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Determination of U, Th and Pu in natural waters, biological materials and clinical samples by ETV-ICP-MS

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A method for the determination of U, Th and Pu in natural water, biological materials and urine samples by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) is described. Carbide formation was minimized using sample vaporization from a tantalum surface for U and additional use of tetrafluoromethane (Freon-23) as a gaseous modifier for Th and Pu. A prior $\text{Ca}_3(\text{PO}_4)_2$ co-precipitation provided an enrichment factor of 50, yielding procedural detection limits (LOD) of 0.013, 0.029 and 0.017 pg g^{-1} for Th, U and Pu, respectively and corresponding absolute LODs of 0.13, 0.29 and 0.17 fg. Recovery of spikes from urine was typically 80%, whereas those from seawater, river water and biological materials averaged 99%. The accuracy of the method was validated by determination of U and Th in NIST SRM 1566b Oyster Tissue and U in a series of NRC natural water CRMs SLRS-4, CASS-4, NASS-5 and SLEW-3. Precision of determination was better than 10% at concentrations of 0.1 ng mL^{-1} .

Introduction

Interest in the determination of long-lived radionuclides is increasing. Uranium and thorium are naturally occurring alpha-emitting elements that are present in the environment as a result of leaching from natural deposits, release from mine tailings and emissions from the nuclear industry. Plutonium, dispersed by global fallout over the past several decades, may be present in the environment due to use and manufacture of nuclear weapons. According to Ganz *et al.*,¹ the natural plutonium concentration in the earth's crust is approximately $10^{-16} \text{ g g}^{-1}$, but its concentration can rise as high as $10^{-13} \text{ g g}^{-1}$ in contaminated regions.²

These elements can be ingested daily with food and drinking water at low concentration levels. For example, the concentration of uranium in natural waters³ varies in the range 0.1–10 $\mu\text{g L}^{-1}$ but mineral waters can contain uranium at a concentration as high as 40 $\mu\text{g L}^{-1}$. The dangerous health effects of this element are well documented; concentrations as low as 500 $\mu\text{g L}^{-1}$ can affect the reproductive capability of aquatic organisms.⁴ Plutonium presents a more significant danger to both short and long-term health.

The maximum permitted concentration of U generally changes from agency to agency, for example in Canada this value is set by Canadian Guidelines⁵ to be 10 $\mu\text{g L}^{-1}$ for U in drinking water, for the US Environmental Protection Agency (EPA) this value is 30 $\mu\text{g L}^{-1}$ ⁶ and the World Health Organization (WHO) revised its provisional guideline value for uranium in drinking water from 9 $\mu\text{g L}^{-1}$ to 15 $\mu\text{g L}^{-1}$.⁷

In relation to Pu, the maximum permitted concentration set by Canadian Guidelines⁵ is 1 Bq kg^{-1} , equivalent to only 0.436 ng L^{-1} for Pu. This same value is used by WHO,⁷ but a 20-fold higher limit is set by EURATOM.⁸

Although these elements have been traditionally measured by radiometric techniques such as alpha spectroscopy,^{9–13} gamma spectroscopy,^{14–16} liquid scintillation^{17–19} and neutron activation analysis (NAA),^{20–24} they are not ideally suited to rapid and/or accurate determination as they generally require large sample volumes, complex sample pre-treatment, extensive time necessary for detection and suffer from poor detection limits.

Inductively coupled plasma mass spectrometry (ICP-MS) is currently considered one of the most powerful analytical methods for trace and ultra-trace analysis, offering low detection limits with minimal analysis time. For long-lived radionuclides in aqueous solutions, quadrupole based instruments typically provide 1 ng L^{-1} detection capability. One of the most important components affecting performance by ICP-MS is the sample introduction system. A variety of these has been evaluated for radionuclide detection, including the cross-flow nebulizer, ultrasonic nebulizer,^{25,26} desolvation systems,^{26–28} micronebulizers²⁹ and electrothermal vaporization (ETV).^{30–37}

The use of ETV coupled to ICP-MS offers several advantages, including improved transport efficiency (20–80% in contrast to 2–5% using solution nebulization), reduced oxide and hydride formation because the solvent is largely removed, minimal sample consumption (10–100 μL), no waste production and accommodation of complex sample matrices, *i.e.*, salts, organic matrices, solids, strong acids and slurries, with very little sample preparation. In addition, the ability to use thermal programming allows selective removal of sample matrix constituents, thereby eliminating or reducing spectroscopic interferences that would otherwise arise from the matrix. This simplifies sample preparation procedures.

