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Analysis of plutonium isotopes in marine samples by radiometric, ICP-MS and AMS techniques

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IAEA reference materials (radionuclides in the marine environment) collected in areas affected by nuclear reprocessing plants and nuclear weapons tests have been analysed by semiconductor alpha-spectrometry (SAS), liquid scintillation spectrometry (LSS) and mass spectrometric techniques (high resolution ICP-MS and AMS) with the aim of developing analytical procedures and to study the geochemical behavior of plutonium in the marine environment. The Pu results obtained by SAS, ICP-MS and AMS were in reasonably good agreement ($R^2 = 0.99$). The mean atom ratios of $^{240}Pu/^{239}Pu$ in IAEA reference materials, IAEA-134, 135 and 381 were (0.212±0.010), (0.211±0.004) and (0.242±0.004), respectively. IAEA-384 (Fangataufa Lagoon Sediment) gave a $^{240}Pu/^{239}Pu$ mean atom ratio of 0.051±0.001. The results of ^{241}Pu obtained by ICP-MS and LSS also show reasonable agreement ($R^2 = 0.91$). Pu isotopic signatures were useful in tracing Pu origin and in interpreting biogeochemical processes involving Pu in the marine environment.

Introduction

The total inventory of Pu in the world's oceans is estimated to be around 20 PBq since its introduction into the marine environment over 50 years ago. The open ocean Pu distribution is due to global fallout, however, there are visible contributions over this background which are mainly due to discharges from reprocessing plants (e.g., Sellafield, La Hague) and close-in fallout from nuclear bomb tests (e.g., the Marshall Islands, Mururoa and Fangataufa Atolls). Because of the different inputs of Pu and its non-conservative behavior, Pu concentrations in seawater, sediment and biota vary considerably.

In the past, large volume samples were required to analyse Pu isotopes in the marine environment as their activities had been decreasing due to biogeochemical (scavenging, sedimentation, etc.) and transportation processes as a result of the moratorium on atmospheric bomb tests which took place in 1963.[1] Therefore, much effort has been made to improve analytical procedures for the analysis of Pu isotopes using various techniques. Semiconductor alpha-spectrometry (SAS) has been the most widely used technique, however, it has several disadvantages, e.g., low sensitivity, long counting times, and problems with the separation of ^{239}Pu and ^{240}Pu isotopes. Liquid scintillation spectrometry (LSS),[2–4] because of its lower energy resolution cannot compete with SAS, however, this technique has proved useful for the analysis of the soft beta-emitter ^{241}Pu. Recently, high resolution inductively coupled plasma mass spectrometry (ICP-MS),[5–8] accelerator mass spectrometry (AMS)[9–11] and thermal ionization mass spectrometry (TIMS)[12–16] have been introduced to improve the sensitivity of the analysis of Pu isotopes in the marine environment.

However, because of financial and operational constraints, at present only a few laboratories are using mass spectrometry techniques for the analysis of Pu in marine samples.

The purpose of this study is to compare various analytical procedures for the analysis of Pu isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu) in the marine environment.

Experimental

Sample preparation, radiometrics and ICP-MS analyses were carried out at the IAEA Marine Environment Laboratory, Monaco and AMS measurements were done at the Australian National University, Canberra.

Materials

Pu analyses of IAEA reference materials IAEA-134, IAEA-135, IAEA-381 and IAEA-384 and sediment and seawater samples from the Marshall Islands and French Polynesia collected in the framework of the research project "World-wide Marine Radioactivity Monitoring"[17] were carried out using SAS, LSS, high resolution ICP-MS and AMS. The materials and procedures used for the treatment of marine samples are described below. The chemical procedures included pre-concentration (water) or total dissolution by concentrated acids (sediment), extraction and purification with anion exchange or extraction chromatography and electrodeposition on stainless steel discs or source preparation for direct ICP-MS and AMS analyses.

Pre-treatment of samples

Seawater samples were pre-treated on ship board. The samples were filtered (0.45 μm), acidified with conc. HCl (pH 1) and ^{236}Pu or ^{242}Pu tracers were added. Afterwards, proper amounts of saturated KMnO$_4$ were added and mixed with 10M NaOH solution adjusting the pH to 9–10. Then 0.5M MnCl$_2$ was added adjusting the pH to 7–8 to co-precipitate plutonium and manganese oxide.

The precipitates were transferred to the laboratory and were dissolved using reducing agent (0.1 g/ml NH$_2$OH·HCl) with HCl. After Pu(III) was converted to Pu(IV) with NaNO$_2$, plutonium was co-precipitated with 50 mg of iron. The residues were dissolved in conc. HCl and evaporated to dryness. 8M HNO$_3$ was added to re-dissolve the sample followed by the purification of plutonium by anion exchange columns.

