Determination of actinides using ICP-SFMS

Ulrika Nygren
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Abstract

Interest in the determination of the actinides using ICP-MS has steadily increased with the development of systems capable of more sensitive and precise measurements. However, the analysis of less abundant actinides such as Pu and Am is not straightforward due to the need for chemical separation of these elements prior to determination. In many applications of mass-spectrometric actinide analysis, isotope ratio measurements are important, either for the analysis of the isotopic composition of, e.g., U or Pu in the sample, or for quantitative determinations using isotope dilution mass spectrometry. In order to achieve high precision and accuracy in an isotope ratio measurement, corrections for instrumentally induced systematic errors, e.g., due to dead-time and mass bias, need to be considered.

In this thesis, different aspects of actinide analysis using ICP-SFMS have been addressed. In Papers I and III, separation procedures based on solid phase extraction for Pu, Am and U were developed and evaluated with respect to chemical yield and separation from elements causing spectral interferences. Applications of the analytical procedures developed comprised measurement of the \(^{240}\text{Pu}/^{239}\text{Pu}\) ratio in environmental reference materials (Paper I), and age determination of Pu based on the \(^{241}\text{Pu}/^{241}\text{Am}\) and \(^{240}\text{Pu}/^{236}\text{U}\) ratios (Paper III). In the application of different separation procedures for Pu (Paper I), previously unidentified spectral interferences were discovered. In Paper II, these interferences were identified as lanthanide phosphate ions and the composition and formation of these species with respect to different instrumental parameters were further examined.

Due to the importance of precise and accurate isotope ratio determination, a thorough investigation of the instrumental dead time of an ICP-SFMS system was performed. The dead time was evaluated via both isotope ratio and electronic measurements of the output from the detector amplifier. It was found that the overall uncertainty in ratio measurements can be significantly reduced by using an electronically determined dead time due to the inherently higher precision compared to traditional isotope ratio based approaches. However, this requires that an correct artificial dead-time is implemented in the pulse counting system (Paper IV).
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List of publications

This thesis is based on the work contained in the following papers and submitted manuscripts, which are referred to by their Roman numerals.

I. Separation of plutonium from soil and sediment prior to determination by inductively coupled plasma mass spectrometry
   Ulrika Nygren, Ilia Rodushkin, Calle Nilsson and Douglas C. Baxter

II. Lanthanide phosphate interferences in actinide determination using inductively coupled plasma mass spectrometry
   Ulrika Nygren, Henrik Ramebäck, Douglas C. Baxter and Calle Nilsson
   *Journal of Analytical Atomic Spectrometry* 20 (2005) 529-534

III. Age determination of plutonium using ICP-SFMS
    Ulrika Nygren, Henrik Ramebäck and Calle Nilsson
    Accepted after minor revision for publication in *Journal of Radioanalytical and Nuclear Chemistry*

IV. The importance of a correct dead time setting in isotope ratio mass spectrometry: Implementation of an electronic determined dead time to reduce measurement uncertainty
    Ulrika Nygren, Henrik Ramebäck, Michael Berglund and Douglas C. Baxter
    Accepted after minor revision for publication in *International Journal of Mass Spectrometry*
1 Introduction

Of the actinides, the two elements of most importance for nuclear energy and weapons production are uranium and plutonium. Uranium is present in the environment in relatively high concentrations\(^1\), and the isotopic composition of naturally occurring U is 99.27% $^{238}\text{U}$ and 0.72% $^{235}\text{U}$\(^2\). The production of uranium nuclear reactor fuel consists of four basic steps, i.e., mining, refining, isotope enrichment and fuel element fabrication.\(^3\) Plutonium is primarily produced in nuclear reactors by (n,\(\gamma\)) reaction of $^{238}\text{U}$ to $^{239}\text{U}$ followed by beta-decay via $^{239}\text{Np}$ to $^{239}\text{Pu}$. Further (n,\(\gamma\)) reactions of $^{239}\text{Pu}$ produce plutonium isotopes of higher masses, while $^{238}\text{Pu}$ is produced by multiple neutron capture of $^{235}\text{U}$ to $^{237}\text{U}$ followed by decay to $^{237}\text{Np}$, and (n,\(\gamma\)) to $^{238}\text{Np}$, which finally decays to $^{238}\text{Pu}$\(^3\),\(^4\),\(^5\). The nuclear reactions producing Pu as well as Am and Cm are outlined in Fig. 1.

![Fig. 1. Nuclear reactions in the irradiation of uranium.\(^3\) Fission and \(\alpha\)-decay have for clarity been omitted from the diagram.](image-url)
The isotopes of primary interest for use in nuclear reactors and nuclear weapons are $^{235}\text{U}$ and $^{239}\text{Pu}$ due to their high fissionability and relatively high availability. Furthermore, the isotopic composition of U or Pu is critical for the intended use of the material, since the manufacture of nuclear weapons requires higher concentrations of $^{235}\text{U}$ or $^{239}\text{Pu}$ compared to the levels required in fuel for production of nuclear energy. U and Pu materials are often divided in different categories depending on isotopic content (Table 1). Depleted uranium is the “left over” material from the isotope enrichment process and hence the amount of $^{235}\text{U}$ is lower than in naturally occurring uranium. Low enriched uranium is the category usually employed for energy production. Highly enriched uranium and weapons-grade uranium can both be used for nuclear weapons production. Reactor grade Pu is produced in regular nuclear power reactors while weapons-grade Pu generally is produced from low burn-up of natural or slightly enriched uranium fuel in so called production reactors. In principle all categories of Pu, with the exception of material containing more than 80% $^{238}\text{Pu}$ can be used to make nuclear devices. Besides information on the intended use, the isotopic composition also reveals the origin and history of the material. The isotopic composition of Pu from potential sources of contamination of the Artic Ocean is summarised in Table 2.

<table>
<thead>
<tr>
<th>Category</th>
<th>$^{235}\text{U}$ (%)</th>
<th>$^{239}\text{Pu}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depleted uranium</td>
<td>&lt; 0.71</td>
<td></td>
</tr>
<tr>
<td>Natural uranium</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>Low enriched uranium (LEU)</td>
<td>0.71-20 (usually 3-5)</td>
<td></td>
</tr>
<tr>
<td>Highly enriched uranium (HEU)</td>
<td>&gt; 20 (usually 90)</td>
<td></td>
</tr>
<tr>
<td>Weapons-grade uranium (WGU)</td>
<td>&gt; 90</td>
<td></td>
</tr>
<tr>
<td>Reactor-grade plutonium (RGPu)</td>
<td>&gt; 19</td>
<td></td>
</tr>
<tr>
<td>Fuel-grade plutonium (FGPu)</td>
<td>7-19</td>
<td></td>
</tr>
<tr>
<td>Weapon-grade plutonium (WGPu)</td>
<td>&lt; 7</td>
<td></td>
</tr>
<tr>
<td>(Super-grade Pu (SGPu))</td>
<td>(&lt; 3)</td>
<td></td>
</tr>
</tbody>
</table>
Table 2  Plutonium isotope ratios for various sources (decay corrected to January 1, 1995). Data extracted from Cooper et al.9

<table>
<thead>
<tr>
<th>Source</th>
<th>$^{238}\text{Pu}/^{239}\text{Pu}$</th>
<th>$^{240}\text{Pu}/^{239}\text{Pu}$</th>
<th>$^{241}\text{Pu}/^{239}\text{Pu}$</th>
<th>$^{242}\text{Pu}/^{239}\text{Pu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric testing (Northern</td>
<td>$(17.7\pm0.32)\cdot10^{-4}$</td>
<td>$0.1808\pm0.0057$</td>
<td>$(2.64\pm0.20)\cdot10^{-3}$</td>
<td>$(4.0\pm0.3)\cdot10^{-3}$</td>
</tr>
<tr>
<td>hemisphere average)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kyshtym, accidental release of</td>
<td>$(3.34\pm0.89)\cdot10^{-5}$</td>
<td>$0.0282\pm0.0001$</td>
<td>$(2.31\pm0.06)\cdot10^{-4}$</td>
<td>$(7.15\pm0.26)\cdot10^{-5}$</td>
</tr>
<tr>
<td>weapons grade Pu</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sellafield discharge</td>
<td>0.0118</td>
<td>0.1838</td>
<td>0.0116</td>
<td>0.0053</td>
</tr>
<tr>
<td>Chernobyl accident</td>
<td>0.00334</td>
<td>0.563</td>
<td>0.14</td>
<td>0.0429</td>
</tr>
</tbody>
</table>

Actinides and other radioactive nuclides have been released to the environment primarily due to nuclear weapons testing, nuclear energy production and reactor accidents.1 Concerning actinides only, additional contamination has occurred due to destruction of the satellites SNAP9A (1964) and Cosmos 954 (1978) in the atmosphere and crashes of nuclear weapons carrying military aircraft in Palomares (1966) and Thule (1968).1 Since the decay mode of most actinides is by the emission of an $\alpha$-particle, the radiotoxicity of these nuclides is relatively high and there is therefore a need to monitor the levels of the actinides in the environment both on a routine basis and in a radiological emergency situation. From a radioanalytical perspective, the requirement on the type and quality of the analysis is dependent on the application of the analytical results. Environmental monitoring and radio-ecological studies often involve low concentrations and hence require low detection limits of the analytical method, while in emergency preparedness a fast response can be more important than high accuracy and sensitivity. In, e.g., nuclear forensics and safeguards, isotope ratio determination with high precision is crucial.

Since the introduction of inductively coupled plasma mass spectrometry (ICP-MS) in the early 1980s, its use for the determination of the actinides has steadily increased. Advantages of the technique include the ability to perform isotope specific analysis, multi-element capability and speed of analysis. In general, actinide isotope ratio measurements have traditionally been performed with thermal ionisation mass
spectrometry (TIMS), while radiometric techniques have been used for concentration
determinations. The development of more sensitive and stable ICP-MS systems has
made this technique an alternative to TIMS for isotope ratio determinations.\textsuperscript{10}

Compared to radiometric determination, ICP-MS is generally more sensitive for long-
lived radionuclides.\textsuperscript{11} This is due to the relationship between the amount, \(N\), and
counting efficiency results in about 49\% relative standard deviation (\(k=2\)) on the
determined activity. The 1mBq level is indicated as a solid line in Fig. 2. Hence, if
1mBq is chosen as a representative practical determination limit for \(\alpha\)-spectrometry,
then the nuclides above the solid line in Fig. 2 have lower determination limits using
\(\alpha\)-spectrometry than ICP-SFMS.

In many applications of elemental analysis using ICP-MS, no chemical treatment other
than simple dissolution of the samples is required. However, for actinide
determinations by ICP-MS, chemical separation of the analyte(s) from the sample
matrix and from other actinides is often necessary to avoid spectral interferences. As
mentioned above, precise isotope ratio measurements are of great value in actinide
determination. Besides removal or correction for spectral interferences, such
determinations also require a thorough knowledge of parameters such as detector
dead-time and instrumental mass-discrimination.
The aim of this work was to improve the capabilities for precise actinide isotope ratio measurements using ICP-SFMS. Different aspects were to be addressed, e.g., improved chemical separation of the analytes (U, Pu and Am), identification and removal of elements causing spectral interferences in the actinide mass region, and examination of the effect of instrumental parameters on the precision and accuracy of actinide isotope ratio determination.

Fig. 2 Relationship between activity and half life for various actinide nuclides for a fixed mass of 10 fg (a practical determination limit for actinide measurement using ICP-SFMS)
2 Radiometric determination of actinides

A short description of two of the most widespread techniques for radiometric, isotope specific determination of actinides, $\alpha$- and $\gamma$-spectrometry, is presented in this chapter.

2.1 $\alpha$-spectrometry

The most common decay mode of the actinides is by emission of an $\alpha$-particle, and hence $\alpha$-spectrometry has been, and still is, a common technique for the determination of these elements. The general procedure of an $\alpha$-spectrometric determination starts with a thorough chemical separation of the analyte(s), preparation of a thin-layer source by electroplating or micro-precipitation and counting using a silicon semiconductor detector. The range of typical $\alpha$-particles (3-8 MeV) in solid material is short (10-100 μm), which explains the requirements for a thin layer geometry and that the counting chamber is maintained under vacuum. The effect of a “thick” source would be peak tailing toward the low energy region, which would consequently reduce the resolution of the spectra. The chemical separation of the analytes is therefore in most cases a requirement for good resolution, but is also necessary to avoid spectral interferences. Common examples of radionuclides with overlapping $\alpha$-energies are $^{238}$Pu (5.499 MeV) and $^{241}$Am (5.486 MeV) as well as $^{239}$Pu (5.157 MeV) and $^{240}$Pu (5.168 MeV). Since $^{239}$Pu and $^{240}$Pu cannot be separated chemically, they cannot be determined individually by regular resolution $\alpha$-spectrometry and the result is often presented as the sum of the activities of these nuclides.

Hence, $\alpha$-spectrometry is a relatively time and labour consuming technique that cannot provide information on the $^{240}$Pu/$^{239}$Pu ratio. However, as mentioned above, for some short-lived $\alpha$-emitting nuclides the detection limits using $\alpha$-spectrometry are favourable compared to those achieved using ICP-SFMS. $\alpha$-spectrometry can also be of use for the determination of isotopes that are severely interfered in mass spectrometric determination, such as $^{238}$Pu. Fig. 3 shows a spectrum from the analysis of the Pu-fraction of Irish Sea sediment using an ion implanted Si detector.
2.2 $\gamma$-spectrometry

The range of $\gamma$-rays is, in contrast to $\alpha$-particles, relatively long (~0.1 m in solid material\textsuperscript{12}), which makes the conditions for $\gamma$-spectrometry quite different from those described for $\alpha$-spectrometry. The detectors most often used for $\gamma$-spectrometry today are High Purity Germanium (HPGe) semiconductor devices. The resolution of these detectors for $\gamma$-spectrometric determinations is generally good with FWHM (full width at half maximum) values of only a few keV.\textsuperscript{12} Due to this, no chemical separation of the analytes is usually required.

The $\alpha$-decay (or in some cases $\beta$-decay) of the actinide nuclides is often followed by the emission of $\gamma$-radiation. However, the abundance and energies of these emissions are generally low which makes $\gamma$-spectrometry a less preferred detection technique for these elements due to lack of sensitivity. Nevertheless, in cases where the sensitivity is sufficient, $\gamma$-spectrometry has the advantage of being a non-destructive technique that can also be used for in-field applications. As an example, $\gamma$-spectrometry was used in Paper III to verify the mass spectrometric dating and isotopic compositional analysis of Pu. A spectrum from such a HPGe analysis of weapons-grade Pu is shown in Fig. 4.
As can be seen in Fig. 4, $^{239}$Pu exhibits several $\gamma$-emission peaks in the energy region depicted. Since the emission probabilities for the different energies are fixed, a relative efficiency curve inherent to each sample for this energy region can be constructed from the $^{239}$Pu peaks. This efficiency curve can then be used for isotope ratio measurements of, e.g., $^{240}$Pu/$^{239}$Pu. The ratio of $^{241}$Pu/$^{241}$Am can also be extracted and used for age determination of the Pu material (see Paper III).

Fig. 4 Spectrum from a HPGe analysis of weapons-grade Pu (reference material IRMM081).
3 Inductively coupled plasma mass spectrometry

There are mainly three different configurations of ICP-MS system, i.e., the quadrupole based (ICP-QMS), the double focusing sector field (ICP-SFMS) and the multi-collector sector field (MC-ICP-MS) devices. Of these, ICP-QMS is the oldest being introduced in the early 1980s, followed by ICP-SFMS (in 1988) and more recently MC-ICP-MS (in 1992). The introduction of ICP-SFMS provided the possibility to perform analyses at higher mass resolution, allowing instrumental separation of many species causing spectral interferences in ICP-QMS. ICP-SFMS also provides lower background and higher ion transmission, and consequently better detection limits compared to ICP-QMS. Another benefit compared to ICP-QMS is higher precision in isotope ratio determinations due to flat-topped peaks in low-resolution mode. The multi-collector system was developed in order to further enhance the precision of isotope ratio measurements by simultaneous detection of the isotopes, thus primarily reducing the influence of plasma fluctuations on the determination.

Another instrumental parameter that varies between different set-ups is the sample introduction system. The traditional set-up is a spray-chamber in combination with a nebuliser, and there are a number of variations of these designed for different applications such as samples with high matrix load, samples containing HF and isotope ratio determinations requiring higher stability. There are also more sophisticated systems available based on, e.g., ultrasonic nebulisation as well as direct injection and electro thermal vaporisation (ETV). Yet other variations involve coupling of chromatographic systems to the nebuliser for on-line separation prior to the analysis, direct sampling of solid materials using laser-ablation ICP-MS and reduction of isobaric interferences using reaction- or collision cells.

The analyses on which this thesis is based were performed using an ICP-SFMS system (Element2, Thermo Finnigan, Bremen, Germany) equipped with either a Scott-type or a cyclonic spray chamber in combination with a conical nebuliser.
3.1 The ICP-SFMS configuration

In principle, an ICP-SFMS system, such as the Element2, consists of the following parts: sample inlet system, ICP ion source, interface region, transfer optics and extraction lens, magnetic sector field analyser, electric sector analyser (ESA) and the detection system. The sample inlet and argon plasma are maintained under atmospheric pressure, while the pressure is reduced to about 10^{-3} mbar in the interface and transfer optics/extraction lens region and further reduced to about 10^{-7} mbar in the mass analyser and detection regions.

In the inlet system, the sample is transformed to an aerosol of which droplets smaller than 10 μm are selected and transferred to the plasma where solvent evaporation, particle vaporisation, atomisation and ionisation occur. The ions are then extracted via the sampler and skimmer cones into the entrance slit of the mass analyser, where they are separated according to their mass to charge ratio (m/z) in the magnetic field and according to their energy by the ESA. After passing the exit slit, the ions are detected by a conversion dynode coupled to a secondary electron multiplier (SEM). Scanning of the mass to charge range is performed either by altering the acceleration voltage or by changing the magnetic field. Changing the magnetic field allows scanning of the whole m/z range (up to about 300) while scanning by changing the acceleration voltage is used for restricted intervals (up to 30% of the start mass set by the magnetic field). Acceleration scanning is substantially faster than magnetic field scanning, and is therefore the preferred mode for, e.g., isotope ratio determination.

Altering the widths of the entrance and exit slits changes the mass resolution. On the Element2, three settings are available; low resolution (m/Δm=300), medium resolution (m/Δm=4000) and high resolution (m/Δm=10000). In low resolution, the entrance slit is wider than the exit slit resulting in the flat-topped peaks that are advantageous for measurement stability due to the resultant insensitivity to shifts in mass calibration during the analysis. However, the intensity of the ion-beam decreases with increasing mass-resolution, which consequently reduces the sensitivity of the analysis. Hence,
low-resolution analysis is to be preferred whenever higher mass resolution is not required to separate the analyte peak from any interfering species.

3.2 Spectral interferences

In spite of the relatively high mass resolution achievable with ICP-SFMS, problems with spectral interferences in actinide determination still exist. These can be divided in three categories, i.e., isobaric overlap, abundance sensitivity and polyatomic species.

3.2.1 Isobaric overlap

Examples of isobaric overlap in actinide determination are $^{238}\text{U}$ and $^{238}\text{Pu}$, $^{241}\text{Pu}$ and $^{241}\text{Am}$ as well as $^{242}\text{Pu}$ and $^{242}\text{Cm}$. The largest difference in mass ($\Delta m$) for these is $0.0012$ u ($m_{238\text{U}}-m_{238\text{Pu}}$), which would require a mass resolution of $\geq190000$ for separation of the corresponding peaks in the mass spectrum. Hence a chemical separation of these elements is required prior to analysis. An example of such a separation for the analysis of $^{241}\text{Pu}$ and $^{241}\text{Am}$ using ICP-SFMS is presented in Paper III.