The principal difficulty encountered with the determination of radionuclides by ETV is their reactivity toward the graphite substrate at high temperatures, leading to carbide formation, severe memory effects and poor sensitivity. Several approaches have been used to overcome this, including use of different chemical modifiers,^{38,39} addition of reactive gases,^{38–42} use of graphite rod direct sample insertion (DSI) devices,⁴³ a carbon cup,⁴⁴ and vaporization from a filament of W, Re or Ta or from platforms coated with these elements.^{45,46}

The aim of this study was to develop an ETV-ICP-MS method for the determination of Th, U and Pu in environmental and clinical samples. Preconcentration by co-precipitation with calcium phosphate and enhancement in sample vaporization efficiency by use of Freon-23 as a gaseous modifier and/or a Ta tube insert placed within the graphite furnace were used to optimize performance.

Experimental

Instrumentation

A Perkin-Elmer Sciex ELAN DRC II spectrometer (used in the standard mode) equipped with an HGA-600MS electrothermal vaporizer and a model AS-60 autosampler was used for this work. Pyrolytic graphite-coated tubes and pyrolytic graphite L'vov platforms were used. The HGA-600MS was housed in a HEPA filtered cabinet to minimize contamination from the laboratory atmosphere. The transfer line between the ETV and the base of the ICP torch was an 80 cm long, 6 mm id Teflon tube.

Operating conditions for the ICP-MS and ETV are given in Tables 1 and 2, respectively. Optimization of the plasma and mass spectrometer was accomplished using solution nebulization, prior to switching to ETV sample introduction.

The electrothermal vaporizer was operated under software control from the host ELAN computer. During the drying and pyrolysis steps, opposing 300 mL min⁻¹ flows of argon originating from both ends of the graphite tube removed water and other vapors through the dosing hole of the graphite tube. During the high temperature vaporization step, the dosing hole was sealed (2 seconds prior to this step) by a pneumatically activated graphite probe. Once the graphite tube was sealed, a valve located at one end of the HGA workhead directed the carrier argon gas flow originating from the opposite end of the graphite tube directly to the ICP at a flow rate of 1000 mL min⁻¹. Total carrier gas flow rate was maintained at 1000 mL min⁻¹, irrespective of contributions from internal purge gas flows.

A 10 µL volume of the calibration solution or sample followed by 5 µL of modifier/carrier (where noted) was automatically delivered to the tube for all measurements. The furnace was maintained at room temperature during the injection of samples and modifiers.

Analyte vaporization from metal-modified graphite surfaces was studied. For this purpose, two different metallic coating procedures were tested: thermal deposition on the interior tube walls and deposition by sputtering onto a L'vov platform. Thermal coating involved the injection of five 100 µL aliquots of a solution of Ta (1000 ppm). After each injection, the solution was slowly dried by heating the furnace to 150 °C with a ramp and hold time of 25 and 40 s, respectively. A second drying step at 200 °C with a ramp rate and hold time of 20 and 30 s, respectively, was then applied, followed by a reduction step at 2000 °C for 5 s.

Deposition by sputtering onto a L'vov platform was performed using ion-beam sputtering (IBS, Spector, Veeco-Ion-Tech, Fort-Collins Co.). In this process an argon ion-beam was used to sputter Ta atoms from a metallic target, the sputtered atoms being then directed at 45° onto a rotating substrate holder. The deposition chamber was evacuated to a pressure of

Table 1 Instrumental conditions and data acquisition

ICP-MS system	
Rf power	1100 W
Total carrier flow rate	1.0 L min ⁻¹
Auxiliary Ar flow rate	1.2 L min ⁻¹
Plasma Ar flow rate	15 L min ⁻¹
Peak scan parameters	
<i>m/z</i> per reading cycle	4 (²³⁸ U, ²³⁵ U, ²³² Th, ²⁴² Pu)
Dwell time	23 ms
Sweeps per reading	1
Reading per replicate	110
No. of replicates	1
Signal measurement	Peak area
Measurement mode	Peak hopping

Table 2 Furnace temperature program^a

Step	Temperature/°C	Ramp/s	Hold/s	Ar flow rate/mL min ⁻¹
1	120	10	20	300
2	150	5	20	300
3	1200	10	20	300
4	20	5	10	300
5	2300	1	10	150 ^b
6	20	5	10	300
7	2650	1	5	300
8	20	5	5	300

^a Sample volume, 10 µL, modifier volume, 5 µL. ^b Read step.

7×10^{-8} Torr prior to the deposition, and 3×10^{-3} Torr during the deposition. Temperature was maintained at 90 °C throughout the process. A coating thickness of about 2 µm was achieved on a L'vov platform using this procedure.

