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Determination of plutonium in seawater using co-precipitation and inductively coupled plasma mass spectrometry with ultrasonic nebulisation[1]

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Abstract

A flow injection–inductively coupled plasma–mass spectrometric (FI–ICP–MS) procedure, utilising ultrasonic nebulisation with membrane desolvation (USN/MD), has been developed for the determination of plutonium (Pu) in seawater at fg l^{-1} concentration levels. Seawater samples (1 l), after filtration, were subjected to co-precipitation with NdF_3, followed by ion exchange to enrich Pu and to reject seawater matrix ions and co-existing uranium. The seawater concentrate (1.0 ml) was then analysed by FI–ICP–MS. The limit of detection for ^{239}Pu in seawater based on an enrichment factor of 1000 was 5 fg l^{-1}, and precision at the 0.80 pg l^{-1} level was 12% RSD. Accuracy was verified via recovery experiments, and by comparing survey data for the Irish Sea with that derived by standard methodology based on co-precipitation and α-spectrometry. Concentrations for dissolved ^{239}Pu and ^{240}Pu in the Irish Sea were in the range of 0.267–0.941 pg l^{-1} (0.614–2.164 mBq l^{-1}) and 0.051–0.196 pg l^{-1} (0.428–1.646 mBq l^{-1}), respectively. © 1998 Elsevier Science B.V. All rights reserved

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1. Introduction

Plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu) and other radionuclides are present in the environment as a result of nuclear weapons detonation, general reactor operations, and from re-processing of nuclear fuels. The concentration of radionuclides in the marine environment can be extremely low, as in the open oceans (fg/sub-fg l^{-1}) [1] but elevated

concentrations (pg l^{-1}) are known to be associated with long-term fuel re-processing operations [2]. The behaviour of plutonium in seawater depends on the chemical form and the oxidation state of the species. Dissolved $^{239+240}$Pu can exist in at least two valence states in seawater. In the Irish Sea dissolved $^{239+240}$Pu has been reported to be predominantly (70%–90%) in the V-valent state [3,4], whereas $^{239+240}$Pu associated with particulate material exists almost entirely (>98%) in the IV-valent state [5]. It has also been suggested that Pu(V) can bind to particulate material and that the uptake of Pu(V) species involves the reduction to Pu(IV) at the particle–solution interface [6]. Moreover, it has

been shown that the distribution coefficient (partitioning between dissolved and particulate phases) for Pu(IV) ($K_d \sim 10^6$) exceeds that of Pu(V) ($K_d \sim 10^4$) [7]. Therefore, it is evident that Pu(IV) is a highly particle reactive species, whilst Pu(V) is relatively soluble. Interconversion between the two valence states may occur, albeit at a slow rate. In experiments to investigate the stability of Pu(IV) and Pu(V) in filtered seawater, Pentreath et al. [8] have shown Pu(IV) to be oxidised to Pu(V) at a slow rate, approximately 0.2% day^{-1}, whilst Pu(V) appeared to be stable over an extended length of time (3 weeks).

To date, the determination of dissolved plutonium in seawater invariably involves a preconcentration/separation step prior to instrumental measurement. This is usually achieved by co-precipitation, ion-exchange or solvent extraction procedures in association with α-spectrometry (Ref. [9] and references therein). Popular preconcentration methods include co-precipitation of reduced Pu(III) and Pu(IV) species onto NdF_3 [10], $Fe(OH)_3$ [11], or CaC_2O_4 [12]. The basic steps in these methods include: (i) filtration of samples at the time of collection (since plutonium is particle-reactive), (ii) adjustment of the oxidation state of plutonium to low valency states, since only Pu(III) and Pu(IV) undergo co-precipitation, (iii) formation of precipitate and co-precipitation of plutonium and the other transuranic species, and (iv) purification of concentrate by ion exchange. With respect to α-spectrometric determination, very large sample volumes, typically 25–200 l, are processed, and for the final measurement step plutonium in the concentrate is electrodeposited onto stainless steel disks prior to counting. A major disadvantage of α-spectrometry relates to the counting period, which can take from days to several weeks depending on the sensitivity and precision required. In addition, ^{239}Pu and ^{240}Pu signals cannot be resolved and reported as independent data.

Studies on the co-precipitation of Pu species with NdF_3 have been summarised by Seaborg and Wahl in Ref. [13]. Pu(III) and Pu(IV), but not Pu(V) and Pu(VI) species, were observed to co-precipitate with NdF_3. This procedure was adapted and modified for the analysis of seawater samples by Lovett and Nelson [10]. These workers used co-precipitation and α-spectrometry to determine the concentration and oxidation state of plutonium in

water and suspended particulate. After sample filtration (0.22 μm) it was demonstrated that retained plutonium was predominantly Pu(IV), whilst plutonium in the filtrate was mainly Pu(VI). The concentrations of Pu(IV) and Pu(VI) in the Irish Sea, an area of known contamination, were reported as 57–15 900 fCi l^{-1} (0.0021–0.59 Bq l^{-1}) and 200–1250 fCi l^{-1} (0.0074–0.046 Bq l^{-1}), respectively. More recent survey data for UK coastal waters is given by Woodhead and Pentreath in Ref. [14], who report ^{239}Pu and ^{240}Pu concentrations to be in the range of 0.01–7 mBq l^{-1}.

