applied in inductively coupled plasma mass spectrometry (ICP-MS).

Due to the low specific activity of long-lived radionuclides, many of these are more conveniently detected using mass spectrometric techniques. Mass spectrometry also enables the individual determination of ^{239}Pu and ^{240}Pu , which cannot be obtained by alpha spectrometry. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are rapidly growing techniques for the ultra-trace analytical determination of stable and long-lived isotopes and have a wide potential within environmental science, including ecosystem tracers and radio ecological studies.

Such instrumentation, of course needs good radiochemical separation, to give best performance.

The simultaneous determination of Pu and Np in one analytical procedure offers the advantages including reducing the consumption of samples and chemical reagents, and remarkably saving the analytical time. Moreover, using ^{242}Pu (sometimes ^{236}Pu or ^{244}Pu) as a chemical yield tracer of Np can avoid the less availability of Np isotopic tracer (such ^{235}Np , ^{239}Np). However, due to the bottle-neck of valence adjustment and maintenance for Pu(IV) and Np(IV), only few works have been reported for the simultaneous analysis of Pu and Np in the environmental samples (Chen et al. 2001; Kenna 2002; Kim et al. 2004; Perna et al. 2001). The traditional analytical methods for Pu and Np are operated manually, therefore tedious, time-consuming, and labor-intensive.

Moreover, the methods require large volumes of organic solvents or mineral acids, and embody the risk of cross-contamination. In this work, we aim at to develop an automated method by exploiting an on-line separation using sequential injection technique and extraction chromatography, which can simultaneously determine Pu and Np in environmental samples (Roos and Povinec 2008).

But also in ICP-MS, there can be masses giving overlap, i.e. uranium hydrates giving overlap into the Pu-239 masses, and high level separation might be needed. So along with actually improving detection limits and performance on the ICP-MS, there is also need for improved chemical separation procedures. At FOI a solid phase extraction procedure has been used for several years for separation of actinides prior to determination using ICP-SFMS (Nygren et al. 2005; Nygren et al. 2003). The procedure is based on the TEVA resin for separation of tetravalent actinides such as Pu⁴⁺ and Th⁴⁺, the UTEVA resin for separation of U⁶⁺ and a combination of TRU and Ln-resin for separation of Am³⁺. A few years ago, Eichrom introduced a new resin, the DGA resin, which is based on N, N, N', N' tetraoctyldiglycolamide (TODGA) (Horwitz et al. 2005). It has been shown that TODGA is very efficient in extracting Am from nitric acid, and according to Horwitz et al, the resin capacity factor, *k'*, for Am on the DGA resin in 3M HNO₃ is about 70 times higher than for Am on the TRU resin. The capacity of the TRU resin for Am is relatively low and the retention is decreased by the presence of other trivalent ions such as Fe³⁺. The use of DGA resin thus has potential to increase the stability of the Am separation in the existing method, and the aim of this study is update the existing method by replacing TRU and Ln-resin with DGA resin.

Also for other longlived nuclides, the ICP-MS can be a good and rapid tool get results. One example is Tc-99 measurements where ICP-MS (Skipperud et al. 2007) has shown excellent performance. Radiometric determination is by far the most common method of ⁹⁹Tc determination, measuring rate of decay through the beta radiation emitted. This method is insensitive as the long half-life and low energy ($E_{\max}=292$ keV) of ⁹⁹Tc make radiometric counting insensitive and non-specific. Environmental samples also need pre-concentration which can introduce error. In addition can the interfering isotopes ¹⁰³Ru, ¹⁰⁶Ru and ⁹⁰Sr (200 and 700, 40 and 500 keV) create difficulties (Keith-Roach et al., 2002). ICP-MS enables measurement of Tc-99 with low determination limit; compared to the classical method beta counting determination limits can be three orders of magnitude lower.

A number of other techniques have been employed in the determination of ⁹⁹Tc. These include neutron activation analysis (NAA) producing ¹⁰⁰Tc which can be measured by both gamma and beta counting (Trautmann, 1993; Yagi et al., 1991), X-ray fluorescence analysis (XRF) (Long and Sparkes, 1988), resonance ionisation mass spectrometry (RIMS) (Trautmann, 1993; Trautmann et al., 2004) and accelerator mass spectrometry (AMS) (Carling, 1999). However, all these methods have different limitations. The use of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine samples in solution introduced by aspiration into the plasma has found many applications, particularly in geology, and has been found to be an excellent method of measuring long lived radionuclides at low levels in environmental samples. For example it has been used with success to measure technetium-99 and is reported to be a quick, robust and relatively easy technique to operate. The main disadvantage is the necessity to correct for the isobaric interference of the stable ruthenium-99 isotope either by chemical means or by the simultaneous measurement of other ruthenium isotopes (Butterworth, 1996; Mas et al., 2004a; Mas et al., 2004b; Mas et al., 2000; Mas et al., 2002; Song and Probst, 2000). The main interferences in the mass spectra of Tc-99 are Ru-99 and hydride of Mo-98. The majority of these isotopes are removed in modern separation methods such as those which apply Eichrom's TEVA resin. However, a complete cleanup of sample from interfering agents is needed when working with environmental samples of low Tc-99 concentration.

Objectives

The objectives of the project is to identify current needs and problems within low-level determination of long-lived radioisotopes by ICP-MS, to perform intercalibration and development and improvement of ICP-MS methods for the measurement of radionuclides and isotope ratios and to develop new methods based on modified separation chemistry applied to new auxiliary equipment.

Sub-goals:

1. Identification of current needs and problems in determining long-lived radioisotopes by ICP-MS in close contact with authorities and other stake holders need
2. Development and optimisation ICP-MS methodology for the determination of long-lived radionuclides by designing suitable separation methods applied to auxiliary equipment to overcome current problems.
3. Method validation of ICP-MS for long-lived radionuclides including assessment of matrix effects, intercomparison excersises, and quality control with respect to reference materials;
4. Application of the new methods to determine actinide elements in low level environmental samples from areas contaminated by Chernobyl accident, by uranium mining or global fallout with the aim of improving environmental impact assessment.

Partners in the project are:

- Lindis Skipperud, Cato Wendel, Jelena M Popic at Norwegian University of Life Science (UMB)
- Per Roos, Jussi Jernström, Jixin Qiao at Risø National Laboratory, Denmark
- Eiliv Steinnes at Norwegian Univeristy of Science and Technology (NTNU), Norway
- Susanna Salminen, University of Helsinki (UH), Finland
- Ulrika Nygren at Swedish Defence Research Agency (FOI), Sweden
- Olgeir Sigmarsson, Sigurdur Emil Palsson at University of Iceland/Icelandic Radiation Protection Institute

Specific tasks in Method MS (year project)

ICP-MS investigations will include method development and optimization for determination of Tc-99, Pu-isotopes, U-isotopes and Np using SF-ICP-MS (1st and 2nd generation) and conventional quadrupole ICP-MS, as well as method development and optimization for other actinides. Specifically:

1. Investigation and documentation of detection levels for actinides and Tc-99 using standard solutions and standard reference materials on ICP-MS and SF-ICP-MS.
2. Documentation of possible matrix effects, interferences and method validation with respect to reference materials.
3. Intercalibration and Quality control documentation for methods in question, and intercalibration with conventional alpha spectrometry measurements.
4. Development of a chromatographic method for measuring Tc-99 in environmental samples by ICP-MS.
5. Development of FI/SI technique for determination of Pu concentration in sample.

6. Look into possibilities of analyzing Pu-238 with ICP-MS if proper separation from U-238 is possible.

Knowledge gaps apply to both anthropogenic and naturally-occurring radionuclides, particularly because of the need to put doses from nuclear activities into context with those from background radiation.

Publications related to Method-MS project

The following publications are published or planned to be published in international scientific journals related to this project:

- Nygren, U., Ramebäck, H., Vesterlund, A., Berglund, M., *Int. J. Mass Spectrom.*, **2010**, *in press*
- Qiao, J., Hou, X., Roos, P., Miró, M. *Anal. Chem.* **2009**, *81*, 8185-8192.
- Qiao, J. X.; Hou, X. L.; Roos, P.; Miró, M. *J. Anal. At. Spectrom.* **2010**, *25*, 1769-1779.
- Qiao, J. X.; Hou, X. L.; Roos, P.; Miró, M. *Anal. Chim. Acta.* **2010**, *in press*
- Qiao, J. X.; Hou, X. L.; Roos, P.; Miró, M. *Talanta.* **2010**, *submitted*
- Qiao, J. X.; Hou, X. L.; Roos, P.; Miró, M. *Anal. Chem.* **2010**, *in press*
- Mrdakovic Popic, J., Salbu, B., Strand, T., Skipperud, L., *J. Env. Mon.* **2011**, *In press*
- Steinnes, E., Skipperud, L., Wendel, C.C., *J. Env. Rad.* **2011**, *In prep*
- Wendel, C.C., Steinnes, E., Salbu, B., Skipperud, L., *J. Env. Rad.* **2011**, *In prep*
- Mrdakovic Popic, J., Salbu, B., Skipperud, L., *Science of the total env.* **2011**, *submitted*

Instrumentation

The use of inductively coupled mass spectrometry (ICP-MS) to measure plutonium and other long-lived radionuclides (including other actinides) have increased the last decade (Baglan et al. 2000; Baglan et al. 2004; Bouvier-Capely et al. 2003; Pointurier et al. 2004; Roos and Povinec 2008; Skipperud et al. 2007).

ICP-MS is an analytical technique that performs elemental analysis with excellent sensitivity and high sample throughput. ICP-MS systems rely on the introduction of sample molecules into an argon plasma at temperatures of 6000–10000 K, where they are dissociated and the resulting atoms ionised. Normally, liquid samples (e.g., a purified actinide in an appropriate acid medium) are transferred by a peristaltic pump to a nebulizer, which feeds a fine aerosol of analyte droplets into the plasma. Analyte ions are extracted from the plasma into a mass spectrometer (held at high vacuum) through a pair of orifices, known as sampling and skimmer cones. These ions are focused by a series of ion lenses into a magnetic quadrupole analyser, which separates the ions on the basis of their mass/charge ratio.

HR-ICP-MS is the most powerful technique for the quantification of trace elements, long lived radionuclides and isotope ratios (Skipperud et al. 2005) in both solid and liquid samples, covering most of the periodic table. Based on the highest sensitivity and the best signal-to-noise ratio, no other ICP-MS system can make this claim: ultimate sensitivity at all resolution settings, ultimate selectivity through high mass resolution, 'hot' and 'cold' plasma conditions, high speed for transient signals, high stability for isotope ratios, full automation for routine productivity and full access to all instrumental parameters for method development. A HR-ICP-MS instrument has the possibilities of:

- Multielement analysis across the periodic table covering a mg/L to sub pg/L concentration range - Compatible with inorganic and organic solution matrices and solids.
- High mass resolution to access spectrally interfered isotopes - Produces elemental spectra (Figure 1).
- A multielemental detector for transient signals when interface with FFF, HPLC, CE, GC and LA.
- High precision isotope ratios on non-interfered or interfered isotopes.
- Fully automated tuning and analysis in conjunction with a comprehensive quality control system.
- Reliability and robustness with high sample throughput.
- High flexibility / accessibility to serve as an advanced research tool.

High mass resolution: The separation of analyte ions from spectral interferences by high mass resolution is a prerequisite of accurate and precise analysis. The argon plasma gas, water, acid and the sample matrix itself can combine to give polyatomic ion species having the same nominal mass as the analyte and thus give a false high value that's needs to be accounted for. High resolution with sector-field mass spectrometer will distinguish the analyte mass from the interference mass in a magnetic and electrostatic field.

Resolution: Low resolution is used for the analysis of non-interfered isotopes, with high sensitivity. Additionally, the flat top peak shape is an advantage for high precision isotope ratio measurements. Medium resolution gives interference-free analysis for most elements in the majority of sample matrices. High resolution is used for the analysis of elements in challenging sample matrices, such as chlorine matrices where high resolution is used to separate As and Se from argon interferences and argon chloride interferences.

Sensitivity and Stability: the highest instrumental sensitivity is essential to achieve the lowest detection limits. However, it is the signal to noise ratio that dictates the detection limits. The HR-ICP-MS gives an of-peak

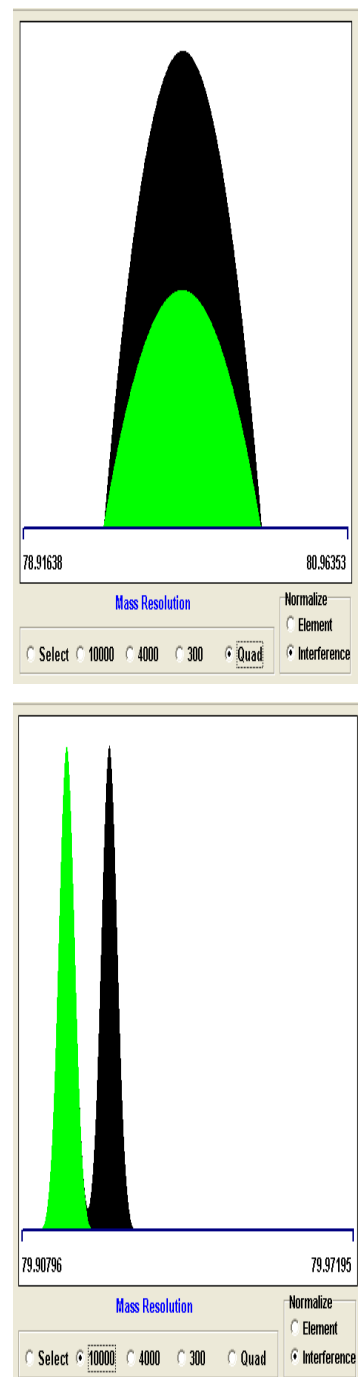


Figure 1. The peak signal of the 40Ar40Ar+ and 80Se+ (in green) shown using an ordinary quadrupole ICP-MS. B) The peak signals are separated in a HR-ICP-MS.

background of < 0.2 cps for all three resolutions. Detection limits in the fg/L range are possible. Furthermore, the HR-ICP-MS enables fast peak top jumping analyses rather than scanning across the whole peak, thus decreasing analysis times. (Thermo 2004).

General Application of HR-ICP-MS in Radioecology

HR-ICP-MS is a powerful technique for the ultra-trace analytical determination of stable and long-lived isotopes, allowing information on specific isotope ratios. The high resolution Sector Field ICP-MS (HR-ICP-MS) offers superior detection limits (fg) for many elements and long-lived radionuclides (half lives of greater than a few thousand years) as interferences are few. Since the radionuclides of interest only need to be separated from isobaric interferences (not alpha or beta emitters), sample preparation is often straightforward. Additionally, the sample measurement time is relatively short, usually requiring a matter of minutes per sample in contrast to radioactivity measurements which need counting times of hours or days (Skipperud et al. 2004; Skipperud et al. 2005).

HR-ICP-MS and isotope ratio measurements can be utilized for tracing, source identification and dating of relevance. The use of Pu- and U- isotopes to identify military or civil sources contributing to U and Pu contamination will be most useful within nuclear forensic, and can be extended to cover more radionuclides/isotope ratios.