Materials and reagents

Stock solutions (1000 mg L⁻¹) of U and Th were prepared by dissolution of appropriate amounts of their oxides (SPEX Industries, Edison NJ). A stock solution of ²⁴²Pu was obtained from NIST (176.6 ng g⁻¹, SRM 4334G, Gaithersburg, Md., USA) and diluted to 1.25 µg L⁻¹ with 1% HNO₃. Working standards were prepared just before use by serial dilutions of the stock solutions using high-purity, deionized, distilled water (DDW) obtained from a Milli-Q system (Barnsted, Dubuque, IA, USA) and acidified to 0.2% with sub-boiling, quartz distilled HNO₃. Modifier solutions of 1% m/v NH₄F (Anachemia Science, ON) were prepared using deionized water. Trifluoromethane (Freon-23) was purchased from Air Liquide Canada Inc. Tantalum foil of 0.127 mm thickness was obtained from Johnson Matthey Electronics (MA, USA) and a tantalum tube of 1 mm thickness and 6.35 mm od obtained from Goodfellow (PA, USA). The flow rate of trifluoromethane was controlled by a thermal mass flow controller (Brooks, USA) or a 610A rotameter flow meter (Matheson, USA) and blended with Ar before reaching the graphite furnace.

All plastic and glassware was cleaned by immersion in 50% (v/v) HNO₃ for at least 24 h and thoroughly rinsed with Milli-Q water before use. Metal vaporization surfaces were inserted manually into the graphite tube.

Samples

Urine samples were collected directly into precleaned 80 ml polyethylene containers, acidified, and stored under refrigeration. Under these conditions they were stable for at least 10 days. As noted by Krystek and Ritsema,⁴⁷ losses occurred when urine samples were stored at room temperature or even if refrigerated but not acidified.

The following Certified Reference Materials were used for validating the accuracy of the proposed method: NIST SRM 1566b Oyster Tissue (Gaithersburg, USA), NRCC (National Research Council Canada) CASS-4 Nearshore Seawater, NASS-5 Open Ocean Seawater, SLEW-3 Estuarine Water and SLRS-4 Riverine Water reference materials for trace metals.

Sample treatment

Oyster Tissue digestion. A nominal 0.25 g sample was accurately weighed into a Teflon digestion vessel (CEM Type) and 7 mL of HNO₃ were added. The vessel was capped and the sample was digested using microwave heating at a pressure of 120 psi for 30 minutes. After cooling, 200 µL H₂O₂ (30%) was added, the samples were recapped and heated again using the

same microwave program. The digested material was then cooled and diluted to 50 ml with DDW.

Co-precipitation procedure. A simplified co-precipitation approach using calcium phosphate was used to achieve matrix separation and analyte preconcentration. A 50 mL aliquot of sample was pipetted into a centrifuge tube, followed by addition of appropriate standards. A 50 μL volume of 1.25 M $\text{Ca}(\text{NO}_3)_2$, 2 drops of phenolphthalein indicator and 200 μL of 3.2 M of $(\text{NH}_4)_2\text{HPO}_4$ were then added. Concentrated NH_4OH was added very slowly until the phenolphthalein end point was reached and precipitation of $\text{Ca}_3(\text{PO}_4)_2$ occurred. The solution was shaken for 2 minutes and then centrifuged for 10 minutes at 3000 rpm. The supernatant fluid was decanted and the precipitate dissolved in 1 mL of 5% HNO_3 . This procedure significantly reduced the total sample treatment time to 30 minutes compared to traditional calcium phosphate precipitation requiring several hours to complete.^{48,49}

Results

An initial study was made to ascertain which nuclides could be recovered by co-precipitation with calcium phosphate. For this purpose, a mixed standard containing Sr, Cs, Pb, Th, U and Pu at concentrations ranging from 50 pg g^{-1} to 5 ng g^{-1} (for Pu the maximum concentration used was 1 ng g^{-1}) was submitted to the precipitation procedure described above and analyzed by ETV. No pyrolysis temperature and a vaporization temperature of 2300 $^\circ\text{C}$ were used. Comparing the results with those obtained from deionized water calibration standards verified that recoveries higher than 90% could be achieved for U, Th and Pu over the concentration range studied. On the other hand, Sr, Cs and Pb were not quantitatively recovered and a high blank signal was obtained for Sr and Pb, most likely due to impurities in the reagents used.

ETV

Selection of chemical modifier. It is well known that the elements studied, especially U, form refractory carbides with the graphite tube substrate,³⁹ inhibiting complete vaporization, producing severe memory effects and decreased analyte transport efficiency. The extent of carbide formation depends mainly on the temperature of the tube and the activity of the graphite surface.