Dry sediment and biota samples (analysed by SAS) were ashed for 24 hours at 600 °C in an electric furnace and the yield determinants (^{236}Pu or ^{242}Pu) were added.

Samples were dissolved in conc. HNO$_3$ for 8 hours and centrifuged to separate the supernate. The residue was totally dissolved in conc. HCl, HF and HClO$_4$.

Purification of plutonium

The combined solution (8M HNO$_3$) was passed through a Bio rad (1-X8, 100-200 mesh, Cl$^-$ form) anion exchange column (ϕ10 mm×120 mm). The column was washed with 100 ml of 8M HNO$_3$ and then was washed with 100 ml of 10M HCl. Finally Pu was eluted by 100 ml of 0.1M NH$_4$I–9M HCl. The eluent was evaporated to dryness and dissolved in 50 ml of 8M HNO$_3$. The above procedure was repeated to purify the obtained plutonium.

Electrodeposition

The effluent was evaporated to dryness and electroplated onto a stainless steel disc for 1 hour at a constant current of 1 A from Na$_2$SO$_4$ solution at pH 2.2.
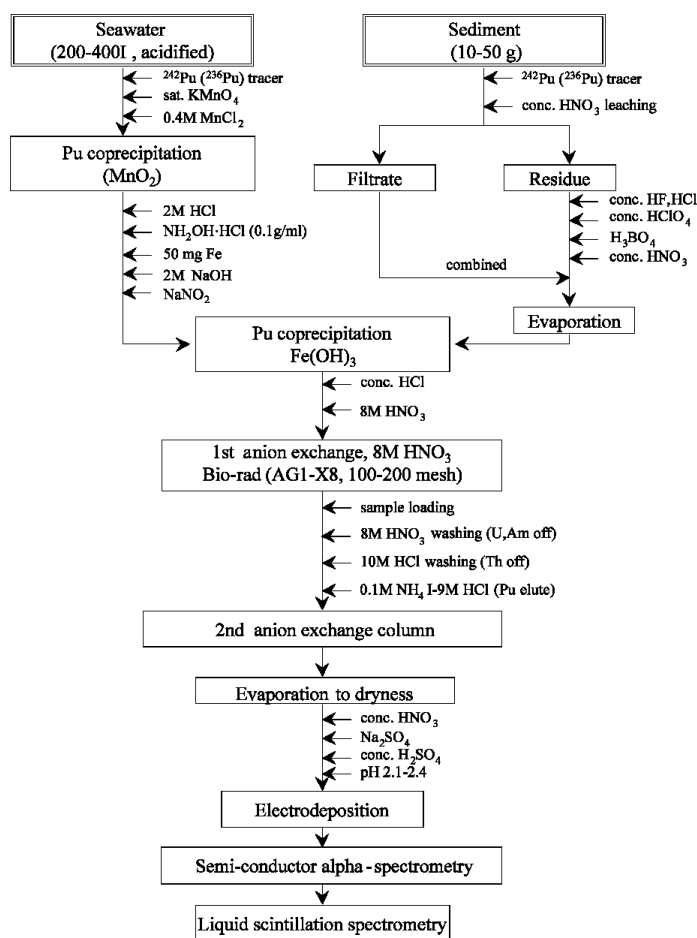