Mass spectrometric (MS) techniques have been used for the determination of long-lived radionuclides, because of their high sensitivity and multi-element/isotopic analysis capability [15–21]. Useful comparisons of mass spectrometric detection vs radiometric detection are available from several sources [22–25], but with reference to ICP–MS, a key advantage of the ICP technique is the rapid measurement time. Kershaw et al. [17] made a detailed study on sediment samples collected from the Irish Sea, in a site close to the Sellafield nuclear reprocessing plant, and determined the isotopic composition of plutonium of samples using TIMS (Thermal ionisation mass spectrometry) and ICP–MS. ICP–MS and α-spectrometry were also used to determine ^{239}Pu and ^{240}Pu concentrations, and good correlation between the two data sets was found. A depth profile for the ^{240}Pu/^{239}Pu isotope ratio was established and a systematic decrease in the ratio with depth was observed. The ratio was approximately 0.21 in the first 10 cm of surface sediment and approximately 0.06 at 200 cm depth. Studies, however, were not extended to seawater.

High resolution ICP–MS with ultrasonic nebulisation has been utilised for the determination of several radionuclides, including plutonium [15]. High sensitivity measurements at the low pg l^{-1} level were achieved, but the application to environmental samples was not demonstrated.

The aim of the present study was to develop rapid and sensitive methodology for the determination of dissolved plutonium in marine waters. The approach relies on exploiting high sensitivity ICP–MS with a powerful preconcentration scheme based on NdF_3 co-precipitation. A key feature of the analytical technology is the use of ultrasonic

nebulisation with membrane desolvation. The methodology was applied to the determination of plutonium isotopes (^{239}Pu and ^{240}Pu) at various locations in the Irish Sea.

2. Experimental

2.1. Reagents and materials

High purity water (Milli-Q Academic, Millipore) and high purity acids (Aristar grade, BDH Chemicals Ltd) were used throughout. Analytical reagent grade chemicals, Nd_2O_3, $(NH_4)_2SO_4.FeSO_4.6H_2O$ and Na_2SO_3 were used to prepare Nd^{3+}, Fe^{2+} and SO_3^{2-} solutions, respectively. Stock Pu solutions (^{239}Pu and ^{242}Pu, 10 ng l^{-1}) were supplied from the Centre for Environment, Fisheries and Aquaculture Science (CEFAS) laboratory of the Ministry of Agriculture, Fisheries and Food (MAFF) at Lowestoft. The ^{242}Pu yield tracer originally obtained from the Isotopes Division of AEA Technology (formerly AERE; Harwell, UK), was calibrated against a standard solution of ^{238}Pu obtained from Amersham (UK). Standard solutions of ^{239}Pu at the sub-ng l^{-1} were prepared from the stock. Polyethylene bottles (1 l) and PTFE beakers (25–50 ml) were used in sample processing for co-precipitation and evaporation stages, respectively.

2.2. Samples and sample processing

Seawater samples were collected (15–19 December, 1996) directly from the Irish Sea, using a purpose-built water pumping system assembled onboard the research vessel Cirolana (MAFF) [26]. In addition, waters containing levels of dissolved plutonium about two orders of magnitude less than that found in the Eastern Irish Sea [14], were collected close to the Scilly Islands (off the south-west coast of the UK). Samples were pumped into large storage reservoirs (polyethylene, 25 l) and then filtered into similar vessels using custom filtration apparatus (cellulose nitrate membrane filter, 0.45 μm, Sartorious GmbH), before acidification with HNO_3 to pH < 2. On return to the laboratory, all samples were kept in a cold room at 4°C until processing. In all determinations ^{242}Pu was used as a yield monitor.

The co-precipitation procedure used in this study was adapted from the work of Lovett and Nelson [10] as follows.

2.2.1. Oxidation state adjustment and NdF_3 precipitation

To filtered seawater (950 ml), ^{242}Pu spike (100 μl, 10 ngl^{-1}), concentrated HNO_3 (50 ml), Nd^{3+} (1 ml, 0.7 M; Nd_2O_3 dissolved in 8 M HNO_3), SO_3^{2-} (10 ml, 1.6 M; Na_2SO_3 dissolved in water) and Fe^{2+} (10 ml, 0.5 M; $(NH_4)_2SO_4.FeSO_4.6H_2O$ dissolved in 1 M H_2SO_4) were added sequentially with good mixing between each addition. HNO_3 was added first to destroy any hydrolysis products or complexes of plutonium in the seawater. Fe^{2+}/SO_3^{2-} served to reduce Pu(VI) to Pu(IV). After 30 min, concentrated HF (10 ml) was added and NdF_3 was precipitated. The precipitate was allowed to develop (30 min) and then the solution was filtered through a membrane filter (0.45 μm).

2.2.2. Removal of excess fluoride and $Nd(OH)_3$ precipitation

The filter containing the precipitate was washed with an HNO_3/HF (0.8 M/0.1 M) solution and placed in a PTFE beaker (50 ml). Concentrated HNO_3 (5 ml) was added and the beaker was covered with a watchglass. The solution was evaporated to dryness. After dissolution of the precipitate in concentrated $HClO_4$ (2.5 ml) and HNO_3 (5 ml), the solution was evaporated to dryness once more. The precipitate was dissolved by warming with HNO_3 (5 ml, 8 M) and saturated H_3BO_3 (2 ml), and the solution was then transferred to a polyethylene centrifuge tube (50 ml). The volume was made up to 40 ml with water and concentrated NH_4OH was added until the solution pH was greater than 9. Thereupon, $Nd(OH)_3$ was precipitated. The mixture was centrifuged and the supernatant was discarded. Concentrated HNO_3 was added to dissolve the precipitate, the final extract being 8 M in HNO_3.