As the temperature required for decomposition of the carbides is 3000–4000 $^\circ\text{C}$, higher than the sublimation temperature of graphite, other means are required to minimize or deal with carbide formation including use of NH_4F as a chemical modifier, coating of the tube or platforms with Ta or W, use of a Ta-lined tube or foil placed inside the graphite tube and use of trifluoromethane (Freon-23) as a gaseous modifier. Results obtained with each of these approaches are described below and Fig. 1 illustrates typical signals obtained with 10 pg of U using the various vaporization scenarios. Similar observations arise for Th and Pu.

Use of NH_4F and trifluoromethane as chemical modifiers. NH_4F decomposes during heating, liberating fluorine radicals that react with metals in the sample, forming compounds which can be more easily vaporized and efficiently transported to the plasma than their atomic counterparts.⁵⁰

Varying masses of NH_4F , ranging from 0.5 to 500 μg , were added before, after or previously mixed with the sample. Use of NH_4F was found to be completely ineffective in preventing carbide formation by U, as shown in Fig. 1. It follows that Th and Pu would be similarly affected. Pozebon *et al.*⁵¹ used about 1000-fold higher masses of NH_4F for the determination of U,

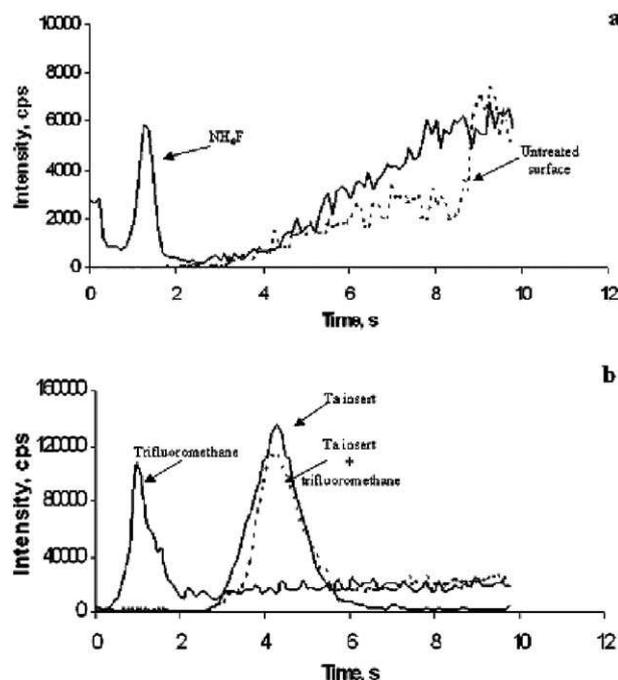


Fig. 1 Response from 10 pg U with (a) vaporization from an untreated surface (dashed line) and in the presence of 20 μL 2% NH_4F , 2600 $^\circ\text{C}$ vaporization temperature (b) with addition of trifluoromethane (8 mL min^{-1}); vaporization from a Ta insert (2600 $^\circ\text{C}$) and vaporization from a Ta insert and addition of trifluoromethane (14 mL min^{-1} , 2300 $^\circ\text{C}$, dashed line).

but even in this case a strong memory effect was observed in the presence of seawater.

The use of Freon in order to minimize carbide formation was first presented by Kirkbright and Snook⁵² for the determination of B, Mo, Zr, Cr and W by ETV-ICP-OES. Similar to the addition of NH_4F , Freon will also promote the formation of volatile compounds. Several other studies have shown the efficiency of use of Freon for the determination of refractory elements,^{38,53,54} rare earths,^{55,56} lanthanides,⁵⁷ titanium⁵⁸ and actinides,^{34,39,40} among others.

Alvarado and Erickson³⁴ were one of the first to report a method for the determination of long-lived radioisotopes (U, Th, Ra and Tc) in waters by ETV-ICP-MS. The authors showed that the use of Freon together with appropriate temporal-thermal programming permitted selective separation of the analytes from the matrix.