Method development and QA

Interferences in the actinide mass-area

The presence of interfering signals is one of the major field in ICP-MS and tightly connected to all QA work, and has been closely investigated by the Danish partners. The interfering signals is usually relatively simple to obtain sufficient signal from most elements in the periodic table in nearly all matrixes but the reliability of the data calculated from such signals depends on knowledge of other sources contributing to such signals. A classical example is determination of the rare earth elements (REE's) in the presence of usually much higher concentrations of barium. If not corrected for, the contribution from BaH, BaO and BaOH will heavily dominate signals to the light REE mass area. In radioecology related areas, determination of many long-lived radioisotopes suffer from the same type of problems, usually to a much higher degree due to the very low concentrations (on a mass basis) which demands either/or very thorough control of interfering signals or a well done separation of the analyte from the interfering elements. The latter is not always possible since knowledge on which elements will interfere in a particular case is not straight forward and knowledge on which elements which appear in a certain sample is not easy to know in advance. Thus, separation schemes to remove such elements can be designed first after a pre-run of the sample itself . The degree of interference depends not only on the matrix composition of the sample but also on the instrument settings usually including some 4-5 lens settings, gas flows, nebuliser type, its geometry and position, analyte uptake rate, torch type, position and condition etc. The complexity with which the magnitude of interferences may form make it nearly impossible to employ generic correction equations. Instead interferences must be evaluated in each individual case by standard addition experiments and then by using a minimum of different conditions relative to the conditions used during ordinary analysis. Standard addition methods and sensitivity analysis of the most critical instrumental parameters is usually required

(eg uptake rate and nebuliser gas flow). In any case, minimizing conditions, which may result in serious interference signals, is often well invested time. In our laboratory where analysis primarily is focused on the actinides we have for some time designed our procedures to include removal of the most common interferences. An example of a problematic sample is shown in figure 2 below. It is a sample of suspected Pu-contaminated paint which contained several percent lead (Pb) to stabilize this particular kind of paint. The separation procedure of lead often include a hydrochloric acid step (maximum absorbance of Pb on anion exchange AG1x4 is at 1.5M HCl) and not careful enough handling may result in a final sample giving the mass-spectra in the figure. The solution contained no actinides so all signals are due to interferences between Pb and Cl isotopes. For Pu-isotopic analysis the pronounced interferences at m/z 241 (eg. $^{206}\text{Pb}^{35}\text{Cl}$) is particularly disturbing since the signal intensity of ^{241}Pu in environmental samples is very weak, typically only a few cps above background. The situation is drastically improved if HCl is omitted from the sample and replaced with more common HNO_3 (Figure 3). Still however interference signals at m/z 241 is higher than what can be accepted. Investigations on decontamination of Pb (and U) in standardized sample processing for Pu and Np analysis by ICP-MS is shown below.

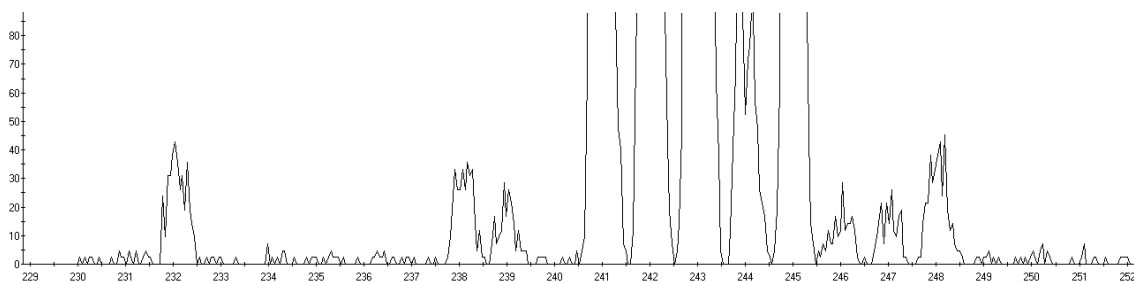


Figure 2. 900 ppb Pb and 3% HCl solution injected with 300 uL/min into a ICP-MS with sensitivity of 450 kcps/ppb of uranium. Standard concentric nebuliser. The sample contained no actinides of measurable quantities. Background count rates in the actinide area are less than 1 cps per mass unit except for ^{232}Th and ^{238}U which have backgrounds of about 10cps each.

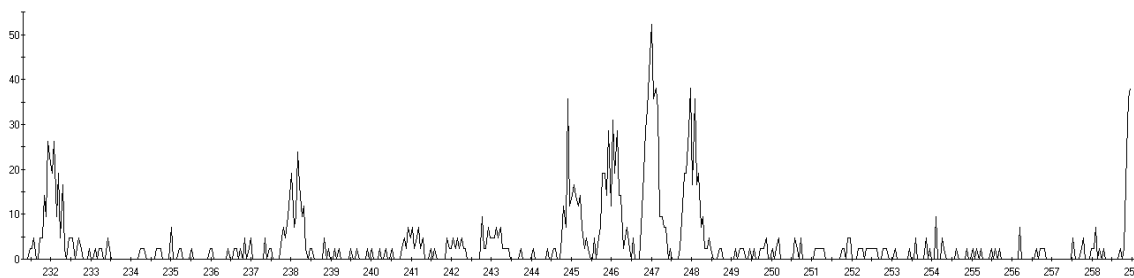


Figure 3. 900 ppb Pb and 3% HNO_3 solution injected with 300 uL/min into a ICP-MS with sensitivity of 450 kcps/ppb of uranium and settings otherwise as in figure 1.

The manual handling of samples from radiochemical separation, standard addition and ICP-introduction requires much time which prevents sample flow. In order to improve and simplify

sample throughput using ICP-MS instrumentation for the analysis of Pu-isotopes and Np-237 we have tried to evaluate an automatic sequential injection procedure which can handle simple soil and sediment samples, which constitute the majority of samples, analysed.

Optimizing Pu-isotope analysis

The work of the Norwegian partners have focused on method development and QA work on both Quadrupole ICP-MS and on high resolution SF-ICP-MS. Pu- and U-isotopes have been prioritized, but also Th has been analyzed.

In this work, samples were analyzed for Pu- and U-isotopes using a Perkin Elmer ELAN 6000 ICP-MS (at UMB) and a Sector field HR-ICP-MS (at NTNU). The sample introduction systems used were an electro thermal vaporisation (ETV) unit and ultrasonic nebulizer (USN) with membrane desolvator, because this gave better detection levels than the more normally used cross-flow nebulizer. The following instrumental parameters were optimized every day before analysis started: torch position, nebulizer gas flow, ionlens versus mass calibration, oxide levels and doubly charged ion level (Table 1). For ETV optimisation, all the parameters except nebulizer gas flow were first optimized with the USN with membrane desolvator. This has the advantage over the cross-flow nebulizer, having less H₂O and giving more compatible signals to the ETV. The nebulizer gas flow was then optimized by repetitive injections of a standard solution in the ETV, while adjusting the gas flow.

Table 1 Typical instrumental operating conditions for the ELAN 6000 ICP-MS.

| | |
|------------------------------|---|
| RF power | 1250 W |
| Plasma argon flow | 15.0 L/min. |
| Auxiliary argon flow | 1.0 L/min. |
| Nebulizer/carrier argon flow | ca. 1.1 L/min. (optimised daily) |
| Ion lens | Scanned with mass (calibrated daily) |
| Sampler and skimmer | Nickel |
| Scan mode | Peak hopping |
| Points pr. peak | 1 |

All standards and samples were in 0.1 M nitric acid solutions when analysed on the ICP-MS for both introduction units. For the USN a peristaltic pump gave a flow of about 1.1 ml min⁻¹. The total sampling time used in this work, including one minute read delay, was 4 minutes. This means that a total of 5.5 ml solution is required using UCN.

Plutonium isotope ratios were also determined by SF-ICP-MS (Thermo Finnegan Element 2), and concentrations of ²³⁹Pu and ²⁴⁰Pu were calculated through the measured ²³⁹Pu/²⁴²Pu and ²⁴⁰Pu/²⁴²Pu ratios. All measurements were performed in the low resolution mode R=m/Δm=300 (full width at 10 % maximum and ²³⁸U was measured in order to account for the ²³⁸U1H+ interference originating from uranium still present in the solutions after ion exchange. Sample solutions were introduced to the instrument by self-aspiration at a rate of ~1.8 ml/min. Masses of 238, 239, 240, 241 (2009) and 242 were registered using magnet scans over the area 238 through 242.

To get precise isotope ratios it is necessary to find the optimal dwell time, i.e. the dwell time that best corrects for noise and drift of the signal. To determine which dwell time that gave the best precision, a plutonium standard was aspirated into the instrument, and the dwell time was varied with total counting time kept constant. When working with isotope ratios it also has to be taken into consideration the expected isotope ratio. If the ratio is very low, the counting statistics on the least abundant isotope will be very poor, which again leads to poor precision. It is known that the $^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratio for the sediment samples determined in this work were around 0.1 – 0.2, and therefore a dwell time 4 times longer on the 240 isotope than on the 239 isotope was used as a compromise between optimum dwell time and counting statistics.

The settling time moving from one isotope to the other was set low (200 μs) to spend as much time as possible on actual measuring the isotopes, optimizing to get the area that gave best isotope ratio precision.

The mass bias correction was carried out by using a plutonium standard with certified isotope ratios. The isotope ratio standard was run before and after the 6 daily determined replicates under the validation of the methods. There was no significant ($p = 0.05$) isotope ratio drift for any of these measurements. However, when performing isotope ratio drift testing over a two-hour period, some isotope ratio drift was observed. Thus, if Pu were to be determined in long series of samples, isotopic re-calibration should be performed periodically.

In the chosen Pu and U separation procedure (Clacher 1995), the samples were taken up in 40 ml of 8 M HNO_3 , and then treated so as to ensure that plutonium was in the correct oxidation state, the Pu^{IV} . About 50 mg of Fe^{II} salt, was added and the sample heated gently for a few minutes to reduce all plutonium to Pu^{III} . After cooling, one ml of 15% NaNO_2 (sodium nitrite) was added and the solution heated gently to oxidise the plutonium to Pu^{IV} (Chen 1991). The solution was then allowed to cool for 30 minutes. If allowed to stand for a longer period than this, disproportionation of Pu^{IV} starts to occur (Toth et al. 1990):



The samples were then loaded onto an anion exchange column. The columns were made from disposable polystyrene columns (Piacars UK Ltd) with a 2 ml bed capacity. The anion exchange resin used was Dowex 1 x 8 (Cl^- form). The resin was contained between two glass-sintered plugs, the top plug having the effect of preventing the column from running dry. The columns were connected to disposable plastic funnels of 25 ml capacity, which acted as reservoirs for the sample solution and acid wash. The columns were pre-treated with 20 ml of 2M NaNO_3 followed by 8 M HNO_3 prior to introduction of the sample solution. The 8 M nitric acid eluant from the column was collected in a beaker. Two further 25 ml washes with 8 M HNO_3 were required to ensure all Am and U was washed through the column. Washes and eluant was retained for later Am and U analysis, if required. At this stage, thorium is retained on the column as $\text{Th}(\text{NO}_3)_6^{2-}$ and is eluted off as ThCl_4 with 50 ml of 10 M HCl . Finally, plutonium is retained on the column as $\text{Pu}(\text{NO}_3)_6^{2-}$ and was eluted as PuCl_3 by 50 ml of 10 M HCl with 0.5 ml of 50% HI dissolved in it immediately prior to use. Samples solutions analyzed by the Inductively Coupled Plasma Mass Spectrometer (ICP-MS) were just dissolved in 10 ml of 0.1M ultra pure HNO_3 and were ready for measurement at the ICP-MS. Standard and certified reference solutions were taken to dryness and diluted directly in 10 ml 0.1 M ultra pure HNO_3 .

Table 2 Pu isotope ratios in two inhouse-standards measured on HR-ICP-MS at NTNU.

| | | |
|------|---------|-------|
| 2626 | Avg | 0,14 |
| | Std dev | 0,02 |
| 3516 | Avg | 0,024 |
| | Std dev | 0,003 |

In the case of ICP-MS, by far the most common method of sample introduction reported is that of pneumatic nebulization, in which a fine aerosol of analyte droplets is injected into the plasma (Gray 1989). This method is, however, very inefficient and alternative techniques such as ultrasonic nebulizer (USN), electro thermal volatilisation (ETV) and laser ablation are increasingly been used. In this work, the USN was chosen as the introduction system for the quadrupole ICP-MS while standard nebulizer was used in the HR-ICP-MS in Trondheim when measuring Pu- and U-isotopes. Looking into the reproducibility of Pu-isotope ratios, two in-house standards have been measured every time there was a run of samples (Table 2). While the precision of Pu measurements have been tested towards an international intercomparison solution provided by NPL, UK (Figure 4).

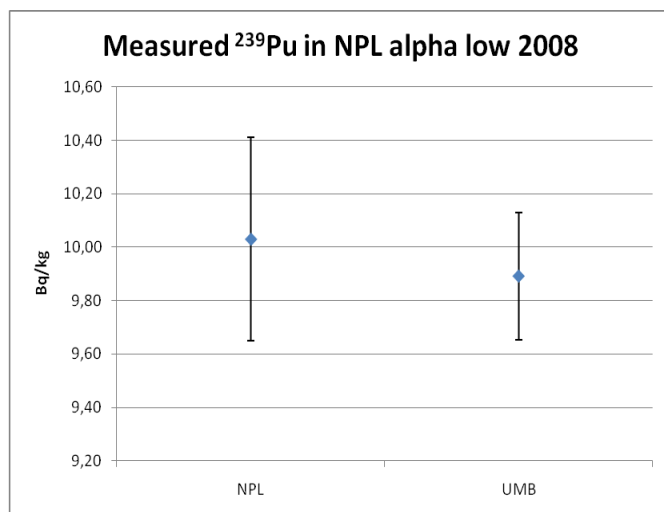


Figure 4. Intercalibration results 2009, measurements (UMB) performed at HR-ICP-MS at NTNU. NPL results are the reference value.

The partners in Finland have focused on method optimization towards Pu-isotope measurements. A preliminary method for determining ²³⁹Pu and ²⁴⁰Pu from environmental samples (soil, sediment, air filters) by quadrupole ICP-MS was developed in Laboratory of Radiochemistry during spring of 2009. The method is not fully optimized yet, and the most challenging problem is the low concentration of ²³⁹Pu and ²⁴⁰Pu in investigated samples, leading to high uncertainties in measured mass concentrations by quadrupole instrument. The most intensive effort for method development will take place in October 2009 – January 2010, when the effect of different parameters on measured Pu isotope concentrations and counting errors can be systematically examined. Quality control of Pu-isotopes measurements will be further improved by increasing reference sample analyses and more effective background count rate control.

In this work, the capability of the instrument for determining Pu isotopes, especially from environmental samples with low concentration, was tested and a preliminary method for measuring Pu isotopes with ICP-MS was created. There was no previous experience or existing method for analysing Pu isotopes by ICP-MS in the Laboratory of Radiochemistry. The Laboratory of Radiochemistry has a share of a quadrupole ICP-MS (Agilent 7500ce). This instrument is normally used for the determination of stable, lighter elements from different kind of samples (trace metals from soil, water etc.). In addition to solution analysis, LA-ICP-MS would be an available option in the Laboratory of Radiochemistry for the direct determination of Pu isotopes from solid samples, if the concentration level would be high enough and there was no significant interference from U. The Laboratory of Radiochemistry has an access to a multicollector HR-ICP-MS in Finland (Geological Research Survey), but it has not yet been utilized for the analysis of transuranium nuclides.

In preliminary work in 2009, some variation in repeatability was observed when measuring concentrations of ^{240}Pu and ^{239}Pu in a reference solution. In addition, due to very low mass concentration of ^{240}Pu and ^{239}Pu in our reference solution ($\sim\text{pg/g}$), RSDs of determined Pu isotope concentrations were sometimes over 5%. In 2010 the method development was continued with attempt to increase the repeatability of the results, especially for real environmental samples, often containing complex matrix and disturbing elements despite of all chemical treatments and separations before ICP-MS-measurement. Old alpha samples (NdF_3 -coprecipitated) were chosen for testing the validity of ICP-MS-method. The samples were originally IAEA-135-reference sediment, air filter, peat and lichen. The alpha samples were re-dissolved and purified by extraction chromatography (UTEVA[®] and TRU[®] resins) for reducing uranium concentration in plutonium fraction. Separated Pu-fractions were measured by Agilent 7500ce quadrupole ICP-MS for determining $^{240}\text{Pu}/^{239}\text{Pu}$ mass ratio in the samples. The $^{240}\text{Pu}/^{239}\text{Pu}$ mass ratio in IAEA-135 reference sediment subsamples, ~ 0.5 , did not correspond with the value $0.210(\pm 0.005)$ reported previously (Hrnecek et al. 2008; Muramatsu et al. 2001; Muramatsu et al. 2000; Muramatsu et al. 2003). The mass ratio $^{240}\text{Pu}/^{239}\text{Pu}$ was as high for other investigated environmental samples. Mass concentration of ^{240}Pu and ^{239}Pu is very low in these samples and the ICP-MS instrument had not been optimised for such low elemental concentrations, therefore the preliminary results for Pu alpha preparations were not correct.