2.2.3. Purification

A column containing a strong anion exchange resin (AG1-X4, 100–200 mesh, Bio-Rad Laboratories) was prepared using a glass pasteur pipette (6 mm i.d.), plugged at the lower end by glass wool. The length of the column was 5 cm. After conditioning with

HNO_3 (5 ml, 8 M) the acidified sample extract was passed through the column, the eluate going to waste. Plutonium in the +4 oxidation state was adsorbed by the ion exchanger, while uranium and neodymium remained in the effluent. The column was then washed with HNO_3 (10 ml, 8 M) to complete the removal of uranium and neodymium, followed by washing with concentrated HCl (6 ml) to elute any thorium or americium. Finally, plutonium was eluted from the column with NH_4I/HCl (6 ml, 0.1 M NH_4I in 12 M HCl) and the eluate was collected in a PTFE beaker (25 ml). (Plutonium is reduced to the trivalent state by the iodide ion in concentrated HCl. It does not form an anionic complex in the +3 state and is released from the column.) The solution was repeatedly evaporated to dryness (2–3 times) with successive additions of concentrated HNO_3 (1–2 ml) to remove iodide ions. Finally, the residue was dissolved in dilute HNO_3 (0.95 ml, 1 M) containing 1.0 $\mu g\ l^{-1}$ [209]Bi (internal standard). The procedure yielded a nominal enrichment factor of 1000 and typically required 3 working days to complete.

2.3. Instrumentation and operating procedures

A schematic of the flow injection–ICP–MS (FI–ICP–MS) facility is given in Fig. 1. A quadrupole-based ICP-mass spectrometer (HP4500, Hewlett Packard) utilising an ultrasonic nebuliser/ membrane desolvation system (USN U-6000AT[+], CETAC Technologies Inc.) was used in all measurements. Operating parameters are summarised in
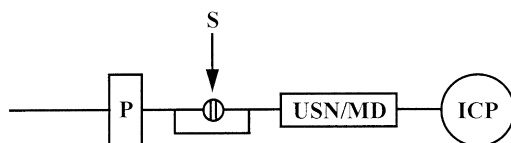

Fig. 1. Flow injection–ICP–MS system. P, peristaltic pump; S, sample and standard; sample volume, 250 μl.

Table 1. The dry aerosol stream exiting the USN/ MD was coupled with a low flow of argon ($< 0.1\ l\ min^{-1}$) from the blend gas port and the mixed flow was injected into the plasma. The function of using argon as a blend gas was to facilitate sample injection. As a result of the small volume (0.95 ml) of concentrate realised from the co-precipitation procedure, a flow injection valve (Omnifit, 250 μl loop) was used in conjunction with a peristaltic pump (Gilson Minipuls 3) for sample introduction. PTFE-lined Tygon tubing was used for all connections.

Instrumental parameters were optimised on a daily basis using a Tl standard solution ([205]Tl, 1 $\mu g\ l^{-1}$). Sensitivity was also checked periodically using [238]U (1 $\mu g\ l^{-1}$). The uranium hydride response was monitored using standard solutions of uranium (1–100 $\mu g\ l^{-1}$) before the measurement of the samples. Background counts were measured at m/z 239 and 240 using a blank solution (1 M HNO_3). Peak hopping in the time resolved mode was used in the measurement of standard solutions and samples. In all experiments, the concentration of [239]Pu in the final extracts was calculated from a calibration graph obtained with aqueous plutonium standards in the concentration

Table 1
ICP–MS operating parameters

● Sample presentation	
Carrier stream	2 ml min^{-1}
Sample volume	250 μl
USN — Heater temperature	140°C
USN — Condenser temperature	2°C
MD — Heater temperature	160°C
MD — Sweep gas flow	1.90 l min^{-1}
● ICP–MS	
Carrier gas flow	0.5–0.6 l min^{-1}
Blend gas flow	0.0–0.1 l min^{-1}
Isotopes monitored	[209]Bi, [238]U, [239]Pu, [240]Pu, [242]Pu
Data acquisition mode	Peak hopping in time resolved analysis
Integration time	[238]U, [239]Pu, [240]Pu, [242]Pu; 0.5 s [209]Bi; 0.1 s

range of $0.025–1.0$ ng l^{-1}, with bismuth (^{209}Bi, 1.0 μg l^{-1}) serving as the internal standard. ^{242}Pu concentrations, which were used to check the chemical yield of the method, were calculated in the same way using ^{242}Pu standards. The isotope ratio ^{239}Pu/^{242}Pu was used to determine ^{239}Pu concentrations in the samples. ^{240}Pu concentrations were calculated considering the ratio of counts at m/z 240–239. Ion responses for ^{239}Pu and ^{240}Pu were assumed to be the same. The limit of detection was calculated as 3 times the standard deviation of the blank solution (1 M HNO$_3$) measured 10 times at m/z 239. Short-term precision was based on ^{209}Bi and ^{238}U signals measured at 1 min intervals for a period of 10 min. Long-term precision was calculated in the same way over a period of 1 h. In experiments concerning hydride formation and calculation of UH/U, pneumatic nebulisation (PN) was also used for comparison purposes. Similar data acquisition parameters were used as with USN, the only difference being the carrier gas flow (1.2 l min^{-1}).

2.4. Alpha spectrometry

The assay of dissolved plutonium by α-spectrometry requires sample preconcentration/separation, in order to overcome radiometric and gravimetric interferences [26]. In the present study, seawater samples were filtered (0.45 μm membrane filter) to separate suspended particulate material. The concentration of dissolved ^{239}Pu and ^{240}Pu was determined according to the standard method routinely carried out at CEFAS, Lowestoft [26]. Briefly, the filtered seawater (25 l) was acidified to pH 2 with HCl and spiked with ^{236}Pu as the yield monitor. ^{239}Pu(V) and ^{240}Pu(V) species were reduced using a combination of SO$_3^{2-}$ and Fe^{2+}, and then co-precipitated onto Fe(OH)$_3$ by

adding Fe^{3+} carrier and NH$_4$OH. The precipitate was collected on a filter (0.45 μm). The filter was then wet-ashed and the Fe(OH)$_3$ redissolved in strong acid. The plutonium was chemically separated from the bulk by co-precipitation onto CaC$_2$O$_4$, and then further purified using a similar ion exchange procedure previously outlined for the NdF$_3$/ICP–MS procedure. Finally, the plutonium in the concentrate was electrodeposited onto a stainless steel disk via a solution of ammonium oxalate. The sources were assayed for ^{239}Pu and ^{240}Pu by counting on silicon-surface barrier detectors for a period of $\sim$2 weeks.