Fig. 1. Flow chart of Pu procedures for SAS and LSS

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┌────────────────────────────┐          ┌────────────────────────────┐
│ Seawater (1-20I, acidified)│          │    Sediment (0.1-0.5 g)    │
└────────────────────────────┘          └────────────────────────────┘
              ◄── ²⁴²Pu tracer                        ◄── ²⁴²Pu tracer
              ◄── sat. KMnO₄                          ◄── conc. mixed acid
              ◄── 0.4M MnCl₂              ┌────────────────────────────┐
┌────────────────────────────┐           │      Microwave system      │
│  Pu coprecipitaton (MnO₂)  │           │  (running time : 30 min)   │
└────────────────────────────┘           └────────────────────────────┘
              ◄── 2M HCl                             │
              ◄── NH₂OH·HCl (0.1g/mL)     ┌─────────────────┐
              ◄── 50 mg Fe                │   evaporation   │
              ◄── 2M NaOH                 └─────────────────┘
              ◄── NaNO₂                             │
        ┌──────────────────────────────────────────────┐
        │      Pu coprecipitation Fe(OH)₃     ◄─────────┘
        └──────────────────────────────────────────────┘
              ◄── 2.5M HNO₃ -0.5M Al(NO₃)₃
              ◄── 0.6M ferrous sulfamate
              ◄── ascorbic acid
        ┌──────────────────────────────────────────────┐
        │       2-Column extraction chromatography      │
        │     Eichrom (UTEVA-TRU, 2 ml bed Vol.)        │
        └──────────────────────────────────────────────┘
              ◄── 5 ml of 2.5M HNO₃
              ◄── sample loading
              ◄── 2.5M HNO₃ + 0.6M ferrous sulfamate
   ┌───────────────┐              ┌───────────────┐
   │    UTEVA      │              │     TRU       │
   │ U(VI), Th(IV),│              │ Pu(III), Am(III)│
   │   Np(IV)      │              └───────────────┘
   └───────────────┘       ◄── 2.5M HNO₃+0.1M NaNO₂
                           ◄── 9M HCl
                           ◄── 4M HCl (Am elute)
                           ◄── 4M HCl+0.1M H₂Q (Pu elute)
          ┌──────────────────┐       ◄── 1M HNO₃
          │   Evaporation    │       ◄── 2 mg of Fe
          └──────────────────┘       ◄── ashing in 550 °C
                                     ◄── mixing with Al powder
  ◄──1M HNO₃    ◄──1M HNO₃
┌──────────┐  ┌──────────┐  ┌──────────┐
│ ICP – MS │  │   TIMS   │  │   AMS    │
└──────────┘  └──────────┘  └──────────┘
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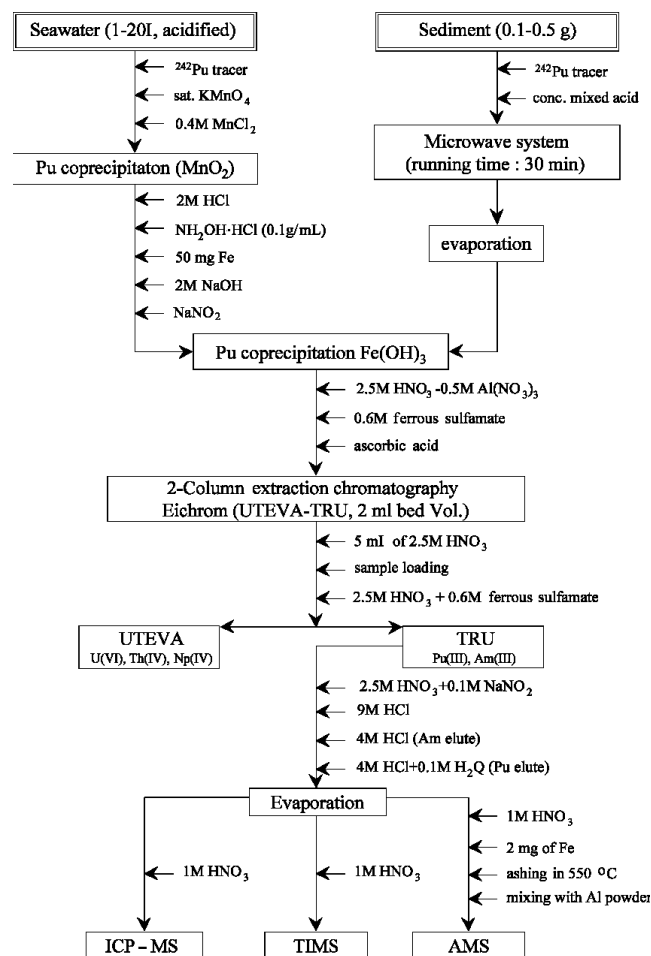
Fig. 2. Flow chart of Pu procedures for mass spectrometry

Source preparations for mass-spectrometry analyses

After SAS measurements, the discs were either directly analysed by LSS (for ^{241}Pu) or leached by concentrated HNO_3 and the remaining samples prepared for ICP-MS and AMS measurements. The sample solutions leached from the discs were purified by anion exchange columns to remove any impurities (polyatomic ions UH^+, organic fragments) which could produce interference or matrix effects. For the measurement of Pu isotopes by AMS, the plutonium was dispersed in an iron oxide matrix, adjusted to the atom ratios of ^{242}Pu:Fe (10^{-10} to 10^{-9}), evaporated to dryness, and baked at 550 °C to obtain Fe_2O_3. The resulting samples were mixed with Al powder (in the proportions of 4:1 by weight), which served as an electrical and thermal conductor, and pressed firmly into the sample holders.[9] All sample preparations were carried out in clean, low-level analytical laboratories. The activities of all Pu isotopes were calculated on the basis of isotopic dilution technique with ^{236}Pu or ^{242}Pu using the half-life of ^{239}Pu (24,119 y), ^{240}Pu (6,563 y), ^{241}Pu (14.35 y) and ^{242}Pu ($3.733 \cdot 10^5$ y), and a few samples (with and without ^{242}Pu tracer) were prepared for measurement of ^{242}Pu. The flow diagrams of the analytical procedures used for alpha and mass spectrometry are summarized in Figs 1 and 2.