It is not possible to re-measure the samples later after adjusting the method due to limited sample amount. The ICP-MS-instrument consumed the sample of 5 ml nearly totally with the preliminary method (7 repetitions) and after adding more repetitions to the method (previously 7, now 10), more solution is consumed during the measurements, The sample of 10 ml is now required for determining Pu isotopes from low-concentration environmental samples. Still the sample has to be concentrated enough in order to detect ^{240}Pu and ^{239}Pu .

We selected special tuning parameters to increase the sensitivity of the instrument for high masses and manual sample introduction was applied for minimising the solution loss at sample introduction tube. The repetitions were increased from 7 to 10 for increasing the reliability from 95% to 99% of determined Pu mass concentrations. After these improvements, mass ratio $^{240}\text{Pu}/^{239}\text{Pu}$ in IAEA-135 reference sediment samples was on the average $0.227(\pm 0.005)$, corresponding well to the previously published values.

A reference solution containing known mass percentages of ^{242}Pu , ^{241}Pu , ^{240}Pu and ^{239}Pu was used as a standard solution in ICP-MS-measurements.

One gram of NKS-sediment (intercomparison sample) was weighed, tracers ^{236}U and ^{242}Pu were added and the sample was leached with concentrated HNO_3 and HCl on a hot plate for 6 hours. After filtration the solution was evaporated to dryness and dissolved to 3 M HNO_3 + 1 M $\text{Al}(\text{NO}_3)_3$. Ferrous sulphamate and ascorbic acid were added for reducing and stabilising the valence state of Pu^{4+} to Pu^{3+} before radiochemical separation. The separation method was modified from the method of Eichrom Technologies. The solution was loaded into preconditioned UTEVA[®] column and the eluate containing Pu^{3+} was collected. The column was rinsed with 3 M HNO_3 and the wash solution was combined with the first eluted Pu^{3+} -fraction. UTEVA[®] column was further washed with 9 M HCl and 5 M HCl + 0.05 M oxalic acid to remove Th and Np from column before eluting U. Uranium was eluted from the UTEVA[®] column with 0.01 M HCl . Uranium-fraction was adjusted to 1 M HCl with conc. HCl and few drops of 15% TiCl_3 was added for reducing U^{6+} to U^{4+} . 1 ml of HF and 50 μg of Nd were added for co-precipitating U with NdF_3 . (In Eichrom's method uranium is directly eluted with 1 M HCl while we used 0.01 M HCl according to older but as functional method (Salminen and Paatero 2009)).

Pu-fraction was loaded into preconditioned TRU[®] column and before eluting Pu the column was washed with 2 M HNO_3 , 2 M HNO_3 + 0.1 M NaNO_2 (for oxidising Pu^{3+} to Pu^{4+}), 0.5 M HNO_3 , 9 M HCl , 4 M HCl (elution of Am) and 4 M HCl +0.1 M HF (elution of residual Th and Po). Pu was eluted with 4 M HCl + 0.02 M TiCl_3 . 1/3 of the solution containing Pu was used for preparing an alpha sample. Pu was co-precipitated with HF and Nd similarly with U.

Both co-precipitated U- and Pu-fractions were filtered to membrane filters and activities of isotopes ^{234}U , $^{235+236}\text{U}$, ^{238}U , ^{242}Pu , $^{239+240}\text{Pu}$ and ^{238}Pu were determined from filters by alpha spectrometry. The counting time of alpha samples was 3-7 days.

2/3 of 4 M HCl + 0.02 M TiCl_3 solution from TRU[®] column was used for mass spectrometric measurement, and before that the Pu-containing solution had to be further purified in order to decrease concentration of ^{238}U in the solution. The solution was evaporated to dryness. Due to Ti in the samples the residue after evaporation was white precipitate which was hard to dissolve.

Previously ammonium oxalate solution has been used for eluting Pu from TRU[®] column in our laboratory, but for some environmental samples, containing high Po concentrations, ammonium oxalate elution caused leaking of Po to Pu fraction (Salminen and Paatero 2009). Elution of Pu with 4 M HCl + 0.02 M TiCl_3 instead of ammonium oxalate produced Pu-fractions and Pu alpha samples free of Po. In the case of mass spectrometric measurements the use of TiCl_3 can decrease the yield of Pu by adsorption of Pu to evaporation residue, precipitate containing TiF_4 and NdF_3 . On the other hand, for alpha spectrometric means it is essential that there are no radionuclides from natural decay series in Pu alpha sample. It should be further investigated which elution method for Pu would be suitable for a sample used both for alpha spectrometric and mass spectrometric purposes.

After evaporation the residue was tried to dissolve to conc. HNO_3 and it was evaporated again. The residue after second evaporation did not dissolve completely to starting solution 3 M HNO_3

+ 1 M $\text{Al}(\text{NO}_3)_3$. Before second UTEVA[®]+TRU[®]-separation the solution was filtered through a 20 μm syringe filter to the UTEVA[®] column. The second UTEVA[®]+TRU[®]-separation procedure was similar as the first separation (before splitting the sample for alpha and mass spectrometric measurements), but after elution and washing of Pu from UTEVA[®] column the column was no longer used. Another exception for the normal procedure was elution of Pu with ammonium oxalate solution from TRU[®] column instead of 4 M HCl + 0.02 M TiCl_3 . Ammonium oxalate solution containing Pu was evaporated into dryness and the residue was handled twice with conc. super pure HNO_3 . The residue was dissolved to 10 ml of 5% super pure HNO_3 for determining Pu by ICP-MS.

Radiochemical yield of Pu was only 10% after four column separations when the yield was about 67% after two column separations. Especially the problem with dissolving Pu from evaporation residue after first separation procedure is considered as main reason for low recovery of Pu in ICP-MS samples. Again, some more suitable eluting reagent than 4 M HCl + 0.02 M TiCl_3 for Pu from TRU[®] column must be adapted, to avoid loss of Pu to evaporation residue precipitate but the new eluting solution should still be selective in order to prevent Po from contaminating Pu fraction, if the sample will be used for both alpha and mass spectrometric measurements.

Method development for rapid determination of plutonium and neptunium using flow-based chromatography and inductively coupled plasma mass spectrometry

In this study, automated analytical methods were developed by Danish partners for rapid determination of plutonium and neptunium in environmental samples using flow-based extraction or anion exchange chromatography combined with inductively coupled plasma mass spectrometry (ICP-MS). Specific objectives achieved in this study include: (I) method development for plutonium determination using flow-based extraction chromatography (TEVA) and ICP-MS detection; (ii) method development for simultaneous determination of Pu and Np using extraction chromatography (TEVA) and ICP-MS detection; (iii) method development for plutonium determination using anion exchange chromatography (AG 1 series) and ICP-MS detection; (iv) reliable determination of neptunium using plutonium as a tracer and anion exchange chromatography (AG 1 series) combined with ICP-MS detection; (i) method development for simultaneous determination of Pu and Np using anion exchange chromatography (macroporous AG MP-1) and ICP-MS detection.

The configurations of SI-manifold utilized in this study for automated separations of plutonium and/or neptunium consisted of an FIALab-3500B SI system (FIALab Instruments, Bellevue, WA) furnished with a syringe pump (SP, Cavro, Sunnyvale, CA, 25 mL capacity), an internal 10-port (or 6-port) multi-position selection valve (SV-1). The central port of the SV-1 was connected to the holding coil (HC), which consisted of a 6.6 m long PTFE tubing with an inner capacity of 30 mL (2.4 mm inner diameter (i.d.)/3.2 mm outer diameter (o.d.)). One external 10-port multiple selection valves, SV-2 (Valco Instruments, USA) were built in the system for collecting effluents. A schematic illustration of the SI-analyzer is shown in figure 5.

Pre-treatment was conducted before the chemical separation, and the procedure is shown in figure 6. The automated chemical separation procedures performed with the SI-analyzer are shown in figure 7 and 8. After elution of Pu and Np, the eluate was evaporated to dryness on the hot-plate with the addition of concentrated nitric acid to decompose HCl and/or $\text{NH}_2\text{OH}\cdot\text{HCl}$. The residue was dissolved in 5mL of 0.5mol/L HNO_3 and the final sample was delivered to X

Series^{II} ICP-MS for measurement of ²³⁷Np, ²³⁹Pu, ²⁴⁰Pu, ²⁴²Pu and interfering nuclides such as ²³⁸U, ²³²Th, ²⁰⁸Pb.

Typical analytical results for determination of plutonium and neptunium using SI-based extraction or anion exchange chromatography are summarized in Table 2 (Hou et al. 2009; Qiao et al. 2010; 2011a; b). Small-sized chromatographic columns (e.g. 2 mL) suffice processing ≥ 10 g of soil samples regardless the category of the selective sorbent materials packed in the column. Chemical yields of plutonium are always better than 85% throughout the work. In the cases of simultaneous determination of Pu and Np using ²⁴²Pu as a tracer, satisfactory Pu and Np chemical yields and excellent agreement between chemical yields of ²⁴²Pu and ²³⁷Np are obtained whenever using a macro-porous anion exchanger (AG MP-1M). While around 25% chemical yields difference between ²³⁷Np and ²⁴²Pu (with a ratio of $Y(^{237}\text{Np})/Y(^{242}\text{Pu})=0.75$) was encountered in the cases of using gel-type anion exchangers (viz. AG 1 series).^{4,5}

In general, the decontamination factors for ²³⁸U using anion exchange resins in this work were generally lower by a factor of 10-100 compared with those of TEVA resin which were in the range of 10^4 - 10^5 . However, no severe interferences from U, Th and Pb in the ICP-MS measurement of plutonium isotopes and ²³⁷Np in the SI-eluates were in any case detected. No significant difference with respect to the decontamination factors for Th (10^3 to 10^4) were observed among distinct analytical methods and those of Pb varied widely from 1×10^3 to 1×10^6 due to external contamination from the vessels and reagents.

The activity concentrations of ²³⁹Pu and ²⁴⁰Pu determined in 10 g of Danish soil in all cases are in very good agreement with the reference value. It should also be borne in mind that based on the application of SI-network, the total on-column separation procedures were expedited to be completed within 2-3 hours for a single sample. Therefore, the proposed SI-based analytical method using a downscaled extraction or anion exchange chromatographic column should be regarded as an appealing approach for rapid determination of Pu and Np at environmentally relevant levels.

The developed methods in this study yield reliable and effective analyses which satisfactorily support the analytical purposes under different situations. The sample throughput is significantly improved compared with the traditional manual method, wherein 2-3 days are needed for processing similar sample amounts because sample treatment and column separation are commonly performed sequentially. Besides, the SI-based multi-stage analytical procedure performed stably and robustly within a long-term continuous operation suggesting its actual applicability to the rapid analysis of large number of samples within a short time frame, as demanded in emergency situations.

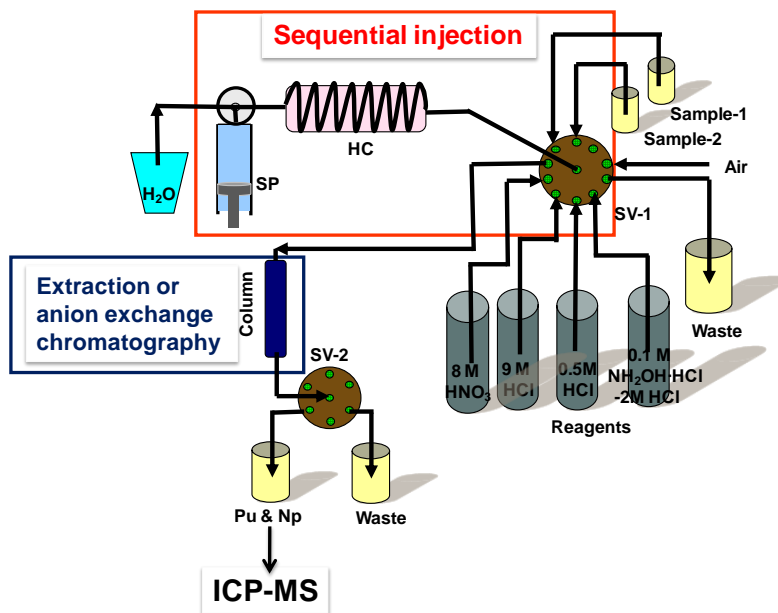


Figure 5. SI-networks in this study for plutonium and neptunium determination using extraction chromatography or anion exchange chromatography. SP: syringe pump, HC, holding coil, Air: port for air aspiration to isolate the carrier from the solution drawn into the holding coil, SV-1-SV-2: selection valves.

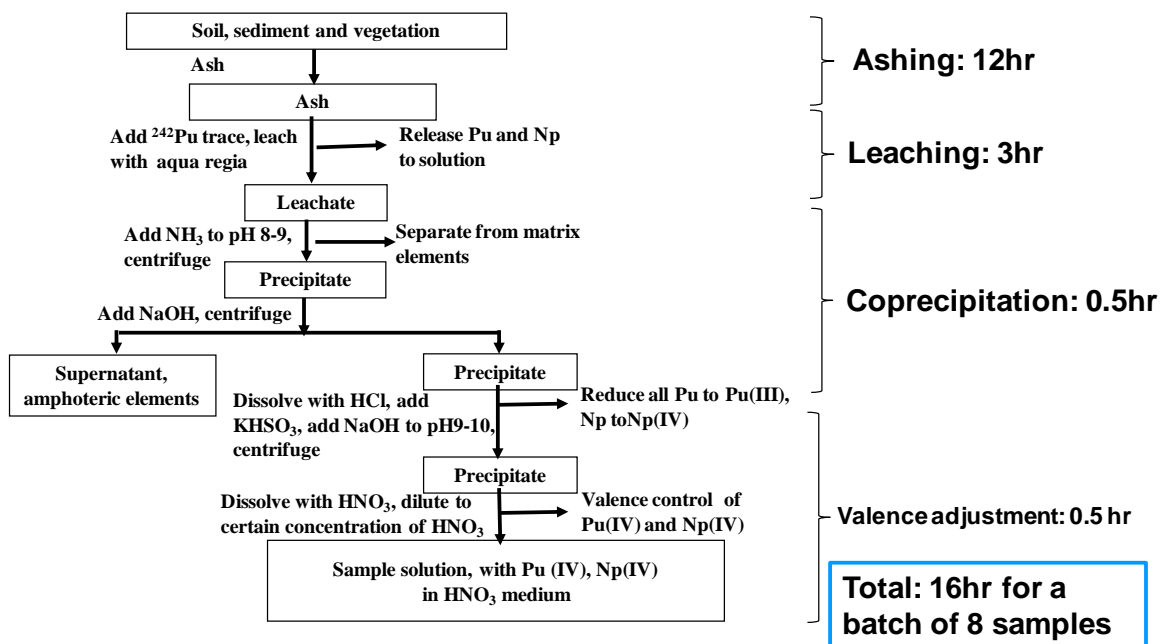


Figure 6. Recommended procedure of sample pre-treatment for simultaneous determination of Pu and Np

