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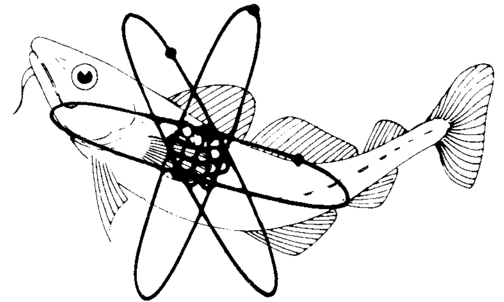
MINISTRY OF AGRICULTURE FISHERIES AND FOOD

DIRECTORATE OF FISHERIES RESEARCH

AQUATIC ENVIRONMENT PROTECTION: ANALYTICAL METHODS



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The determination of alpha-emitting nuclides of plutonium, americium and curium in environmental materials: Part 1. Sea water

M. B. Lovett, S. J. Boggis and P. Blowers

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LOWESTOFT, 1990

The authors:

M. B. Lovett, LRSC, is a Senior Scientific Officer, S. J. Boggis, CChem MRSC, at the time of writing, was a Higher Scientific Officer but has since left the Ministry and P. Blowers is an Assistant Scientific Officer within Aquatic Environment Protection Division 4 of the Directorate of Fisheries Research at the Fisheries Laboratory, Lowestoft.

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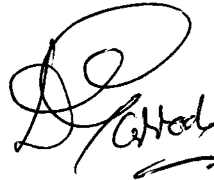
Foreword

As part of its responsibilities under various Acts of Parliament, MAFF Directorate of Fisheries Research has a duty to carry out a substantial programme of monitoring, surveillance and research in relation to the quality of the aquatic environment in and around the United Kingdom. In the course of that programme, a wide variety of methods of analysis are used for a wide variety of contaminants, both inorganic and organic, stable and radioactive. This series of publications describes the main methods used in the course of this work and parallels the existing Aquatic Environment Monitoring Report series, in which much of the resulting data is published. Regardless of whether the analytical procedure relates to a radionuclide or a non-radioactive contaminant, each report contains a step-by-step guide to analytical procedures and an explanation of the calculation of results.



D. J. Garrod

Director
Ministry of Agriculture, Fisheries and Food
Directorate of Fisheries Research

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1. Introduction

Within the Aquatic Environment Protection Division of the Directorate of Fisheries Research (DFR), the Radioanalytical Group routinely analyses a wide range of environmental materials for a substantial number of radionuclides. Gamma-emitting nuclides can usually be determined with a minimum of preparative chemistry, depending upon total quantity present and concentration, whereas alpha-emitting and pure beta-emitting nuclides require radiochemical separation for quantitative determination. A wide variety of radiochemical procedures have been developed at different laboratories but there are no 'standard' methods because the methods are continually developing. Nevertheless, it is useful, as in this present series, periodically to draw together the methods which are in routine use at a laboratory and to discuss their development and application.

Since the first microgram quantities were produced during 1941, plutonium has probably been studied more intensively than any other element (Seaborg, Katz and Manning, 1949; Coleman, 1965). The motivation to investigate the physical, chemical and environmental behaviour of this 'man-made' element with such thoroughness has been more than purely academic. Long-lived nuclides of plutonium are now present in the environment in measurable quantities as a result of nuclear weapons' testing, nuclear power production, and accidental releases.

Americium and curium have not attracted so much attention, chiefly because their nuclides of major interest have, in general, half-lives shorter than those of plutonium. Nevertheless, together with plutonium they constitute, in radiological terms, a significant fraction of the low-level aqueous radioactive waste discharges which have arisen from the nuclear industry (Pentreath, 1988). It must also be borne in mind that ^{241}Am is generated in situ in the environment as a result of the decay of its parent, the beta-emitting nuclide ^{241}Pu. A separate report is being prepared on this nuclide (Boggis and Lovett, in preparation).

In order to obtain a proper understanding of the environmental impact of these 'man-made' elements and their potential return to man, it is essential to be able to make accurate determinations of their concentrations in a wide range of materials. Inevitably, much of the radioactive material released has found its way to the marine environment where its ultimate distribution will be determined by the way in which it reacts with this environment, coupled with the movement of the water masses. The accurate determination of the various nuclides of these elements in the water column is, therefore, a logical starting point towards a total understanding of their environmental behaviour.

Table 1 lists the environmentally-important alpha-emitting nuclides of the transuranium elements and provides details of their half-lives and principal energies. The concentration of these nuclides in filtered sea water is extremely variable; for example, the concentrations of $^{239+240}$Pu range from some 10^5 µBq l^{-1} in parts of the eastern Irish Sea, to less than 10 µBq l^{-1} in deep oceanic waters. The relative proportions of the different nuclides present is also variable, depending upon the source of release, the age of the material and the extent to which materials from different sources have become mixed. The source of release can often be identified from the unique isotopic signal of the actinide element nuclides present (Sholkovitz, 1983). Table 2 gives an indication of the variability of concentration and isotopic composition of plutonium, americium and curium in filtered sea water in different sea areas.

Table 1. Alpha-emitting transuranic nuclides of importance in the environment

Nuclide	Principal energy (MeV)	Half-life (years)
^{237}Np	4.788	2.14×10^6
^{238}Pu	5.499	87.70
^{239}Pu	5.156	2.41×10^4
^{240}Pu	5.168	6.55×10^3
^{241}Am	5.486	432
^{242}Cm	6.113	0.446
^{243}Cm	5.785	30.00
^{244}Cm	5.805	18.11

This table was compiled from data in ICRP (1983)

Table 2. Concentration in sea water filtered through a 0.22 μm filter

Cruise	Sea area	$^{239+240}Pu$ ($\mu Bq\ l^{-1}$)	^{238}Pu ($\mu Bq\ l^{-1}$)	^{241}Am ($\mu Bq\ l^{-1}$)	^{242}Cm ($\mu Bq\ l^{-1}$)	$^{243+244}Cm$ ($\mu Bq\ l^{-1}$)
CIR 7/81	Arctic Ocean	16.7	0.823	1.77	ND	ND
CIR 4/85	English Channel	29.9	18.7	4.96	0.598	3.03
CIR 4/84	Eastern Irish Sea	24 100	7 530	4 840	274	33.9

ND - Not determinable as analysed.