Results and discussion

IAEA reference materials

The results of analyses of IAEA reference materials by SAS, LSS, ICP-MS and AMS are presented in Tables 1 to 4. The concentrations of ^{239,240}Pu in IAEA-134 (Irish Sea Cockle Flesh) analysed by SAS ranged from (15.5±1.4) to (16.0±1.4) Bq·kg^{-1} (mean value: (15.8±1.0) Bq·kg^{-1}), these results are in good agreement with the recommended value of (15.0) Bq·kg^{-1}.

Table 1. The results of plutonium isotopes obtained by SAS and ICP-MS in IAEA-134 (Irish Sea Cockle Flesh)

Method	^{238}Pu, Bq·kg^{-1}	^{239}Pu, Bq·kg^{-1}	^{240}Pu, Bq·kg^{-1}	^{239,240}Pu, Bq·kg^{-1}	^{238}Pu/^{239,240}Pu	^{240}Pu/^{239}Pu
SAS	3.1 ± 0.4	–	–	16.0 ± 1.4	0.191 ± 0.030	–
SAS	2.8 ± 0.4	–	–	15.5 ± 1.4	0.183 ± 0.028	–
ICP-MS	–	9.8 ± 0.8	7.7 ± 0.6	17.5 ± 1.0	–	0.212 ± 0.008
Mean	3.0 ± 0.2	9.8 ± 0.8	7.7 ± 0.6	16.3 ± 0.8	0.187 ± 0.020	0.212 ± 0.008
Recommended value	3.1*	–	–	15	–	–
95% confidence interval	3.0 – 3.4*			13.8 – 16.2		

* Information value.

Table 2. The results of plutonium isotopes obtained by SAS, ICP-MS, AMS and LSS in IAEA-135 (Irish Sea Sediment)

Method	^{238}Pu, Bq·kg^{-1}	^{239}Pu, Bq·kg^{-1}	^{240}Pu, Bq·kg^{-1}	^{241}Pu, Bq·kg^{-1}	^{242}Pu, Bq·kg^{-1}	^{239,240}Pu, Bq·kg^{-1}
SAS	41 ± 2	–	–	–	–	216 ± 9
SAS	43 ± 2	–	–	–	–	228 ± 10
ICP-MS	–	126 ± 11	96 ± 8	3930 ± 300	–	222 ± 13
ICP-MS	–	128 ± 10	100 ± 8	4020 ± 320	0.056 ± 0.006	228 ± 18
AMS	–	129 ± 13	92 ± 9		0.033 ± 0.001	221 ± 16
LSS	–	–	–	2780 ± 300	–	–
LSS	–	–	–	3170 ± 300	–	–
Mean	42 ± 1	127 ± 8	96 ± 6	3500 ± 500	0.046 ± 0.003	223 ± 5
Recommended value	43					213
95% confidence interval	41.6 – 45.0					205 – 226

Method	^{238}Pu/^{239,240}Pu	^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu	^{242}Pu/^{239}Pu
SAS	0.190 ± 0.012	–	–	–
SAS	0.186 ± 0.013	–	–	–
ICP-MS	–	0.204 ± 0.008	0.0217 ± 0.0011	–
ICP-MS	–	0.210 ± 0.008	0.0224 ± 0.0011	0.0068 ± 0.0007
AMS	–	0.192 ± 0.027	–	0.0041 ± 0.0041
AMS	–	0.246 ± 0.043	–	–
Mean	0.188 ± 0.002	0.207 ± 0.006	0.0221 ± 0.0080	0.0055 ± 0.0021

The results obtained by ICP-MS are higher than the recommended value (an average of (17.5±1.0) Bq·kg^{-1}), but within 2σ in a 95% confidence interval. The atom ratio of ^{240}Pu/^{239}Pu is (0.212±0.010) and agrees with the previous result (0.200±0.010)[18] within 1 standard deviation (σ).