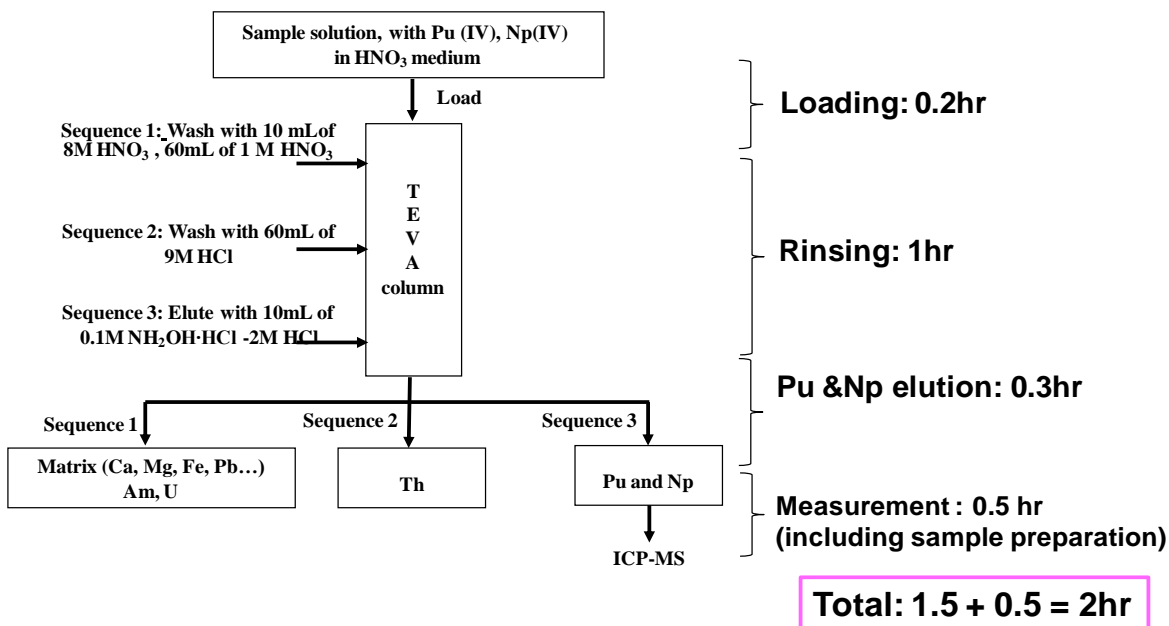


Figure 7. Recommended procedure of simultaneous chemical separation of Pu and Np using extraction chromatography

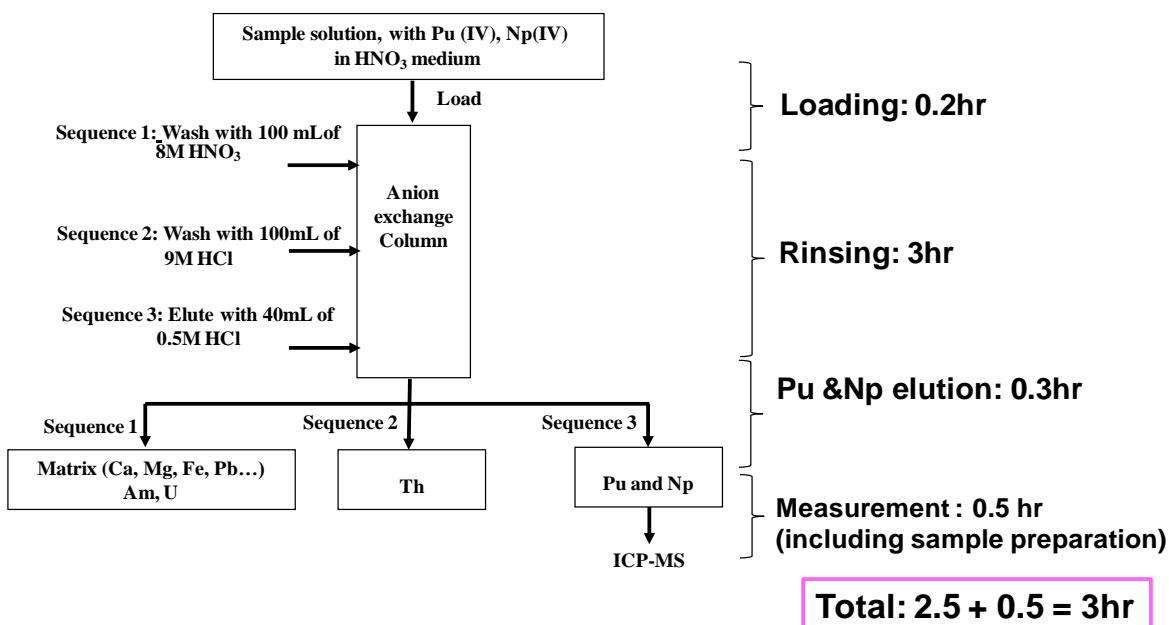


Figure 8. Recommended procedure of simultaneous chemical separation of Pu and Np using anion exchange chromatography

Table 3. Selected analytical results for determination of plutonium and neptunium using SI-based extraction or anion exchange chromatography combined with ICP-MS detection

| Method | Analyte | Resin | Chemical yield of ^{242}Pu , Y_{Pu} (%) | Chemical yield of ^{237}Np , Y_{Np} (%) | Ratio of $Y_{\text{Np}}/Y_{\text{Pu}}$ | ^{239}Pu measured (Bq/kg)* | ^{240}Pu measured (Bq/kg)* | Decontamination factor ** | | |
|---------------------------|---------------------------------|--|---|---|--|-------------------------------------|-------------------------------------|---------------------------|-------------------|-------------------|
| | | | | | | | | ^{238}U | ^{232}Th | ^{208}Pb |
| Extraction chromatography | Pu^1 | TEVA (100-150 μm) (2mL, ϕ 0.7 \times 5 cm) | 97.7 ± 3.4 | - | - | 0.14 ± 0.01 | 0.09 ± 0.01 | 7.5×10^4 | 2.5×10^4 | 1.3×10^5 |
| | $\text{Np} \& \text{Pu}^2$ | TEVA (100-150 μm) (2mL, ϕ 0.7 \times 5 cm) | 88.1 ± 3.4 | 85.7 ± 3.9 | 0.97 | 0.14 ± 0.01 | 0.09 ± 0.01 | 1.0×10^4 | 7.0×10^3 | 1.0×10^4 |
| Anion chromatography | $\text{Pu} \text{ (&Np)}_{3,4}$ | AG 1- \times 4 (50-100 mesh), (2mL, ϕ 0.5 \times 10cm) | 103.0 ± 5.2 | 84.8 ± 5.3 | 0.75 | 0.14 ± 0.02 | 0.09 ± 0.01 | 3.9×10^3 | 2.4×10^4 | 2.7×10^4 |
| | | AG 1- \times 4 (100-200 mesh), (2mL, ϕ 0.5 \times 10cm) | 91.6 ± 4.6 | 75.8 ± 4.6 | 0.77 | 0.14 ± 0.01 | 0.10 ± 0.01 | 6.9×10^3 | 1.7×10^4 | 1.0×10^3 |
| | $\text{Np} \& \text{Pu}^5$ | AG MP-1M (100-200 mesh), (2mL, ϕ 0.5 \times 10cm) | 86.5 ± 4.3 | 85.3 ± 4.3 | 0.99 | 0.14 ± 0.02 | 0.10 ± 0.01 | 3.9×10^3 | 2.5×10^4 | 1.0×10^3 |

*The sample used in the study is 10 g of Danish soil, the reference values of ^{239}Pu and ^{240}Pu activity concentrations in Danish soil is 0.140 ± 0.008 and 0.098 ± 0.006 Bq/kg, respectively. ** The relative standard deviations were in all instances better than 10%.

Method development towards Am-measurements

The purpose of the work done by Swedish partners, has been to investigate the suitability of TODGA (tetraoctyldiglycolamide) resin for separation of Am prior to determination using high resolution ICP-MS. TODGA has previously been reported to show relatively high uptake of Am compared to the widely used CMPO/TBP based TRU resin (Horwitz et al. 2005). The work consists of 3 parts:

1. Preliminary tests of DGA resin for Am retention and elution
2. Evaluation of U, Pu and Am separation factors on DGA in combination with TEVA and UTEVA resins
3. Test of separation procedure for Am using DGA on soil materials

Of these, the first has been conducted, the second is ongoing and the third has not been started yet.

The results so far is that 10 mM ammoniumhydrogenoxalate can elute Am from the DGA resin in only 2 bed volumes, and the eluate can be analysed directly using ICP-MS with a standard conical nebuliser and cyclonic spray chamber. The initial test of the novel separation procedure is very promising with high yield for Am and U. The investigations of the relatively low yield of Pu and Th from the TEVA resin packed in cartridge are progressing.

The method development has begun with finding a suitable elution media for Am from DGA resin. The aim has been to find a media that can elute Am in a small volume, and that is suitable for direct introduction into the ICP-MS in order to avoid subsequent evaporations.

An initial test of separating U, Pu, Th and Am using TEVA, UTEVA and DGA resins has also been performed. However, it was found that when switching from self packed columns to cartridges the separation of Pu and Th on the TEVA resin showed decreased yields and several studies to find the reason for this has been performed.

The quality assurance of the ICP-MS determinations of actinides done at FOI is obtained by analyzing suitable reference materials that correspond with the kind of analyses that are performed. For isotope ratio determinations, the IRMM073 series is used to control dead-time and mass-bias effects, and natural matrix reference materials from NIST and IAEA are used to verify the analyses of such samples. Partitioning in international intercomparisons is done when suitable intercomparisons are available and when time allows for it. Research with respect to the quality of the produced results has been continuously ongoing, addressing, e.g., separation procedures, polyatomic interferences and the effects of detector dead time in isotope ratio determinations. The research is published in peer-reviewed journals such as Journal of Analytical Atomic Spectrometry, International Journal of Mass Spectrometry and Journal of Radioanalytical and Nuclear Chemistry. During 2010, a paper concerning problems in dead-time correction when determining isotope ratios using ion counting detectors in mass spectrometers was accepted for publication in IJMS (Nygren et al. 2006).

The work that was initiated in the previous NKS Methode MS project on developing a novel separation procedure for the determination of Am in combination with U and Pu) has continued this year. It has been shown that the use of the N, N, N', N' tetraoctyldiglycolamide (TODGA) resin facilitates the separation of Am with respect to time and number of columns compared with our previous procedure. The overall method has been tested on spiked solutions and the chemical yield of Am varies between 91 – 95%. The method was also tested in the analysis of U, Pu and

Am in a particle from Thule, work that was co-sponsored by the NKS – financed “HOTRATE” project. The results were good concerning chemical yields of U (89%), Pu (100%) and Am (103%). Furthermore, the Pu in the particle was dated using the ^{241}Pu and ^{241}Am ratio and the separation of Am from Pu and Pu from Am was more than sufficient for that purpose. Less than 1 % of the Am remained in the Pu fraction, and < 1 % of the Pu remained in the Am fraction after separation.

In the preceding Method MS project it was found that the chemical yield of Pu decreased to as low as 20% when TEVA cartridges instead of columns were used. There is no obvious reason for this, and further investigations have shown that the Pu is retained on the resin in spite of increased volume of the eluent 0.01% hydroxyethylene-diphosphonic acid. Other eluents such as 10 mM ammonium-bis-oxalate and 3M HNO_3 -0.2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ that previously has been reported to work well concerning elution of Pu(IV) from TEVA (Nygren et al. 2003) has also been tested without success. Recent findings suggest that the flow rate of 1 ml/min recommended by the manufacturer may be too high for this application, and work will continue by further investigating this.

Method development towards U on ICP-MS

Ordinary alpha-spectrometry is an excellent method in determining uranium isotope ratios in most samples. There are however important examples where there is a need for mass spectrometry if the origin of the uranium sample is to be determined. An alpha spectrum of depleted uranium is shown in figure 9 below.

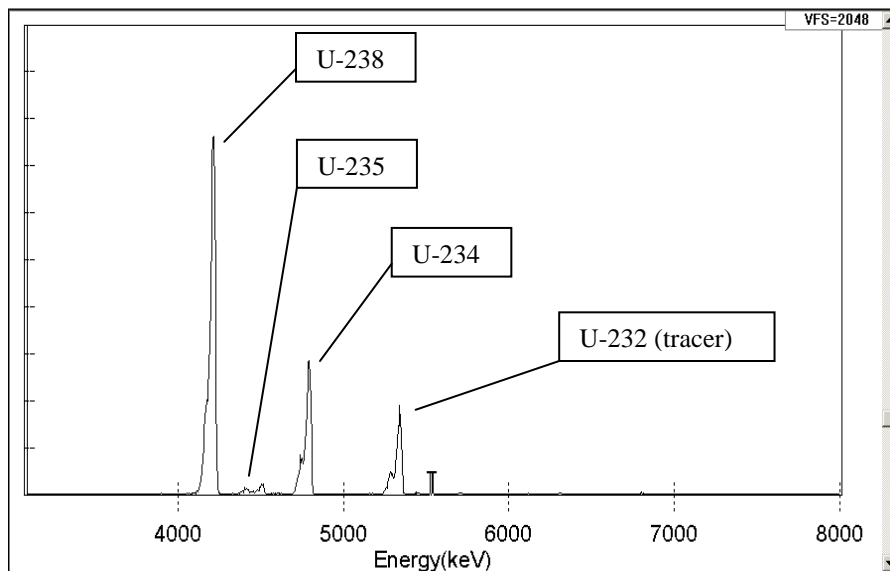


Figure 9. Alpha spectrum of depleted recycled uranium.

The ^{235}U and the ^{234}U isotopes are depleted relative to ^{238}U . The ^{235}U peak is however disturbed by an additional peak on its right hand side which in this case is ^{236}U . The uranium is thus both depleted and recycled (it has passed through a nuclear reactor and later the uranium has been reprocessed – most probably the origin is uranium from the high mass side of an enrichment plant

being feed with a mixture of uranium sources). Due to the complex ^{235}U peak, the unknown depletion and the poor separation between the ^{235}U peak and the ^{236}U peak the $^{235}\text{U}/^{238}\text{U}$ ratio is difficult to determine, as is the $^{236}\text{U}/^{235}\text{U}$ ratio. A logarithmic scaled figure of the same alpha spectrum shows the difficulties better (figure 10). Due to the importance of the $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{235}\text{U}$ ratios in safeguard work, mass-spectrometric measurements are usually employed instead of alpha spectrometry. Also precision in these ratios obtained by mass-spectrometry can reach one or two orders better uncertainty than alpha spectrometry.

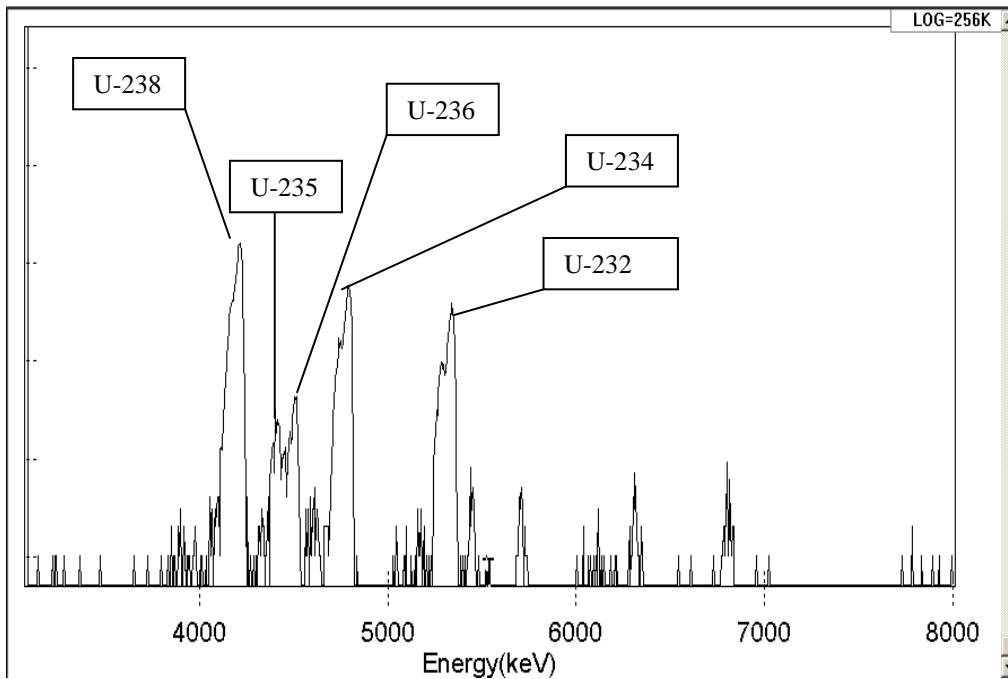


Figure 10. Same alpha spectrum as in figure 9 but with logarithmic scaled abscissa.