3. Results and discussion

In order to monitor plutonium in seawater by ICP–MS, there is a need to devise methodology which affords both high analyte preconcentration in the sample processing stage and efficient sample utilisation in ICP–MS measurement. In this work method, sensitivity to the fg l^{-1} level was realised by employing ultrasonic nebulisation for sample introduction, and by using a co-precipitation technique to effect analyte preconcentration. A further feature of the ICP–MS methodology was the use of a membrane desolvation device (in conjunction with USN) to reduce the aerosol water loading to the plasma and, hence, minimise formation of residual ^{238}U^{1}H, a potential interferent on mass 239.

Experiments were first performed to document the value of using USN for signal enhancement, and to clarify the extent to which signals resulting from ^{238}U might compromise the determination of ^{239}Pu. Basic performance data with respect to uranium are presented in Table 2 for three sample introduction systems investigated, i.e. pneumatic nebulisation, ultrasonic nebulisation and ultrasonic nebulisation

Table 2
Analytical performance with pneumatic nebulisation (PN), USN and USN/MD

	PN	USN	USN/MD
Counts/s[a] (100 μgl^{-1} ^{238}U)	7.4×10^6	3.4×10^{8} [b]	3.4×10^8
^{238}U^{1}H/^{238}U ratio[c]	7.8×10^{-5}	7.1×10^{-5}	0.95×10^{-5}

[a] Measurements were carried out in the spectrum mode, 3 points/peak.
[b] Normalised to the counts obtained with USN/MD to have a better UH/U comparison.
[c] Calculated using the parameters in Table 1.

with membrane desolvation. It is clear that the count rate is significantly enhanced for USN, either alone, or with membrane desolvation relative to pneumatic nebulisation, and this is a direct consequence of the increase in analyte transport efficiency for USN [27,28]. The potential benefit of using membrane desolvation can also be seen in Table 2; with membrane desolvation there is a 7-fold reduction, relative to direct USN, for the UH/U ratio, consistent with a corresponding reduction in water loading to the plasma. Mass spectra obtained using USN with and without membrane desolvation for $100 \mu g l^{-1}$ U solution are shown in Fig. 2.

There have been few studies in the ICP–MS literature which attempt to characterise the formation of UH species [20,29]. From the standpoint of seawater analysis and given that uranium concentrations in seawater would typically be at least 10^6 in excess over plutonium (i.e. U, $> 1 \mu g l^{-1}$; Pu, $< 1 pg l^{-1}$), additional experiments were undertaken in an attempt to clarify the magnitude of this potential interference.

Using recommended ICP–MS operating conditions uranium standard solutions $(1–100 \mu g l^{-1})$ were processed (triplicate injections) in the FI–ICP–MS system using USN with and without membrane desolvation. The transient ion-time responses corresponding to masses 238 and 239 were monitored, and are presented in Fig. 3. It is evident that in the absence of membrane desolvation, Fig. 3(a), there is appreciable hydride formation, and the onset is

significant at uranium concentrations of $\sim 5 \mu g l^{-1}$. With membrane desolvation, interference levels are markedly reduced, and UH response is not significant until the uranium concentration is at least $25 \mu g l^{-1}$, as shown in Fig. 3(b). Irrespective of the nebulisation system, under FI conditions, hydride formation is reproducible, and given the good proportionality between uranium concentration and the UH response, as revealed in Fig. 4, correction factors based on the knowledge of uranium concentrations can be computed for both USN configurations. (As shown later, the uranium content of seawater concentrates was less than $1 \mu g l^{-1}$ and, hence, correction was not necessary.) It is clear that FI–ICP–MS with ultrasonic nebulisation and membrane desolvation is the preferred route for the determination of plutonium, from the standpoint of detection capability, precision, measurement time and low UH/U ratio, as documented in Tables 2 and 3. Nevertheless, sensitivity is insufficient to quantify plutonium at the $pg l^{-1}$ level and below, hence the need to undertake sample preconcentration.

3.1. Co-precipitation and analytical performance

Concentrations of dissolved plutonium (^{239}Pu and ^{240}Pu) in coastal waters of the UK have been reported to be in the range of $0.01–7 mBq l^{-1}$ (assuming $^{240}Pu/^{239}Pu$ isotope ratio to be 0.21, this range corresponds to $0.002–2 pg l^{-1}$ and
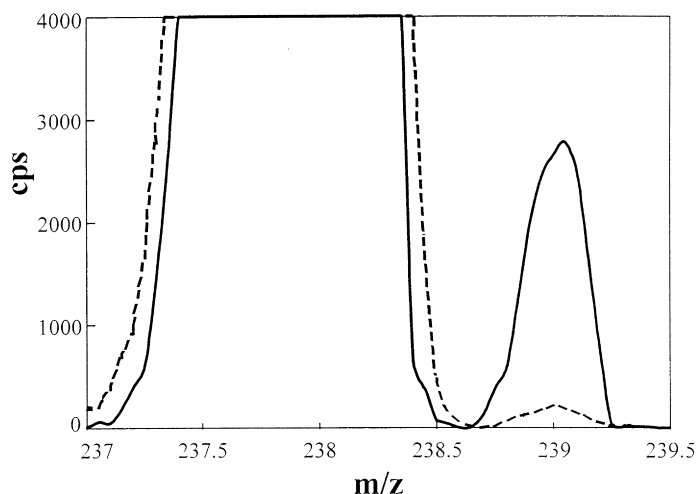