3.2.2 Abundance sensitivity

Abundance sensitivity is defined as the ratio of the signal measured one mass unit below (or above) a specific isotope to that acquired on peak, and thus describes the tailing from an intense peak on neighbouring masses. The tailing is due to scattering of the ion beam through interaction with residual gas in the mass spectrometer, and hence increases under poorer vacuum conditions. Again, if the intense peak corresponds to an isotope of a different element than the analyte, a chemical separation of the two will reduce the problem. However, if isotopes of the same element are to be analysed, the abundance sensitivity will provide a practical limit to the magnitude of the ratio that may be determined.

One example is the determination of $^{236}\text{U}$ in environmental samples. $^{236}\text{U}$ is primarily produced via $(n,\gamma)$ reaction of $^{235}\text{U}$ in nuclear reactors, and the abundance of this nuclide in the environment is extremely low. Boulyga et al. have examined the
magnitude of tailing from $^{238}\text{U}^+$ on m/z 236 for different ICP-MS systems. They reported values of $(5.0 - 5.3) \times 10^{-6}$ for ICP-SFMS depending on the sample introduction system. In Paper III, $^{236}\text{U}$ was determined in soil from the Trinity “ground zero” (Trinitite) and sediment from the Marshall Islands (reference material IAEA367) contaminated with nuclear weapons debris. The tailing from $^{238}\text{U}^+$ on m/z 236 during that study was about $(1.9 \pm 0.3) \times 10^{-6}$ ($k=2$), i.e., slightly lower than the values reported by Boulyga et al.\textsuperscript{19} In Fig. 5, spectra from the mass regions 233 to 243 for the U fractions of the two materials are shown. As can be seen, the determination of $^{236}\text{U}$ in Trinitite was not severely affected by $^{238}\text{U}^+$ (Fig. 5a), while for IAEA367 measurement was impossible due to tailing from $^{238}\text{U}^+$ (Fig. 5b). In that study, it was also necessary to correct for abundance sensitivity from $^{239}\text{Pu}$ on $^{241}\text{Pu}$ since the tailing resulted in an increased signal for $^{241}\text{Pu}$ of about 6%. However, the $^{241}\text{Pu}/^{239}\text{Pu}$ amount ratio found in this material, average $2.85 \times 10^{-5}$, was unusually low (see Table 2) and Trinitite is exceptional due to the initial high concentration of $^{239}\text{Pu}$ and the high age of the material.

**Fig. 5** Spectra from ICP-SFMS analysis of the U fraction of a) Trinitite and b) IAEA367.

### 3.2.3 Polyatomic species

Probably the most common interference from polyatomic species in actinide determination is the interference from $^{238}\text{U}^+\text{H}^+$ on $^{239}\text{Pu}$. The mass-difference between these two is 0.0065 u,\textsuperscript{27} hence requiring a mass-resolution of $\geq 37000$. In Fig. 5a, a good example of the effect of $^{238}\text{U}^+\text{H}^+$ formation in combination with abundance sensitivity on m/z=239 is shown. The formation of $\text{UH}^+$ is dependent on instrumental
parameters such as sample introduction system and nebuliser gas flow-rate, which can be adjusted to somewhat decrease this interference.\textsuperscript{31, 32} However, during the analysis of samples containing natural U, the concentration of \textsuperscript{238}U is generally several orders of magnitude higher than that of \textsuperscript{239}Pu, and consequently a chemical separation of the two is required in order to remove this interference. In Paper \textbf{I}, different separation procedures based on solid phase extraction (SPE) are evaluated with respect to their abilities to separate Pu from U as well as to provide high chemical yields of Pu. In that study, a single column separation procedure was sufficient for the sample materials (soil and sediment reference material) and quantities used (\(\leq 2\) g). However, when materials containing even lower concentrations of Pu and larger sample quantities are required, repeated separation is often required to sufficiently remove U.\textsuperscript{33}

Besides \textsuperscript{UH}\textsuperscript{+}, interferences from other polyatomic species in the actinide mass-region have also been reported. Examples are \textsuperscript{PbCl}\textsuperscript{+},\textsuperscript{34} \textsuperscript{PtNO}\textsubscript{2}\textsuperscript{+},\textsuperscript{35} as well as \textsuperscript{ReO}\textsubscript{3}\textsuperscript{+} and \textsuperscript{ReO}\textsubscript{3}\textsuperscript{H\textsuperscript{+}}.\textsuperscript{36} In Paper \textbf{I}, seemingly elevated concentrations of Pu were obtained when Pu had been separated in the trivalent oxidation-state. This could be explained by the finding of interfering peaks when scanning the region \(m/z\) 237 – 243 in medium resolution. In Fig. 6, spectra from the scanning of Pu fractions obtained after separation of Pu(III) and Pu(IV) are shown. The interfering peaks in Fig. 6a are at about 0.18 u lower masses than the Pu isotopes and \textsuperscript{238}U. In Paper \textbf{II}, these interferences could be identified as lanthanide-phosphate ions, which was somewhat surprising since interferences from molecules composed of such large numbers of atoms is rarely considered.\textsuperscript{28} It was found that the formation of the lanthanide phosphates was favoured by “cold” plasma conditions, i.e., reduced rf power and increased sample-gas flow rate, as well as larger sampler and skimmer cone orifices. A larger skimmer-cone orifice increases the ion-beam catchment’s diameter and thus the transmission of molecular ions formed in the boundary layer around the sampler cone. Since the gas kinetic temperature is expected to decrease with distance from the centre of the ion-beam, a larger “cool” area is formed thus providing more favourable conditions for the formation of complex polyatomic species.\textsuperscript{37}
3.3 Isotope ratio determination

Actinide determinations by ICP-MS are most often based on isotope ratio measurements, either for the analysis of the isotopic composition of, e.g., U or Pu in the sample, or for quantification whereby a spike is added prior to the chemical separations, i.e., IDMS. In order to achieve accurate isotope ratio measurements, there are certain instrumental offset factors that need to be addressed, i.e., mass discrimination and dead time. In addition to accuracy, high precision is sought for and the factors primarily influencing the uncertainty in ratio determinations are described and discussed below.

3.3.1 Mass discrimination

In ICP-SFMS, the sensitivity increases with increasing mass of the ions analysed. Although this increase becomes less pronounced in higher atomic mass regions pertinent to the actinides, it is still necessary to correct for mass discrimination (or mass bias) in actinide isotope ratio measurements. This correction is usually done via the so-called $K$-factor

$$K = \frac{R}{r}$$

Fig. 6 Spectra from medium resolution scanning ($m/\Delta m = 4000$) of the Pu-fractions from separation of IAEA135 (Sellafield sediment). In a), Pu was separated as Pu(III) and in b) as Pu(IV)
where $R$ is the true (certified) ratio and $r$ is the measured ratio. Several different models based on, e.g., linear, exponential or power-law functions have been proposed for the evaluation of $K$, of which the simplest and most commonly used in ICP-SFMS is the linear function

$$K_{\text{lin}} = 1 + B_{\text{lin}} \Delta m$$

(3)

where $B_{\text{lin}}$ is the mass discrimination per unit mass. Although the relationship of instrumental sensitivity to atomic mass is not strictly linear, the differences between the results returned by different models are generally within the uncertainty obtained for ratio determinations using ICP-SFMS. Hence, the linear model has been used for correction of measured isotope ratios in Papers I, III and IV.

It has also been found that mass bias varies between different elements, although these variations are usually too small to have a significant impact on isotope ratio measurements with the precision achievable using ICP-SFMS. Taylor et al. compared the mass bias factors obtained for U and Pu using MC-ICP-MS and found agreement to within 0.01% \( u^{-1} \) for both elements, and concluded that an isotopic standard of U could be used to correct data acquired for Pu-isotope ratio measurements. That is also the procedure used in Papers I and III, where an isotopic standard containing U of natural composition (IRMM184) was used to evaluate the mass bias.

3.3.2 Dead-time

The detection system in ICP-SFMS is based on pulse counting. In such systems, a finite time is required to process each individual pulse and during this period no further pulses can be registered, i.e., the detector is “dead”. The detector dead time is generally denoted by the symbol $\tau$ (s). These detectors suffer from counting losses and the effect of the dead time increases with increasing count-rate. It is generally assumed that the detection systems used in ICP-SFMS are non-paralysable, i.e., the dead time is fixed and is not extended by the impact of other ions during the processing of a
The measured count-rate for an isotope ion beam, \( I \) (counts s\(^{-1}\)), is related to the true interaction rate, \( ^{0}I \) (counts s\(^{-1}\)), in a non-paralysable system by the relationship

\[
I = (1 - \tau) \cdot ^{0}I; \quad ^{0}I = \frac{I}{1 - \tau}
\]  

(4)

The dead time of an ICP-SFMS system is usually evaluated by analysing different concentrations of an element with a known (certified) isotope ratio, \( R \), and monitoring the change in the measured ratio, \( r \), as a function of concentration. A requirement for this method is obviously that the isotope ratio used is not unity, since the change in the measured ratio is due to the greater effect of \( \tau \) on the intensity of the more abundant isotope. In addition, the measured ratio has to be corrected for mass bias.

Several different approaches to the evaluation of dead time based on ratio measurements have been reported\(^{41}\), of which the more recent are based on linear models followed by regression analysis.\(^{42, 43, 44}\) In Paper I and III, the model presented by Appelblad and Baxter\(^{43}\) was used. This model allows simultaneous evaluation of mass bias and dead time, according to the relationship

\[
r_{M/m} = \frac{I_M}{I_m} = \frac{R}{K} + \tau \left(1 - \frac{R}{K}\right) I_M
\]  

(5)

where \( I_M \) and \( I_m \) are the measured count-rate for the major and minor isotopes respectively. Hence, \( \tau \) can be evaluated from the slope and \( K \) from the slope and intercept of the regression line. This concept requires that the mass bias is relatively constant during the measurement, which is usually the case in ICP-SFMS.\(^{28}\) Another approach, presented, e.g., by Held and Taylor\(^{42}\) and Ramebäck et al.,\(^{44}\) involves the use of two known isotope ratios of which one is near unity. Hence, mass bias can be evaluated from the near-unity ratio and a correction can be made to every individual measured ratio, making this approach less sensitive to changes in mass bias during the
measurement. The dead-time can be evaluated using this approach from the relationship

$$\frac{1}{K r_{Ml/M}} = \frac{1}{R} + r I_M \left( \frac{1}{K} - \frac{1}{R} \right)$$

(6)

Note that, in contrast to Eq. (5), the ratio is here defined with the major isotope as the denominator, which is statistically advantageous since the uncertainty in the determination of the major isotope is generally less than that of the minor isotope. However, a small systematic error is introduced using this expression, since correction for mass bias must be performed before correcting for dead time. Strictly speaking, dead time should be corrected first, since the two operations are not commutative.

In Paper IV, the dead time of the Element2 was determined by measurement of IRMM073, a series of uranium reference materials with near unity $^{235}\text{U}/^{238}\text{U}$ ratio and variable $^{233}\text{U}/^{238}\text{U}$, and by electronic analysis of the pulse amplifier output using an oscilloscope. In that study, the dead times were also evaluated on three different instrumental settings. A dead-time circuit implemented in the pulse amplifier of the detector determines these settings. The default setting when the instrument is delivered from the factory is 10 ns, but a slight modification allows switching the dead time to 20 or 70 ns as well.

The results of the electronically determined dead times, as well as values derived from isotope ratio measurements, via both Eqs. (5) and (6), are displayed in Fig. 7. As can be seen from the latter, no significant differences (at the 95% confidence level) between the dead times evaluated using Eqs. (5) and (6) could be found. However, discrepancies between the electronically- and ratio-determined dead times at instrumental settings of 10 and 20 ns were obtained. This indicates that other components in the detection system, e.g., the electron multiplier, also have dead times long enough to affect the total value of the system when the setting implemented on the amplifier is relatively short. The benefit of introducing a relatively large, well
known artificial dead time is that of masking the contributions of other individual components in the detection system. Another benefit is that the functional dead time of the whole system can be determined via electronic measurements, which provide much higher precision than ratio-based approaches (see section 3.3.3).

![Dead-time determination on Element2. Three different dead-time settings implemented on the pulse amplifier of the detector (10, 20 and 70 ns) were evaluated. The solid lines represent the upper- and lower limits of the electronically determined dead time of the amplifier with \( k = 2 \), viz., \( (11.0 \pm 0.4) \), \( (21.8 \pm 0.4) \) and \( (71.8 \pm 0.4) \) ns, respectively. The symbols represent the dead times determined via isotope ratio analysis for the three setting, where squares represent 10 ns, triangles 20 ns and circles 70 ns; open symbols are for evaluations using Eq. (5) and filled symbols for Eq. (6). Uncertainty bars represent \( U \) where \( k = 2 \).]

### 3.3.3 Precision in isotope ratio measurement

The precision of isotope ratio using ICP-SFMS is affected by two different kinds of parameters, i.e., noise in the actual measurement and uncertainty contributions due to mathematical corrections of the measured data. The two primary sources of noise are counting statistics and flicker noise. Counting statistics is a term used to describe the natural, fundamental variation in the rate at which ions arrive at the detector. This variation is generally considered to be Poisson distributed, and the standard deviation
is consequently defined as the square root of the total number of counts. Hence, the relative uncertainty attributed to counting statistics decreases with increasing number of counts collected. Flicker noise is due to fluctuations in ion-production in the plasma in combination with the sequential sampling of the ion beam used in ICP-SFMS. The root mean square of the flicker noise has been reported to be inversely proportional to the frequency, but also proportional to the number of counts. Hence, acquisition of data by fast “jumping” between the analyte peaks is beneficial due to reduced contribution of flicker noise, while a high count-rate increases the absolute contribution of flicker noise.

Typical mathematical corrections of the measured data are, as described above, for dead time and mass discrimination as well as for blank, abundance sensitivity and spectral interferences. Of these, corrections for dead time and mass discrimination are generally applied to all ratio determinations. Examples of the magnitude of the contributions to the expanded combined uncertainty, \( U \), of a determined isotope ratio are shown in Fig. 8. In the figure, \( U \) for the isotope ratio \( ^{233}\text{U}/^{238}\text{U} \) is shown as a function of the intensity of the major isotope \( ^{238}\text{U} \). The relative contributions of the major sources to the combined uncertainty are shown as well. The data used for the figure are from the analysis of IRMM073/7 made for Paper IV, and the \( ^{233}\text{U}/^{238}\text{U} \) isotope ratio is certified to 0.0198570±0.0000060 (k=2) in this material. The values used for correction of mass bias and dead time in Fig. 8a, and the uncertainties of these values are typical for those obtained in that study (for an instrumental dead-time setting of 10 ns). In Fig. 8b, the input data are the same except for the uncertainty in \( \tau \), where the value obtained from the electronic dead time determination was used. In Fig. 8a, it can be seen that the major contribution to \( U \) at lower count-rates is from the measurement of the minor isotope \( ^{233}\text{U} \), while at count-rates above ~0.9 Mcps for \( ^{238}\text{U} \), the contribution from dead-time correction is dominating. However, in Fig. 8b, it is shown that by reducing the uncertainty in \( \tau \) to that achieved by electronic measurements, \( I_{^{233}\text{U}} \) remains the dominant contribution to \( U \) even at higher count-rates. As expected from Poisson statistics, \( U \) then decreases with increasing count-rates.
Fig. 8 Expanded combined uncertainty, $U$, for the ratio $^{233}$U/$^{238}$U as a function of the intensity of $^{238}$U. The combined uncertainty ($k=2$) is represented by filled diamonds, while the contributions to $U$ from the correction for $\tau$ and mass bias are shown as open squares and open triangles, respectively. The contributions from the measured intensities are shown as crosses for $^{238}$U and open circles for $^{233}$U. The correction for mass bias was performed according to Eq. (3) with $B_{\text{lin}} = 0.001721 \pm 0.000135$. In a) the correction for dead time was made using $\tau = (15.9 \pm 2.2)$ ns and in b) $(15.9 \pm 0.4)$ ns ($k=2$). The data used are from the analysis of IRMM073/7 from Paper IV. The uncertainties have been evaluated using the GUM Workbench$^{48}$. 
4 Chemical separation of the actinides

The solution chemistry of the actinide elements is largely dependent on the oxidation state of the ions. Generally, chemical behaviour is similar for actinide elements in the same oxidation state. The most common oxidation states for actinides in solution are III, IV, V and VI, of which the two latter are oxygenated to the general form \( \text{MO}_2^+ \) and \( \text{MO}_2^{2+} \). Due to the close proximity of the energy levels of the 7s, 6d and 5f electrons, several oxidation states are possible for the same actinide element although some are more stable than others.\(^4\) As an example, for the elements U, Np, Pu and Am, the III to VI states are all possible in solution, but the preferred state varies from VI for U followed by V, IV and III for Np, Pu and Am respectively.\(^4\)

As mentioned above, chemical separation of actinides prior to analysis is in most cases required both for radiometric and mass spectrometric analysis. Several different procedures have been used in the separation of actinides for analytical purposes, e.g., precipitation, solvent extraction and solid phase extraction (SPE). Examples of the separation of U, Pu, Np and Am via selective red-ox adjustment and co-precipitation with rare-earth fluorides have been presented, e.g., by Rao and Cooper\(^49\) and Sill.\(^50\)

Solvent extraction is a widely used technique in actinide separation for industrial purposes, as well as separations for analytical applications.\(^51\) The principle of solvent extraction is the use of two immiscible liquids, e.g., water and an organic solvent, and transfer of solutes between the two phases. In actinide analysis, the sample is usually dissolved in water and the actinides are extracted as uncharged metal complexes to an organic phase. Hence the purpose of the complex formation is both to neutralise the charge of the actinide ion and to produce a complex that is soluble in the organic phase. The desired effect of the extraction is both concentration of the analyte(s) and separation of the analyte(s) from the bulk matrix of the sample as well as from elements that can cause interference in the subsequent analysis. The complexes formed can be divided in three main categories, i.e., chelate type complexes, adduct type complexes and ion pairs.\(^3\),\(^51\) The extent of the extraction is described by the distribution ratio, \( D \), which is defined as “the total analytical concentration of the
substance in the organic phase to its total analytical concentration in the aqueous phase, usually measured at equilibrium\textsuperscript{51} according to

\[ D = \frac{[A]_{\text{org}}}{[A]_{\text{aq}}} \]  \hspace{1cm} (7)

However, for analytical actinide separation, both precipitation and solvent extraction are successively being replaced by solid phase extraction procedures due to the high selectivity and ease of operation. It should also be mentioned for clarity that for most radioanalytical applications, SPE is usually denoted “extraction chromatography”\textsuperscript{52}. Compared to solvent extraction, SPE also reduces the use of organic solvents, which is beneficial from environmental aspects. The separations used in Papers I and III are all based on SPE.

4.1 Solid-phase extraction procedures

A SPE system consists of three parts, the inert solid support, the stationary phase and the mobile phase. The inert solid support usually consists of particles of porous silica or an organic polymer ranging in size from 50 – 150 μm. The stationary phase is composed of extracting molecules, which are either covalently bound to the solid support or sorbed to the particles, with or without an organic solvent. The mobile phase consists of the aqueous based sample-, rinse- or eluting solutions. In actinide analysis, the sample is usually dissolved in a mineral acid, e.g., nitric or hydrochloric acid. In SPE, the retention of a solvent is described using the capacity factor, \( k' \), which is related to the distribution ratio used in solvent extraction as

\[ k' = D \frac{V_s}{V_m} \]  \hspace{1cm} (8)

where \( V_s \) and \( V_m \) are the volumes of the stationary- and the mobile phase, respectively.\textsuperscript{53} Another description of \( k' \) is the number of free column volumes to peak maximum.\textsuperscript{52} As in all chromatographic systems, separation is not only dependent on
the distribution ratio, but also on band spreading which is described by the height of a theoretical plate. Several factors control the plate height of a system, e.g., extraction kinetics, flow phenomena and diffusion in the stationary phase. However, actinide separation using SPE has perhaps more similarities to solvent extraction than modern chromatographic systems since separation is generally achieved by changing the composition if the mobile phase for element specific elution, rather than utilising differences in retention volume.