In the presence of trifluoromethane, sensitivity, based on integrated response, increased substantially (about 100-fold) compared to that obtained using the untreated graphite furnace and well-defined signals were realized having greatly reduced memory effects. The concentration of trifluoromethane added to the argon carrier gas was optimized with best results occurring with a flow of 8 mL min^{-1} of trifluoromethane bled into an internal purge gas flow of 300 mL min^{-1} of Ar (*i.e.*, about 0.8% trifluoromethane in total carrier Ar flow). Increased background, especially for U, occurred at higher trifluoromethane flow rates. When trifluoromethane was added to the graphite furnace during each step of the temperature program, tube lifetime decreased substantially, as noted earlier by Truscott *et al.*³⁷ Although these authors introduced the gas only during the ashing stage, improved response can be obtained when trifluoromethane is present during all steps except the cleaning stage. The graphite tube lifetime under these conditions is 200–300 firings. It is also necessary to pre-clean the tube (especially those earlier used for U) before use, as a high background is observed for U when trifluoromethane is first used, likely due to the efficient removal

of contaminants. For this purpose, 2 or 3 heating cycles were undertaken with an empty furnace.

Improved day-to-day reproducibility (peak area and signal profile) was obtained when trifluoromethane was added to the internal purge gas directly at the furnace workhead, rather than being introduced into the graphite furnace *via* the alternative gas line where it was previously blended with Ar. This is likely due to differences in operating pressure between the Ar and trifluoromethane, which may occur from day-to-day, causing slightly different flow rates of trifluoromethane to be added to the graphite furnace. Use of a pre-mixed source of trifluoromethane in Ar will eliminate this problem.

Vaporization from metallic surfaces. Another procedure that can be used in order to avoid the carbide formation is the modification of the tube surface with high-melting carbides. Elements such as Ta, W, Mo, Ti and Zr may decrease the reactivity of the graphite surface due to competition for active sites between the modifying elements and carbide-forming analyte.⁵⁹

When sample vaporization occurs from metallic surfaces, sensitivity (based on integrated response) similar to or higher than that realized when using trifluoromethane can be obtained. Well-defined signals arise and memory effects are also greatly reduced, although Th vaporizes slightly later than Pu and U. Additionally, the vaporization temperature can be reduced by 200 °C, increasing the lifetime of the ETV graphite components. Signal tailing is also significantly decreased compared with the use of trifluoromethane alone. The improvement in sensitivity is largely due to the effect of the metallic surface preventing losses of U by intercalation into the graphite and carbide formation.

With sample vaporization occurring from either a thermally coated tube or a sputter coated L'vov platform, the Ta coating was shortlived. These coatings needed to be reapplied after a few heating cycles (less than 30 for thermal deposition and 100 for sputter coatings). When using the Ta sputtered platform, a ramp time of 5 s was required during the vaporization step (as opposed to zero ramp) because the signal appeared before the beginning of the read step. Attempts to reduce the pyrolysis temperature or eliminate the read delay did not eliminate this problem.

A 0.127 mm thick Ta foil was subsequently used to line the interior of the graphite tube following the procedure suggested by SenGupta,⁶⁰ thereby covering the entire inner surface. Unfortunately, after only a few firings the foil became brittle, fragile and began to crack, exposing the graphite to the sample solution and degrading response. The same problem arose with use of a W foil.^{61,62}

A Ta tube of 1 mm thickness and 6.35 mm od was cut in half axially and the resulting 10 mm long "platform" was inserted into the graphite tube, establishing firm contact with the interior graphite surface. This provided the best approach when using metallic surfaces. Precision better than 10% and a tube lifetime of about 160 firings could be achieved.

It should be noted that the upper half of the graphite tube remains exposed to the high temperature vapor. The Ta-lined tube serves only to prevent condensed phase interactions. Although the geometry of the Ta-lined tube had no effect on the U signal, day-to-day reproducibility was worse than when operating with no insert, as there was a need to insure good contact between the metal and graphite surface for reproducible temperature programming to be achieved. A 1 cm length, positioned beneath the dosing hole in a manner such that the sample did not come into contact with the graphite tube, was optimal. Goltz *et al.*⁶³ showed that significant quantities of metal are volatilized from this surface during the high temperature heating step, thereby serving as a physical carrier^{64,65} and enhancing analyte transport efficiency.

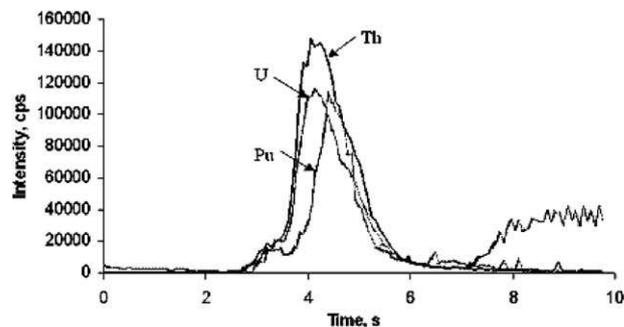


Fig. 2 Response from 10 pg Th, U and Pu with vaporization from Ta insert and addition of trifluoromethane (14 mL min⁻¹, vaporization temperature 2300 °C).