Fig. 2. Mass spectra obtained using USN with (dotted line) and without membrane (solid line) desolvation; U concentration, $100 \mu g l^{-1}$.
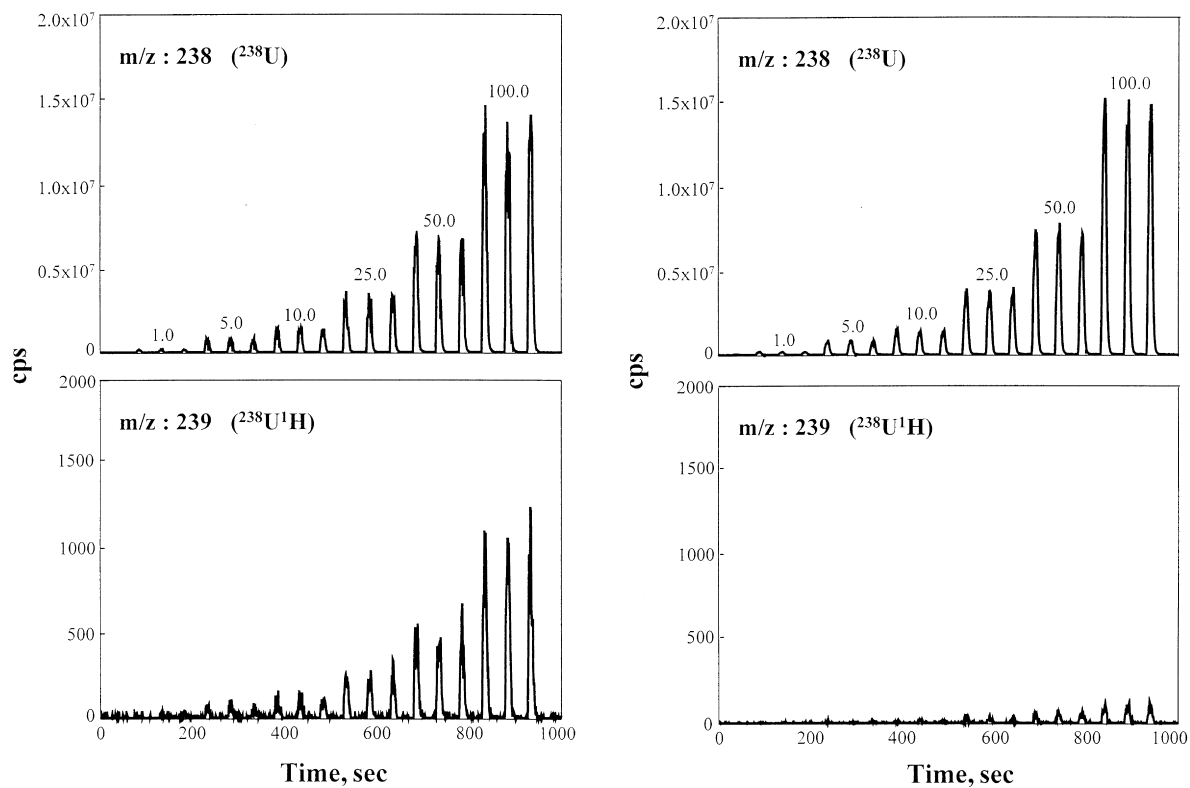
Fig. 3. Ion time responses: (a) USN without membrane desolvation, and (b) USN with membrane desolvation (numbers shown refer to U concentrations (μg l^{-1}).
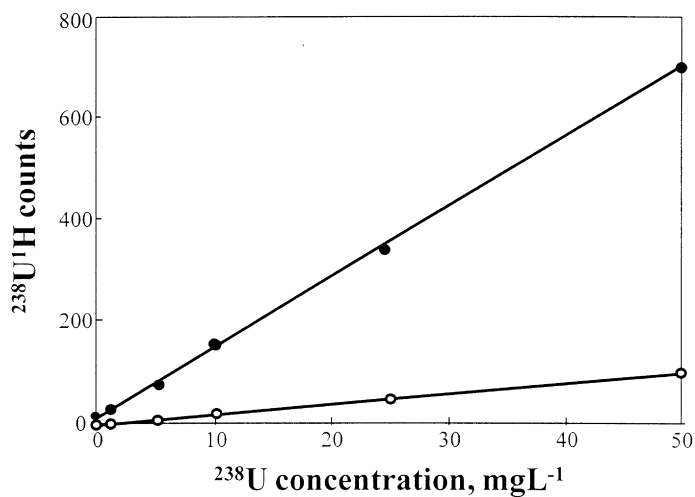

Fig. 4. Variation of UH response as a function of uranium concentration. ($\bullet$) USN without membrane desolvation ($y = 13.0204 + 13.9102 \times$ ($r = 0.9988$) ($\bigcirc$) USN with membrane desolvation ($y = -5.9796 + 2.1102 \times$ ($r = 0.9991$).

0.0005–0.4 pg l^{-1} for ^{239}Pu and ^{240}Pu, respectively) [14]. Given such ultra-low concentration levels, there is a need to undertake sample preconcentration prior to quantitation by ICP–MS. In addition to analyte enrichment, it is highly desirable that seawater salts are rejected, otherwise, on sample introduction, instability and interference effects might ensue as a result of the gradual build-up of matrix ions on the interface cones. As already indicated, a key requirement for sample pre-treatment is the rejection of co-existing uranium which is in considerable excess over that of plutonium.