For the separations described in Papers I and III, four different SPE resins were used, i.e., TEVA, TRU, UTEVA and Ln-resin (all from Eichrom, Darien, IL, USA). The TEVA resin was used for the extraction of tetravalent actinides, e.g., Pu(IV). This resin contains trialkyl (R=C₈ and C₁₀) methylammonium nitrate (Aliquat336) as the stationary phase (see Fig. 9). Aliquat336 extracts tetravalent actinide nitrate complexes either as negatively charged complexes via anion exchange according to

\[
\text{Pu(NO}_3\text{)}_4^{2-} + 2E\cdot\text{NO}_3\text{)}_3^{(\text{org})} \leftrightarrow E_2\cdot\text{Pu(NO}_3\text{)}_4^{(\text{org})} + 2\text{NO}_2^- \quad (9)
\]

or as electrically uncharged complexes according to

\[
\text{Pu(NO}_3\text{)}_4^{(\text{aq})} + 2E\cdot\text{NO}_3\text{)}_3^{(\text{org})} \leftrightarrow E_2\cdot\text{Pu(NO}_3\text{)}_4^{(\text{org})} \quad (10)
\]

where E represents Aliquat336. The TRU resin has a mixture of octyl(phenyl)-N,N-diisobutyl carbamoylmethyl-phosphine oxide (CMPO) and tri-n-butyl phosphate (TBP) as stationary phase. The structure of CMPO is shown in Fig. 9. This resin generally shows high retention of tri-, tetra-, and hexavalent actinides, but was used in Papers I and III primarily for retention of trivalent Pu and Am. The TRU resin extracts trivalent actinides as neutral nitrate complexes according to

\[
\text{Am(NO}_3\text{)}_3^{(\text{aq})} + 3\text{CMPO}_{\text{org}} \leftrightarrow \text{Am(NO}_3\text{)}_3^{(\text{org})}\cdot\text{CMPO}_{\text{org}} \quad (11)
\]
The extractant in UTEVA is diamyl amylphosphonate (DAAP) which was used for separation of U(VI) (see Fig. 9). Similar to the TRU resin, UTEVA also extract actinides as neutral nitrate complex. The uranyl ion, UO$_2^{2+}$, is extracted by diamyl amylphosphonate according to

$$\text{UO}_2\text{(NO}_3\text{)}_2\text{(aq)} + 2\text{DAAP}_{\text{org}} \leftrightarrow \text{UO}_2\text{(NO}_3\text{)}_2\text{DAAP}_{2\text{org}}$$

Since all three of the described resins extract actinides as nitrate complexes, they exhibit high or optimum $k'$ at about 3M HNO$_3$. Hence, the same loading solution is suitable for all resins, which facilitates a serial arrangement. The Ln-resin is based on dialkyl phosphoric acid (HDEHP) as the stationary phase (see Fig. 9), which forms a chelate type complex with the extracted actinide ion. The extraction reaction of trivalent ions by HDEHP is

$$\text{M}^{3+\text{aq}} + 3\text{(HDEHP)}_{2\text{org}} \leftrightarrow \text{M(H(DEHP))}_2\text{H}_{3\text{aq}} + 3\text{H}^+$$

Hence, charge neutralisation is provided by the extractant, and, in contrast to the other extractants described above, no nitrate ions are required. Since HDEHP is a weak acid the extraction efficiency is decreased at lower pH, although a dilute acid is recommended for sample loading in order to avoid hydrolysis of the actinides.

![Structural formulae for the extractants used in the SPE procedures described in Papers I and III.](image-url)
In Paper I, several different combinations of SPE resins and loading/elution solutions were investigated for separation of Pu prior to ICP-SFMS determination. The procedures were evaluated with respect to the chemical yield of Pu and the decontamination of U. Of the procedures tested, separation of Pu(IV) on TEVA and separation of Pu(III) on a serial arrangement of UTEVA and TRU in combination with elution using 0.1% HEDPA (hydroxylethylidene diphosphonic acid, Fig. 9) provided the best results. HEDPA is a strong complexing agent for tri-, tetra- and hexavalent actinides and provided a faster elution of Pu than any of the other solutions tested. It was also found that using HEDPA in the sample solution for the ICP-MS determination decreased sorption of Pu to the tubing of the sample introduction system, which reduces wash time and the risk of between sample contamination. Hence, a relatively concentrated Pu fraction was obtained that could be introduced without further treatment to the ICP-SFMS system and which also provided reduced memory effects in comparison to, e.g., 1 or 5% HNO₃. The separation procedure using TEVA and elution with 0.1% HEDPA was successfully applied to soil and sediment reference materials.

However, the combination of separation of Pu in the trivalent state and elution using 0.1% HEDPA resulted, as mentioned above, in spectral interference from lanthanide-phosphates. Lanthanide ions are preferably trivalent, and the chemistry of these resembles the chemistry of trivalent actinides. Hence, when Pu is separated as Pu(III), a large portion of the lanthanides found in the sample end up in the Pu-fraction as well. The separation of Pu is often based on Pu(IV) and the concentration of lanthanides in this fraction is then too small for spectral interferences to occur. However, Am is almost always separated as Am(III) and therefore a phosphate based sample solution should be avoided in the ICP-MS-based determination of Am.

In Paper III, a chemical separation procedure for U, Pu and Am based on all four resins described above was developed. Application of the method was to the age determination of Pu based on analysis of the ²⁴¹Pu/²⁴¹Am and ²⁴⁰Pu/²³⁶U ratios, and hence a thorough Pu-Am separation was required to avoid spectral interference. The
use of TEVA, UTEVA and TRU in series for Pu, U and Am separation has been proposed previously.\textsuperscript{54, 62} However, the magnitude of the Pu-Am separation utilising this combination of resins has not been reported, which is also often the case with other separation procedures applied in mass spectrometric determination of \textsuperscript{241}Am and \textsuperscript{241}Pu.\textsuperscript{63, 64, 65}

Owing to the relatively low loading capacity for Am on TRU\textsuperscript{52, 56}, a larger amount of this resin was used compared to TEVA and UTEVA. Due to the potential interferences described above, elution of Am could not be done by HEDPA but was instead performed by lowering the HNO_3 concentration to 0.01M. This resulted in a relatively large elution volume and hence a more dilute Am fraction. An extra step for further concentration of the Am fraction was provided by eluting Am from TRU onto a small volume of Ln-resin. In 0.01M HNO_3 the complexion of Am(III) by HDEHP is relatively high.\textsuperscript{60} Am was then eluted from Ln-resin using a small volume of 0.5M HNO_3. This method was applied on Pu reference material solutions as well as Pacific Ocean sediment and Trinitite, and the resulting separation factors, defined as the added amount divided by that found in each fraction, were \textgtr=3560 for Pu in the Am-fraction and \textgtr=696 for Am in the Pu-fraction. Since the ratio of \textsuperscript{241}Pu/\textsuperscript{241}Am will vary from 20 to 0.06 for Pu ages from 1 to 60 years, the achieved separations are more than sufficient (see Fig. 10 and section 5.1).
Applications of actinide determination using ICP-SFMS

Actinide determinations find application in many different areas, e.g., in nuclear facilities, tracer experiments, environmental monitoring, bioassay and geochronology. An overview of fields where measurements of long-lived radionuclides are utilised has been given Becker.66 A selection of applications for actinide determination using ICP-SFMS is presented and discussed below.

5.1 Nuclear forensics

As mentioned in the introduction, the isotopic composition of nuclear material is crucial for the intended use of the material, and an accurate and precise isotope ratio determination is of value in several different areas, such as nuclear safeguards, verification of a future fissile material cut-off treaty (FMCT) and nuclear forensics. In nuclear forensic analysis, the purpose is, e.g., to provide information so that the source of nuclear and radiological materials used in illegal activities can be identified.67, 68, 69 Parameters such as the isotopic composition and age of nuclear material, as well as trace element content, are of great importance for this application.

The dating of nuclear material is based on the relationship between the isotopes of the material and their daughter nuclides according to

\[
t = \frac{1}{\lambda_1 - \lambda_2} \ln \left[ 1 - \left( \frac{\lambda_2}{\lambda_1} - 1 \right) \frac{N_2}{N_1} \right]
\]

(14)

where \( t \) is the age of the material, \( \lambda_1 \) and \( \lambda_2 \) are the decay constants of the mother and daughter nuclide and \( N_1 \) and \( N_2 \) are the amounts of the mother and daughter nuclide at the time of analysis. As an example, the ratio of Pu isotopes and their daughter nuclides as a function of the age of the Pu material is displayed in Fig. 10.
In Paper III, the applicability of ICP-MS for age determination was examined. As mentioned above, a chemical separation based on SPE was performed and the age of Pu in two reference standard solutions, a Marshall Island sediment and in Trinitite was determined. The features of these materials are rather different, i.e., the two reference solutions (IRMM081 and IRMM083) are relatively pure, while the Pu in the Marshall Island sediment (IAEA367) and Trinitite is mixed with an environmental matrix as well as with other elements from the nuclear device. Furthermore, the IRMM solutions contain Pu of very different isotopic composition since IRMM081 is weapons-grade Pu (95% $^{239}$Pu) and IRMM083 is a $^{240}$Pu standard (99% $^{240}$Pu). The Pu in IAEA367 and the Trinitite originates from nuclear weapons fall-out, which in the case of the former is primarily due to the detonation of thermonuclear devices and in the latter due to the detonation of a single fission device. All these parameters affect the possibility to perform an accurate dating. For instance, it was found that dating based on $^{240}$Pu/$^{236}$U was either biased due to formation of $^{236}$U via (n,$\gamma$) of $^{235}$U in the detonation of the nuclear devices or impossible due to tailing on m/z = 236 from $^{238}$U$^+$ (as mentioned above). It shall also be mentioned that none of the other Pu/U ratios was applicable due to the content of $^{238}$U and $^{235}$U in environmental matrices, a problem that also was recognised by Wallenius et al. when dating Pu-particles using secondary ion mass spectrometry (SIMS). Hence, it was found that the $^{241}$Pu/$^{241}$Am ratio is the
most reliable for dating of Pu in nuclear weapons fallout. However, dating of IRMM081 using $^{241}\text{Pu}/^{241}\text{Am}$ was biased from residual $^{241}\text{Am}$ remaining after the last purification of the Pu, a problem that was also encountered by Wallenius and Mayer in the dating of reference Pu solutions from NBS using TIMS.$^{69}$

It is also interesting to compare the uncertainties of the determined ages based on TIMS analysis reported by Wallenius and Mayer$^{69}$ with the ones obtained in Paper III. The uncertainties in the ages determined by TIMS varied between 0.08 and 0.39 yr ($k=1$)$^{69}$ which are of the same magnitude as obtained for IRMM083 using ICP-SFMS, i.e., 0.3 – 0.4 yr ($k=2$) (see Paper III). The uncertainties in the ages obtained for the other materials in Paper III varied from 0.7 to 3.0 yr. However, the intensity of at least one of the nuclides that the dating were based on was in those cases less than 200 cps, which increases the uncertainties due to counting statistics (see discussion in section 3).

5.2 Environmental monitoring

Due to the relatively high toxicity of the actinides, it is of interest to monitor the concentrations of these elements in the environment. The relatively low concentrations of transuranium elements found in nature sets special demands on both chemical separation processes and detection techniques. The use of larger sample quantities can pose problems in, e.g., the SPE separation of Am due to large quantities of Fe$^{3+}$ that compete with the retention of Am$^{3+}$. Also, since the ratio of naturally occurring $^{238}\text{U}$ to $^{239}\text{Pu}$ can be on the order of $10^6$ to $10^9$, high demands are set on a thorough Pu-U separation in order to avoid too much interference from $^{238}\text{U}^+\text{H}^+$ on m/z = 239. In Paper I, the separation factor for U found in the Pu fraction varied from 1800 to 59000 in the analysis of Pu in soil and sediment reference materials, which was sufficient to avoid a significant contribution from $^{238}\text{U}^+\text{H}^+$ on the determination of $^{239}\text{Pu}$. However, the large variation in the magnitude of Pu – U separation implies that for samples with lower concentration of Pu, an improved procedure based on, e.g., repeated chromatography will be required to decrease the U content to a level where the $^{238}\text{U}^+\text{H}^+$ interference is insignificant.
However, the high sensitivity (as well as the high sample throughput) of ICP-SFMS is an advantage for these types of samples (see Fig. 1).\textsuperscript{10, 66} As in nuclear forensics, isotope ratio determinations are of interest in environmental studies for determining the origin of nuclear material. The ratios of Pu isotopes have been utilised for this purpose by several authors.\textsuperscript{9, 74}

5.3 Emergency preparedness
In the response to a radiological emergency situation, fast analysis of radionuclide deposition levels or contamination will be required in order to assess the need for protective actions.\textsuperscript{75} Scenarios of radiological emergency can be nuclear power plant incidents, such as the Chernobyl accident in 1986, contamination due to terrorist attacks, such as the use of a radiological dispersion device (RDD, or “dirty bomb”) or intentional contamination of food and drinking water, or even a nuclear weapons attack generating extensive fall-out. Under such circumstances, the capability to deliver results rapidly is likely to be more crucial than high precision and accuracy.

The use of ICP-MS for actinide determination in emergency preparedness is advantageous primarily due to the high sample throughput of this technique. Also, since relatively high levels of actinides are more likely to occur and be of special interest under such circumstances, small sample quantities can be used which provides the opportunity to optimise sample dissolution and actinide separation procedures for this purpose. In an IAEA technical evaluation of analytical procedures in a radiological or nuclear emergency, the proposed methods for determination of Am, Cm and Pu isotopes require from 10 to 48 h depending on the sample matrix.\textsuperscript{75} In comparison, the method for the determination of U, Pu and Am described in Paper III requires about 4 h for the SPE separation and, if microwave assisted digestion is used, about 1-2 h for sample dissolution. The analysis time of individual samples using ICP-MS is about 5 min. Hence a batch of 14 samples can be processed and analysed by one person in a single working day.
For some of the more short-lived nuclides that might be of interest in emergency preparedness, e.g., $^{242}$Cm ($t_{1/2} = 0.446$ y) and $^{244}$Cm ($t_{1/2} = 18.1$ y), the determination limits are poorer for $\alpha$-spectrometry than ICP-SFMS (see Fig. 1). However, it is important to carefully consider the characteristics of interest in emergency preparedness. As an example, the generic action levels for $\alpha$-emitting actinides (exemplified by the Pu isotopes and $^{241}$Am) in foodstuffs recommended by the IAEA are 10 Bq·kg$^{-1}$ for general consumption and 1 Bq·kg$^{-1}$ for milk, infant food and drinking water.\textsuperscript{76} The lower limit of 1 Bq·kg$^{-1}$ corresponds to about 8 fg·kg$^{-1}$ $^{242}$Cm and 330 fg·kg$^{-1}$ $^{244}$Cm. This means that the determination of $^{242}$Cm at the generic action level in for instance one litre of drinking water will be difficult using ICP-SFMS, but the determination of $^{244}$Cm will be well above the determination limit. However, due to the relatively short half-life of $^{242}$Cm the recommended annual limit on intake (ALI) for ingestion of this nuclide is about 20 times higher than the corresponding ALI for $^{241}$Am and the $\alpha$-emitting Pu isotopes.\textsuperscript{77} This indicates that a higher detection limit can be allowed for this nuclide when determined in emergency preparedness situations.
6 Concluding remarks and reflections on future research

In this thesis, different aspects have been addressed in order to facilitate and improve actinide determinations using ICP-SFMS. Concerning sample pre-treatment, separation methods based on solid phase extraction of U, Pu and Am have been developed. In Paper I, the separation of Pu using various SPE procedures was examined with respect to the ability to separate Pu from U and the chemical yield of Pu. It was found that separation based on retention of Pu(IV) on an Aliquat336 containing resin in combination with elution using HEDPA provided the best results. Elution using HEDPA was found to be advantageous from several aspects, e.g., for providing concentrated Pu fractions and reduced memory effects of Pu from the sample introduction system. It was also found that HEDPA (and other phosphate containing substances) in combination with high concentrations of lanthanides in the sample fraction (which was the case when Pu was separated as Pu(III)) resulted in the formation of lanthanide phosphates that interfered in the Pu determination using low resolution mode (m/Δm = 300). The formation of these polyatomic species was found to be favoured by “cold” plasma conditions, i.e., high sample gas flow and reduced rf-power, as well as increased diameter of the sampler and skimmer cones (Paper II).

The developed separation procedures were applied to the measurement of Pu in soil and sediment (Paper I) and to the age determination of Pu in reference material solutions along with samples contaminated by nuclear weapons fall-out (Paper III). The age determination was based on two different mother/daughter nuclide relationships, i.e., \(^{240}\text{Pu}/^{236}\text{U}\) and \(^{241}\text{Pu}/^{241}\text{Am}\). It was found that dating of Pu based on \(^{241}\text{Pu}/^{241}\text{Am}\) provided the most reliable results for all materials tested. Dating of Pu using \(^{240}\text{Pu}/^{236}\text{U}\) was reliable in the reference material solutions, but for the other materials this approach was biased by the formation of \(^{236}\text{U}\) in the detonation of nuclear devices as well as abundance sensitivity from \(^{238}\text{U}\) in the ICP-SFMS determination.

Throughout this thesis, isotope ratio measurements have been used, both for the determination of the isotopic composition of, e.g., Pu and for the quantification of U,
Pu and Am isotopes using IDMS. Since corrections for, e.g., dead-time effects are of importance for high precision and accuracy in isotope ratio measurements, a more thorough study on the dead time of an ICP-SFMS system was conducted. The dead time was determined using experimental isotope ratio-based approaches and direct electronic measurement of the pulse amplifier output. It was found that when using the highest available setting on the amplifier circuitry, the electronic measurements corresponded with the ratio based ones, i.e., the entire system could be characterised by a single dead time (Paper IV). By applying the electronically determined dead time, the combined uncertainty of isotope ratio determinations at high count-rates could also be minimised.

As mentioned above, separation of the actinides in order to purify and concentrate the analyte(s) is generally required prior to determination by ICP-SFMS. This procedure is by far the most time- and labour consuming part in the analytical process and thus the continued development of new separation procedures is of interest for future work. Refinements in ICP-SFMS instrumentation and the provision of improved detection limits are also beneficial for actinide determinations since low-level determinations are often of interest for, e.g., environmental samples. However, since measurement at ever-lower levels often entails the observation of hitherto undetected spectral interferences, studies concerning the formation of polyatomic species and improving the abundance sensitivity remain of equal importance. The use of ICP-SFMS for isotope ratio measurements, as a tool in nuclear forensics and safeguards can also be further exploited. While TIMS and MC-ICP-MS may be capable of higher precision, this is generally only true for samples containing relatively high concentrations. At lower levels, where uncertainties are governed by counting statistics, ICP-SFMS can provide comparable precision, in most cases requiring shorter analysis times. Another application of ICP-MS in actinide determination, where little has been reported so far, is for use in nuclear emergency preparedness, a field where this technique should benefit, e.g., due to its high sample throughput.
7  References


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The purpose of this work was to develop an optimised sample-preparation procedure for the determination of Pu in soil/sediment with ICP-MS. To start with, several different procedures were screened for their ability to separate plutonium and remove uranium. After the screening, two methods were applied on one soil (IAEA Soil6) and two sediment reference materials (IAEA300 and IAEA135). These methods were based on separation of Pu using TEVA and a combination of UTEVA and TRU resins, followed by elution of Pu with 0.1% hydroxyethylene diphosphonic acid (HEDPA). A comparison was also made between sample preparation based on acid-leaching and complete digestion using lithium borate fusion. The highest yield of Pu (80%) was found with the procedure consisting of fusion followed by TEVA, while the decontamination from U showed large variations (RSD varying from 16–52%) with all procedures. No difference in the recovery of Pu was found between the two sample preparation techniques. The results of the quantitative determination in low resolution of $^{239}\text{Pu}$ and $^{240}\text{Pu}$ from the UTEVA + TRU-separation were significantly higher than those obtained by the TEVA procedure. An analysis in higher mass resolution displayed interfering peaks in the mass-region of Pu, and lanthanide-containing polyatomic ions were found to be a likely cause for these interferences. The procedure based on lithium borate fusion and separation using the TEVA-resin avoided such interferences and was therefore tested for repeatability over time on IAEA300. The stability of the method was good (RSD = 2.49% (n = 8)), with the exception of one value being significantly higher than the others. This result was confirmed by analysis in higher mass-resolution, which indicates an inhomogeneous distribution of Pu in the reference material, despite a sample intake of about 1 g.