The concentrations of ^{239,240}Pu in IAEA-135 (Irish Sea Sediment) analysed by SAS ranged from (216±9) to (228±10) Bq·kg^{-1} (mean value: 222±7), and agreed with the recommended value (213 Bq·kg^{-1}). The ICP-MS results showed values between (222±13) to (228±18) Bq·kg^{-1} (the mean value of (224±10) Bq·kg^{-1}) is still within the 95% confidence interval. The mean atom ratio of ^{240}Pu/^{239}Pu is (0.207±0.006), which is similar to the previous result (0.211±0.004).[18] The result of ^{239,240}Pu obtained by AMS showed (221±16) Bq·kg^{-1}, this value agrees well with the values of SAS and ICP-MS. Also, the mean atom ratio of ^{240}Pu/^{239}Pu is (0.219±0.022), which is in agreement with the ICP-MS results. The atom ratios of ^{242}Pu/^{239}Pu measured by AMS and ICP-MS in IAEA-135 are (0.0041±0.0041) and

(0.0068±0.0002), respectively. The value obtained by ICP-MS is higher than the global fallout ratio (0.0039±0.0010).[13]

The concentrations of ^{239,240}Pu analysed by SAS in IAEA-381 (Irish Sea Water) ranged from (0.014±0.001) to (0.015±0.001) Bq·kg^{-1} (mean value: (0.014±0.001) Bq·kg^{-1}) are in good agreement (within 1σ) with the recommended value (0.0142) Bq·kg^{-1}. The ICP-MS results showed (0.014±0.001) to (0.016±0.001) Bq·kg^{-1} (the mean value: (0.015±0.001) Bq·kg^{-1}), within the 95% confidence interval. The mean atom ratio of ^{240}Pu/^{239}Pu is (0.242±0.004). This atom ratio is higher than the global fallout ratio (0.176±0.014)[19] and comparable to those of IAEA-134 and IAEA-135. The results of ^{239,240}Pu obtained by AMS in IAEA-381 showed (0.016±0.001) Bq·kg^{-1}, this value is higher than the recommended value, but agrees well (within 1σ) with the results of SAS and ICP-MS. The mean atom ratio of ^{240}Pu/^{239}Pu is (0.242±0.028), which is in good agreement with the ICP-MS results. The atom ratio of ^{242}Pu/^{239}Pu in IAEA-381, measured by ICP-MS was

(0.0084±0.0004) and (0.0093±0.0005), higher than the global fallout ratio in the Northern Hemisphere. The atom ratios of ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu in IAEA-134, IAEA-135 and IAEA-381 were also higher than the global fallout ratio. This means that Pu in these reference materials has the same origin, discharges from Sellafield reprocessing plant, in which ^{240}Pu and ^{242}Pu were enriched in comparison to global fallout.

Table 3. The results of plutonium isotopes obtained by SAS, ICP-MS and AMS in IAEA-381 (Irish Sea Water)

Method	^{238}Pu, mBq·kg^{-1}	^{239}Pu, mBq·kg^{-1}	^{240}Pu, mBq·kg^{-1}	^{242}Pu, mBq·kg^{-1}	^{239,240}Pu, mBq·kg^{-1}
SAS	3.4 ± 0.3	–	–	–	14 ± 1
SAS	3.5 ± 0.3	–	–	–	15 ± 1
SAS	3.0 ± 0.3	–	–	–	14 ± 1
SAS	–	–	–	–	14 ± 1
ICP-MS	–	8.0 ± 0.8	8.3 ± 0.8	0.0043 ± 0.0002	16 ± 1
ICP-MS	–	8.3 ± 0.8	7.0 ± 0.7	0.0047 ± 0.0002	15 ± 1
ICP-MS	–	7.8 ± 0.8	6.3 ± 0.6	–	14 ± 1
ICP-MS	–	8.1 ± 0.8	7.1 ± 0.7	–	15 ± 1
AMS	–	8.7 ± 0.3	7.0 ± 0.2	–	16 ± 1
Mean	3.3 ± 0.2	8.2 ± 0.3	7.1 ± 0.5	0.0045 ± 0.0001	15 ± 1
Recommended value	3.17	–	–	–	14.2
95% confidence interval	3.10 – 3.50				13.2 – 15.2

Method	^{238}Pu/^{239,240}Pu	^{240}Pu/^{239}Pu	^{242}Pu/^{239}Pu
SAS	0.214 ± 0.024	–	–
SAS	0.237 ± 0.023	–	–
SAS	0.212 ± 0.022	–	–
ICP-MS	–	0.282 ± 0.010	0.0084 ± 0.0004
ICP-MS	–	0.226 ± 0.008	0.0093 ± 0.0005
ICP-MS	–	0.218 ± 0.008	–
ICP-MS	–	0.240 ± 0.009	–
AMS	–	0.242 ± 0.028	–
Mean	0.221 ± 0.011	0.242 ± 0.022	0.0089 ± 0.0006

Table 4. The results of plutonium isotopes obtained by SAS, ICP-MS and AMS in IAEA-384 (Fangataufa Lagoon Sediment)