A co-precipitation procedure based on NdF_3 and originally utilised for α-spectrometry was adapted for ICP–MS. The scheme, outlined in Fig. 5, achieved a nominal enrichment factor of 1000 based on processing 1 l sample aliquots, hence, permitting the determination of plutonium in seawater at the low fg l^{-1} level. The effectiveness of the co-precipitation procedure in terms of the rejecting matrix ions and uranium was first examined. As shown in Table 4, concentrations of major elements in the seawater concentrate were at the mg l^{-1} level. Furthermore, chemicals employed in sample processing, i.e. Fe, Nd and I were also of relatively low concentration in the final extract.

To test the effectiveness of the co-precipitation procedure in rejecting uranium, three aliquots of open ocean water (uranium concentration, ~ 3 μg l^{-1}) with no detectable plutonium, were processed and then subjected to ICP–MS analysis. The concentration of uranium in the concentrate was determined to be less than 1 μg l^{-1}. At this concentration level and based on previous findings, the formation of significant UH was not anticipated as confirmed in the mass spectrum for a seawater concentrate, as shown in Fig. 6.

Table 3
FI–ICP–MS performance data with USN/MD

Calibration response curve[a]	$y = 1.5532 + 97.5128x$ ($r = 0.9999$)
Limit of detection[b]	5.15 pg l^{-1}
Short-term stability[c]	$< 1\%$
Long-term stability[d]	$< 2\%$

[a] Obtained by plotting $^{239}Pu/^{209}Bi$ vs ^{239}Pu concentration

[b] Based on 3 s of blank signal at m/z: 239.

[c] Based on the measurement of 1.0 μg l^{-1} U solution every minute over a period of 10 min at m/z: 238.
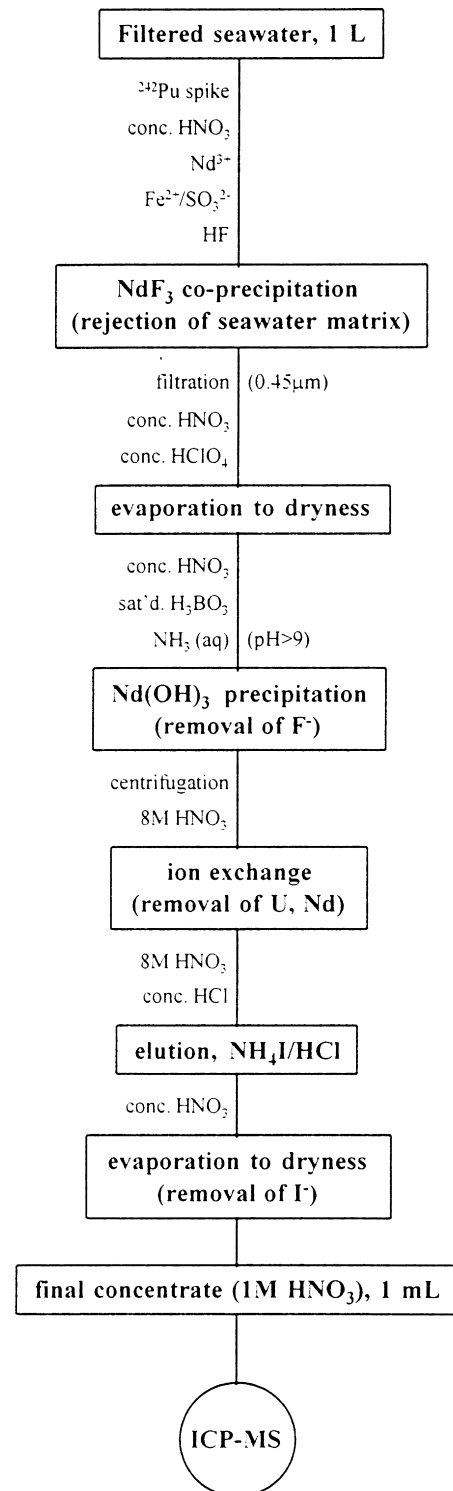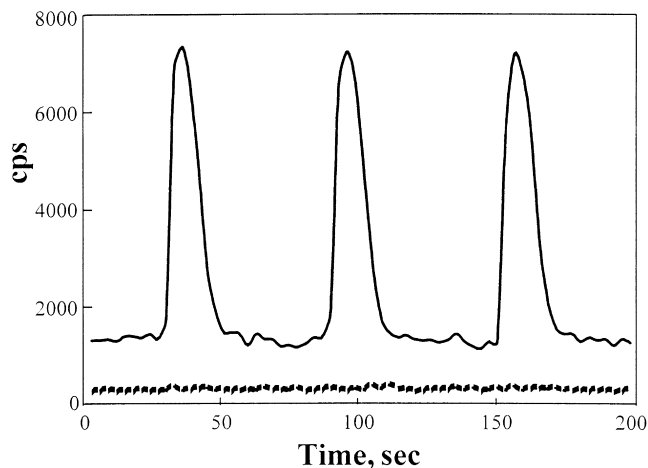

Fig. 5. Flowchart of co-precipitation procedure.

Fig. 6. Ion time responses for open ocean water concentrate; solid line, *m/z*: 238; dotted line, *m/z*: 239; uranium concentration, 0.5 μg l^{-1}.