**Introduction**

Plutonium has been introduced to the environment from several different sources, such as activities related to nuclear weapons development/production and accidental or authorised discharges from nuclear power plants. The determination of plutonium concentrations is not only of interest for monitoring purposes due to the high radiotoxicity of this element, but also in radio-ecological studies concerning the behaviour of plutonium in the environment. The potential use of plutonium in, e.g., nuclear weapons production or nuclear power plants is determined by the isotopic abundances of primarily the two major isotopes $^{239}\text{Pu}$ and $^{240}\text{Pu}$. The isotope amount ratio of these isotopes, as well as the total isotopic pattern of Pu, can be used to identify the source of contamination in environmental samples. For instance, the isotope amount ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ in weapons-grade Pu is typically around 0.05, while the ratio in mixed oxide fuel is approximately 0.4. The average ratio found in environmental samples contaminated by fall-out from nuclear weapons testing is about 0.2, and samples contaminated with debris derived mainly from the Chernobyl accident show ratios of around 0.4.

There are several different techniques available for the determination of plutonium. Of these, the most widely used has traditionally been alpha spectrometry for quantitative determinations and thermal-ionisation mass spectrometry (TIMS) for isotope ratio measurements. The advantages of alpha-spectrometry are generally long counting-times and lack of isotopic information on $^{238}\text{Pu}$ and $^{240}\text{Pu}$ due to the spectral overlap of the alpha-energies of these isotopes. TIMS provides the ability to perform isotope ratio determinations with high precision, but the analysis is rather time consuming. Inductively coupled plasma-mass spectrometry (ICP-MS) has, during the last decade, gained increasing prominence as an alternative in both quantitative and isotope amount ratio measurements of long-lived radionuclides such as plutonium. The advantages of this technique include good sensitivity and short analysis times, but the precision in isotopic ratio determination achievable with the most common single collector ICP-MS is less than that achieved with TIMS. This is primarily due to the instability of the ion-source. However, multi-collector ICP-MS instruments have been shown to be able to reach about the same precision as TIMS due to simultaneous detection of ion-beams. Of the single collector instruments, double focusing sector-field ICP-MS (ICP-SFMS) provides higher sensitivity compared to the quadrupole based (ICP-QMS) systems. The former also offers the ability to perform analyses at higher mass-resolution. In the determination of Pu by ICP-MS at the low levels often found in the environment (pg g$^{-1}$ - ng g$^{-1}$ in soil and sediment), care needs to be taken to avoid interferences from, e.g., polyatomic species formed in the interface region and abundance sensitivity from elements present in high amounts in the sample. In the case of Pu, the most dominant interferences are $^{238}\text{U}^+$ plus tailing of $^{238}\text{U}^+$ on $^{239}\text{Pu}^-$. The intensity-ratio of $^{238}\text{U}^+$ to $^{239}\text{U}^+$ has been reported to be in the region of $4 \times 10^{-1}$ to $10^{-2}$, and it is not possible to separate this interference from the analyte peak at the resolution achievable with current ICP-SFMS instruments. Due to the relatively high content of U (often 6–9 orders of magnitude higher than that for Pu) in especially soil and sediments, it is necessary to chemically separate U from Pu prior to determination. This separation can
be, and often is, performed in the same way as for alpha-spectrometric determinations. There are, however, somewhat different demands on separation for ICP-MS compared to alpha-spectrometry, such as the strong need for decontamination from U in ICP-MS and the requirement of a thorough Pu-Th separation in alpha-spectrometry due to spectral overlap of 238Pu and 232Th. As in all determinations with ICP-MS, it is also of importance to avoid, e.g., clogging of the sample introduction systems and sorption of the analyte(s) in the tubing by properly adjusting the sample solution with respect to total salt content, pH and complex forming agents. Other polyatomic species with the potential of interfering with the Pu-isotopes, such as PbCl\textsuperscript{+}, have also been reported.\textsuperscript{10,11} These interferences can generally be separated from the Pu-peaks with a mass-resolution of approximately 4000, but the attendant loss in sensitivity makes the use of low resolution (300) the most preferred mode for these analyses.

In the determination of Pu in, e.g., soil and sediment, the most common technique reported for sample preparation is acid-leaching, although it has been shown that this procedure may not always dissolve all of the Pu present in the sample.\textsuperscript{12,13} Some procedures have, however, been described where a complete dissolution of the sample is applied.\textsuperscript{14,15} These procedures are based on sample digestion using either strong acids or fusion of the sample with fluxes such as lithium borate. The drawback of a total digestion compared to an acid leaching is a higher salt content in the resulting solution caused by the flux as well as by the siliceous matrix of the sample. This may cause problems in the separation of Pu and provide a higher risk for polyatomic interferences in the mass-spectrometric determinations.

The aim of this study was to develop an optimised sample-preparation procedure for the determination of Pu with ICP-MS in environmental materials such as soil and sediment. Important aspects that have been considered are sufficient clean-up of Pu from potentially interfering elements as well as simplicity to perform and high sample throughput. For the separation of Pu, the focus has been on methods based on extraction chromatography or ion-exchange resins, due to the ease of performance of the resin separations and the elimination of organic solvents compared to, e.g., liquid-liquid extraction.

**Experimental**

**Instrumentation**

An Element2 double-focusing sector field ICP-MS (Thermo-Finnigan, Bremen, Germany) was used for the determination of the U and Pu isotopes addressed in this paper. The instrument was equipped with a Meinhard nebuliser and a Scott-type double-pass spray chamber. The measurements were performed in self-aspirating mode, resulting in a sample flow rate of approximately 0.2 ml min\textsuperscript{-1}. An autosampler (ASX-500, Cetac Technologies, Omaha, NE, USA) was used in the study of variations in intensity for Pu in various solutions. Throughout the measurements, a grounded platinum electrode inserted between the torch and load-coil ("CD2-2 Guard Electrode") was used. The intensity for 238U\textsuperscript{+} after daily optimisation of torch position and Ar-gas flows was typically about 2000 cps per ng l\textsuperscript{-1} in low resolution mode (m/\lambda m = 300) and approximately ten times lower in medium resolution mode (m/\lambda m = 4000). Operating conditions and measurement parameters are reported in Table 1.

**Materials**

A standard solution of 242Pu (NIST SRM 4334G; National Institute of Standards and Technology, Gaithersburg, MD, USA) was used to spike the soil and sediment for yield determinations. For monitoring of instrumental performance and quantification of 238U, an aliquot of 238U (IRMM 040a); Institute of Reference Materials and Measurements, Geel, Belgium) was added to the Pu-fractions from the soil and sediment samples. For the initial screening of various separation procedures, standard solutions of 238Pu (IRMM-083) and natural U (IRMM-184) were used in addition to 233U and 240Pu. The sediment reference materials used were Irish Sea Sediment (IAEA135), Baltic Sea Sediment (IAEA100) and soil from Austria (IAEA Soil6), all from the International Atomic Energy Agency (Vienna, Austria).

The reagents used were HNO\textsubscript{3}, HCl, NH\textsubscript{3}, NaNO\textsubscript{2}, amidosulfuric acid, Fe(s), ascorbic acid, NH\textsubscript{4}I and hydroquinone (all of p.a. grade, Merck, Darmstadt, Germany), HNO\textsubscript{3} (s.p. grade, Merck), lithium borate flux (Spectroflux 100B, Johnson Matthey, Paris, France), polyethylene glycol (PEG2000, for synthesis, Merck) and hydroxyethylidenediphosphonic acid (HEDPA; Briquet ADPA 60A, industrial grade 60%, Albright & Wilson UK Ltd, Oldbury, UK). An anion-exchange material (Bio-Rad AG1-X8 100–200 mesh, Bio-Rad, Hercules, CA, USA) and extraction chromatographic materials (TEVA, UTEVA and TRU, 100–150 μm, Eichrom, Darien, IL, USA) were used for the separation of Pu. The TEVA-resin is based on an aliphatic (R = C\textsubscript{8} and C\textsubscript{10}) quaternary ammonium salt as extractant, while UTEVA is based on dipentyl pentylenphosphonate as extractant and the TRU-resin is based on extraction by octylphenyl-N,N-diisobutylcarbamoyloxyphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP). The Bio-Rad AG1-X8 is, similar to TEVA, based on trimethylammonium chloride

**Table 1** Instrument and data acquisition settings for the Element2

<table>
<thead>
<tr>
<th>Instrument settings</th>
<th>Sample uptake rate</th>
<th>Argon flow rates</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>~0.2 ml min\textsuperscript{-1} (self aspiration)</td>
<td>14 l min\textsuperscript{-1}</td>
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<tr>
<td></td>
<td></td>
<td>11 l min\textsuperscript{-1}</td>
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<tr>
<td>Auxiliary gas</td>
<td>~0.2 ml min\textsuperscript{-1} (optimised daily)</td>
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<tr>
<td>Nebuliser gas</td>
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<tr>
<td>RF power</td>
<td>Torch</td>
<td>Menhard</td>
</tr>
<tr>
<td></td>
<td>Nebuliser</td>
<td></td>
</tr>
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<td>Spray chamber</td>
<td>Scott type (double pass)</td>
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**Data acquisition settings**

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<tr>
<td></td>
<td>237\textsuperscript{Th}, 239\textsuperscript{Pu}, 241\textsuperscript{Pu}</td>
</tr>
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<td></td>
<td>No. of scans 3 × 50</td>
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<tr>
<td></td>
<td>Acquisition window (%) 5</td>
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<tr>
<td></td>
<td>Sample time (ms) 5</td>
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<tr>
<td></td>
<td>Medium resolution (m/\lambda m = 4000):</td>
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<tr>
<td>Isotopes</td>
<td>Quantitative determination</td>
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<td>Acquisition mode Local E-scan (peak jumping)</td>
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<td>No. of scans 3 × 50</td>
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<td></td>
<td>Acquisition window (%) 80</td>
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<tr>
<td></td>
<td>Samples per peak 6</td>
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<td>Sample time (ms) 5 for 238\textsuperscript{U}, 30 for 239\textsuperscript{Pu}, 100 for 241\textsuperscript{Pu}</td>
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<td>Scanning Mass region 237.033–243.054</td>
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<tr>
<td></td>
<td>No. of scans 1</td>
</tr>
<tr>
<td></td>
<td>Samples per peak 2000</td>
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<tr>
<td></td>
<td>Sample time (ms) 0.05</td>
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</tbody>
</table>


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covalently bound through a methyl-phenyl chain to the polymer of the resin. The separations were performed in disposable plastic 10 ml columns (Poly-prep, Bio-Rad). Graphite crucibles (Alfa, Karlsruhe, Germany) were used for fusion of samples, and filters (Munktell OOH, Gryckwyo Pappstruktur AB, Gryckwyo, Sweden) were used for the separation of flocculated Si.

**Screening of various separation procedures**

Separation procedures using different resins and elution media were tested with respect to chemical yield of Pu and decontamination of U. In the screening, both extraction-chromatographic resins such as TEVA and a combination of UTEVA + TRU and an anion-exchange resin were examined together with elution media based on either complexation of Pu (HEDPA and ammonium oxalate) or reduction of Pu to Pu(III) (HCl in combination with NH4I or hydroquinone). The screening was performed using 5 ml of load-solutions spiked with 240Pu and 238U to concentrations of 44 and 300 ppt, respectively. The load-solutions were 3 M HNO3 for the extraction-chromatographic resins and 8 M HNO3 for the anion-exchange resin. The free column volume (FCV) of the resin was determined to be 0.8 ml per ml resin.

**UTEVA and TRU resins.** To reduce, e.g., Pu species to Pu3+ and Fe6+ to Fe3+, iron(II) sulfamate (0.6 M) and ascorbic acid were added to the sample solution to final concentrations of 0.12 M and 20 g l−1, respectively.19 The solution was stirred until the ascorbic acid was completely dissolved. Columns containing 1 ml UTEVA resin and 1 ml TRU resin were mounted in series and the resins were conditioned with 5 ml 3 M HNO3. The sample was loaded on the UTEVA column and allowed to drain through both columns. Uranium and thorium are, under these conditions, mostly retained on the UTEVA while the trivalent Pu and Am pass through and are retained on the TRU resin.18 The sample beaker was rinsed with 2×2.5 ml 3 M HNO3, which was also transferred to the column, followed by an additional rinsing of the TRU resin with 5 ml 3 M HNO3 (s.p. grade). Plutonium was eluted from the TRU resin with 3×3 ml 0.1% HEDPA or 3×5 ml 0.1 M ammonium oxalate, and the fractions were taken to measurement by ICP-SFMS without further treatment.

**TEVA resin.** NaNO2 was added to a concentration of 0.2 M, and the sample solution was heated at 90 °C for 20 min and cooled to room-temperature. This treatment transfers Pu to the tetravalent state. A column was packed with 1 ml TEVA resin and conditioned with 5 ml 3 M HNO3. The sample was loaded on the resin and the beaker was rinsed with 2×2.5 ml 3 M HNO3, which was also transferred to the column. Under these conditions, the retention of tetravalent Pu and Th is strong, while the hexavalent U and trivalent Am pass through or are only weakly retained on the resin.18 When 0.1% HEDPA was used as eluting agent, the resin was first rinsed with 5 ml 9 M HCl (to remove Th which will be present in soil-samples), followed by 3×5 ml 3 M HNO3 (s.p. grade) to remove traces of U. Pu was then eluted with 3×5 ml 0.1% HEDPA (this elution is based on complexation of Pu). When 9 M HCl + 0.1 M NH4I or 9 M HCl + 0.1 M hydroquinone was used, followed by 3×5 ml 3 M HNO3 (s.p. grade) to remove traces of U. Pu was then eluted with 3×5 ml 0.1% HEDPA. The precipitate was filtered (Munktell OOH) and the filtrate was taken to measurement by ICP-SFMS.

**BioRad AG1-X8.** The separation using the anion-exchange resin was performed in the same way as for the TEVA-resin, with the exception that the elution using 9 M HCl + 0.1 M hydroquinone was excluded. After separation, the plutonium-fractions were spiked with 240Pu (~0.19 ng) and 238U (~2.0 ng) for quantification. The determinations were performed according to procedures 1, 2, and 3 (Table 2). Blank samples consisting of 0.1% HEDPA, 0.1% HEDPA spiked with 240Pu and 238U and reagent blanks from the whole separation procedures were analysed with each batch of samples.

**Sample dissolution**

**Lithium borate fusion:** Samples were weighed and mixed with Spectroflux 100B (Li2B4O7 4 : LiBO2, w/w 4 : 1) at a flux to sample ratio of 3 : 1 (w/w). The amount of sample used varied between 0.2 and 2 g depending on the reported concentration of Pu in the materials. The mixture was transferred to a carbon crucible and 0.2 ml of a spiking solution of 337 pg 242Pu g−1 was added for yield determinations. The added spike-solution was weighed for greater accuracy. Care was taken to avoid contact of the spike-solution with the carbon crucible. The samples were fused for 10-15 min and left to cool to room temperature. The melt was transferred to a glass beaker, 100 ml 1.4 M HNO3 per gram of initial sample was added and the melt was dissolved under stirring and boiling. The dissolution of the melt usually required 20 min and no solid residues could be observed in the dissolved sample.

In order to prevent clogging of the columns due to precipitation of silicate acids, it was necessary to remove Si prior to separations. This was done by floculation of Si with polyethylene glycol (PEG2000) according to the method described by Smith et al.,17 where PEG2000 was added to a concentration of 0.002 M and the colloidal silica that formed was allowed to settle before centrifugation. It was found, however, that it was necessary to evaporate the sample to half of the original volume and to allow the precipitate to settle overnight in order to prevent later precipitation of Si. The evaporation also concentrates the HNO3 to approximately 3 M, which is suitable for the following separations. The precipitate was filtered (Munktell OOH) and the filtrate was taken to further separations according to procedures 1 and 3 (Table 2).

**Acid leaching:** The leaching of samples was performed according to the procedure described by Muramatsu et al.9 Samples were weighed into a beaker and 240Pu was added (the same amounts as in the fusion procedure were used). The samples were covered with a watch-glass and leached with
8 M HNO₃ under boiling for 3 h. The mixture was then filtered and the residue boiled again two times with 8 M HNO₃ for 30 min. The combined filtrates were evaporated to dryness, dissolved in 10 ml 3 M HNO₃ and taken to further separations according to procedures 1 and 3 (Table 2).

Extraction-chromatographic separation. The separation of Pu was performed using the procedures described above for TEVA and UTEVA & TRU when using 0.1% HEDPA as elution agent. The only deviation from the procedures used in the screening is that the volume used for elution of Pu was 5 ml, since this volume was found to be sufficient.

Determination by ICP-MS. The determination of Pu and U by ICP-MS was performed according to the conditions given in Table 1. The effect of abundance sensitivity from 238U and 238U⁻¹H⁻ formation in the 239Pu region was determined for each batch of samples analysed. The ratio of abundance sensitivity plus 238U⁻¹H⁻ to 238U was usually around 5 × 10⁻². Dead-time and mass-discrimination correction factors were determined using IRMM-184. The model used for the calculations was according to Appelblad and Baxter.

Calculations and statistical treatment of data. The decontamination from U was calculated as the initial amount in the sample divided by the amount in the Pu-fraction after separation. The chemical yield of Pu was determined as the amount of 242Pu in the final fraction divided by that added initially.

In order to compare the obtained results with the reference values, several statistical treatments were performed. The original data for the reference materials were obtained from IAEA reports. Due to the similarities between the mean and the geometric mean for each of the reference materials, the results were considered to be normally distributed. To identify possible outliers, Grubbs’ test was performed which resulted in Table 2.