Method	^{238}Pu, Bq·kg^{-1}	^{239}Pu, Bq·kg^{-1}	^{240}Pu, Bq·kg^{-1}	^{242}Pu, mBq·kg^{-1}	^{239,240}Pu, Bq·kg^{-1}
SAS	41 ± 3	–	–	–	107 ± 7
SAS	39 ± 4	–	–	–	108 ± 9
SAS	44 ± 2	–	–	–	120 ± 5
SAS	38 ± 2	–	–	–	107 ± 4
ICP-MS	–	102 ± 8	19 ± 2	–	121 ± 8
ICP-MS	–	101 ± 8	18 ± 1	1.93 ± 0.46	119 ± 8
AMS	–	109 ± 11	14 ± 1	0.66 ± 0.03	123 ± 11
Mean	40 ± 2	104 ± 4	17 ± 2	1.30 ± 0.23	115 ± 7
Recommended value	41	–	–	–	–
95% confidence interval	38.1 – 39.1	–	–	–	–

Method	^{238}Pu/^{239,240}Pu	^{240}Pu/^{239}Pu	^{242}Pu/^{239}Pu
SAS	0.379 ± 0.037	–	–
SAS	0.361 ± 0.046	–	–
SAS	0.368 ± 0.023	–	–
SAS	0.355 ± 0.023	–	–
ICP-MS	–	0.052 ± 0.002	–
ICP-MS	–	0.051 ± 0.002	0.0003 ± 0.0001
AMS	–	0.042 ± 0.005	0.0001 ± 0.0001
AMS	–	0.048 ± 0.002	–
Mean	0.370 ± 0.016	0.048 ± 0.004	0.0002 ± 0.0001

IAEA-384 reference material (Fangataufa Lagoon Sediment) measured by SAS showed ^{239,240}Pu concentrations from (107±4) to (120±5) Bq·kg^{-1}, the mean value is (111±3) Bq·kg^{-1}. The ICP-MS mean value is (120±6) Bq·kg^{-1} and the AMS value is (123±11) Bq·kg^{-1}, both in agreement with the SAS value. The mean atom ratio of ^{240}Pu/^{239}Pu is (0.052±0.001) by ICP-MS and (0.046±0.005) by AMS, which are much lower than the global fallout ratio. IAEA-384 is enriched in ^{239}Pu as a result of low burn-up atmospheric nuclear bomb tests carried out at Fangataufa Atoll (a tropospheric component).[13] It was reported that weapons-grade Pu (thermonuclear and fission) was mainly composed of ^{239}Pu (^{240}Pu less than 5%), while Pu from global fallout had a different composition [^{239}Pu (80%) and ^{240}Pu (20%)].[16] The atom ratios of ^{242}Pu/^{239}Pu measured by AMS and ICP-MS were (0.0001±0.0001) and (0.0003±0.0001), lower than the global fallout ratio (due to ^{239}Pu enrichment in samples).

The ^{241}Pu results measured by LSS and ICP-MS in IAEA-135 are presented in Table 2. The ^{241}Pu results obtained by LSS in IAEA-135 showed concentrations from (2,780±300) to (3,170±300) Bq·kg^{-1}, with a mean value of (2,980±200) Bq·kg^{-1}. ICP-MS showed (3,930±300) to (4,020±320) Bq·kg^{-1}, with a mean value of (3,980±200) Bq·kg^{-1}, which are much higher than the LSS results. But both results are in the range of values

reported for intercomparison exercise IAEA-135[20] from (2,260±280) to (3,990±50) Bq·kg^{-1}. The mean atom ratio of ^{241}Pu/^{239}Pu in IAEA-135 is ten times higher than the global fallout value (0.0019±0.0003) for the Northern Hemisphere.[13] It suggests that sediment was enriched in ^{241}Pu originating from Sellafield reprocessing plant.