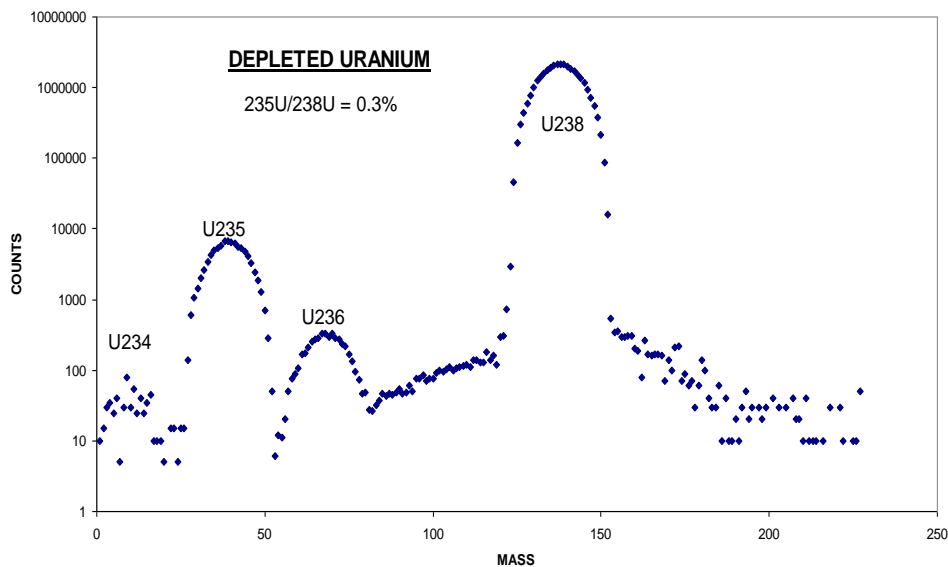


Figure 11. Corresponding mass spectrum of the uranium sample in figure 9 and 10 above. Sample analysed using a sector field ICP-MS with poor abundance sensitivity.

The same type of analytical problems appear when analyzing enriched uranium. A typical spectrum of low-enriched uranium is shown in figure 12. Just as with the depleted sample above ^{236}U is present. The mass-spectrum in figure 13 makes the determination of the $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{235}\text{U}$ ratios easier to determine.

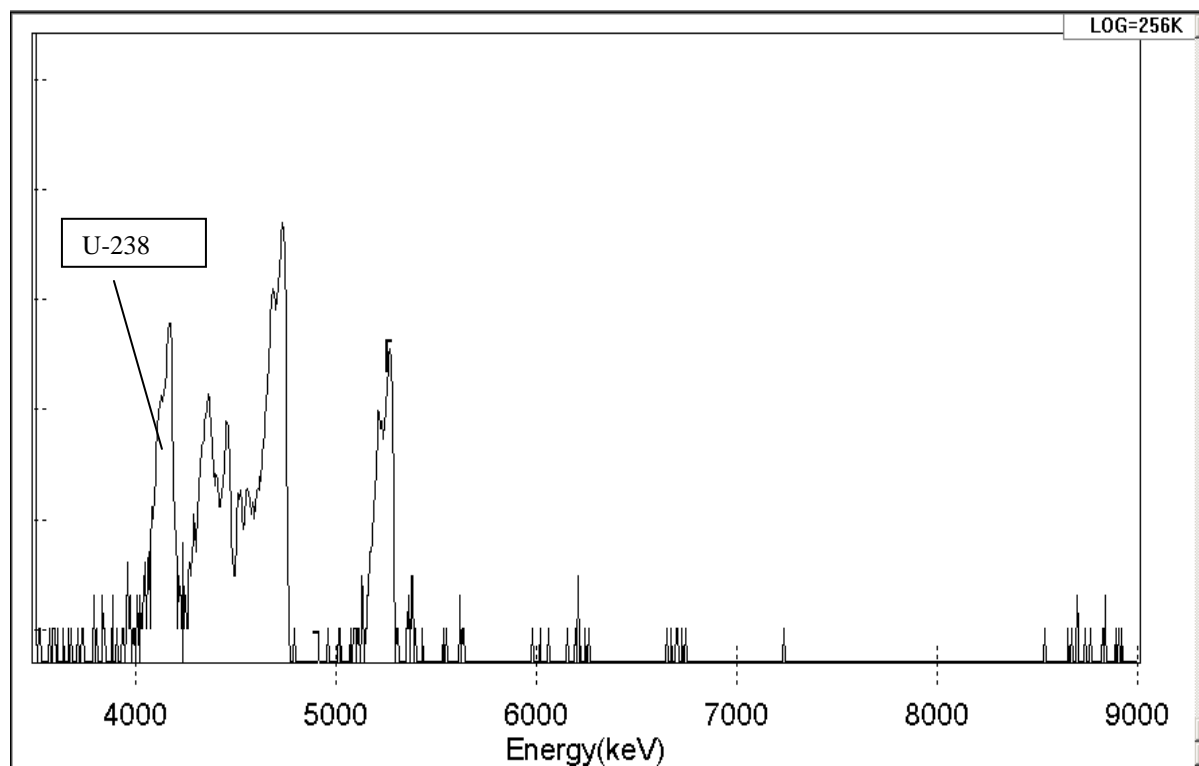


Figure 12. Alpha spectrum of low-enriched uranium.

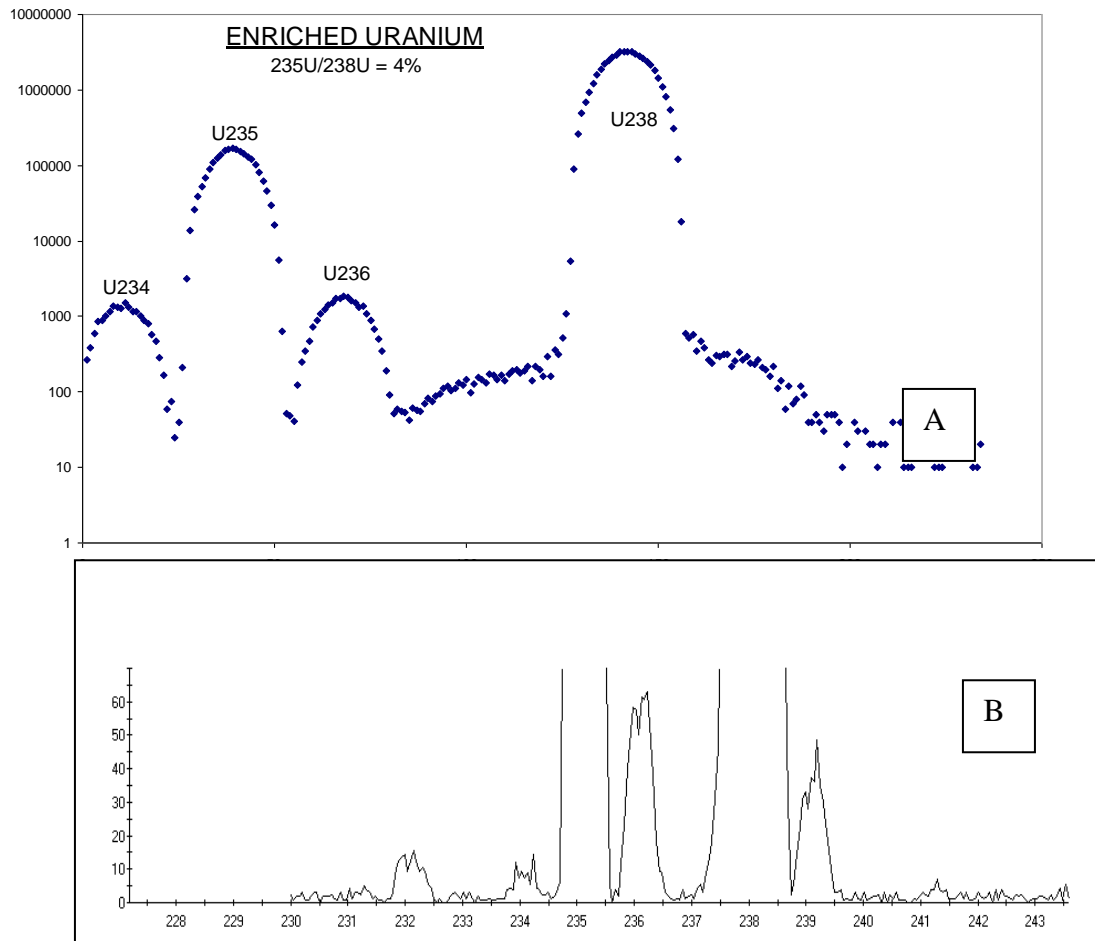


Figure 13. Mass-spectrum of the low-enriched uranium shown in figure 6. Spectrum A) with a poor abundance sector field ICP-MS and spectrum B) using a quadrupole ICP-MS with improved abundance sensitivity.

Although uranium in most cases are rather abundant in a sample chemical separation is needed to be able to determine especially the low abundant ^{234}U which otherwise will be influenced by ^{232}Th tailing, ^{232}ThH tailing and $^{232}\text{ThH}_2$. Figure 14 below shows a typical spectrum of a soil sample analysed without chemical separation using a poor abundance sensitivity ICP-MS (sector field).

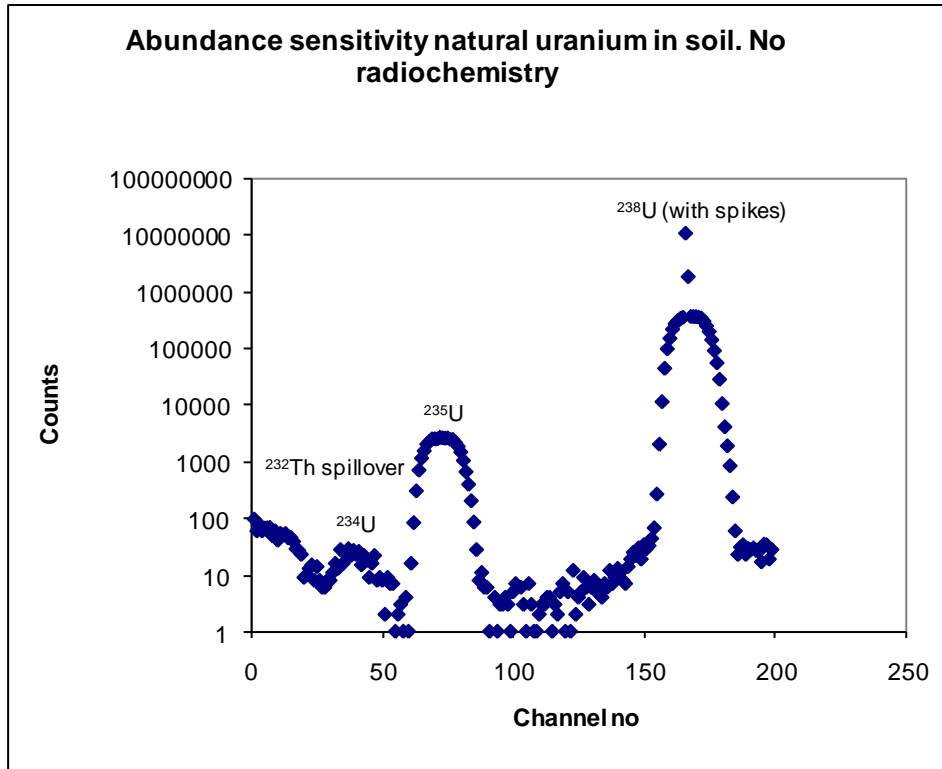


Figure 14. Mass spectrum of uranium in a soil sample analyzed without chemical purification.

Even when spectra appears to be easy to interpret there is still a need to obtain stable signal intensities to be able to determine isotope ratios with the best possible precision. Optimizing of the signal stability and ion transmission (sensitivity) simultaneously is a tedious work and may take a whole working day. Just as with most analytical instrumentation the statistics is determined both by the sample concentration and the inherent variability of the instrument. Ratios of $^{235}\text{U}/^{238}\text{U}$ may be determined down to about 0.2% (two sigma) during the most favorable conditions provided concentrations are above about 0.1ppb of the low abundant isotope ^{235}U (corresponds to about 12 $\mu\text{Bq/g}$ ^{238}U for a sample with natural isotope composition). Usually the count rate of the ^{238}U signal is such that it requires the detector to go from count rate to current mode or to pass over to a Faraday type of detector. Cross calibration of the two detector modes/types is then of large importance for the isotope ratio precision since the ^{235}U isotope is counted using the pulse counting detector while the ^{238}U isotope is counted using the current (Faraday) or analogue detector. This type of detector usage is even more pronounced when determining the $^{234}\text{U}/^{238}\text{U}$ ratio. Sometimes when natural uranium is analysed (with a well determined $^{235}\text{U}/^{238}\text{U}$ atom ratio of 0.00715) it is advantageous to determine the $^{234}\text{U}/^{235}\text{U}$ ratio instead of the $^{234}\text{U}/^{238}\text{U}$ ratio since both isotopes then may be counted on the pulse counting detector thus avoiding the uncertainty associated with the detector cross-calibration. To further improve isotope measurements mass-bias measurements should be performed. Mass-bias is sample matrix dependent and a standard addition procedure should thus be performed. For low concentration samples blank contribution problems also must be considered. The magnitude of the blank and the instrument background when analyzing small (100mg) samples of plant material is shown in figure 15. The dependence of the analyte concentration in determination of

the $^{235}\text{U}/^{238}\text{U}$ ratio is shown in figure 16. The sensitivity of the instrument was such that 1000 ^{235}U counts corresponded to a concentration of 0.1 ppt natural uranium.