Use of both the Ta tube insert and trifluoromethane was investigated. In this case, optimum trifluoromethane gas flow was 14 mL min⁻¹ (about 1.4% trifluoromethane in total Ar). Enhancements in sensitivity (peak area) for Th and Pu of about 1.4- and 1.8-fold were obtained compared to data generated using just trifluoromethane or only a Ta-tube insert, respectively. The appearance time for all analytes studied was the same. Higher background was noted for U when trifluoromethane was added to the system, likely due to impurities present in the graphite furnace and graphite contacts.

Fig. 2 illustrates typical signals obtained with 10 pg of U, Th and Pu using the Ta tube insert and added trifluoromethane.

Optimization of ETV parameters

Vaporization temperature. The drying step was set at 120 °C and pyrolysis at 1200 °C; no detectable losses of analyte occurred in either step. Selection of the vaporization temperature is not as critical with ETV as it is for GFAAS; the temperature must only be sufficiently high to ensure vaporization of the analytes. Uranium signals appear at tube temperatures higher than 1800 °C, thorium and plutonium at 2000 °C. These analytes produce a maximum response at a temperature of 2300 °C. Although it was verified that plasma loading, observed by monitoring the argon dimer (Ar₂⁺) intensity,^{63,66} starts to occur at temperatures higher than 2100 °C, a temperature of 2300 °C was chosen to ensure complete vaporization.

Transport gas flow rate. The total gas flow rate used to transfer the volatilized analyte to the ICP corresponds to the sum of the carrier gas (nebulizer gas) and internal gas flow rates through the graphite tube. During the vaporization step, the internal gas is directed to the plasma with the carrier gas. In this study, the carrier gas flow rate was initially optimized using conventional solution nebulization (1000 mL min⁻¹). The internal gas flow rate was varied from 0 to 300 mL min⁻¹. Maximal signal intensities are achieved at 150 mL min⁻¹ for all analytes studied. When the internal flow rates exceed 200 mL min⁻¹, the precision is significantly degraded: for 150 mL min⁻¹ the RSD for replicate signals is about 7% while at 250 mL min⁻¹ it is about 15%, as shown in Fig. 3 for U.

Memory effects. Memory effects have been reported during solution sample introduction with ICP-MS detection of U⁶⁷ and especially Th.⁶⁸ Even with ETV, it was necessary to read one blank signal after a high concentration solution (higher than 5 ng g⁻¹) of analyte in order to avoid memory effects caused by incomplete vaporization. This does not occur for concentrations less than 1 ng g⁻¹.

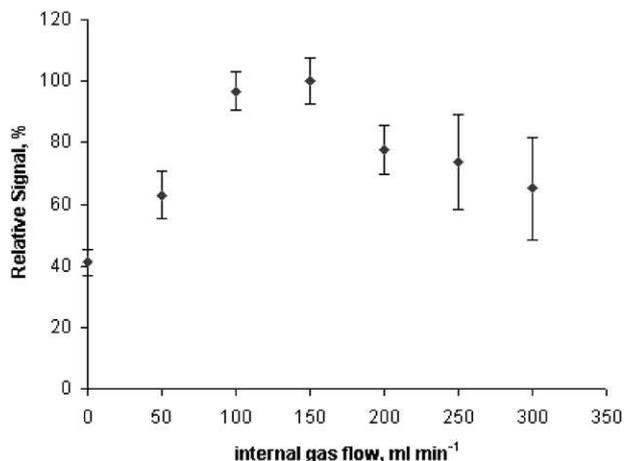


Fig. 3 Influence of the internal gas flow rate on the sensitivity (1 ppb U); vaporization temperature of 2300 °C (Ta tube insert, trifluoromethane flow rate 14 mL min⁻¹).

Effect of Ca₃(PO₄)₂ matrix

Depending on sample composition, varying masses of Ca₃(PO₄)₂ may be formed during co-precipitation due to the different concentrations of Ca²⁺ originally present in the sample. To examine the effect of Ca₃(PO₄)₂ matrix on the analyte signal, a range of Ca₃(PO₄)₂ concentrations was studied to simulate conditions commonly encountered when analyzing real samples; results are shown in Fig. 4.

Under the conditions selected, formation of a precipitate occurs when the concentration of calcium phosphate exceeds about 0.8 ppm. For Ca₃(PO₄)₂ concentrations higher than 100 ppm, a plateau in U response is reached. Thorium and plutonium showed similar characteristics. With the proposed sample preparation procedure, about 6 mg of Ca₃(PO₄)₂ is formed, leading to a concentration of 6000 ppm in the final concentrate and having no influence on the analyte signals.