**Table 2.** a) Resins, rinse- and elution media used in the initial screening of various separation procedures and the resulting chemical yields of Pu and U decontamination factors. The predominant oxidation state of Pu is stated for the load- and elution steps. b) Intensity of 242Pu in different elution media (where σ is the standard deviation of the individual measurement and n = 3)

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Resin(s)</th>
<th>Load media</th>
<th>Oxidation state reagent</th>
<th>Rinse media</th>
<th>Elution medium</th>
<th>Reference</th>
<th>Pu-yield</th>
<th>Decont. from U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>UTEVA &amp; TRU</td>
<td>3 M HNO₃</td>
<td>Fe(II) sulfate and acrobic acid</td>
<td>3 M HNO₃</td>
<td>0.1% HEDPA</td>
<td>Pu(a)</td>
<td>—</td>
<td>96% 6760</td>
</tr>
<tr>
<td>2</td>
<td>UTEVA &amp; TRU</td>
<td>3 M HNO₃</td>
<td>Fe(II) sulfate and acrobic acid</td>
<td>3 M HNO₃</td>
<td>0.1 M ammonium oxalate</td>
<td>Pu(a)</td>
<td>17</td>
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<td>3</td>
<td>TEVA</td>
<td>3 M HNO₃</td>
<td>NaNO₂</td>
<td>3 M HNO₃</td>
<td>0.1% HEDPA</td>
<td>Pu(a)</td>
<td>—</td>
<td>96% 1430</td>
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<tr>
<td>4</td>
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<td>3 M HNO₃</td>
<td>NaNO₂</td>
<td>3 M HNO₃</td>
<td>9 M HCl</td>
<td>Pu(a)</td>
<td>—</td>
<td>95% 2790</td>
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<tr>
<td>5</td>
<td>TEVA</td>
<td>3 M HNO₃</td>
<td>NaNO₂</td>
<td>3 M HNO₃</td>
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<td>Pu(a)</td>
<td>—</td>
<td>95% 2790</td>
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<td>BioRad AGI-X8</td>
<td>8 M HNO₃</td>
<td>NaNO₂</td>
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<td>0.1% HEDPA</td>
<td>Pu(a)</td>
<td>—</td>
<td>37% 47</td>
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<td>7</td>
<td>BioRad AGI-X8</td>
<td>8 M HNO₃</td>
<td>NaNO₂</td>
<td>3 M HNO₃</td>
<td>9 M HCl</td>
<td>Pu(a)</td>
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<table>
<thead>
<tr>
<th>Medium</th>
<th>Intensity 242Pu/cps ng⁻¹</th>
<th>σ</th>
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<tr>
<td>1.0% HNO₃</td>
<td>2125</td>
<td>19</td>
</tr>
<tr>
<td>5.0% HNO₃</td>
<td>2763</td>
<td>16</td>
</tr>
<tr>
<td>0.01% HEDPA</td>
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<td>15</td>
</tr>
<tr>
<td>0.05% HEDPA</td>
<td>3026</td>
<td>9</td>
</tr>
<tr>
<td>0.1% HEDPA</td>
<td>3036</td>
<td>8</td>
</tr>
<tr>
<td>1% HEDPA</td>
<td>3461</td>
<td>18</td>
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<tr>
<td>0.10 M ammonium oxalate</td>
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<td>10</td>
</tr>
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</table>

Fig. 1 Separation procedures applied on soil and sediment reference materials.
Results and discussion

Screening of various resins and elution media

The chemical yields and U decontamination factors for the various separation procedures are shown in Table 2. As can be seen from the table, the decontamination from U is generally more efficient for the extraction-chromatographic resins compared to anion-exchange, with the UTEVA + TRU combination providing the highest clean-up. With all resins, quantitative recoveries but also relatively poor yields are found, depending on the eluent. Elution with 0.1% HEDPA resulted, however, in good yields on both the extraction-chromatographic systems. Good chemical yields of Pu were found, depending on the eluent. Elution with 0.1% HEDPA provided complete elution of Pu from the anion-exchange resins. In Fig. 2, the elution profiles of Pu from the various separation procedures are shown. It can be seen that 0.1% HEDPA can be used to elute Pu from the extraction-chromatographic resins in less than 8 free column volumes (FCV), whereas the other procedures often require tens or even more than 12 FCVs. An efficient elution is of importance to decontamination, 238U was found in the Pu-fractions at levels of 1 except for TEVA/HEDPA and UTEVA + TRU/HEDPA where n ~ 3 and the error bars represent 1 σ.

In one identified outlier per reference material. This is much less than reported following application of the non-parametric box-and-whisker test for outliers in the IAEA summaries for the respective materials. After the outlier identified by Grubbs test was removed, the mean-value and standard deviation for each material was calculated. An F-test was used to compare the standard deviations of the reference data and the obtained results, followed by a t-test for comparison of the mean values.

For comparison with reported data, the values obtained for 239Pu and 240Pu determination by ICP-MS were transformed from mass (g kg−1) to activity (Bq kg−1) concentrations at an assumed density of 1 g cm−3. The half-lives used in the calculations are 24065 years for 239Pu and 6537 years for 240Pu.

Application to soil and sediment analysis

As described above, three different sample-preparation procedures were applied on three soil and sediment reference materials. The chemical yields of Pu and decontamination from U for the various combinations are shown in Table 3. The chemical yield of Pu varies between 44% and 83%, the highest chemical yields being found with the combination of lithium borate fusion and TEVA-separation (procedure 3). The average Pu-yield obtained with this method was 80%. The average decontamination from U shows large variations (from 1800 to 59000 with RSD varying from 16–52%), and none of the procedures provides a significantly higher clean-up level than the others. The decontamination seems to be more related to the type of sample and sample amount (i.e., initial amount of U) than to the separation procedure per se. In spite of the decontamination, 238U was found in the Pu-fractions at levels in the fraction used for determination. The use of HEDPA in combination with these resins has not been reported previously, however, its strong ability to form complexes with trivalent- and hexavalent actinides has been demonstrated previously.

Table 3 Chemical yield of Pu and decontamination from U from various sample-preparation procedures and reference materials (n = 3)
soil samples that interfere with the determination of $^{239}$Pu. The combined contribution of $^{234}$U-tailing and $^{235}$U$^+$ on $^{239}$Pu was therefore determined and subtracted from the measured count-rate. The ratio of the contribution from $^{234}$U and the net count-rate at $m/z$ 239 varied from less than 0.1% to 33% in this work. During the study, blank levels of 0.1% HEDPA, 0.1% HEDPA spiked with $^{233}$U and $^{242}$Pu and reagent blanks from entire separation procedures were monitored. The average blank levels of $^{239}$Pu and $^{240}$Pu in 0.1% HEDPA varied between 1–2 cps, while the levels of the spiked HEDPA varied between 2–3 cps. The levels in the reagent blanks varied between 1–5 cps with slightly higher blank levels for the fusion compared to the acid-leaching procedure. The reagent blank levels of $^{238}$U from the entire procedures were generally a few percent of the levels of $^{238}$U found in the final Pu-fractions of the samples.

The results of $^{239}$Pu and $^{240}$Pu determinations (in Bq kg$^{-1}$) are listed in Table 4. Data for the two nuclides have also been summed for comparison with the recommended values provided for the reference materials. As described above, the data for the reference materials were re-evaluated in order to obtain average values that could be used for a comparison of the obtained results using a t-test. As can be seen from the table, the re-evaluated mean values are, for two of the materials, higher than the recommended values. This difference is mainly due to the large discrepancies in the outcomes of tests for outliers. The application of the t-test showed no significant difference between the obtained results and the averages of the procedures ($P = 0.05$). The fusion/UTEVA + TRU procedure resulted in higher values than the other two, and there is a large difference in the values obtained for IAEA300 and Soil6.

To examine the reason for these elevated values, a scan of the mass-region 237–243 amu was performed at medium resolution (see settings in Table 1). The resulting spectra from IAEA135 provided no such interferences. To examine the origin of these treated by fusion/UTEVA + TRU and fusion/TEVA are shown in Fig. 3. The spectra clearly display interfering peaks at approximately 0.18 amu lower than the analyte peaks from the TRU procedure, while the TEVA-separation provides no such interferences. To examine the origin of these

### Table 4

<table>
<thead>
<tr>
<th>Reference material</th>
<th>Procedure</th>
<th>$^{239}$Pu/ $^{240}$Pu</th>
<th>$^{240}$Pu</th>
<th>$^{239}$ + $^{240}$Pu</th>
<th>$^{239}$Pu</th>
<th>$^{240}$Pu</th>
<th>Rec. value</th>
<th>Re-evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA135 Fusion/TEVA</td>
<td>126</td>
<td>10</td>
<td>96.4</td>
<td>8.8</td>
<td>222</td>
<td>19</td>
<td>0.207</td>
<td>0.002</td>
</tr>
<tr>
<td>IAEA135 Fusion/TEVA</td>
<td>125</td>
<td>3.9</td>
<td>96.5</td>
<td>5.8</td>
<td>222</td>
<td>10</td>
<td>0.209</td>
<td>0.006</td>
</tr>
<tr>
<td>IAEA135 Fusion/UTEVA + TRU</td>
<td>135</td>
<td>3.3</td>
<td>112</td>
<td>3.2</td>
<td>247</td>
<td>6.5</td>
<td>0.225</td>
<td>0.001</td>
</tr>
<tr>
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<td>2.22</td>
<td>0.065</td>
<td>1.54</td>
<td>0.054</td>
<td>3.77</td>
<td>0.12</td>
<td>0.188</td>
<td>0.003</td>
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<tr>
<td>IAEA135 Leaching/TEVA</td>
<td>2.22</td>
<td>0.11</td>
<td>1.59</td>
<td>0.079</td>
<td>3.80</td>
<td>0.11</td>
<td>0.194</td>
<td>0.015</td>
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<tr>
<td>IAEA135 Fusion/UTEVA + TRU</td>
<td>19.2</td>
<td>0.69</td>
<td>28.9</td>
<td>1.1</td>
<td>48.1</td>
<td>1.8</td>
<td>0.407</td>
<td>0.002</td>
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<tr>
<td>Soil6 Fusion/TEVA</td>
<td>0.679</td>
<td>0.017</td>
<td>0.475</td>
<td>0.002</td>
<td>1.15</td>
<td>0.0188</td>
<td>0.189</td>
<td>0.004</td>
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<tr>
<td>Soil6 Fusion/UTEVA + TRU</td>
<td>0.655</td>
<td>0.026</td>
<td>0.531</td>
<td>0.066</td>
<td>1.19</td>
<td>0.0715</td>
<td>0.220</td>
<td>0.029</td>
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<tr>
<td>Soil6 Fusion/TEVA</td>
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<td>1.29</td>
<td>9.50</td>
<td>0.63</td>
<td>16.4</td>
<td>1.9</td>
<td>0.378</td>
<td>0.042</td>
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</table>

### Table 5

<table>
<thead>
<tr>
<th>Reference material</th>
<th>Procedure</th>
<th>Chemical procedure</th>
<th>Analysis instrumentation</th>
<th>$^{240}$Pu/$^{239}$Pu</th>
<th>s</th>
<th>n</th>
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</thead>
<tbody>
<tr>
<td>IAEA135</td>
<td>9</td>
<td>Leaching/TEVA or anion exchange</td>
<td>ICP-QMS</td>
<td>0.211</td>
<td>0.004</td>
<td></td>
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<tr>
<td>IAEA135</td>
<td>10</td>
<td>Leaching/anion exchange</td>
<td>Element MCN6000</td>
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<td>0.008</td>
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</tr>
<tr>
<td>IAEA135</td>
<td>33</td>
<td>Leaching/anion exchange + 3M Empore discs</td>
<td>JMS-PLASMA MAX2 + U5000 + AT</td>
<td>0.255</td>
<td>0.03</td>
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</tr>
<tr>
<td>IAEA135</td>
<td>34</td>
<td>Microwave digest/UTEVA + TRU</td>
<td>ICP-SMS</td>
<td>0.240</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>IAEA135</td>
<td>34</td>
<td>Microwave digest/UTEVA + TRU</td>
<td>ICP-SMS</td>
<td>0.21</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>IAEA135</td>
<td>35</td>
<td>Leaching/TEVA + Sr-resin</td>
<td>PlasmaTrace 2 + USN U-5000</td>
<td>0.19</td>
<td>0.02</td>
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</tr>
<tr>
<td>IAEA135</td>
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<td>Leaching/TEVA + Sr-resin</td>
<td>PlasmaTrace 2 + USN U-5000</td>
<td>0.1779</td>
<td>3</td>
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<tr>
<td>Soil6</td>
<td>35</td>
<td>Leaching/TEVA or anion exchange</td>
<td>PlasmaTrace 2 + USN U-5000</td>
<td>0.18</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Soil6</td>
<td>9</td>
<td>Leaching/TEVA or anion exchange</td>
<td>ICP-QMS</td>
<td>0.191</td>
<td>0.005</td>
<td></td>
</tr>
</tbody>
</table>

interferences, a semi-quantitative determination was made on the Pu-fractions from the UTEVA TRU separation. Fig. 4 shows the concentrations of the major elements (e.g., Zr and lanthanides, and the same pattern was found in the other reference materials. Based on these findings and potential interferences from Pb previously reported by Wyse et al. and Becker and Dietze, solutions of 1 mg l⁻¹ Zr, Pb and Ce in 0.1% HEDPA and 0.3 M HNO₃ were analysed by scanning of the mass region 230-244 amu at medium resolution. The spectra displayed peaks at 235.884 and 236.874 amu in the 1 mg l⁻¹ Ce solution, which indicate that
the lanthanides could be a contributing factor to the formation of the interferences. No interfering peaks (intensities = 0 cps) were found under applied experimental conditions in the mass spectra resulting from Zr and Pb solutions.

The mass differences between the major isotope of Ce, i.e., 140Ce (88.48%), and the masses of the interfering peaks are 95.979 and 96.969 amu. No previously reported polyatomic species can explain such a large difference in mass. A number of potential polyatomic species that could interfere with the actinides has been listed by Truscott et al.\textsuperscript{22} The formation of polyatomic species from Pb, Ti, Hg, Pt, Bi in combination with one isotope of P, S, Cl or Ar is mentioned for the mass range 238–243 amu. Due to the findings from the semi-quantitative determination, the absence or low abundance of S and Cl in the Pu-fraction from the UTEVA + TRU separation and the negative test for Pb in HEDPA, it is difficult to explain all the interferences in the region 238–243 amu from this list. Becker and Dietze\textsuperscript{23} have reported interferences from ReO\textsubscript{3H} and ReO\textsubscript{3} on the mass region 233–236 amu. The formation of tri-oxides from Os, Ir or Pt could cause interferences at 238–243 amu, but the concentrations of these elements in the Pu-fraction from the UTEVA + TRU separation were less than 0.5 µg per 1\textsuperscript{a}. The elevated levels of lanthanides from the UTEVA + TRU separation, the fact that the interferences were found at relatively equal intensities over such a broad mass range, and the initial positive tests with Ce indicate that the lanthanides are at the origin of the interferences. Further and more extensive investigations need to be conducted, however, before a satisfactory explanation of these interferences can be presented.

The separation with TEVA is dependent on retention of tetravalent Pu, while that using UTEVA and TRU is based on retention of Pu in trivalent form.\textsuperscript{18} In the latter procedure, americium, as well as the lanthanides, also exists as trivalent ions and will partly follow plutonium in the separations. Initially this was not considered to be a problem since no interferences from the lanthanides were expected and only the minor isotopes, 239Pu and 240Pu, were to be determined, which makes the isobaric interference of 241Am on 240Pu inconsequential. It is, however, possible to separate Am and the lanthanides from Pu when using a combination of UTEVA and TRU,\textsuperscript{17,18} but these steps were excluded in this work in order to simplify the procedure. Since the separation based on TEVA eliminates the problem with these interferences, this alternative should be preferred instead.

The isotopic amount ratio of 240Pu/239Pu was also determined and the results are included in Table 4a. Since there is no information on this ratio in the reference values, a summary of data reported in the literature was compiled (Table 4b). The ratio for the two procedures based on TEVA-separation agree well with the reported results, while those determined in the UTEVA + TRU fractions appear to be excessive. This is most likely caused by the interferences identified above. The precision of the isotopic amount ratio determination obtained in this study was comparable to, or better than, values reported in the literature.

As mentioned above, there are some concerns in the literature regarding the suitability of acid-leaching of soil and sediment for the determination of Pu.\textsuperscript{12,14} In this study, both acid-leaching and complete dissolution based on lithium borate fusion were applied, and no significant differences in Pu-concentrations could be detected. The chemical yields of Pu were slightly higher for the fusion procedure, and although a complete dissolution should result in higher concentrations of 235U, no difference could be seen in the decontamination from 235U for the two methods. Although the semi-quantitative determination revealed higher concentrations of, e.g., lanthanides from the fusion/TEVA procedure, the levels were not high enough to cause any interference in the determination of Pu. The time required for the fusion procedure is longer due to the overnight flocculation of Si, but requires less hands-on time compared to acid-leaching. It should also be emphasised that the fusion-procedure is to be preferred over a complete digestion using acids, since the usage of HF is avoided and such procedures are often time consuming and labour intensive.\textsuperscript{14} The recommended procedure based on these findings is therefore the lithium borate fusion.

Based on the results obtained, the fusion/TEVA procedure was chosen for further testing of the repeatability over time. Two additional batches of three aliquots of IAEA300 were prepared and analysed. The results are shown in Table 5. The method provides good stability and all the results are in agreement, except for sub-sample 1 in batch 2, where the concentration of 241Pu was found to be almost twice as high as the rest of the results. To determine whether this was caused by interferences similar to those detected earlier, the fraction was re-analysed using medium-resolution. The result from this determination was, however, in agreement with the first. An explanation for this high result could be inhomogeneity of the reference material, which would also explain the large variations in the reported concentrations in the evaluation of the recommended reference value.\textsuperscript{27} It has been shown previously that radionuclides such as Pu can be incorporated in hot-particles in environmental samples,\textsuperscript{30,31} which makes the homogenisation of samples difficult. It is also interesting to notice that the isotopic amount ratio of 240Pu/239Pu in sub-sample 2.1 is higher than the ratio found in the other sub-samples (0.228 compared to an average of 0.187). Calculations show that the additional activity should have an isotope amount ratio of ~0.28 which is in between the average ratio of global fall-out and the ratio reported in debris originating from the Chernobyl accident.

### Conclusions

The separation based on the TEVA-resin followed by elution with 0.1% HEDPA is well suited as a medium for Pu-determination since it provides a fast and efficient elution of Pu from the resins and minimizes memory effects in the sample introduction system. Neither significant differences in the efficiencies of

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**Table 5.** Repeated measurements of IAEA300 using the fusion/TEVA procedure

<table>
<thead>
<tr>
<th>Batch</th>
<th>Subsample</th>
<th>239Pu/Bq kg(^{-1})</th>
<th>240Pu/Bq kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2.15</td>
<td>0.067</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.23</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.29</td>
<td>0.076</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>4.03</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.24</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.20</td>
<td>0.020</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2.17</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.15</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.15</td>
<td>0.052</td>
</tr>
</tbody>
</table>

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Pu recovery from the samples were detected when comparing acid-leaching to lithium borate fusion, nor did the fusion seem to cause more problems in the separation and determination than the acid leaching. This suggests fusion to be a more suitable procedure due to the potential for encountering refractory Pu in certain samples. It was also found that the potential interference of polyatomic species must be considered in the determination of actinides with ICP-MS. Further investigations need to be carried out to identify the interferences found in this study. The importance of an accurate and precise determination of the contribution from $^{238}$U on $^{239}$Pu must also be stressed, since this interference can be significant in spite of chemical separation of Pu from U. The results of this study also highlight the problem of sample homogenisation when performing determinations of Pu in soil, a problem which must be considered both in the use of reference materials and in the preparation of routine samples.

Acknowledgements

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References

Lanthanide phosphate interferences in actinide determination using inductively coupled plasma mass spectrometry

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The determination of actinides at low levels using ICP-MS can be interfered by polyatomic ions appearing at the same nominal mass-to-charge ratio. In this work, interferences initially found when analysing plutonium in soil and sediment samples were identified as lanthanide phosphates and the formation of these species examined. It was found that high sample gas flow rates and low rf powers enhanced the formation of lanthanide phosphates. All lanthanides studied (La, Ce, Pr and Nd) formed phosphates, albeit to various extents and of slightly different compositions. Furthermore, the lanthanide phosphate formation was verified by introducing the source of phosphorus, hydroxyethylidene diphosphonic acid (HEDPA), in an 18O enriched water solution. This experiment also revealed that the HEDPA is essentially completely dissociated in the plasma and that the interfering species are most likely formed during ion extraction.

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) has been widely used for the determination of actinides for several years now. The benefits of this analytical technique, as compared with the more traditionally used γ-spectrometry, include shorter analysis times, less demands on chemical separation and the ability to separate 238Pu and 239Pu. The development of double focusing sector field (ICP-SFMS) instruments has improved the sensitivity and allowed the determination of actinides at sub-pg l−1 levels. However, as in all determinations using ICP-MS, care needs to be taken to avoid spectral and non-spectral interferences.1 Although the influence of spectral interferences from polyatomic ions and isobaric elements is considered to be relatively low for the analysis of actinides compared with elements in the lower mass region, certain problems persist, of which the most common are probably 238U1H+ on 239Pu1+ and 238U1+ on 239Pu1+. Generally a chemical separation is performed to decrease the influence of 238U1H+ on 239Pu since the resolution of the ICP-MS instruments available is insufficient to resolve this interference (would require a resolution (m/Δm) of about 37000).