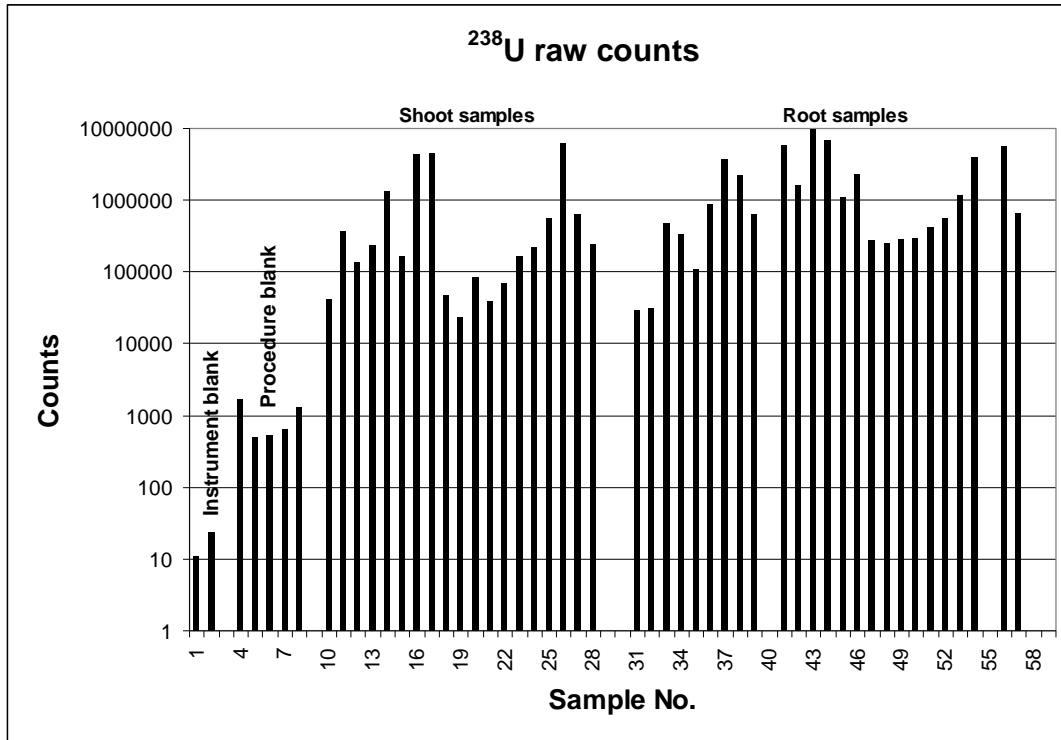


Figure 15. Raw ^{238}U counts when analyzing small (100mg) plant material samples. Contribution from instrument and procedure blank shown separately.

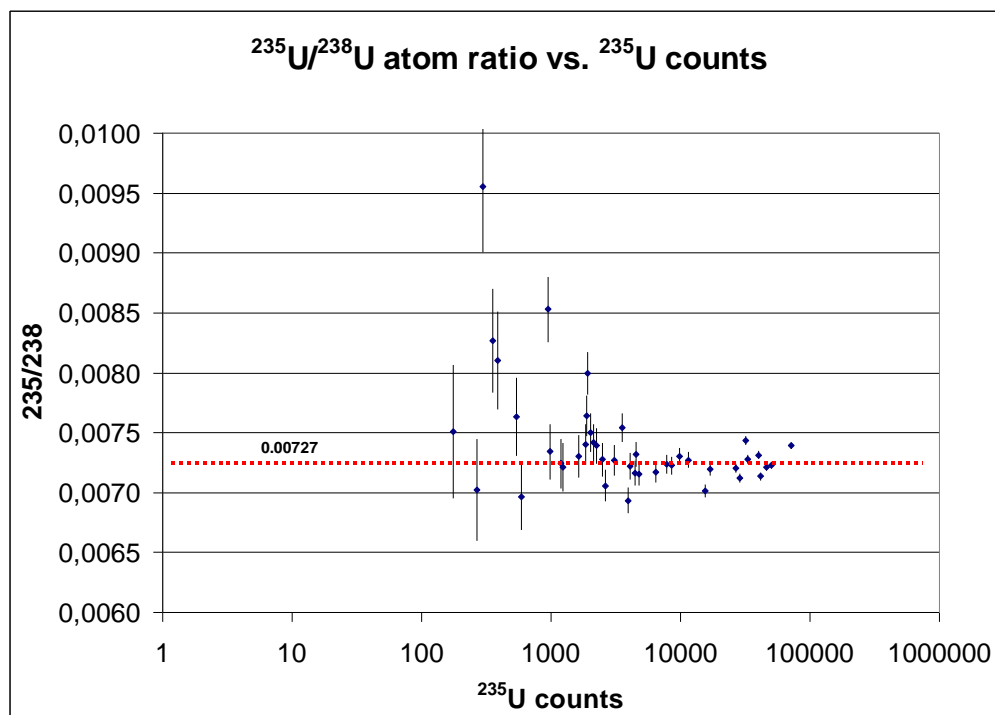


Figure 16. The dependence of the analyte concentration in determination of the $^{235}\text{U}/^{238}\text{U}$ ratio. The sensitivity of the instrument was such that 1000 ^{235}U counts corresponded to a concentration of 0.1 ppt natural uranium.

Specific work to be done by the Icelandic partner was defined as:

“Optimizing and quality control of long lived U and Th radionuclide determination by ICP-MS comparing Quadrupol and LA-ICP-MS on volcanic glasses, application to tephra layers and international dissemination.”

In the preparation for measuring U- and Th-isotopes, the Icelandic partners have assessed instrument capabilities by analyzing lead 206 and 208 isotopes in spiked natural samples. First step concerned dissolution of natural silicate sample into which precisely weighted 206-enriched Pb-spike (206/208= 4345.565) had been added. In order to minimize the error magnification due to spiking, we aimed for a ratio close to 40 and in all cases higher than 5 (ideal theoretical ratio is 44.706, and below 5 the amplification factor reaches 1.10). During the second step, lead is isolated from all other elements using element specific extraction chromatography, and finally diluted to 10 ml with 0.7M nitric acid. Chemical blank was prepared in the same manner. Third step is the measurement of the 206/208 lead ratio in dynamic mode by the Agilent 7500c ICP-MS using the following parameters:

- RF power 1500W
- Gas flow rates: Plasma 15 l min⁻¹, Makeup 0 l min⁻¹, Nebulizer micromist, Sampling cone Ni, 1mm aperture diameter, Skimmer cone Ni, 0.4mm aperture diameter
- Ion lenses: Extract lens 3.2V, Einzel lens (1, 2 and 3) -80V, 10V, -80V, Octapole parameters, OctP RF 190V, OctP bias -7.8V
- Quadrupole parameters: AMU gain 127V, AMU offset 124V, QP bias -5V
- Detector parameters: Discriminator 8mV , Analog HV 1670V , Pluse HV 1060V

Data acquisition was in ten cycles (NBS982, blank, sample, NBS982, blank, sample etc) with an average 2RSD of 0.5-1% on the 206/208 (3-6% for the blank). Measured 206/208 were corrected for instrument mass-bias using exponential fractionation law deduced from the NBS982 standard ($\delta_{exp} = -0.05$). The variations observed for NBS 982 during the analytical session was less than the analytical uncertainties or 0.03 ‰. Calculated Pb concentrations were in the range 0.656 to 8.79 ppm, or very close to anticipated values (as deduced from linear correlations with those of Th).

They were able to conduct the work on U and Th but due to the eruption at Eyjafjallajökull and the need for rapid investigation of the eruptive products, our scheduled work on the ICP-MS Quadrupol for Ra concentration measurements has been delayed. Nevertheless, the partners progressed significantly with the in-situ analysis using an LA-ICP-MS and whole-rock trace-element analysis using the same instrument. The techniques are described in the application chapter. Below are given the average concentrations in ppm and standard deviation of point analyses of the A-THO standard.

Table 4. average concentration in ppm and standard deviation of point analysis of A-THO standard

| | X | SD | | X | SD |
|----|----------|---------|----|--------|------|
| Li | 29.79 | 0.50 | La | 52.47 | 0.60 |
| Si | 351339 | 7316.98 | Ce | 134.10 | 1.53 |
| Ca | 12006.98 | 134.28 | Pr | 13.83 | 0.15 |
| Sc | 7.32 | 0.09 | Nd | 58.97 | 0.68 |
| Ti | 1565.20 | 19.39 | Sm | 13.82 | 0.16 |
| V | 2.72 | 0.03 | Eu | 2.63 | 0.03 |
| Rb | 64.03 | 0.72 | Gd | 13.98 | 0.16 |
| Sr | 82.41 | 0.91 | Tb | 2.28 | 0.03 |
| Y | 90.27 | 1.02 | Dy | 15.76 | 0.18 |
| Zr | 530.76 | 6.01 | Ho | 3.26 | 0.04 |
| Nb | 59.93 | 0.69 | Er | 9.74 | 0.11 |
| Ba | 606.12 | 6.85 | Tm | 1.44 | 0.02 |
| | | | Yb | 9.91 | 0.11 |
| Pb | 5.73 | 0.08 | Lu | 1.44 | 0.02 |
| Th | 7.03 | 0.09 | Hf | 12.44 | 0.14 |
| U | 2.34 | 0.03 | Ta | 3.76 | 0.04 |

Determination of ^{232}Th and $^{230}\text{Th}/^{232}\text{Th}$ ratios using ICP-MS

Determination of ^{230}Th and ^{232}Th is most simply done using alpha spectrometry and there are few arguments for using ICP-MS if only a few samples are to be analyzed. The advantage in using ICP-MS comes when a larger number of samples are to be analyzed. Figure 17 shows the sensitivity of Th in natural soil, measured without any radiochemical separation prior to analysis.

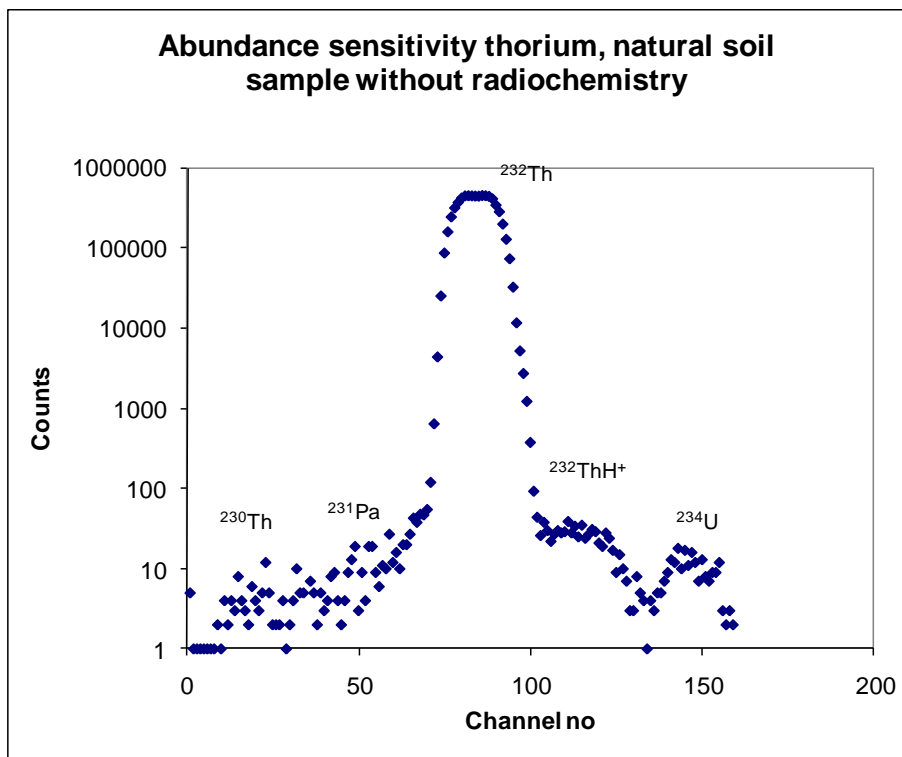


Figure 17. The sensitivity of ICP-MS measurements of Th in soil, with no chemical purification prior to analysis.

Tc-99 measurement improvement

The aim of this work by Danish partners was to apply ion chromatography column (CS5A, Dionex) for producing an interference-free Tc-99 sample in the end of a separation chain which also includes iron hydroxide precipitation and anion exchange. Prior to the ion chromatography column Tc is complexed with oxalate in reduced form Tc(IV) and eluted with oxalic acid solution. By this way a complete separation of Tc from Mo and Ru is achieved. The method has been developed by using tracer solutions and carbonate-rich soil.

Measurement of ^{99}Tc with ICP-MS is feasible due to low determination limit. When compared to classical method beta counting the modern ICP-MS instruments reach even three orders of magnitude lower determination limits. However, for efficient analysis the sample needs to be free of interfering agents such as isotopes of other elements and polyatomics. The main interferences in the mass spectra of ^{99}Tc are ^{99}Ru and, to some extent, ^{98}MoH , $^{59}\text{Co}^{40}\text{Ar}$, $^{87}\text{Sr}^{12}\text{C}$, $^{87}\text{Rb}^{12}\text{C}$, $^{43}\text{Ca}^{16}\text{O}^{40}\text{Ar}$, $^{40}\text{Ar}_2^{18}\text{OH}$ and $^{40}\text{Ca}^{18}\text{OH}^{40}\text{Ar}$. These can be removed in the chemical separation procedure, for example, by using TEVA resin (Eichrom Industries), but when working with large samples and using large amounts of reagents, absolute clean up can be difficult (Keith-Roach et al. 2002). The amount of Ru in the sample can be calculated from its relatively undisturbed isotope ^{101}Ru , however, this decreases the determination limit of ^{99}Tc which is problematic with samples of low ^{99}Tc concentration. Large amounts of Mo in samples create a problem for measurement of Tc via the interference of ^{98}Mo -hydride. Another issue with Mo is the interference of ^{97}Mo isotope when ^{97}Tc is used as yield tracer. Furthermore, not only ICP-MS but also AMS which is the most sensitive technique for measuring ^{99}Tc , suffers from the presence of ^{99}Ru in ^{99}Tc determination. It is thus important to find a way to purify Tc sample from interfering Ru and Mo.

The aim of this work was to apply ion chromatography column for removing interfering elements Ru and Mo for enabling efficient measurement of Tc with ICP-MS. The work includes testing the method with tracers and further applying it to environmental sample material.

The method applies a HPLC system (Thermo SpectraSystem) and ICP-MS (Thermo X-Series II). For the separation of Tc from interfering elements an ion chromatography column (Dionex CG5A-CS5A) was applied. For measuring chemical yield of Tc in the procedure $^{99\text{m}}\text{Tc}$ tracer milked from ^{99}Mo generator (Drytec) was used. For further improving the limits for ^{99}Tc determination with ICP-MS we have an Electrothermal Vaporization (ETV) equipment (SpectraSystem ETV4000).

Work performed included testing different complexing agents in order to elute Tc through the Dionex ion chromatography column in a fraction which is free from any Ru and Mo. Both reducing and non-reducing conditions have been tested; reducing conditions being achieved with a mixture of hydroxylamine and ascorbic acid. An anion exchange HPLC column coupled to ion chromatography column has been tested for pre-concentrating oxidic Tc to enhance the separation of Tc in the ion chromatography column. Preliminary tests have been done with tracer solutions, after which carbonate-rich soil has been used for method testing representing environmental sample material. Digestion and radiochemical separation of Tc in environmental samples has been performed following procedure printed in Keith-Roach et al. (2003; Keith-Roach et al. 2002).

Three different complexing agents were tested for the separation; oxalic acid, dipicolinic acid (PDCA) and EDTA. It was found out that oxalic acid complexes efficiently with Tc in reducing conditions and enables the separation efficiently in tracer conditions. EDTA complexes and enables separation in reducing conditions but with poor quantitativity leaving part of Tc in the chromatographic column. Both oxalic acid and EDTA did not elute Tc (TcO_4^-) in non-reducing conditions in a variety of pH conditions. PDCA was found to form complex with Tc and enable separation in reducing conditions but to elute with poor quantitativity. However, in non-reducing conditions separation with PDCA was very good and quantitative (Figure 18).