An indication of the efficiency of the preconcentration scheme was obtained by subjecting dilute aqueous standard solutions of ^{239}Pu and blank seawater spiked at 0.33, 0.65 and 1.32 pg l^{-1} to preconcentration and ICP analysis. As shown in Fig. 7, slopes of the response plots for the aqueous standards and the spiked waters were similar, indicating that the seawater matrix did not have a suppressive effect on analyte recoveries. By referring the integral counts for the three seawater concentrates to a calibration plot derived from simple aqueous ^{239}Pu standards (0.025–2.0 ng l^{-1}), and, based on an enrichment factor of 1000 (sample aliquots 950 ml,

extract 0.95 ml), spike recoveries were calculated as 104% $\pm$ 11% (aqueous solution) and 104% $\pm$ 17% (seawater).

3.2. Survey analysis

It is clear that the proposed FI–ICP–MS technique offers considerable potential for rapid and sensitive determination of plutonium in seawater. It was, therefore, decided to undertake survey analysis of the Irish Sea and also to obtain comparative data by α-spectrometry. The Irish Sea, in relation to open ocean water, is known to contain elevated
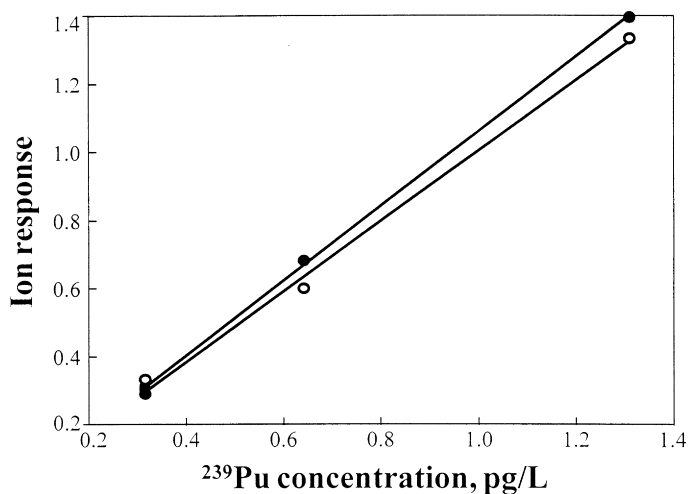

Fig. 7. Ion response (^{239}Pu) as a function of Pu concentration: (●) high purity water, (○) seawater.
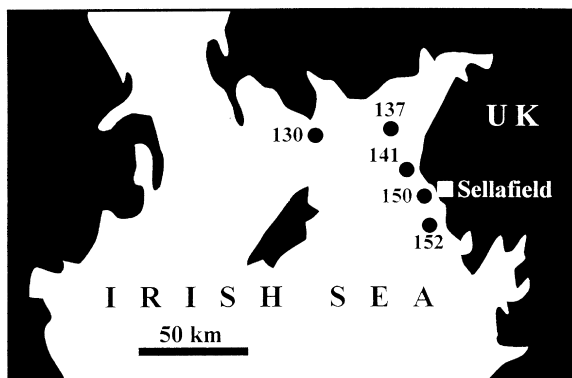
Fig. 8. Sampling stations in the Irish Sea.

concentrations of plutonium, 0.5–7 mBq l^{-1} (assuming ^{240}Pu/^{230}Pu ratio to be 0.21, this range corresponds to 0.1–2 pg l^{-1} and 0.02–0.4 pg l^{-1} for ^{239}Pu and ^{240}Pu, respectively) as a result of low level

discharges from the Seallafield nuclear fuel reprocessing plant, and, hence, sampling stations were selected for monitoring as shown in Fig. 8. Plutonium was detected in all samples collected, and typical ion-time responses for ^{230}Pu and ^{240}Pu are presented in Fig. 9. Mass spectra were recorded for the Irish Sea samples, and, as an additional check that UH did not comprise ^{239}Pu measurement, uncontaminated water collected off the Scilly Isles was also analysed. The mass spectra given in Fig. 10 are consistent with method development studies, in that ICP–MS with USN and membrane desolvation provides a sensitive and interference-free route for the determination of ^{239}Pu (and ^{240}Pu). The survey data are presented in Table 5 and it is seen that ^{239}Pu and ^{240}Pu concentrations (1–4 mBq l^{-1}) are consistent with literature values. Significantly, the FI–ICP–MS data compare very favourably with the data of
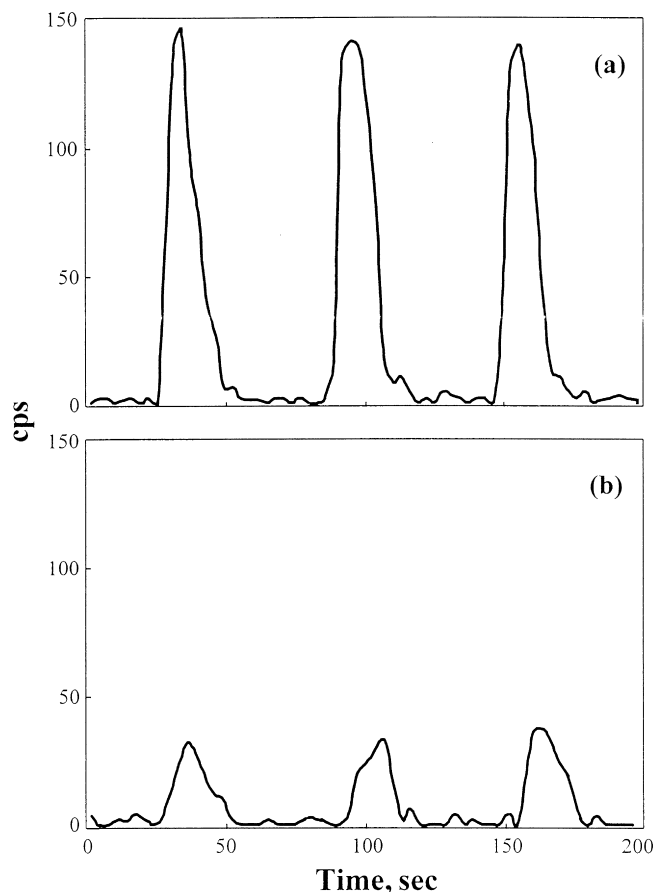

Fig. 9. Ion time responses for Irish Sea concentrate: (a) ^{239}Pu, (b) ^{240}Pu.