Analyses of actinides at the low concentrations possible today can also be interfered by other, less abundant polyatomic ions. Examples of such species which have been found or suspected to interfere in actinide measurements are PbC3− (in digested soil samples),2 PbNO3− (in leachates of samples electrodeposited in Pt-discs)3 and ReO4−/ReO3H+ (in reactor waste water spiked with Re).4 Shen et al.5 observed interferences in the mass region 229–237 when determining U and Th in geological material and sea-water particulate. These interferences caused elevated signal levels of up to 20 times for the measurement of 240Pu5+ and up to 10 times for 239Pu5+, and the resulting isotope ratio of 240Pu/239Pu was increased by a factor of two at worst. The cause of these interferences was suspected to be related to high levels of lanthanides since they only appeared when Pu was separated in the trivalent oxidation state. This separation resulted in concentrations up to 6 mg l−1 of individual lanthanides in the Pu fraction while the concentration of 240Pu was 10 pg l−1 at the lowest. However, no satisfactory explanation of the composition could be provided at that time. The intention of the present study was to further examine the composition and behaviour of these interferences.

Experimental

Reagents and standards

The lanthanides used were lanthanum nitrate hexahydrate 99.99%, cerium(III) nitrate hexahydrate 99.999%, neodymium(III) nitrate hexahydrate 99.9% (all from Aldrich, Milwaukee, WI, USA) and praseodymium nitrate 99.9% (City Chemical Corporation, New York, USA). Other reagents used were nitric acid 65%, phosphoric acid min. 85%, oxalic acid dihydrate (all of p.a. grade, Merck, Darmstadt, Germany) and hydroxyethylidene diphosphonic acid (HEDPA; Briquest ADPA 60A, industrial grade 60%, Albright & Wilson UK Ltd., Oldbury, UK). A standard solution of 242Pu (NIST SRM 4334G; National Institute of Standards and Technology, Gaithersburg, MD, USA) was used for optimising the instrument for Pu measurements. Water, 18O min. 99 at% (Rotech, Miamisburg, OH, USA), was used for the isotope enriched study of the lanthanum phosphates formation. All other solu-
tions were prepared using deionised water from a Milli-Q Element system (Millipore, Molsheim, France).

**Instrumentation**

Measurements were performed using an Element2 ICP-SFMS instrument (Thermo-Finnigan, Bremen, Germany). The instrument was equipped with a semi-demotionable Fassel quartz torch and a CD-2 Guard Electrode. Sample introduction was performed using an auto sampler (ASX-500, Cetac Technologies, Omaha, NE, USA), a conical nebuliser (GlassExpansion, Melbourne, Australia) and a Scott-type double-pass spray chamber. Self-aspiration, resulting in a sample flow rate of approximately 0.2 ml min^{-1}, was used throughout. The guard electrode was grounded and the automatic dead time correction activated. Torch position, lens parameters and nebuliser gas flow rates were optimised daily to obtain a maximum sensitivity for $^{238}\text{U}$ and to minimise UO$_2$ electrode formation in order to check the instrumental performance. The instrument was then tuned for highest intensity of $^{242}\text{Pu}$ in 0.1% HEDPA.

**Data evaluation**

Throughout this study, the “raw data” or “channel data” that can be obtained from the instrument software were used in the evaluations. For quantitative determinations, the four central samples (or channels) of each peak have been used (corresponding to an integration window of 40%) and no blocking of the data was performed. For the scanning of larger mass areas, averages of 10 scans were used to create the spectra shown.

**Results and discussion**

As mentioned above, the interferences found in the actinide region were suspected to derive from high levels of lanthanides since problems only occurred in solutions where Pu had not been separated from these elements. Furthermore, analysis of a solution of 1 mg l\(^{-1}\) Ce in 0.1% HEDPA, using a medium resolution ($m$/Am = 4000), showed the $^{139}$La peak approximately 95.98 and 96.97 u higher than the most abundant Ce isotope ($^{139}\text{Ce} 139.905$ u). No previous reports of polyatomic ion formation in ICP-MS analysis could explain such a large difference between the “parent” isotope and the polyatomic ion. Calculations based on the composition of the solution yielded a hypothesis that the interference could be caused by formation of a lanthanide in combination with HPO$_4$ (95.96 u) or H$_2$PO$_4$ (96.97 u).

**Influence of instrumental parameters on interference formation**

The rf power and nebuliser gas flow rate were varied in order to examine the influence of these parameters on the formation of the interferences. For this study, a solution containing $^{139}$La, $^{92}$Ce (9.92 mg l\(^{-1}\)) and $^{244}$Pu (153 ng l\(^{-1}\)) in 0.1% HEDPA was used. The rf power was varied while the other settings were unchanged: the same procedure was followed for the nebuliser gas.

**Table 1**

<table>
<thead>
<tr>
<th>Instrument settings</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Argon flow rates</strong></td>
</tr>
<tr>
<td>Cooling gas</td>
</tr>
<tr>
<td>Auxiliary gas</td>
</tr>
<tr>
<td>Nebuliser gas</td>
</tr>
<tr>
<td>RF power</td>
</tr>
<tr>
<td>Sample cone</td>
</tr>
<tr>
<td>Skimmer cone</td>
</tr>
</tbody>
</table>

**Data acquisition settings**

| Resolution (m/Am) | 4000 |
| Detection mode | Pulse counting |
| Data acquisition mode | E-scan |

<table>
<thead>
<tr>
<th>Quantitative determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotopes and polyatomic ions</td>
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<tr>
<td>$^{139}$La$^{31}$P$^{16}$O$_4$</td>
</tr>
<tr>
<td>$^{139}$La$^{31}$P$^{16}$O$_4$</td>
</tr>
<tr>
<td>$^{238}$U (235.075–241.026 u)</td>
</tr>
<tr>
<td>$^{244}$Pu (241.043–247.084 u)</td>
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<tr>
<td>Mass window</td>
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<tr>
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<td>Number of scans</td>
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<td>Settling time</td>
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<td>Magnet mass</td>
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**Scanning of larger mass areas**

<table>
<thead>
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<th>Isotopes and corresponding mass regions</th>
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</thead>
<tbody>
<tr>
<td>$^{238}$U (233.094–238.996 u)</td>
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<tr>
<td>$^{244}$Pu (241.043–247.084 u)</td>
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<tr>
<td>Sample time</td>
</tr>
<tr>
<td>Mass window</td>
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<tr>
<td>Samples per peak</td>
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<tr>
<td>Number of scans</td>
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<tr>
<td>Settling time</td>
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<td>Magnet masses</td>
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</tbody>
</table>

It was also found that changing the sampler and skimmer orifices affected the lanthanum phosphate formation significantly. A pair of previously used cones resulted in increased intensities for $^{139}$LaHPO$_4^-$ and $^{139}$LaH$_2$PO$_4^-$ by factors of 4 and 18, respectively. By comparison, the intensity for $^{238}$U was increased by a factor of 1.5. The orifices of the cones were measured using a microscope, and it was found that the cones causing more lanthanum phosphate formation had larger orifices (sampled 1095 ± 2 μm (one standard uncertainty); skimmer 830 ± 10 μm) than the ones inducing less formation (sampled 1059 ± 3 μm; skimmer 751 ± 6 μm).

Gas flows through the sampler and skimmer cones are each proportional to the orifice areas. Thus, the set of cones with larger diameter orifices would be expected to yield about 30% higher U sensitivity, in reasonable agreement with the experimental result considering that the measurements were performed on different days. Clearly though, the behaviour of parameters. An increased nebuliser gas flow rate, as well as a decreased rf power (down to 1000 W) results in more pronounced $^{139}$LaHPO$_4^-$ formation. Both these settings result in a “cooler” plasma that might suppress the dissociation of polyatomic ions. The figures also show that, fortunately, the maximum interference for $^{244}$Pu$^+$ is achieved at different settings from that of $^{139}$LaHPO$_4^-$.
Influence of rf power and nebuliser gas flow on the intensity of $^{139}$LaHPO$_4$.

The term n.d. is used when the relative standard uncertainty ($\frac{k}{\sqrt{n}}$) is above 100%.

**Table 2** Intensities of lanthanum phosphates in various media. The intensities are given in cps with the combined standard uncertainties ($\frac{k}{\sqrt{n}}$).

![Fig. 1](image-url) Influence of (a) rf power and (b) nebuliser gas flow on the intensity of $^{139}$LaHPO$_4$.

Interference formation in various media

In order to verify that the interference was due to the formation of lanthanide phosphates, solutions of $^{139}$La in different media were prepared. The compositions of the solutions are specified in Table 2. Oxalic acid and phosphorous acids were chosen to somewhat match the elemental composition of HEDPA with and without phosphorus, and the nitric acid was chosen since it is a common matrix in ICP-MS determinations. The formation of $^{139}$LaPO$_3^-$, $^{139}$LaHPO$_4^-$, $^{139}$LaH$_2$PO$_4^-$ and $^{139}$LaH$_3$PO$_4^-$ was monitored and two instrumental settings were used, one optimised for $^{242}$Pu in 0.1% HEDPA (nebuliser gas flow rate 0.946 l min$^{-1}$, rf power 1300 W) and the other for $^{139}$LaHPO$_4$ formation in 0.1% HEDPA (nebuliser gas flow rate 0.946 l min$^{-1}$, rf power 1020 W). The results are shown in Table 2.

It can be seen from the table that the interferences can only be found in the matrices containing phosphorus, which strongly supports the theory that the interferences are caused by lanthanide phosphates. Furthermore, it can be seen that $^{139}$LaHPO$_4^-$ is the most abundant species at both instrumental settings, followed by $^{139}$LaH$_3$PO$_4^-$. The intensities of the phosphates are approximately the same for both HEDPA and H$_2$PO$_4$ which could be expected since the concentration of phosphorus is the same in these two solutions. A scan of further mass areas using the solution of La in HEDPA (rf power 1300 W) also shows the formation of $^{139}$LaPO$_3^-$, $^{139}$LaHPO$_4^-$ and $^{139}$LaH$_2$PO$_4^-$ at intensities approximately the same or slightly lower than $^{139}$LaHPO$_4^-$. Analysis of lower mass areas displays the formation of all combinations of H$_2$PO$_4^-$ (where $x = 0$–3 and $y = 1$–4).

Interference pattern from various lanthanides

In order to examine the interference pattern from various lanthanides, solutions of approximately 10 mg l$^{-1}$ of La, Ce, Pr and Nd in 0.1% HEDPA were prepared. A larger mass area was scanned (see Table 2 for actual mass areas and instrumental settings) and the corresponding spectra are shown in Fig. 2. The spectra show the formation of interferences for all of the lanthanides studied. The combinations of a lanthanide with HPO$_4$ or H$_2$PO$_4$ dominate, but the relative intensities vary for different lanthanides. The absolute intensities also vary between different elements, e.g., the cerium phosphates are more abundant than the phosphates of the other lanthanides. Moreover, the isotopic compositions of Nd and Ce phosphates depicted in Fig. 2 correspond well with the natural isotopic compositions of Nd and Ce.

As mentioned above, it was found that the sizes of the cone orifices affect the formation of the lanthanide phosphates. Spectra from analysing solutions of La and Pr in HEDPA, using more worn cones with slightly larger orifices, are shown in Fig. 2. The nebuliser flow rate is kept at 0.95 l min$^{-1}$.
in Fig. 3. As can be seen, the intensities are significantly increased and the most abundant lanthanum phosphate has changed from $^{139}$LaHPO$_4$ to $^{139}$LaH$_2$PO$_4$.

Overall, it is clear that these lanthanide phosphates can cause interferences in a large part of the actinide mass area, from m/z 235 and above. It is also evident from these spectra that the interfering peaks found in our previous study$^8$ can be explained by phosphates of Ce, Pr and Nd. Gwiazda et al.$^7$ showed an interfering peak at m/z 234.81 when determining $^{235}$U in urine that could be removed when U was separated using anion exchange prior to the analysis. The mass of 234.81 u corresponds relatively well with the mass of $^{139}$LaHPO$_4$ (234.89 u).

In a study by Themelis et al.,$^{13}$ the concentration of phosphate in urine varied between 0.9 and 1.5 g l$^{-1}$, which is in accordance with the concentrations used in this study. According to Minoia et al.,$^{14}$ the concentration of La in urine can be expected to vary between 0.015 and 3.6 g l$^{-1}$. This is significantly lower than the concentration used here. The linearity of the formation of lanthanide phosphates with concentration has not been examined but the intensities of the phosphates have been observed to vary substantially over time in spite of “identical” instrument settings. Taking this into account makes LaHPO$_4$ a possible explanation for the interference found by Gwiazda et al.$^7$

Study of interference formation using H$_2^{18}$O

In order to further confirm the formation of lanthanide phosphates, a solution of Pr (15.7 mg l$^{-1}$) and HEDPA (0.1%) in $^{18}$O enriched (99 at%) water was prepared. The resulting 16O content of the solution was $\sim$0.2% of the total amount of oxygen. It should be noticed that no isotopic exchange of oxygen in H$_3$PO$_4$, and by inference HEDPA, takes place unless the reaction is catalysed by the addition of an enzyme or elevated temperatures.$^{15}$ The solution was analysed by scanning a large mass area (as described above) and the resulting mass spectrum is shown in Fig. 4, together with that for a solution of Pr and HEDPA in water with natural oxygen isotopic composition.

The relatively large peak from PrH$_2$PO$_4$ in the regular water matrix has been divided into five different peaks in the H$_2^{18}$O matrix. These peaks are at 0, 2, 4, 6 and 8 u higher than the original peak, which indicates the replacement of 0, 1, 2, 3 and 4 $^{16}$O atoms in the phosphate moiety with $^{18}$O. The intensities of the peaks were compared with a theoretical distribution based on the binominal expression $(a+b)^n$, where $a$ is the mole fraction of $^{16}$O and $b$ is the mole fraction of $^{18}$O.$^{16,17}$ The best fit of the experimental distribution to the
ionisation energies of 10.49, 10.5 and 8.39 eV, respectively.\textsuperscript{20} Substantial proportions of at least the two former species will remain in neutral form.\textsuperscript{7} Atomic phosphorus and its neutral oxides are therefore potential precursors for H\textsubscript{3}PO\textsubscript{4} formation following collisions in the extraction process.

Assuming complete dissociation of the water introduced into the plasma, Niu and Houk\textsuperscript{9} have calculated that the combined number density of H and O atoms may reach 17% of the total density. In combination with estimates of the number of collisions experienced during the expansion (about 250),\textsuperscript{9,21} there appears to be ample opportunity for the production of the observed lanthanide phosphate ions downstream of the sampler. Note that the presence of molecular ions containing the PO\textsubscript{4} moiety also shows that recombination reactions are involved, since HEDPA actually contains phosphonic acid groups, i.e., \text{–PO\textsubscript{2}H\textsubscript{2}}.

Conclusions

This study has shown that polyatomic species consisting of lanthanide phosphates constitute a potential source of spectral interference in the determination of low levels of actinides using ICP-MS. The formation of these species is favoured by "cold" plasma conditions, \textit{i.e.}, lower rf power settings or increased sample gas flow rates. Owing to the large mass range of the lanthanides, the phosphates of these elements have the potential to interfere in the whole actinide mass-region. Because of the chemical similarities of the lanthanides to trivalent actinides such as Am, Cm and, in some cases, Pu, the lanthanides will, in these cases, to some extent follow the actinides through most chemical separation processes. The latter are often based on liquid-liquid or solid-phase extraction procedures using phosphorus-containing complexing agents, thus providing a potential source of phosphorus for interference formation.\textsuperscript{22–24} This problem may also occur when no chemical separation is applied, \textit{e.g.}, when analysing minor isotopes of U in phosphorus containing matrices such as urine. A strategy to avoid the problem of lanthanide phosphates interfering with actinide determination can be to modify the separation procedures to avoid the combination of high lanthanide and phosphorus concentrations in the sample solution. For the determination of Pu, a separation based on tetravalent Pu is preferable since this provides a separation of lanthanides from Pu.\textsuperscript{8} The use of a phosphorus-containing medium such as HEDPA in Pu determination with ICP-MS is not a common procedure, but has the advantage of providing an efficient elution of Pu from solid phase extraction columns and reducing adsorption of Pu in the sample introduction system. The problem of adsorption is not as pronounced for, for example, Am or Cm and hence the use of other eluting media is advisable, since the alternative of separating these elements from the lanthanides requires additional sample pre-treatment.\textsuperscript{25} Other options to avoid interference from lanthanide phosphates include adjustment of plasma parameters to suppress formation of these compounds or determination in medium resolution, although this latter alternative would reduce the sensitivity by about a factor of ten.

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References

Age determination of plutonium using inductively coupled plasma mass spectrometry

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Abstract

The time since the last chemical separation, i.e. the age, of plutonium materials can be determined by analysing the isotope amount ratio of the plutonium isotopes and their daughter nuclides. In this paper, a method for age determination based on analysis of $^{241}\text{Pu}/^{241}\text{Am}$ and $^{240}\text{Pu}/^{236}\text{Pu}$ using ICP-SFMS is described. Separation of Pu and Am was performed using a solid phase extraction procedure including UTEVA, TEVA, TRU and Ln-resins. The procedure provided separation factors adequate for this purpose. Age determinations were performed on two plutonium reference material solutions, IRMM081 ($^{239}\text{Pu}$) and IRMM083 ($^{240}\text{Pu}$), on sediment from the Marshall Islands (reference material IAEA367) and on Trinitite. The observed ages based on the $^{241}\text{Am}/^{241}\text{Pu}$ ratio corresponded well with the actual ages of all the materials. The ages derived from the $^{236}\text{U}/^{240}\text{Pu}$ ratio were in agreement for the IRMM materials, but for IAEA367 the determination of $^{236}\text{U}$ was interfered by tailing from $^{238}\text{U}$, and for Trinitite the determined age was biased due to formation of $^{236}\text{U}$ in the detonation of the “Gadget”.

Introduction

Knowledge of the origin and history of nuclear material is of importance in many different areas, e.g., nuclear forensics (illicit trafficking), environmental studies, emergency preparedness, and in a verification regime for a future fissile material cut-off treaty (FMCT). In the analysis of the origin of plutonium, information on isotopic composition and age of the material is of vital importance.
Wallenius and colleagues have, in a series of publications, exploited different types of mass spectrometers for determining the age and origin of Pu. They applied secondary ion mass spectrometry (SIMS) for the dating of single plutonium particles.\textsuperscript{1} Thermal ionisation mass spectrometry (TIMS) and quadrupole-based inductively coupled plasma mass spectrometry (ICP-QMS) were used for the age determination of plutonium reference materials and plutonium pellet samples.\textsuperscript{2, 3} The age determinations using mass spectrometry were primarily based on the $^{238}$Pu/$^{234}$U, $^{239}$Pu/$^{235}$U and $^{240}$Pu/$^{236}$U ratios, and the results were generally in good agreement with the reported ages. However, some discrepancies were identified, e.g., too low determined ages from the $^{238}$Pu/$^{234}$U ratio and too high from the $^{239}$Pu/$^{235}$U ratio when analysing PuO$_2$ and MOX (mixed oxide fuel) particles using SIMS.\textsuperscript{1} This was due to interference from $^{238}$U in the determination of $^{238}$Pu causing overestimation of the $^{238}$Pu/$^{234}$U ratio, and contamination from $^{235}$U causing an underestimated $^{239}$Pu/$^{235}$U ratio.