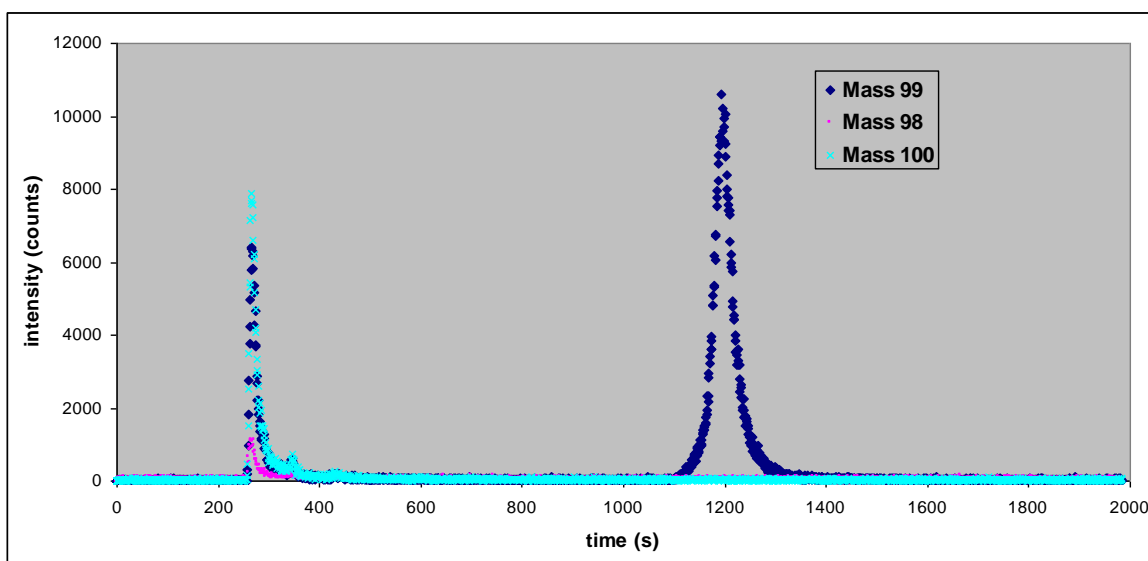


Figure 18. Separation of ^{99m}Tc from Mo (mass 98) and Ru (mass 100) by using dipicolinic acid eluent in non-reducing conditions.

Oxalic acid in reducing conditions applied to environmental sample material has shown to enable the separation but being very sensitive to chemical conditions making it difficult to establish repeatable elution behaviour. From the experiments it can be suggested that in the simultaneous reduction/complexation process variable amount of Tc-oxalate complexes are formed which is then shown in elution curves. When PDCA was tested with environmental sample material the conditions were non-reducing and thus more easy to handle. It was found out that elution of Tc with PDCA enables the separation from Ru and Mo, however, the quantitativity being dependent on complexation time. This can also be seen when anionic column is coupled with chromatographic column; short complexation time causes inefficient elution of Tc-PDCA from the anionic column. Time factor in Tc-PDCA elution is currently under investigation.

Experiments have shown that the applied ion chromatography column is able to separate Tc quantitatively from Ru and Mo. This separation can be achieved by different complexing agents in different chemical conditions. Further work will adjust the method so that it is fully applicable to environmental samples of various kinds.

Successful application of methods developed

Applications (Norway)

Pu-isotopes in Norway top soil

Several soil samples from all regions of Norway, top soils collected in 1990 and 2005. 1990-series measured for activity of ^{137}Cs and $^{239,240}\text{Pu}$ and isotope ratios of Pu. Attempt to measure U-concentrations and isotope ratios failed due to contamination issues. Similar works in Finland (Ikaheimonen 2000; Paatero and Jaakkol 1994; Paatero et al. 2002) and Sweden (Lindahl et al. 2004) indicates Pu-isotope ratios deviant from global fallout and Chernobyl influence, Chernobyl signal found for ^{137}Cs in these samples. Samples from Sweden were lichens sampled a few months to years after the accident, the samples from Finland (Paatero et al. 2002) were probably sampled in the same period. The Swedish samples had 240/239 values clearly deviant from global fallout.

Some 40 topsoil samples analysed successfully with 2 – 5 replicates, the majority of the samples were found to be within the range of global fallout regarding the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio (0.18), some were slightly above, and one found to be below. All but one ^{239}Pu concentrations found to be above the determination limit, three ^{240}Pu concentrations below determination limit of which one was also below detection limit. Intercomparison test samples were analysed for Pu to secure high precision.

The most important results was isotope ratios $^{240}\text{Pu}/^{239}\text{Pu}$ found in the range 0.166 - 0.22, and concentrations between $2.6 \times 10^{-10} - 5.6 \times 10^{-9}$ g/kg and $4.9 \times 10^{-11} - 9.3 \times 10^{-10}$ g/kg for ^{239}Pu and ^{240}Pu respectively. Therefore, the analysis gave successful results for post-Chernobyl soil samples from Norway utilizing aqua regia leaching and HR-ICP-MS. Results found to indicate strong global fallout influence, although global fallout consists of small and relatively soluble Pu-particles (Bermudez). More thorough digestion methods might reveal an underlying signal stemming from more refractive Chernobyl-fallout.

U, Th and metals in Fen area, Norway

Concentrations of radionuclides ^{232}Th , ^{238}U and metals As, Cr, Pb, Cd, Ni, Cu and Zn in all samples were measured with ICP - MS analysis of extracts after microwave decomposition (Milestone Inc., Ultraclave High performance reactor, Shelton, CT), employing high - grade purity HNO_3 acid for soil and rocks and HNO_3 in combination with H_2O_2 for plant samples.

Working conditions were set on 6 consecutive steps, with increasing temperature $24\text{ }^\circ\text{C} - 260\text{ }^\circ\text{C}$ and increasing pressure 40 – 170 bar. Internal standard that contained 4 mg/L of In, Tl and Rh in 2 % HNO_3 was added systematically to each sample before decomposition.

ICP - MS analysis was done using a Perkin ElmerSciex Elan 6000 (Norwalk CT, USA) with electro thermal vaporization (ETV) unit. All rock and soil samples were measured in 1 % HNO_3 solutions and all plant samples in 3.5 % HNO_3 solutions. Each sample was determined by 3 injections. Detection limits were calculated as three times standard deviation of blank samples measurements.

The accuracy of the analysis was assured using certified reference materials NCS DC 73325 for soil and NCS DC 73348 for plants. Calibration standards, reagent blanks and method blanks were also systematically used throughout ICP - MS measurements.

Results of soil analysis (Table 5) showed wide ranges in radionuclides activity concentrations, 69 - 6581 Bq/kg and 49 - 130 Bq/kg, for ^{232}Th and ^{238}U , respectively. These values clearly exceed the world average values for soil 30 Bq/kg for ^{232}Th and 35 Bq/kg for ^{238}U given by (Unsear 2000).

Table 5. Concentrations of ^{232}Th and ^{238}U (mg/kg) and corresponding activity concentrations (Bq/kg) in soil samples (mean \pm st.dev), n = 5.

| Site | ^{232}Th (mg/kg) | ^{238}U (mg/kg) | ^{232}Th (Bq/kg)* | ^{238}U (Bq/kg)* |
|------|------------------------------|-----------------------------|-------------------------------|------------------------------|
| S1 | 17 \pm 2 | 4 \pm 1 | 69 \pm 8 | 49 \pm 12 |
| F3 | 988 \pm 274 | 9 \pm 3 | 4011 \pm 1108 | 111 \pm 37 |
| F4 | 1124 \pm 23 | 9 \pm 3 | 4563 \pm 93 | 111 \pm 37 |
| T1 | 261 \pm 7 | 10.5 \pm 0.4 | 1059 \pm 28 | 130 \pm 5 |
| G11 | 1621 \pm 91 | 7 \pm 5 | 6581 \pm 364 | 86 \pm 62 |
| G13 | 1424 \pm 209 | 5.5 \pm 0.5 | 5781 \pm 848 | 68 \pm 6 |
| G14 | 1192 \pm 31 | 6.9 \pm 0.4 | 4839 \pm 126 | 85 \pm 5 |

*Activity concentrations (Bq/kg) obtained by multiplying concentrations with factor 4.06 and 12.35 for ^{232}Th and ^{238}U , respectively.

The highest ^{232}Th concentration was found in soil at site G11, area Gruvehaugen, and the lowest at site S1, area Søvgruve. The pattern of ^{232}Th distribution in soil of whole area is in connection to the abundance of rock type rødberg (with high ^{232}Th level) at sites Gruvehaugen and Fenguve and with the abundance of rock type søvite (considerable lower ^{232}Th level) in area of Søvgruve. Also, as mentioned above, former niobium mining site Søvgruve was covered with a protective layer of clay and sand material which contributed to lower radionuclides results for soil obtained in our investigation. Comparison of ^{232}Th concentration median in TENORM rich and background soil samples showed significant difference (Kruskal-Wallis test, $H = 31.50$, $p < 0.05$). Maximum ^{238}U concentration, 130 Bq/kg, was measured on site T1, what is an unexpected high value considering that this sampling site was chosen to represent background area (outside main investigated past mining Fen area). It indicated that high radionuclides concentrations could be measured not only on TENORM, but on other, non-disturbed sites in the area. Correlation analysis of ^{232}Th and ^{238}U did not show any significant relationship. The most likely explanation is that different and not connected minerals are origins for these two radionuclides in rocks. Generally, soil concentration results suggested that erosion and weathering of rocks led to formation of soil layers significantly enriched in radionuclides. Intensive mining activities from the past and excavation of radionuclide rich materials, additionally, gave increase of radiation locally. Similar results for soil ^{232}Th and ^{238}U distribution were obtained in study of Ramli et al (2005) and Lee et al. (2009), where soils from region of Johor in Malaysia with abundance of

basic volcanic rocks rich in monazite were investigated. Investigation of carbonatite rocks, type søvite, in Uganda (Kisolo and Barifaijo 2008) showed higher, but comparable values for ^{232}Th and similar for ^{238}U .

The dependence of air measured gamma dose rates on ^{232}Th activity concentration in soil was confirmed by significant positive linear correlation found (figure 19) ($r = 0.78$, $p < 0.001$, $n = 30$).

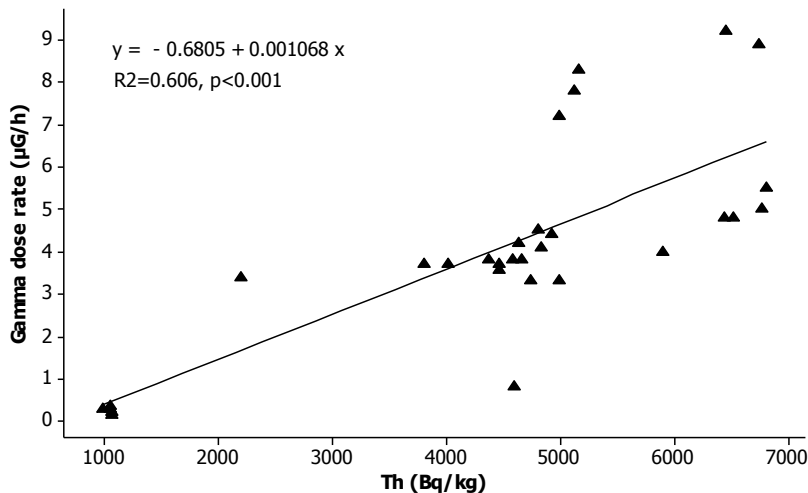


Figure 19. Relationship between ^{232}Th activity concentration in soil and terrestrial gamma dose rate measured in Fen wood.

However, it is possible that some mother–daughter equilibriums in ^{232}Th and ^{238}U radionuclides decay chains were disturbed due to Ra mobility or radon (Rn) emission, giving the high gamma daughters that contributed to some extremely high measured dose rate. Thus, this relationship showed the need for more investigation into the actual concentration of thorium and uranium daughter products.

To check the possibility for a multiple radiological and metal contamination in this area, soil samples were simultaneously analyzed for metals such as As, Cr, Ni, Cd, Pb, Cu and Zn. Obtained concentrations of metals are given in Table 6. Default upper limit values for soil that can be consider as non-polluted in Norway, given by Norwegian Pollution Control Authority (Klif), are also presented in Table 6 in comparison purpose (Klif 2009).

Arsenic concentrations in soil samples (with an exception of site S1 with protective sand layer) were higher than value of 8 mg/kg for non-polluted Norwegian soil. Earlier investigation of soil samples from Fen area (NGI and UMB 2010) showed similar high values of As. Analysis of relationship between As and ^{232}Th concentration showed strong positive linear correlation ($r = 0.86$, $p < 0.05$, $n = 35$) (figure 20). However, no correlation between As and ^{238}U was found. This result could indicate that As is metal follower of radionuclide ^{232}Th , i.e., present in same minerals as ^{232}Th . The concentration range for Pb in samples of soil taken in Fen area was 47 - 287 mg/kg, with median value of 65 mg/kg. Obtained results for 4 of 7 investigated sites are higher than KLIF (2009) value, but in accordance with results obtained for southern Norway and correlated to pollution due to long range transport (Amap 1998; Steinnes and Ruhling 2002).

Table 6. Metals concentrations (mg/kg) in soil samples (mean ± st.dev), n = 5

| Site | As | Cd | Pb | Cr | Ni | Cu | Zn |
|------|----------|-------------|----------|----------|----------|-----------|----------|
| S1 | 4±4 | 0.26±0.01 | 47 ± 5 | 26±23 | 14±15 | 45 ± 24 | 210± 52 |
| F3 | 20±5 | 0.60 ± 0.14 | 134 ± 95 | 33±19 | 37±20 | 9 ± 12 | 47 ± 5 |
| F4 | 17±1 | 0.73 ±0.07 | 121 ± 23 | 40±8 | 34±11 | 9±7 | 891± 334 |
| T1 | 7±1 | 0.48±0.02 | 287± 10 | 30.0±0.3 | 22.1±0.3 | 11.7±0.1 | 242±3 |
| G11 | 20±6 | 1.88±0.59 | 55±7 | 54±14 | 57±13 | 5±2 | 1021±300 |
| G13 | 20±1 | 0.68 ± 0.07 | 65± 10 | 66±4 | 76±11 | 6.4 ± 0.5 | 258± 28 |
| G14 | 16.7±0.2 | 0.54 ± 0.07 | 59 ± 2 | 89±3 | 54±2 | 5.9 ± 0.4 | 268 ± 27 |
| SFT* | 8 | 1.5 | 60 | 50 | 60 | 100 | 200 |

* SFT (Norwegian Pollution Control Authority) standard values - criteria for non-polluted soil

Moderate positive correlation was found between Pb concentrations and ^{238}U concentrations in soil ($r = 0.61$, $p < 0.05$, $n = 35$), but only weak negative correlation was found with ^{232}Th ($r = -0.37$, $p = 0.028$, $n = 35$). Opposite to As, it is likely that Pb is ^{238}U follower, connected with it in same mineral types. Cd concentrations in soil were in ranges often given for soil in the vicinity of sedimentary or Fe rich rocks and soil in different parts of Norway (Berg and Steinnes 2005; Cook and Marrow 1995; Klif 2009; Salbu and Steinnes 1995; Steinnes and Ruhling 2002). Zn was found to be present in different levels in soil, from 205 - 706 mg/kg. These values are 3 - 10 times higher than those found in Norwegian surface soil, by Steinnes and Ruhling (2002). Cr and Ni exceeded KLIF (2009) values in samples taken at sites G11, G13 and G14, in wooden area of Gruvehaugen where high radionuclides levels were also found. Results of Cu levels in soil were in agreement with the different abundance of Cu, from 2 - 250 mg/kg, in different soil types (Salbu and Steinnes 1995; Steinnes and Ruhling 2002). Cd, Zn and Cr showed moderate positive linear correlation with ^{232}Th concentrations ($r = 0.63$, $r = 0.58$ and $r = 0.44$ respectively, all $p < 0.05$, $n = 35$). Relationship of soil Ni concentrations and ^{232}Th was, as in case of As, strong positively correlated ($r = 0.74$, $p < 0.05$, $n = 35$) (figure 21). Cu levels were negatively correlated to ^{232}Th in soil.

In general, distribution of all metals was found to be very inhomogeneous and variable even on close sampling points. High levels of As, Pb, Cr, Ni and Zn on some sampling locations in Fen area are results of local loading due to weathering of bedrocks and leaching upon different environmental conditions, and especially during the mining and milling activities in past centuries. Positive correlations of mentioned metals with ^{232}Th could indicate that these metals have origin in ^{232}Th rich rocks.