Evaluation of results obtained by SAS, LSS, ICP-MS and AMS

Generally, the results of ^{239,240}Pu analyses obtained by SAS, ICP-MS and AMS for IAEA reference materials were in reasonable agreement ($R^2 = 0.99$, confidence interval 95%) (Fig. 3). Nevertheless, ICP-MS results were a little higher than the recommended values by up to 10%. These discrepancies could have been caused by experimental errors contributing to the total uncertainty. This has often been noticed in ICP-MS analyses of Pu isotopes and in most cases, it was suspected that some matrix or interference effects (like a contribution of ^{238}U or ^{m}Pb^{35}Cl) could have contributed to the final results. There were no differences between the results of atom ratios obtained by ICP-MS and AMS [$R^2 = 0.99$, confidence interval 95% (Fig. 4a)], both methods have proved to be very useful tools for identifying the origin of Pu in the marine environment.
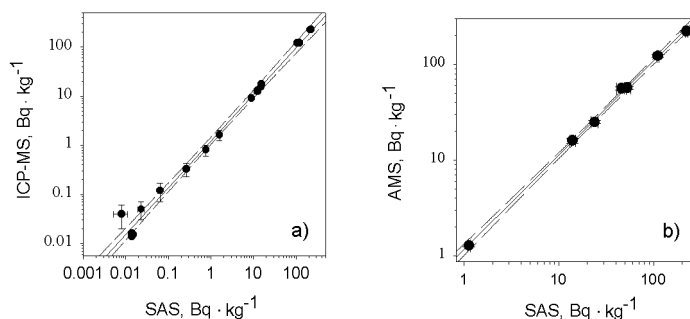

Fig. 3. Comparisons of plutonium data obtained by ICP-MS and SAS (a), and by AMS and SAS (b)
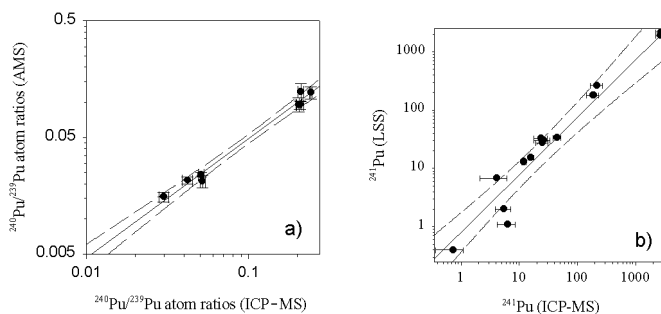

Fig. 4. Relationships between ^{240}Pu/^{239}Pu atom ratios as obtained by AMS and ICP-MS (a), comparison of ^{241}Pu data as obtained by ICP-MS and LSS (b)

SAS is still a powerful technique because of simplicity of measurement, good resolution and reasonable sensitivity for specific radionuclides, especially with short half-lives. However, long counting times for low activity samples are needed and separation of ^{239}Pu and ^{240}Pu is difficult, but possible with a suitable deconvolution software.[21]

ICP-MS has been proved to be the most powerful tool to analyse Pu isotopes because of its many advantages (high sensitivity, fast analysis, multi-isotopic composition including beta-emitters, low cost per analysis and small sample size). In spite of the many advantages, we found in our studies that ICP-MS requires good separation of ^{238}U for ^{239}Pu analysis and the elimination of matrix effect such as polyatomic chlorides and oxides which could pose problems.[7] Therefore, before the ICP-MS measurements are carried out more careful purification procedures by extraction chromatography are needed.

AMS can minimize the sample size requirement due to its low detection limits of below 10^6 atom of ^{239}Pu. Further, AMS has low matrix and interference effects compared to ICP-MS. Therefore, the purification of plutonium leached from the discs after SAS measurements is not necessary. However, AMS operation is more complex and a well experienced team is required. Also, the analysis is more expensive.

^{241}Pu results obtained by LSS and ICP-MS were in reasonable agreement with a correlation coefficient of $R^2 = 0.91$ (Fig. 4a). ICP-MS measurements often showed low count rates (similar to background values), peak shifts due to matrix effects and over-estimations caused by interference. The ^{241}Pu measurements by LSS showed several advantages such as relatively simple measurements, and it is often not necessary to strip Pu from the disc, therefore, discs can be retrieved again for other purposes (mass-spectrometry measurements) after LSS analysis. However, several problems have been registered, e.g., if some contaminants (like Fe, Pt) are electroplated with Pu, they can produce quenching effects which could decrease the detection efficiency, shift alpha and beta spectra and mis-classify alpha events.[4] On the other hand, the calculation of LSS results depends on the chemical recovery given by SAS, therefore, the exact chemical yield should be determined by SAS. The relative precision of Pu results as obtained in the presented analyses were by SAS (^{239,240}Pu), ICP-MS (^{239,240}Pu), AMS (^{239,240}Pu) and LSS (^{241}Pu) 5%, 7%, 10% and 8%, respectively. However, these values can differ for different types of samples, sensitivity of instruments, etc.

It is believed that mass spectrometry techniques will be used more frequently in future for the analysis of Pu isotopes in the marine environment.

Conclusions

Pu isotopic signature provided good information on Pu origin in analysed samples. IAEA reference materials (IAEA-134, IAEA-135 and IAEA-381) are characterised by ^{240}Pu/^{239}Pu atom ratios of (0.212±0.010), (0.211±0.004) and (0.242±0.004), respectively, confirming the origin of Pu in the samples from Sellafield reprocessing plant. IAEA-384 (Fangataufa Lagoon Sediment) gave a ^{240}Pu/^{239}Pu atom ratio of (0.051±0.001).