Table 4
Concentrations of matrix elements in seawater concentrate after co-precipitation and ion exchange

Element	Conc. (mg l^{-1})	Element	Conc. (mg l^{-1})
Na	2-10	Fe	0.4–0.7
K	0.5-1	Nd	0.04–0.2
Mg	0.4-1	I	0.2–0.7
Ca	3-6	U	$(0.3–0.9) \times 10^{-3}$

α-spectrometry, thus implying accurate measurement (correlation coefficient between the two data sets is 0.995).

As mentioned above, one of the key features of the ICP–MS methodology is that it permits the determination of Pu isotope ratios (^{240}Pu/^{239}Pu). Such isotope ratio data serve as a source indicator.

The ^{240}Pu/^{239}Pu isotope ratio values found [0.165–0.243 (0.21 ± 0.03)] are consistent with values for the Irish Sea sediment samples analysed using ICP–MS and TIMS [17]. In the aforementioned study, the ^{240}Pu/^{239}Pu isotope ratios were found to vary between 0.169 and 0.255 for sediments originating close to the surface. (The surface of the sediment can be considered to resemble the recent situation of the Irish Sea water in terms of ^{240}Pu/^{239}Pu isotope ratio.)

4. Conclusions

It has been demonstrated that ICP–MS utilising USN with membrane desolvation, in conjunction with co-precipitation, provides a powerful new route
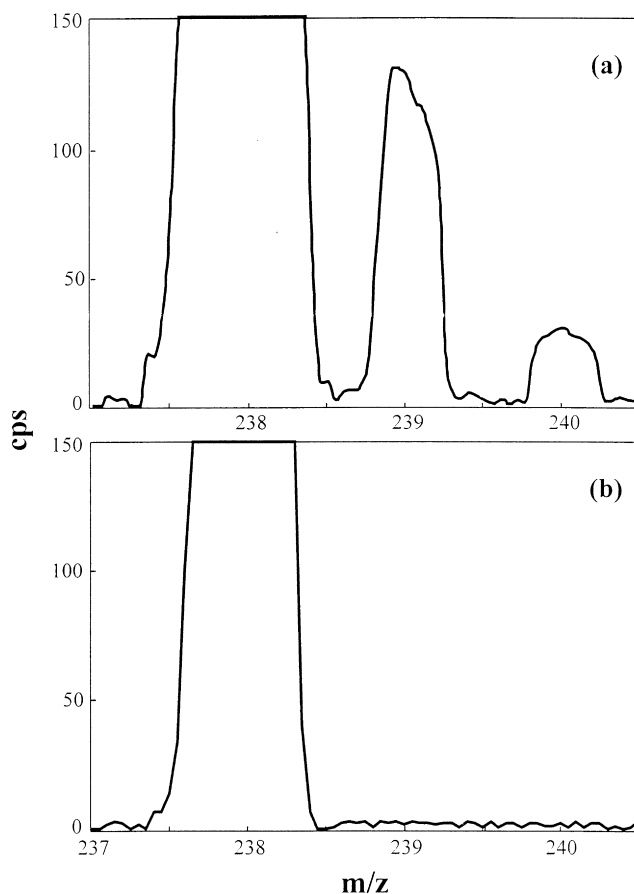

Fig. 10. Typical mass spectra for seawater concentrates: (a) Irish Sea, and (b) open ocean water (background).

Table 5
Plutonium concentrations in the Irish Sea by ICP–MS and α-spectrometry

	ICP–MS [a]				α-spectrometry [b]
Sample	^{239}Pu, pg l^{-1} (mBq l^{-1})	^{240}Pu, pg l^{-1} (mBq l^{-1})	^{240}Pu/^{239}Pu	^{239}Pu$+^{240}$Pu (mBq l^{-1})	$^{239}+^{240}$Pu (mBq l^{-1})
130	0.267 (0.614)	0.051 (0.428)	0.191	1.042	1.113
137	0.393 (0.904)	0.065 (0.546)	0.165	1.450	1.691
141	0.489 (1.125)	0.119 (1.000)	0.243	2.125	2.156
150	0.941 (2.164)	0.196 (1.646)	0.208	3.810	3.741
152	0.786 (1.808)	0.174 (1.462)	0.221	3.270	3.053

[a] 1 l sample, measurement time: 4 min.
[b] 25 l sample, measurement time: 14 days.
1 pg l^{-1} ^{239}Pu = 2.3 mBq l^{-1}.
1 pg l^{-1} ^{240}Pu = 8.4 mBq l^{-1}.
ICP–MS, mean of 3 replicates.

for the quantitation of Pu in seawater at the fg l^{-1} level. Key aspects of the methodology are the high enrichment factor for Pu, rejection of co-existing U, and the reduction in water loading to the plasma (via USN with membrane desolvation), such that there is negligible formation of the potentially interfering species, ^{238}U^{1}H. In relation to α-spectrometry, ICP mass spectrometry offers significant advantages, including isotopic information (as distinct from ^{239}Pu and ^{240}Pu), short analysis time, and substantial reduction in sample size. These benefits should ensure an increasing use of ICP–MS technology for surveillance of long-lived radio-nuclides, particularly in the marine environment. It is planned to extend work to Tc and other radionuclides, and to develop new on-line preconcentration systems for field use.

Acknowledgements

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