Of the Pu-U pairs, the $^{240}$Pu/$^{236}$U ratio is the one expected to be least sensitive to interference from contamination by natural U since the occurrence of $^{236}$U in nature is extremely low.\textsuperscript{4} However, $^{236}$U is produced from $^{235}$U(n,$\gamma$)$^{236}$U reactions in nuclear reactors and concentrations of $^{236}$U up to 0.5\% (atomic) can be found in spent nuclear fuel.\textsuperscript{5} Since in most cases $^{236}$U will be present together with larger amounts of $^{238}$U and $^{235}$U, corrections for abundance sensitivity and hydride formation needs to be made when analysing $^{236}$U using ICP-MS. Due to these interferences and the generally low concentrations of $^{236}$U found in nature, the determination of this nuclide using ICP-MS poses some difficulties. Boulyga et al. have examined the potential of different ICP-MS systems for $^{236}$U determination with application to soil-samples contaminated with fall out from the Chernobyl nuclear power plant accident.\textsuperscript{6, 7} In these studies, abundance sensitivity from $^{238}$U on m/z=236 for a sector field (ICP-SFMS; ELEMENT) instrument was reported to be $(5 - 5.3) \cdot 10^{-6}$ depending on the sample introduction system used.\textsuperscript{6}

A possibility to avoid the problem of uranium contamination is to base the dating of Pu material on the ratio $^{241}$Pu/$^{241}$Am. This ratio has been used in age determination of plutonium with $\gamma$-spectrometry\textsuperscript{8, 9}, but also for the characterisation and dating of Pu found in Chernaya Bay based on measurements by TIMS.\textsuperscript{10}
Since $^{241}$Pu and $^{241}$Am are isobars and cannot be separated by the highest resolution available with ICP-SFMS, a thorough chemical separation will be required prior to analysis using mass spectrometry. Determination of plutonium isotopes, including $^{241}$Pu, in environmental samples by ICP-MS or TIMS has been reported previously, e.g., in the analysis of the origin of Pu in the environment\textsuperscript{11, 12, 13, 14}, although in most cases the magnitude of the separation of Pu and Am has not been reported. Compared to the determination of Pu using ICP-MS, little has been published concerning the determination of $^{241}$Am in environmental samples using ICP-MS. Agarande et al. have compared results of $^{241}$Am analysis in sediment from the vicinity of a French nuclear site using ICP-SFMS and alpha spectrometry.\textsuperscript{15} In that study, a rather time consuming separation procedure (requiring 15 days) based on ion exchange and solid phase extraction was used, and the magnitude of the achieved separation of Pu and Am was not reported. Boulyga et al. determined $^{239}$Pu, $^{240}$Pu and $^{241}$Am in mosses by laser ablation ICP-SFMS.\textsuperscript{16} Solid phase extraction was used for the separation of Pu and Am, but the achieved separation factor was not reported although the concentrations of $^{241}$Am obtained by LA-ICP-SFMS were higher compared to concentrations obtained by alpha spectrometric determinations.

The aim of this study was to develop a method for age determination of plutonium material based on chemical separation and the analysis of $^{241}$Pu/$^{241}$Am and $^{240}$Pu/$^{238}$U using ICP-SFMS. The method has been applied on plutonium reference material solutions and environmental material contaminated with nuclear weapons debris.

**Experimental**

**Reagents and Standards**

The reagents used for sample preparation were nitric acid 65%, hydrochloric acid 37% and NaNO$_2$ (all of p.a. grade, Merck, Darmstadt, Germany), NH$_2$OH·HCl (98%, A.C.S. reagent grade, Scharlau Chemie S.A., Barcelona, Spain), polyethylene glycol (PEG2000, for synthesis, Merck, Darmstadt, Germany), LiBO$_2$ (99.997% Johnson Matthey, Karlsruhe, Germany), Silicagel 60 (Fluka, Buchs, Switzerland) and hydroxyethylidene diphosphonic acid (HEDPA; Briquest ADPA 60A, industrial grade 60%, Albright & Wilson UK Ltd, Oldbury, UK). Graphite crucibles (Alfa, Karslruhe, Germany) were used for fusion of samples, and
filters (Munktell OOM, Grycksbo Pappersbruk AB, Grycksbo, Sweden) were used for separation of flocculated Si. Deionised water from a Milli-Q Element system (Millipore, Molsheim, France) was used for all sample and standard preparations.

For the separation of Am, Pu and U, solid phase extraction based on UTEVA, TEVA, TRU and Ln-resin (all 100-150 μm, Eichrom, Darien IL, USA) was used. The separations were performed in disposable plastic 10 ml columns (Poly-prep, Bio-Rad, Hercules, CA, USA). Standard solutions of $^{233}$U (IRMM 040a), $^{242}$Pu (NIST SRM4334G) and $^{243}$Am (NIST SRM4332D) were used as spike solutions for quantification of the analytes. A standard solution containing U of natural composition (IRMM184) was used for monitoring instrumental dead-time, mass discrimination, $^{238}$U/H$^+$-formation and abundance sensitivity.

The age determinations were performed on two plutonium reference material solutions, IRMM081 ($^{239}$Pu) and IRMM083 ($^{240}$Pu) (both Institute of Reference Materials and Measurements, Geel, Belgium), and on one sediment sample from the Enewetak Atoll, Marshall Islands (reference material IAEA367, International Atomic Energy Agency, Vienna, Austria). Age determinations were also performed on “Trinitite”, i.e., soil from the test-site in New Mexico where the first nuclear weapons test ever was conducted.

Sample pre-treatment

**Lithium borate fusion:** The sediment reference material was dissolved using lithium borate fusion. Approximately 0.2 g (Trinitite) or 4 g (IAEA367) was weighed and mixed in a graphite crucible with LiBO$_2$ at a flux to sample ratio of 3:1. Approximately 0.2 ml of a spike solution containing about 100 pg g$^{-1}$ $^{233}$U, $^{243}$Am and $^{242}$Pu was added to the sample (this amount was also weighed to the accuracy of 0.1 mg, which also was the accuracy used for all sample and spike weighing in this work). Samples were then fused at 1050°C in a furnace for 10-15 minutes and transferred (after cooling) to a glass beaker containing 1.4 M HNO$_3$. The volume of 1.4 M HNO$_3$ used was approximately 100 times the sample weight. The melt was dissolved under heating (≥100°C) and stirring, and the solution was allowed to evaporate to half of the initial volume. In order to prevent precipitation of silicic acids during the following separation procedure, PEG2000 was added to a concentration of 0.002 M to flocculate the dissolved Si. The samples were left at room temperature overnight and then the precipitate was removed by filtering. This resulted in a HNO$_3$ concentration of approximately 2.8 M which was suitable for the following solid phase extraction procedure.
It was also found that the analysis of IRMM081 required a lithium-borate fusion in order to achieve similar chemical behaviour of the Pu in IRMM081 and the added $^{242}$Pu spike. If fusion was not conducted, the Pu from IRMM081 was lost to a higher degree than the $^{242}$Pu spike in the following solid phase extraction separation. The reason for this is not known at present, but one explanation might be that some of the Pu in IRMM081 is in polymeric form. The IRMM has since June 2005 withdrawn this material due to instability and varying concentrations. In order to achieve an amorphous melt in the fusion of this material, SilicaGel was added to LiBO$_2$ in a ratio of 1:5. Of this mixture, 1 gram was used for the fusion of 0.2 ml IRMM081 sample (containing 10.21 ng $^{239}$Pu g$^{-1}$) and 0.2 ml spike solution. The fusion procedure was performed in the same way as described above, with the exceptions that 20 ml 1.4 M HNO$_3$ and 0.08 g PEG2000 were used.

Material not pre-treated by fusion, i.e., IRMM083, was added to a load solution of 5 ml 3 M HNO$_3$ together with 0.2 ml spike solution as described above. Aliquots of 0.2 ml IRMM083 diluted to 13.48 ng $^{240}$Pu g$^{-1}$ were used for the analysis.

**Solid phase extraction separation:** The separations of Pu, U and Am were performed using solid-phase extraction. A red-ox procedure, first described by Moore and Hudgens$^{17}$, was used to adjust Pu to Pu(IV) while keeping Am as trivalent. First, Pu was reduced to the trivalent state by adding NH$_2$OH·HCl to a concentration of 15 mg ml$^{-1}$ and heating at 90°C for 5 minutes. After cooling to approximately 40°C, NaNO$_2$ was added at a concentration of 18 mg ml$^{-1}$ to oxidise Pu(III) to Pu(IV).

UTEVA (1 ml), TEVA (1 ml) and TRU resin (2 ml) were added to 10 ml plastic columns and the resins were conditioned with 5 ml 3 M HNO$_3$. The columns were mounted in series starting with TEVA followed by UTEVA and TRU. The sample was loaded on the resins and the beaker was rinsed with 3 ml 3 M HNO$_3$, which was added to the columns. Under these conditions, Pu(IV) is retained on the TEVA resin, U(VI) on UTEVA while Am(III) is retained on TRU.$^{18}$ The columns were then separated from each other and the TEVA column was rinsed with 20 ml 3 M HNO$_3$ to remove uranium. Plutonium was then eluted using 5 ml 0.1% HEDPA.$^{19}$ The UTEVA column was rinsed using 5 ml 5M HCl and 5 ml 3M HNO$_3$ after which U was eluted using 5 ml 0.1% HEDPA. The TRU-column was mounted on top of a column containing 0.5 ml Ln-resin that had been pre-conditioned with 1 ml 0.01 M HNO$_3$. 20
ml 0.01 M HNO₃ was then added to the columns to transfer americium from TRU to the Ln-resin. Americium was eluted from the Ln-resin using 3 ml 0.5 M HNO₃.

Sample preparation for γ-spectrometric determination of Pu-ratios: An aliquot of 4 g of Trinitite was dissolved using LiBO₂ and Si was removed by flocculation with PEG2000 (as described above). The sample was then loaded on 4 ml TEVA resin and the resin was rinsed using 40 ml 3M HNO₃. The resin was transferred to a 5 ml vial for γ-spectrometric measurement.

Instrumentation

Mass spectrometric measurements were performed using an Element2 ICP-SFMS instrument (Thermo-Finnigan, Bremen, Germany). The instrument was equipped with a semi-demountable Fassel quartz torch and a CD-2 guard electrode. Sample introduction was performed using a conical nebuliser and a cyclonic spray chamber (“Twister” – both from GlassExpansion, Melbourne, Australia). Self-aspiration, resulting in a sample flow rate of approximately 0.2 ml min⁻¹, was used throughout the investigation. The guard electrode was grounded and the automatic, soft-ware induced dead time correction inactivated. Torch position, lens parameters and nebuliser gas flow rates were optimised daily to obtain a maximum sensitivity for $^{238}\text{U}^+$. All measurements were performed using low resolution ($m/Δm = 300$). Instrument and data acquisition settings are shown in Table 1.

Gamma spectrometric measurements were performed using a coaxial high-purity germanium (HPGe), low-energy photon detector (EG&G Ortec, USA).

Data acquisition and evaluation

Instrumental dead-time, mass discrimination, $^{238}\text{U}^+\text{H}^+$ formation and abundance sensitivity were monitored using solutions containing uranium of natural composition (IRMM184) in 0.1% HEDPA. Dead-time and mass discrimination were calculated according to Appelblad and Baxter²⁰ and the results from the sample determinations were correspondingly corrected. The determinations of $^{239}\text{Pu}$ and $^{236}\text{U}$ were also corrected for possible contribution from UH⁺ formation and abundance sensitivity of $^{238}\text{U}$ and $^{235}\text{U}$. The determination of $^{241}\text{Pu}$ was also corrected for abundance sensitivity from $^{239}\text{Pu}$ when necessary. Throughout this study, the “raw data” or “channel data” that can be obtained from the instrument software were used, and the evaluations of these data were performed manually. This was done due to the
The uncertainties of the results were calculated according to ISO/GUM\textsuperscript{22} using the software GUM Workbench\textsuperscript{9} (Metrodata GmbH, D-79639 Grenzach-Whylen, Germany). All reported uncertainties are expanded uncertainties with a coverage factor of two ($k = 2$).

The age determination based on $\gamma$-spectrometric analysis of $^{241}\text{Pu}$ and $^{241}\text{Am}$ were evaluated using the software PC/FRAM (EG&G Ortec, USA). The determination of $^{240}\text{Pu}/^{239}\text{Pu}$ in Trinitite using $\gamma$-spectrometry was based on the 51.6 keV and 45.2 keV $\gamma$-emissions for $^{239}\text{Pu}$ and $^{240}\text{Pu}$ respectively. The 38.6 keV $\gamma$-emission for $^{239}\text{Pu}$ was used to establish a relative efficiency function for the energy region.

### Table 1  Instrument and data acquisition settings for the ICP-SFMS determinations

<table>
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<th>Instrument settings</th>
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<td>Argon flow rates</td>
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| Cooling gas         | 14 l min$^{-1}$  
| Auxiliary gas       | 11 l min$^{-1}$  
| Nebuliser gas       | 0.95 l min$^{-1}$  
| RF power            | 1300W  
| Sample cone         | Nickel, 1.1 mm orifice diameter  
| Skimmer cone        | Nickel, 0.8 mm orifice diameter  
|  
| Data acquisition settings |  
| Resolution (m/\delta m) | 300  
| Detection mode      | Pulse counting  
| Data acquisition mode | E-scan  
| Quantitative determination of Am and Pu |  
| Isotopes             | $^{232}\text{Th}^+, 233\text{U}^+, 234\text{U}^+, 235\text{U}^+, 236\text{U}^+, 238\text{U}^+, 239\text{Pu}^+, 240\text{Pu}^+, 241\text{Pu}/^{241}\text{Am}^+, 242\text{Pu}^+, 243\text{Am}^+$  
| Sample time          | 10 ms (except for $^{232}\text{Th}^+$ and $^{238}\text{U}^+$ where 2 ms was used)  
| Mass window          | 5%  
| Samples per peak     | 100  
| Number of scans      | 500  
| Settling time        | 1 ms (default minimum)  
| Magnet mass          | 232.038 u  
| Monitoring of dead-time, mass discrimination and abundance sensitivity/UH$^+$ formation |  
| Isotopes and polyatomic ions | $^{234}\text{U}^+, 235\text{U}^+, 236\text{U}^+, 237\text{U}^+, 238\text{U}^+, 55\text{U}/\text{H}^+, 55\text{U}/\text{H}_2^+$  
| Sample time          | 2 ms for $^{234}\text{U}^+$, 5 ms for $^{238}\text{U}^+$ and 10 ms for all others  
| Mass window          | 5%  
| Samples per peak     | 100  
| Number of scans      | 900  
| Settling time        | 1 ms (default minimum)  
| Magnet mass          | 234.040 u  

Calculation of the age of Pu-material

The determination of the age of Pu-material was based on the mother/daughter relationship between $^{241}\text{Pu}^{241}\text{Am}$ or $^{240}\text{Pu}^{236}\text{U}$. This relationship is described by the following equation

$$t = \frac{1}{\lambda_1 - \lambda_2} \ln \left[ 1 - \left( \frac{\lambda_2}{\lambda_1} - 1 \right) \frac{N_1}{N_2} \right] \tag{1}$$

In this equation, $t$ is the age of the material, $\lambda_1$ and $\lambda_2$ are the decay constants of Pu and the respective daughter nuclide and $N_1$ and $N_2$ are the amounts of the mother and daughter nuclide at the time of analysis. The half-lives used in the calculations were obtained from the Evaluated Nuclear Structure Data File (ENSDF).23

Results and discussion

The obtained ages based on ICP-SFMS determined $^{241}\text{Am}^{241}\text{Pu}$ and $^{236}\text{U}^{240}\text{Pu}$ ratios are shown in Table 2. Determinations were performed on three sub-samples of each material, plus one $\gamma$-spectrometric analysis of IRMM081 and IRMM083. No $\gamma$-spectrometric dating could be performed on IAEA367 and the Trinitite due to low concentrations of the analytes in these materials. The table also specifies the reference ages of the materials. These are based on the date of purification for the IRMM materials24, and the date of the detonation of “the Gadget” for the Trinitite.25 For IAEA367, the time period when the US conducted testing of thermonuclear weapons at the Enewetak Atoll was used as reference date (see discussion below).25, 26

As can be seen from the table, the ages determined by the $^{241}\text{Am}^{241}\text{Pu}$ ratio correspond well (as indicated by the expanded standard uncertainties, $k=2$) with the reference ages as well as with the $\gamma$-spectrometric determinations. A condition for age determination based on this kind of mother/daughter nuclide ratio is that there is no amount of daughter nuclide present at $t=0$, or that this initial amount is known. In the case of IRMM081, it was known that the material contained $^{241}\text{Am}$ at a concentration of 250 $\mu$g g$^{-1}$ directly after purification.24 Calculations based on this concentration and the concentration of $^{241}\text{Pu}$ at the time of separation using Eq. 2 results in an off-set in the age of 2.4 years for which the determined age in Table 2 has been
corrected. It should be noticed that the purification process used for IRMM081 at the reference time $t=0$ was electrolysis, while anion-exchange of Pu(IV) was used for IRMM083.\textsuperscript{24} Hence, it seems as if Am, at least to some extent, has not been separated from Pu in the electrolysis process while the use of anion exchange has resulted in a more thorough separation. A small bias in the age determination based on TIMS analysis of the $^{241}\text{Am}^{241}\text{Pu}$ ratio in NBS Pu-reference material was also reported by Wallenius and Mayer.\textsuperscript{2} This was also explained by incomplete Pu-Am separation in the purification of the Pu material.

Table 2 Results of the age determinations. The results from the $\gamma$-spectrometric measurements are included as well (numbers in italics). The determined age of IRMM081 has been corrected for an off-set age of 2.4 y due to residual of $^{241}\text{Am}$ after purification of the plutonium material.

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<thead>
<tr>
<th>Date of analysis</th>
<th>Determined age (y) based on:</th>
<th>Reference age (y)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{241}\text{Am}^{241}\text{Pu}$</td>
<td>$^{236}\text{U}^{236}\text{Pu}$</td>
</tr>
<tr>
<td>IRMM083:1</td>
<td>Dec 13, 2005</td>
<td>12.2 ± 0.3</td>
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<td>12.3 ± 0.3</td>
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<td>IRMM083:7</td>
<td></td>
<td>$12.1 ± 1.4$</td>
</tr>
<tr>
<td>IRMM081:1</td>
<td>Oct 27, 2005</td>
<td>30.7 ± 0.7</td>
</tr>
<tr>
<td>IRMM081:2</td>
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<td>30.7 ± 0.7</td>
</tr>
<tr>
<td>IRMM081:3</td>
<td></td>
<td>29.8 ± 0.7</td>
</tr>
<tr>
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<td>$29.3 ± 0.4$</td>
</tr>
<tr>
<td>IAEA367:1</td>
<td>Nov 17, 2005</td>
<td>51.8 ± 2.7</td>
</tr>
<tr>
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<td></td>
<td>50.8 ± 2.7</td>
</tr>
<tr>
<td>IAEA367:3</td>
<td></td>
<td>49.5 ± 2.8</td>
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<tr>
<td>Trinitite:1</td>
<td>Oct 27, 2005</td>
<td>58.4 ± 1.4</td>
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<tr>
<td>Trinitite:2</td>
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<td>59.4 ± 1.4</td>
</tr>
<tr>
<td>Trinitite:3</td>
<td></td>
<td>58.8 ± 1.3</td>
</tr>
</tbody>
</table>

The ages determined by the $^{236}\text{U}^{240}\text{Pu}$ ratio are in agreement with the reference values for the two Pu reference material solutions. For the materials containing nuclear weapons debris, two problems arose in the measurement of $^{236}\text{U}$. In the IAEA367 sediment, $^{236}\text{U}$ could not be significantly quantified due to abundance sensitivity from primarily $^{238}\text{U}$. The magnitude of the abundance sensitivity, defined as the net intensity on m/z 236 divided by the net intensity of $^{238}\text{U}$, was $1.94 ± 0.26 \cdot 10^{-6}$ in this study. When analysing the Trinitite, abundance sensitivity was small compared to the intensity from $^{238}\text{U}$ but the determined ages are much
higher than the reference ages. An explanation to these high results is production of $^{236}\text{U}$ via $(n,\gamma)$ reactions of $^{235}\text{U}$ in the detonation of the nuclear weapon

A critical parameter in developing this method was a thorough separation of $^{241}\text{Pu}$ and $^{241}\text{Am}$ since these nuclides would otherwise mutually interfere during the measurements. The performance of the separation was evaluated by monitoring the amounts of $^{241}\text{Am}$ in the Pu fraction and $^{242}\text{Pu}$ in the Am fraction. The resulting separation factors, defined as the added amount divided by the amount found in respective fraction were $\geq 3560$ for $^{242}\text{Pu}$ in the Am-fractions and $\geq 696$ for $^{243}\text{Am}$ in the Pu-fraction. Considering that the expected ratios of $^{241}\text{Pu}/^{241}\text{Am}$ will vary from 20 to 0.06 for ages from 1 to 60 years, these separation factors are more than adequate. The chemical yields for the separation were $(61\pm8)$ % for Am, $(73\pm5)$ % for Pu and $(64\pm10)$ % for U.