Analyte recovery

Table 3 summarizes recoveries of spikes of U, Th and Pu added at several concentrations to DDW, seawater, digested oyster tissue and urine. The following CRMs were investigated: CRM NASS-5 Nearshore Seawater and SRM 1566b Oyster Tissue. A pool of urine was prepared by mixing several samples in screw-capped plastic vials and characterized for U, Th and Pu. Uranium levels of about 40 ng L⁻¹ were detected, whereas the Th and Pu were present at concentrations below their LODs.

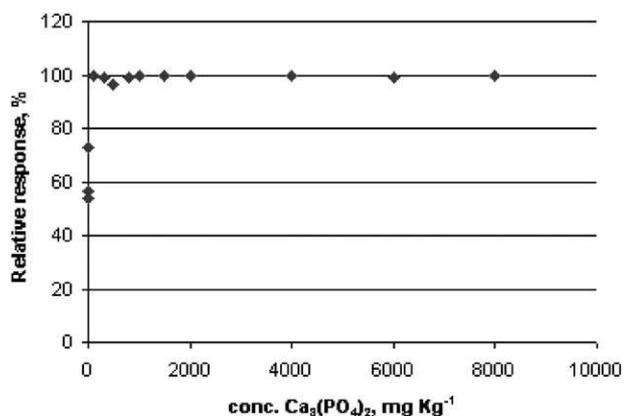


Fig. 4 Effect of Ca₃(PO₄)₂ matrix on response from 1 ppb ²³⁸U; vaporization temperature of 2300 °C (Ta tube insert, trifluoromethane flow rate 14 mL min⁻¹).

Table 3 Recovery studies

Sample	Content	Recovery (%)		
		U	Th	Pu
Standard solution	50 ppt	97 ± 2	98 ± 3	100 ± 3
	200 ppt	98 ± 2	99 ± 2	98 ± 2
	2 ppb	100 ± 2	98 ± 3	—
Seawater	50 ppt	99 ± 3	99 ± 3	97 ± 3
	200 ppt	98 ± 2	100 ± 2	99 ± 3
	2 ppb	101 ± 3	99 ± 3	—
Oyster tissue	50 ppt	100 ± 4	97 ± 2	98 ± 3
	200 ppt	98 ± 3	99 ± 3	101 ± 3
	2 ppb	101 ± 3	99 ± 2	98 ± 2
Urine	50 ppt	85 ± 4	83 ± 5	83 ± 5
	200 ppt	88 ± 3	82 ± 4	81 ± 3
	2 ppb	89 ± 3	85 ± 5	—

As samples containing high concentrations of U and Th (ppb levels) can cause serious memory effects, these elements were removed (no Pu was present in these samples). For this purpose, all samples were acidified with 3 M nitric acid and passed through a UTEVA resin to extract the analytes.⁶⁸ The resulting concentration of both Th and U in these samples was below the ppt level. Spikes were then added, followed by the calcium phosphate precipitation.

Results are based on analyses of 3 replicates using matrix-matched calibration. Quantitative recovery can be achieved for both the natural water samples, independent of their salinity, and for the digested oyster tissue. Recoveries are lower from the urine matrix, possibly because of the presence of complexing agents that may inhibit co-precipitation. A recovery factor was applied to correct all data generated for analysis of urine samples.

Figures of merit

Table 4 summarizes the detection limits for Th, U and Pu obtained using various vaporization environments.

Detection limits (LOD) are based on a 3σ criterion, where σ is the estimated standard deviation of at least 7 repetitive measurements of a dilute HNO₃ solution representing the blank. Better LODs were obtained for Th and Pu when a Ta tube insert was used in conjunction with trifluoromethane. For U, use of trifluoromethane caused an elevated background, which deteriorated the LOD.

Instrumental detection limits calculated from 7 replicate measurements of an unloaded ETV fitted with a Ta tube insert and supplied with trifluoromethane were 0.38, 0.63 and 0.33 pg mL⁻¹ for Th, U and Pu, respectively.

The estimated procedural LODs, using a Ta tube insert together with Freon-23, are 0.013, 0.029 and 0.017 pg mL⁻¹ for Th, U and Pu, respectively, based on processing a 50 mL sub-sample to a final volume of 1 mL. Corresponding absolute detection limits are 13 × 10⁻¹⁷, 29 × 10⁻¹⁷ and 17 × 10⁻¹⁷ g for ²³²Th, ²³⁸U and ²⁴²Pu, respectively. Similar procedural LODs were recently reported by Becker *et al.*^{69,70} using an ELAN 600 ICP-MS fitted with a DIHEN⁶⁹ (for U and Th) or ultrasonic nebulizer⁷⁰ but without sample preconcentration.