Generally, results on ^{239,240}Pu analysis by SAS were in good agreement with ICP-MS and AMS measurements ($R^2 = 0.99$). The comparison of ^{241}Pu measurements between ICP-MS and LSS showed a reasonably good agreement ($R^2 = 0.91$), as well.

Sample purification after leaching of discs used in SAS analyses is necessary to avoid interference and matrix effects in ICP-MS measurements.

ICP-MS and AMS have proved to be high sensitive techniques which will be used more frequently in the future for analysis of Pu isotopes in the marine environment.

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References

1. K. HIROSE, Y. SUGIMURA, M. AOYAMA, Appl. Radiation Isotopes, 43 (1992) 349.
2. J. MORENO, J. J. LA ROSA, P. R. DANESI, K. BURNS, P. DE REGGE, N. VAJDA, M. SINOJMERI, Radioact. Radiochem., 9 (1998) No. 2, 35.
3. M. YAMAMOTO, S. IGARASHI, K. CHATANI, K. KOMURA, K. UENO, J. Radioanal. Nucl. Chem., 138 (1990) 365.
4. O. M. CONDREN, L. L. VINTRO, P. I. MITCHELL, T. P. RYAN, Appl. Radiation Isotopes, 47 (1996) 875.
5. R. CHIAPPINI, J-M. TAILLADE, S. BREBION, J. Anal. At. Spec., 11 (1996) 497.
6. R. F. CHIAPPINI, R. F. POINTURIER, J. C. MILLIES-LACROIX, G. LEPETIT, P. HEMET, Sci. Total Environ., 237/238 (1999) 269.
7. R. R. ROSS, J. R. NOYCE, M. M. LARDY, Radioact. Radiochem., 4, 1 (1993) 24.
8. P. J. KERSHAW, K. E. SAMSON, W. McCARTHY, R. D. SCOTT, J. Radioanal. Nucl. Chem., 198 (1995) 113.
9. L. K. FIFIELD, R. G. CRESSWELL, M. L. DI TADA, T. R. OPHEL, J. P. DAY, A. P. CLACHER, Nucl. Instr. Meth. Phys. Res., B117 (1996) 295.
10. D. H. OUGHTON, L. SKIPPERUD, B. SALBU, L. K. FIFIELD, R. C. CRESSWELL, J. P. DAY, in: Marine Pollution, IAEA-TECDOC-1094, 1999, p. 123.
11. T. W. LINICK, P. E. DAMON, D. J. DONAHUE, A. J. T. JULL, Quat. Intern., 1 (1989) 1.

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12. J. N. Smith, K. M. Ellis, K. Naes, S. Dahle, D. Matishov, Deep Sea Res., 242 (1995) 1471.

13. J. M. Kelly, L. A. Bond, T. M. Beasley, Sci. Total Environ., 237/238 (1999) 483.

14. A. McCormick, Appl. Radiation Isotopes, 43 (1992) 271.

15. R. N. Taylor, I. W. Croudace, P. E. Warwick, S. J. Dee, Chem. Geol., 144 (1998) 73.

16. I. Croudace, P. Warwick, R. Taylor, S. Dee, Anal. Chim. Acta, 371 (1998) 217.

17. P. Povinec, L. Huynh-Ngoc, L. Liong Wee Kwong, S. Mulsow, B. Oregioni, O. Togawa, I. Goroncy, H. H. Uhde, R. Rengarajan, K. Hirose, Y. Ikeuchi, T. Ito, S. Shima, M. Fukasawa, H. Moriya, T. Kazama, S. Ozawa, A. So, S. Yasuzumi, S. H. Lee, S. K. Park, H. B. L. Pettersson, in: Marine Pollution, IAEA-TECDOC-1094, 1999, p. 399.

18. Y. Muramatsu, S. Uchida, K. Togami, S. Yoshida, T. Fujikawa, J. Anal. At. Spectrom., 14 (1999) 859.

19. P. I. Mitchell, L. Leon Vintro, H. Dahlgaard, C. Gasco, J. A. Sanchez-Cabeza, Sci. Total Environ., 202 (1997) 147.

20. P. P. Povinec, M. K. Pham, S. Ballestra, AQCS Report, IAEA/MEL/66.

21. L. Leon Vintro, P. I. Mitchell, O. M. Condren, M. Moran, J. Vives, I. Battle, J. A. Sanchez-Cabeza, Nucl. Instr. Meth. Phys. Res., A369 (1996) 597.