In the analysis, the ratios of the Pu-isotopes were also determined. The ratios obtained for the IRMM Pu reference materials were compared with the certified ratios for these materials and the values were in agreement with each other at the 95% confidence level. The ratios obtained for IAEA367 and the Trinitite are shown in Table 3. The obtained ratios for both $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ in IAEA367 are higher than the average values of global fall-out, i.e., $0.1808\pm0.0057$ for $^{240}\text{Pu}/^{239}\text{Pu}$ and $0.00264\pm0.00020$ for $^{241}\text{Pu}/^{239}\text{Pu}$ ($k=1$). Different constructions of nuclear weapons were tested at Enewetak, both fission and thermonuclear (fusion) weapons. The first thermonuclear device ever tested, “Mike”, detonated at the Enewetak Atoll on October 31, 1952 with a yield of 10.4 Mton. The $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ ratios in the debris from this test have been reported to be $0.363\pm0.004$ and $0.0030\pm0.0004$ (decay corrected to November 17, 2005 and $k=1$). A relatively high $^{240}\text{Pu}/^{239}\text{Pu}$ ratio is characteristic of thermonuclear weapons due to high neutron fluencies, thus creating $^{239}\text{Pu}$ and $^{240}\text{Pu}$ from neutron capture by $^{238}\text{U}$ present in the uranium blanket. Hence, the ratio of 0.30 found in this study indicates significant contribution of debris from thermonuclear devices. Further “successful” thermonuclear tests yielding more than 1 Mton were conducted at Enewetak in 1954 (“Nectar” 1.69 Mton), 1956 (“Apache” 1.85 Mton) and 1958 (“Koa” 1.37 Mton, “Oak” 8.9 Mton and “Pine” 2 Mton). This limits the actual reference date for the age determination to the range 1952 to 1958, as indicated in Table 2. The results displayed in Table 2 are centred around 1955.
The Pu ratios found in the Trinitite are also shown in Table 3. Parekh et al. have recently published a study of the radioactive content of Trinitite, where the $^{239}$Pu, $^{240}$Pu and $^{241}$Pu (via $^{241}$Am) were quantified using $\gamma$-spectrometry.30 The isotope amount ratios calculated from the results of that study are $0.0129\pm0.0030$ for $^{240}$Pu/$^{239}$Pu and $(3.33\pm0.14)\cdot10^{-5}$ for $^{241}$Pu/$^{239}$Pu (decay corrected to 05-11-17 and $k=1$). Although the uncertainties in these results are high, the ratio of $^{240}$Pu/$^{239}$Pu is significantly different from the ratios obtained by ICP-SFMS determinations presented in Table 3. In order to verify the ICP-SFMS results, a $\gamma$-spectrometric analysis was also performed on the Trinitite. It was found necessary to do a Pu-separation on the sample prior to analysis to reduce interference from, e.g., $^{152}$Eu (see details under “Experimental”). The resulting $^{240}$Pu/$^{239}$Pu ratio was in agreement with the mass spectrometric results (see Table 3). In a study conducted by the U.S. EPA on the levels of Pu around the Trinity site31, the $^{240}$Pu/$^{239}$Pu ratio of a “high” plutonium concentration sample was $0.0254\pm0.0007$ (calculated from Table 3 in ref. 31, $k=1$) which is also in agreement with the results found in this study.

Table 3 Obtained isotope amount ratios from analysis of IAEA367 and Trinitite. The result of the $\gamma$-spectrometric measurement of $^{240}$Pu/$^{239}$Pu in the Trinitite is included as well (in italics).

<table>
<thead>
<tr>
<th></th>
<th>Determined Pu-ratios (n/n)</th>
<th>$^{240}$Pu/$^{239}$Pu</th>
<th>$^{241}$Pu/$^{239}$Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA367:1</td>
<td>0.299 ± 0.004</td>
<td>(2.65 ± 0.35) $\cdot 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>IAEA367:2</td>
<td>0.295 ± 0.004</td>
<td>(2.75 ± 0.36) $\cdot 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>IAEA367:3</td>
<td>0.296 ± 0.004</td>
<td>(2.97 ± 0.40) $\cdot 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Trinitite:1</td>
<td>0.02493 ± 0.00009</td>
<td>(2.93 ± 0.18) $\cdot 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Trinitite:2</td>
<td>0.02487 ± 0.00009</td>
<td>(2.77 ± 0.18) $\cdot 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Trinitite:3</td>
<td>0.02486 ± 0.00009</td>
<td>(2.86 ± 0.16) $\cdot 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>**Trinitite:**4</td>
<td><strong>0.0249 ± 0.0047</strong></td>
<td><strong>(2.80 ± 0.17) $\cdot 10^{-5}$</strong></td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

It is shown in this paper that an accurate and precise age determination of Pu can be obtained with the presented method. The separation procedure developed yielded a more than adequate separation of Pu and Am, and the chemical yields of U, Pu and Am were satisfactory. Of the two ratios used, the $^{241}$Pu/$^{241}$Am ratio provided reliable results with the exception the analysis
of IRMM081 where initial $^{241}$Am was present. After correction for this, the resulting ages were in agreement with the reported age of the material. For the samples containing nuclear weapons debris, the age determination based on the $^{240}$Pu/$^{236}$U was limited due to formation of $^{236}$U in the detonation of the weapon. The determination of $^{236}$U was also hampered due to abundance sensitivity from relatively large quantities of naturally-occurring U in the sample. The results show the importance of basing age determinations of Pu on more than one ratio in order to avoid interferences from, e.g., amounts of the daughter nuclide present at $t=0$.

Acknowledgement

The authors would like to thank Douglas C. Baxter for valuable comment of the manuscript and Annika Tovedal for assisting in the age determination using γ-spectrometry. Martin Goliath is acknowledged for valuable discussions concerning the formation of heavy isotopes in nuclear weapon detonations.
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The importance of a correct dead time setting in isotope ratio mass spectrometry: Implementation of an electronic determined dead time to reduce measurement uncertainty

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Abstract

Dead time determinations on a mass spectrometry system with ion counting detection can either be done using an isotope ratio measurement approach or via electronic interrogation of individual components, e.g. the pulse amplifier. Depending on the dead time of each component in the signal chain, the electronically determined result may not represent the true value for the total system, i.e. there might be a series of hardware related dead times. However, a hardware set artificial dead time in the pulse counting system that is long enough might yield a system dead time that can be represented by this set dead time solely. It is shown in this work that a carefully-chosen, artificially-introduced set dead time yields a system that may be characterized to a much lower uncertainty than is possible using ratio-based measurement approaches. Ultimately, the impact of the dead time on the combined uncertainty of an isotope abundance ratio measurement may be negligible even at very high count rates, i.e.>1 Mcps. In other words, incorporating the dead time contribution in a combined uncertainty calculation would no longer be necessary.

1. Introduction

In any pulse counting system there is a specific time interval after which no new events can be counted. This interval is defined as the dead time. The dead time of the detection system is one of several factors that may contribute to bias as well as to uncertainty in isotope
abundance ratio measurements using mass spectrometers in counting mode. An accurate and precise determination of the dead time is therefore required. While an error in the value used for dead time correction will lead to bias in an isotope ratio measurement, any uncertainty will contribute to the combined uncertainty in the result. The effect on the combined uncertainty of a ratio measurement will depend on both the magnitude of the dead time uncertainty and the difference in intensities between the signals forming the ratio to be measured. Basically two approaches can be adopted to minimize the contribution of the dead time uncertainty; one is to suppress the signals in order to reduce the effect of the dead time [1], the other is to determine the dead time with a higher precision.

Ratio-based methods are usually applied for dead time determination in inductively coupled plasma mass spectrometry (ICP-MS). By observing the change in signal ratio upon an intensity change, the dead time of the detection system can be determined. Several different approaches for evaluating the dead time based on isotope ratio measurements have been reported [2-6]. However, one limitation of this method is the precision with which the dead time can be determined. Nelms et al. [6] reported uncertainties in the range of 4-20 ns (k=1) for different methods, and Appelblad and Baxter [4] reported uncertainties down to about 1 ns (k=1) at best. If the dead time instead is determined via electronic measurement [5], the precision is mainly governed by the sampling rate of the measuring device. However, an electronically determined value may not represent the total counting system, but rather, only the dead time of the component measured, e.g. the pulse amplifier. In addition, different parts of a signal chain each have their own dead time, e.g. the electron multiplier and the pulse amplifier are each characterized by their individual values. In the case of the electron multiplier, its dead time may be difficult to determine, and it may also only be approximately constant [7]. In the case of the pulse amplifier, a well-defined artificial dead time may be implemented electronically. One reason for this is that, if long enough compared to the dead time of the electron multiplier, it will represent the dead time of the total system [8]. Furthermore, a well known, although large, correction is preferable to a small but uncertain one [7].

It is also possible to implement different types of dead times in an electronic circuit [8], the two types considered being termed paralyzable and non-paralyzable [9]. The difference between the two types is that, in the paralyzable case, a new dead time is extended by additional events, i.e. the irresponsive period is not fixed in duration. A non-paralyzable detection system is in general preferred, since the paralyzable system may, at very high count...
rates, show apparently low readings [9]. An artificial dead time is also introduced in order to mask afterpulses that occur promptly after a main event in the detector [5, 10].

The common model used for dead time correction in both nuclear spectroscopy and mass spectrometry using ion counting detection is [9]

\[
I_i = \frac{I_m}{(1 - I_m \cdot \tau)}
\]

where \( I_i \) is the corrected intensity, \( I_m \) is the observed intensity and \( \tau \) the dead time. This model applies only for the non-paralyzable dead time type and for a Poissonian process at the detector [8, 9].

In this work, the pulse counting system of a sector field ICP-MS instrument was studied by means of dead time measurements. Dead times were determined both electronically and with ratio based methods using the certified reference materials IRMM 073/3, 5 and 7. The 073-series has two certified uranium ratios. First, \( R_{235/238} \) can be used for an inherent mass bias correction since this isotope ratio is close to unity and will not be affected by a dead time. The other isotope ratio, \( R_{233/238} \), is varied over almost six orders of magnitude and can, with the exception of 073/1 for which \( R_{233/238} < 1 \), be used for dead time determination. Furthermore, since a circuit with three different possible dead time settings is implemented in the pulse amplifier of the instrument used in this study, all three settings were examined. In this paper the consequences of using too low dead time setting are outlined, and some recommendations are made.

2. Materials and methods

IRMM 073/3, /5 and /7 materials were used for the ratio-based dead time measurements. Sub-boiling distilled nitric acid and water from a Milli-Q Element system (Millipore, Molsheim, France) was used for all preparation and dilution of these materials, these operations being carried out in a class 1000 clean-room in order to avoid contamination by natural uranium.

All ICP-MS measurements were performed using an Element2 (Thermo-Finnigan, Bremen, Germany). The instrument was equipped with a semi-demountable quartz Fassel torch and a CD-2 Guard Electrode. Sample introduction was performed using a conical nebulizer (GlassExpansion, Melbourne, Australia) and a cyclonic spray chamber (“Twister”, GlassExpansion). Self-aspiration, resulting in a sample uptake rate of approximately 0.2 ml
min⁻¹, was used throughout the investigation. The guard electrode was grounded and the software induced dead time correction inactivated. Torch position, lens parameters and the nebulizer gas flow rate were optimised daily to obtain maximum sensitivity for ²³⁸U⁺. All measurements were performed using low resolution (m/Δm=300) with the instrument and data acquisition settings shown in Table 1.

Electronic dead time measurements was done using a Gage CompuScope 82G (Gage Applied Technologies Inc., Lachine, Canada), plugged in to the J2801 contact of the pulse amplifier board. A solution containing natural uranium of about 1 μg l⁻¹ was used, and the magnet mass was set constant to m/z=238. Waveforms were sampled for about 2 h at a scope sampling rate of 2 GHz. The minimum pulse-to-pulse time then represents the dead time, i.e. the time between the trigger pulse and the next nearest visible pulse on the scope. The CompuScope was also used to measure pulses directly from the electron multiplier. It was then plugged in to the contact from the electron multiplier located on the housing of the electrostatic analyzer (ESA).

The pulse amplifier (part no. 2030200) originally delivered with the Element2 was factory fixed at the lowest dead time setting (about 10 ns), and was therefore modified in order to facilitate manual changing of the dead time by a jumper on the electronic board. Thus, the amplifier could then be configured to different artificial dead time settings of about 10, 20 and 70 ns. Dead time measurements with the ratio method were evaluated both according to Appelblad and Baxter [4] and Ramebäck et al. [5].

Throughout this study, the “raw data” or “channel data” that can be obtained from the instrument software were used, and evaluations of these data were performed manually. This was done due to the discovery of a post-acquisition introduced bias in the software evaluations [11]. The uncertainties in the results were calculated according to ISO/GUM [12] using the software GUM Workbench® (Metrodata GmbH, D-79639 Grenzach-Wyhlen, Germany). All reported uncertainties are expanded uncertainties with a coverage factor of two (k=2), unless otherwise stated.

### 3. Results and discussion

Table 2 shows the results of both ratio and electronically determined dead times for all settings of the pulse amplifier. It is clearly seen that consistency between the two approaches is only reached for the longest dead time setting of the pulse amplifier, i.e. for about 70 ns.
The plausible explanation for this is that the pulse counting system at this setting can be characterized by the dead time implemented in the pulse amplifier alone. For the other settings, the pulse amplifier contribution is not long enough to mask the dead times of the other components [10]. It can also be seen from Table 2 that the uncertainties of the electronically determined dead times are lower than those of the ratio methods.

An interesting fact is that the pulse width from the electron multiplier was measured to about 16 ns. The dead time of the electron multiplier will probably be on the order of the width of the pulses produced by this device [9]. At the lowest dead time setting on the amplifier board the ratio method probably determines a value dominated by the electron multiplier. Overlapping pulses were observed from the electron multiplier, which indicates paralyzable behavior.

The ratio determined dead times were evaluated using two methods reported by Appelblad and Baxter [4] and Ramebäck et al. [5]. In principal, both methods are based on regression analysis for the determination of $\tau$. The difference between the methods is that in the Appelblad and Baxter approach, the mass bias is also evaluated from the regression analysis while the method used by Ramebäck et al. is based on corrections for mass bias in each measuring point. In Table 2, all individual results obtained by the Appelblad and Baxter approach are displayed, while the average of the dead-times evaluated according to Ramebäck et al. is inserted for comparison. There was never any significant discrepancy between these two ratio methods.

In Fig. 1 the result from a dead time determination with the electronic method is shown. The obvious advantage with this method is the precision with which the dead time can be determined. However, it is important to realize that, in this case, the electronically determined dead time is only that of the pulse amplifier of the detection system. The very first component in the signal chain, the electron multiplier, has its own dead time. Therefore, there is a series of components in the signal chain all having their own inherent dead time. Such series of dead times will be complicated to correct for [8], and Eq. 1 will not apply for such situations. However, if a sufficiently long dead time is introduced late in the signal chain, this component will effectively determine both the magnitude and type of dead time of the entire system[8]. As mentioned above, this seems to be the case for the longest dead time setting of the pulse amplifier.
Fig. 2 shows the calculated combined uncertainty in the determined natural uranium isotope abundance ratio for different dead time uncertainties ($k=1$). A variable dead time will provide a significant contribution to the isotope abundance ratio uncertainty when pulse counting is used [13]. It can be seen in Fig. 2 that with the precision in electronic dead time determination achieved in this work, the contribution of the dead time to the combined isotope abundance ratio uncertainty is negligible. In fact, it only increases from 0.28% to 0.32% going from a zero dead time uncertainty to ±0.4 ns at a count rate of 3.5 Mcps on the major isotope. Ultimately, inclusion of the dead time contribution to a combined uncertainty calculation in mass spectrometry will therefore not be necessary. Furthermore, the stability of an electronic dead time should be expected to be good, which was noticed by Schönfeld and Janssen [14]. Over a three year period of electronic measurements they observed only sub-nanosecond variability in the determined dead time. The same has been observed in our laboratory using sector field ICP-MS, which has shown no significant variations in the electronic dead time, $\tau=71.8\pm0.4$ ns, over the last two years.

4. Conclusions

We have shown that it is possible to configure the pulse detection system for an ICP-MS such that consistency between ratio and electronically determined dead times is achieved. Moreover, the study shows the importance of a correct dead time setting in a pulse counting system used in mass spectrometry in order to achieve a low uncertainty in the measured dead time. With electronic measurements, a dead time uncertainty of ±0.4 ns was reached, which is about an order of magnitude better than can be obtained by ratio-based methods. More importantly, this high level of precision will obviate the need to implement the otherwise considerable dead time contribution at high count rates in a complete uncertainty budget of isotope abundance ratio measurements.

Acknowledgement

Melker Nordstrand is greatly acknowledged for the modification of the Element2 pulse amplifier, and Dr. Anna Sjögren for the preparation of the IRMM 073 solutions.
References

Table 1

Instrument and data acquisition settings for the ICP-SFMS measurements.

**Instrument settings:**

- **Argon flow rates**
  - Cooling gas: 14 l min$^{-1}$
  - Auxiliary gas: 1.1 l min$^{-1}$
  - Nebulizer gas: ~0.95 l min$^{-1}$
- **RF power**: 1300W
- **Sample cone**: Nickel, 1.1 mm orifice diameter
- **Skimmer cone**: Nickel, 0.8 mm orifice diameter

**Data acquisition settings:**

- **Resolution (m/ǻm)**: 300
- **Detection mode**: Pulse counting
- **Data acquisition mode**: E-scan
- **Isotopes**: $^{233}\text{U}^+$, $^{235}\text{U}^+$, $^{238}\text{U}^+$
- **Sampling time**: 5 ms (except for $^{235}\text{U}^+$ where 10 ms was used)
- **Mass window**: 10%
- **Samples per peak**: 50
- **Number of scans**: 2000
- **Settling time**: 1 ms (default minimum)
- **Magnet mass**: 233.0391 u

Table 2

Results from the different dead time determinations.

<table>
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<tr>
<th>Material</th>
<th>$\tau$ (ns)</th>
<th>$U_c$ ($k=2$)</th>
<th>$\tau$ (ns)</th>
<th>$U_c$ ($k=2$)</th>
<th>$\tau$ (ns)</th>
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<tr>
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<tr>
<td>IRMM073/7</td>
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<td>IRMM073/5</td>
<td>14.7</td>
<td>0.6</td>
<td>22.7</td>
<td>2.3</td>
<td>70.8</td>
<td>1.9</td>
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<td>16.0</td>
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<td>4.5</td>
<td>73.6</td>
<td>4.9</td>
</tr>
<tr>
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<td>17.3</td>
<td>4.4</td>
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<td>5.1</td>
<td>71.0</td>
<td>8.6</td>
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<td>0.6</td>
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<td>26.2</td>
<td>2.2</td>
<td>71.2</td>
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</tr>
<tr>
<td>Average according to [5]:</td>
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<td>1.7</td>
<td>24.6</td>
<td>2.9</td>
<td>71.6</td>
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<tr>
<td>Electronic method:</td>
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<td>21.8</td>
<td>0.4</td>
<td>71.8</td>
<td>0.4</td>
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</table>
Fig. 1  Electronic dead time determination. The measured dead time is the interval from the leading edge of the trigger pulse to the next nearest pulse. The observed dead time from this specific measurement was 71.1±0.4 ns.

Fig. 2  The impact of dead time on the combined uncertainty in an observed isotope abundance ratio (natural uranium, \( \tau = 71.8 \) ns and a non-paralyzable dead time type). Observe that the uncertainty in the dead time is expressed for \( k=1 \) whereas \( k=2 \) is applied to the uncertainty of the isotope abundance ratio.