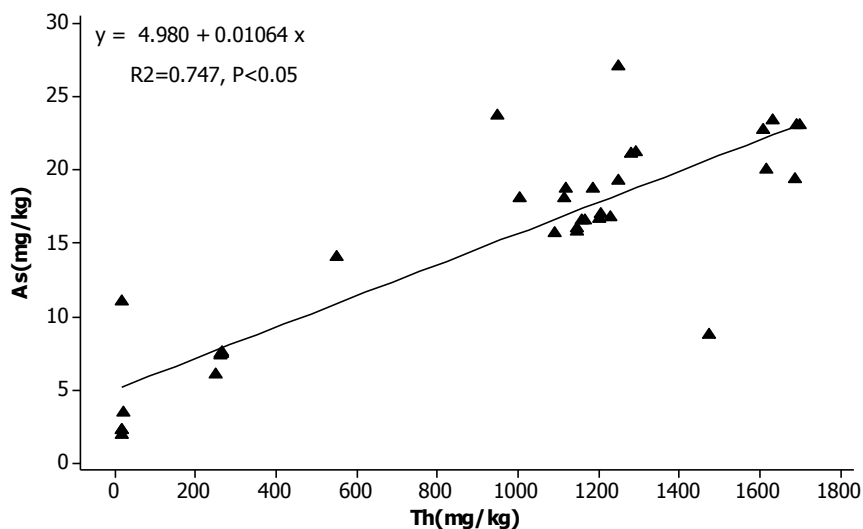


Figure 20. Relationship of As concentrations with ²³²Th concentrations in soil samples

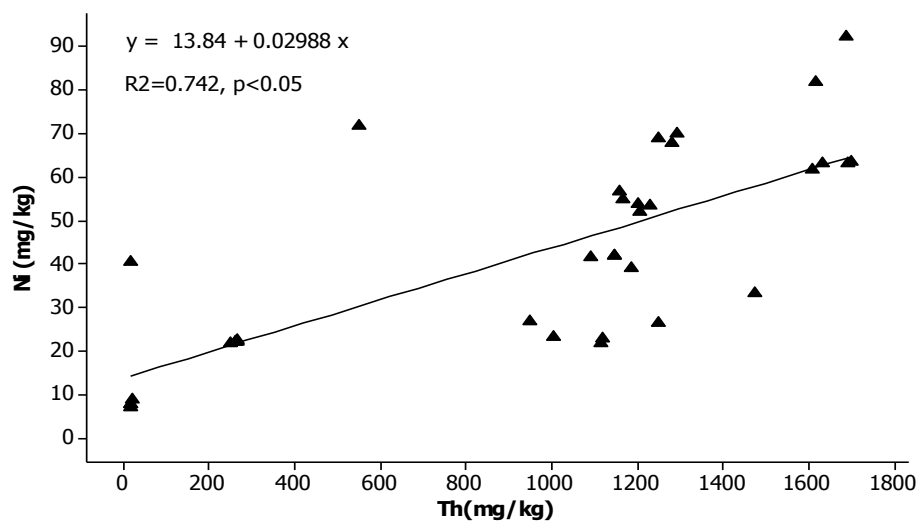


Figure 21. Relationship of Ni concentrations with ²³²Th concentrations in soil samples

The presence of metals like As, Pb and Cr together with extremely high ²³²Th and ²³⁸U concentration in soil gives both chemical and radiological toxicity. These contaminants, when taken up by biota, could cause diverse biological effects – consequences of additive or synergistic acting (Salbu et al. 2005). Thus, future work will be focused on radionuclides and metals mobility and transfer factors into vegetation and animal species of the region, measured on ICP-MS.

Applications (Finland)

With Pu reference solution, the measured isotope concentrations corresponded well to the calculated concentration values. On the other hand, the measured concentrations of ^{239}Pu and ^{240}Pu in reference sediment and soil samples were sometimes significantly different from literature values, probably due to matrix effects and very low Pu concentration in samples (small sample size). The optimization of the method for determining ^{239}Pu and ^{240}Pu from environmental samples must be continued in the Laboratory of Radiochemistry. Low concentration of ^{239}Pu and ^{240}Pu in most environmental samples leads to high uncertainties in measured mass concentrations, although this problem can be partially solved by adjusting the instrumental settings. In this work, RSD of 1-5% was achieved for mass concentrations of ^{239}Pu and ^{240}Pu in Pu reference solution and with the reference soil/sediment samples the RSDs were even greater. High uncertainties of isotope concentrations results in large error for $^{240}\text{Pu}/^{239}\text{Pu}$ ratio, which decreases the reliability of Pu source estimation.

Pu mass concentrations of ppt level in investigated environmental samples and NKS intercomparison sample were the lowest elemental concentrations that have ever been measured with our instrument. After adjustments of the ICP-MS instrument, we finally have a method which is functional and reliable for determining ^{239}Pu and ^{240}Pu from environmental samples by ICP-MS. However, the method will be further modified, for improving the radiochemical recovery of Pu in separation procedure and it will be found out if the tuning parameters of the ICP-MS instrument can be altered more for getting even better detection sensitivity for ^{239}Pu and ^{240}Pu .

After gaining an optimized method for determining Pu isotopes, it is possible to focus on even more challenging determination procedure of ^{237}Np by HR-ICP-MS in near future.

Application (Iceland)

Whole-rock analysis

Approximately 100 mg rock powder was dissolved in concentrated HF-HNO₃, evaporated to near dryness and re-dissolved in 7M HNO₃. The aliquot was evaporated to near dryness and subsequently diluted in HNO₃ 0.4 M to reach a total dilution factor of 5000 for determination of trace element abundances by quadrupole ICP-MS (Agilent 7500, Laboratoire Magmas et Volcans, Clermont-Ferrand, France). The signal was calibrated externally with a reference basaltic standard (BHVO-2, batch 759) dissolved as samples, and employing the GeoReM preferred values (<http://georem.mpch-mainz.gwdg.de/>). Both standards and pure HNO₃ 0.4 M were measured every 4 samples. The external reproducibility of the method, as estimated by running repeatedly different standards (BCR-2, BIR, BEN) is < 5% (2 σ) for most lithophile elements and < 15% for chalcophile elements.

In-situ analysis

Laser ablation inductively coupled plasma mass spectrometry

Trace element analyses in glasses were performed at the Laboratoire Magmas et Volcans using a Resonetics M50 EXCIMER laser (193 nm) coupled to an Agilent 7500cs ICP-MS. The laser was operated at 6 mJ energy, 2 Hz repetition rate and a 11 μm spot size diameter. Ablation gas was

pure helium; nitrogen (7ml/min) and argon was mixed with the carrier gas via Y-connectors between the ablation cell and ICP-MS. Analysis duration was split up in two distinct parts: 40s background acquisition followed by 50 s data acquisition from the sample. Stability of signal intensity during ablation provided a good indicator of the analytical spot homogeneity.

The raw analyses were reduced with the Glitter software (van Achterberg et al., 2001) using CaO concentrations (measured earlier by electron microprobe) as internal standard. NIST 612 glass was used as the primary standard; NIST 612, BCR2-G and A-THO, periodically analyzed during the laser sessions, were used as reference materials to estimate precision and accuracy. Despite the small spot size, precision and accuracy were always better than 10% for all the elements at 95% confidence level.

Intercalibration exercise within NKS Method project

Subsamples of an unknown standard reference sample purchased from National Institute of Standards and Technologies (USA), were distributed to NKS Method participants in 2010. The participants analyzed radionuclides of their choice, and the results are presented in Figure 22 and 23. The intercomparison showed that the results obtained by Method-MS labs were in good agreement with certified values.

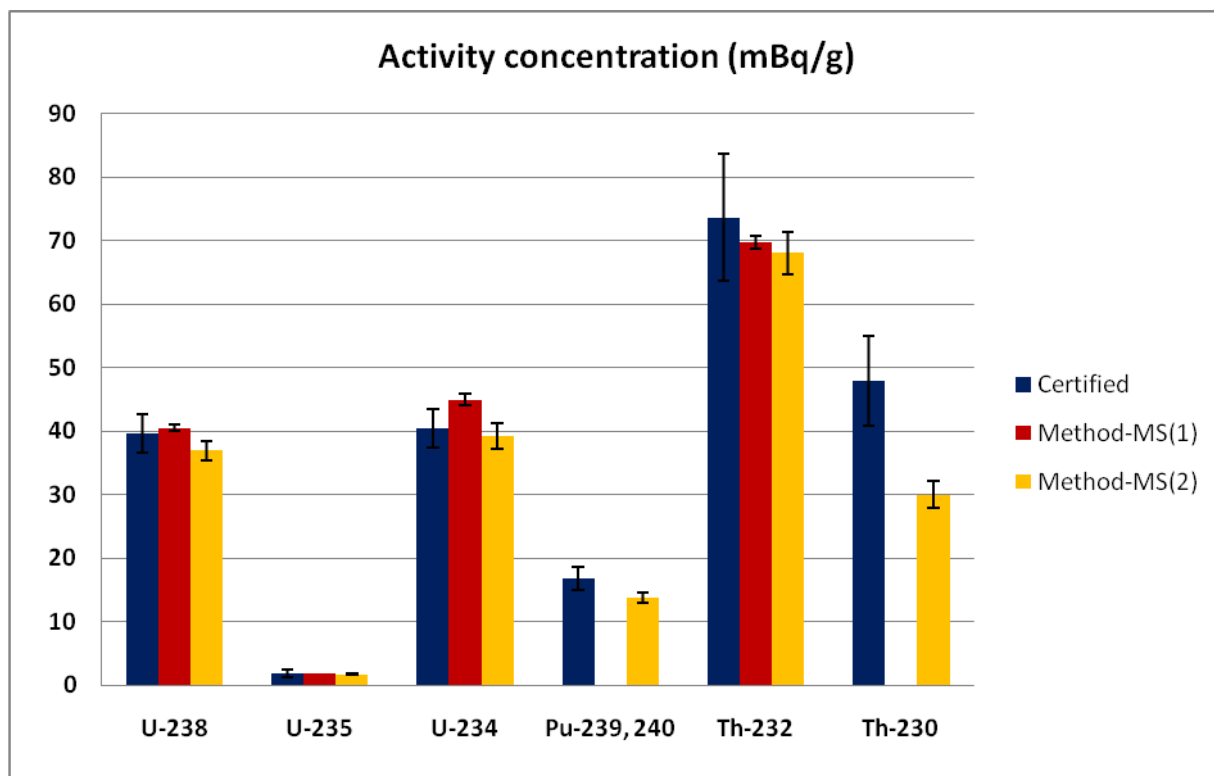


Figure 22 Intercomparison results. Blue bars are activity certified value, while red and yellow bars are activity concentrations reported by Method-MS labs.

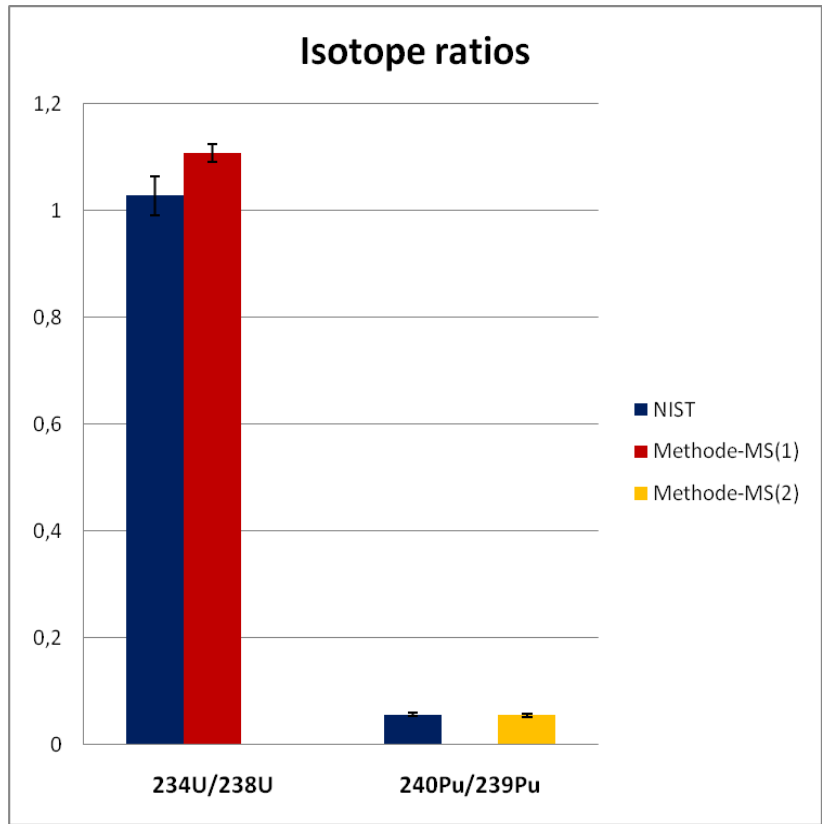


Figure 23. Intercomparison results. Blue bars are isotope ratio (mass) certified value, while red bars are isotope ratio (mass) reported by Method-MS labs.

Conclusion

In recent years, the field of ICP-MS has expanded into many areas of science. Despite its maturity, growth continues at a rapid pace, both in terms of new facilities and in the diversity of applications. Applications of ICP-MS methods in environmental sciences is expected to expand further in the foreseeable future with long-lived radionuclides contributing to a large body of knowledge on processes involving atmosphere, oceans, ice sheets, biosphere, soils and sediments. Finally, the range of heavier radioisotopes now detectable by ICP-MS, including plutonium and other actinide isotopes, is increasing applications on the consequences and uses of releases from nuclear energy. The ICP-MS measurements itself is not too expensive, and in science there may be big reductions in total cost from using ICP-MS, because sample sizes can be much smaller than for other techniques, and sample preparation (particularly for actinide work) is far less labor intensive.

The methods developed during the NKS-Method project, will show themselves useful within a variety of applications. The generally low levels of radionuclides in environmental samples, often combined with limited sample sizes, necessitate reliable low-level techniques for determination of Pu isotopes. ICP-MS has proven to be a good tool together with traditional α -spectrometry when it comes to determining total uranium, plutonium and other long lived nuclides and their isotope ratios in contaminated areas. The methods precision is good and will take the scientific and analytical perspective and possibilities within the Nordic countries to a new level.

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| Abstract | <p>Radiometric determination methods, such as alpha spectrometry require long counting times when low activities are to be determined. Mass spectrometric techniques as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Thermal Ionisation Mass Spectrometry (TIMS) and Accelerator Mass Spectrometry (AMS) have shown several advantages compared to traditional methods when measuring long-lived radionuclides. Mass spectrometric methods for determination of very low concentrations of elemental isotopes, and thereby isotopic ratios, have been developed using a variety of ion sources. Although primarily applied to the determination of the lighter stable element isotopes and radioactive isotopes in geological studies, the techniques can equally well be applied to the measurement of activity concentrations of long-lived low-level radionuclides in various samples using "isotope dilution" methods such as those applied in inductively coupled plasma mass spectrometry (ICP-MS).</p> <p>Due to the low specific activity of long-lived radionuclides, many of these are more conveniently detected using mass spectrometric techniques. Mass spectrometry also enables the individual determination of Pu-239 and Pu-240, which cannot be obtained by alpha spectrometry. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are rapidly growing techniques for the ultra-trace analytical determination of stable and long-lived isotopes and have a wide potential within environmental science, including ecosystem tracers and radio ecological studies. Such instrumentation, of course needs good radiochemical separation, to give best performance.</p> <p>The objectives of the project is to identify current needs and problems within low-level determination of long-lived radioisotopes by ICP-MS, to perform intercalibration and development and improvement of ICP-MS methods for the measurement of radionuclides and isotope ratios and to develop new methods based on modified separation chemistry applied to new auxiliary equipment.</p> |
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