Precision, expressed as relative standard deviation of 10 consecutive replicates, was 4–6% at analyte concentrations approximately 100-fold higher than the procedural LOD.

The accuracy of the proposed methodology for U and Th was validated by the analysis of several Certified Reference Materials. Results, summarized in Table 5, are based on processing 3 subsamples with 3 replicate analyses per sample. Unfortunately, few such materials are available with which to corroborate results for Th and no material was readily available for Pu.

Table 4 Detection limits for Th, U and Pu in calibration standards

Vaporization environments	²³² Th		²³⁸ U		²⁴² Pu	
	Absolute/pg	Relative/pg mL ⁻¹	Absolute/pg	Relative/pg mL ⁻¹	Absolute/pg	Relative/pg mL ⁻¹
Trifluoromethane	0.014	1.4	0.019	1.9	0.011	1.1
Ta tube insert	0.009	0.9	0.010	1.0	0.008	0.82
Ta tube insert with trifluoromethane	0.006	0.56	0.012	1.2	0.007	0.71

Table 5 Analytical results

	U	Th	Pu
SRM 1566b			
Certified values/mg kg ⁻¹	0.2550 ± (0.0014)	0.0367 ± (0.0043)	NC
Found/mg kg ⁻¹	0.2539 ± (0.0027)	0.0363 ± (0.0023)	<LOD
SLRS-4			
Certified values/μg L ⁻¹	0.050 ± (0.003)	0.018 ± (0.003) ^b	NC
Found/μg L ⁻¹	0.055 ± (0.08)	0.021 ± (0.003)	<LOD
CASS-4			
Certified values/μg L ⁻¹	3.05 ± (0.04) ^a	NC	NC
Found, μg L ⁻¹	3.04 ± (0.07)	0.0005 ± (0.0001)	<LOD
NASS-5			
Certified values/μg L ⁻¹	2.63 ± (0.022) ^a	NC	NC
Found/μg L ⁻¹	2.59 ± (0.06)	0.0006 ± (0.0001)	<LOD
SLEW-3			
Certified values/μg L ⁻¹	1.85 ± (0.022) ^a	NC	NC
Found/μg L ⁻¹	1.82 ± (0.03)	0.0012 ± (0.0002)	<LOD

^a Information value only—isotope dilution results. ^b Information value only—ref. 74. Standard deviations in parentheses ($n = 5$). NC—not certified.

Results presented in Table 5 are based on integrated response using matrix-matched calibration. It is evident that good agreement with accepted values has been established for these materials and that no matrix interferences are present.

For the determination of ²³⁵U, the more pronounced background with trifluoromethane made use of the Ta tube insert the method of choice. Values of 0.70 pg mL⁻¹ and 0.017 pg mL⁻¹ could be achieved for an instrumental LOD and procedural LOD, respectively.

With respect to other isotopes of Pu, LODs of 0.81 and 0.90 pg mL⁻¹ were achieved with procedural detection limits of 0.019 and 0.021 pg mL⁻¹ for masses 238 and 239, respectively.

The most significant problem associated with the determination of long-lived radionuclides in environmental samples (or in radioactive waste) is interference from isobars of other radioactive and stable isotopes. This is the case for ²³⁸Pu, which also temporally overlaps U, as both elements are involatile. Fortunately, Tanner *et al.*⁷¹ have demonstrated that U and Pu can be readily resolved using a DRC, wherein U is selectively and quantitatively reacted with ethylene, permitting a mass shift away from Pu.

For the determination of ²³⁹Pu, interference caused by high concentrations of U arises. Despite the ratio UH/U being one order of magnitude lower with ETV than when using solution nebulization, Aridus desolvation or ultrasonic nebulization introduction systems,^{25,27,72} in the presence of a 10 ppm solution of U a ratio of 2.5×10^{-6} was obtained for UH/U, and the signal for mass 239 corresponding to an equivalent concentration of 0.25 ppt ²³⁹Pu arises. Decreasing interference could be accomplished by column separation⁷³ or using D₂O as the solvent.^{25,72}

Conclusions

A rapid and sensitive method for the determination of U, Th and Pu in natural waters, biological material and urine by ETV-ICP-MS based on Ca₃(PO₄)₂ co-precipitation provides sufficient detection power and throughput to be useful for

screening exposed samples and individuals. In addition, the simplified sample preparation procedures used significantly reduce the total analysis time.

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