Numerous methods have been proposed for the extraction of plutonium, americium and curium from sea water but the most practical of these for use with large volume samples (say, up to 1000 litres) are based on coprecipitation with iron hydroxide (Wong, 1971), and this method provides the basis of the procedures described here.

2. Analytical techniques

The analytical procedures described in this report have evolved over the past fifteen years, changes having been incorporated as necessary to accommodate different sample sizes and working conditions, particularly on research vessels. There were three basic requirements:

(i) the procedures should be capable of eliminating both gravimetric and radiometric interferences;

(ii) the chemical and analytical manipulations should be made as simple as possible to cater for operation by staff with little knowledge of chemistry or who may well not be trained in analytical skills; and

(iii) the whole operation must have a proper regard for economy in the use of materials, equipment, time and manpower.

The successful determination of alpha-emitting nuclides by alpha spectrometry depends on the ability of the separation scheme to remove the following:

(i) all matter which would electrodeposit along with the determinand nuclides causing spectral degradation; and

(ii) any other alpha-emitting nuclides which would cause spectral interference. Such interferences are discussed in Sub-section 5.2.

It is fortunate that alpha-emitting nuclides such as ^{236}Pu or ^{242}Pu and ^{243}Am, which do not as yet occur in the environment in sufficient quantities to prejudice their use, are available in a pure state for use as yield monitors. Precise measurement of chemical recovery is unnecessary, because these isotopes are used as standards in isotope dilution analyses. The philosophy behind the use of such monitors was discussed in detail by Harvey and Lovett (1984) and their application in the present procedure is described in Section 3.

It is important to note that the techniques detailed here will not distinguish between ^{239}Pu and ^{240}Pu; they are, therefore, determined together and quoted as $^{239+240}Pu$. Such a separation can only be achieved using mass-spectrometric techniques. A similar situation pertains to ^{243}Cm and ^{244}Cm, although in this case the ^{244}Cm is far more likely to be present.

In order to extract the maximum analytical information from the analyses of sea water, it has always been the custom at DFR to filter the water through 0.22 µm or 0.45 µm membrane filters and to analyse the filtrate and particulate fractions separately (the determination of suspended load being carried out on a sub-sample). Plutonium, americium and curium are strongly particle reactive. The average distribution ratio (concentration on particulate matter/concentration in solution) for plutonium is $> 10^5$ and for americium and curium is $> 10^6$ (Kershaw _et al_., 1986). Such information can be of considerable value in studies of their environmental behaviour.

2.1 Sample collection and pre-treatment

In the past, surface seawater samples had usually been collected using the inbuilt pumping systems of the research vessels. Sub-surface samples have always been collected by devices (e.g. Niskin bottles and Gerard barrels) independent of the ship. Early in the 1980s, following the use of the ship for prolonged periods in the eastern Irish Sea, it became obvious that the ship's pumping system had become thoroughly contaminated and was introducing this contamination into samples in a random fashion long after the ship had left the Irish Sea. The extent of this contamination, and its implications, have already been discussed (Kershaw _et al_., 1986; Harvey, Lovett and Boggis, 1987). Following this discovery, all surface seawater samples have been taken with an acid-cleanable pumping system totally independent of that of the ship. Incidentally, it was the practice of analysing the sample in two fractions - filtrate and particulate - that enabled the extent of this problem to be identified reasonably quickly.

Another phenomenon has been noted at DFR which, although not introducing contamination, can seriously prejudice the determination of a reason-

ably accurate distribution ratio: when samples of high suspended load are filtered, the rate of filtration can become extremely slow resulting in the removal of normally soluble species onto the particulate material (Harvey, Lovett and Boggis, 1987). In such circumstances, this effect can be minimised by changing filters when the rate of filtration becomes slow.

2.2 Separation from the matrix

It is of fundamental importance in any radiochemical scheme to ensure complete chemical equilibration between the determinand and yield monitor before any treatment is given which could differentiate between them. The usual way to achieve this is to perform an unequivocal redox cycle. Of the elements being considered in this study, this is particularly important in the case of plutonium, which has the unique property of being able to exist in solution as an equilibrium mixture of all of its four common oxidation states (Pu^{3+}, Pu^{4+}, PuO_2^+ and PuO_2^{2+}). The equilibrium composition is dependent on the chemical make-up of the solution - in sea water it is most likely that the Pu^{4+} and PuO_2^+ oxidation states will predominate (Orlandini, Penrose and Nelson, 1986). Americium will be present in sea water predominantly in the trivalent form, Am^{3+}, but the possible existence of a small amount of pentavalent americium cannot be ruled out (Pentreath, Harvey and Lovett, 1985). There is no evidence that curium will be present in any state other than as Cm^{3+}.

Actinide elements in their lower oxidation states (M^{3+} and M^{4+}) will readily coprecipitate with small quantities of iron hydroxide (Figure 1) whereas in their higher oxidation states (MO_2^+ and MO_2^{2+}) they do not coprecipitate. Equilibration of the multivalent determinand with the added tracer is achieved by ensuring reduction to the lower oxidation states. This reduction is achieved either by adding sodium sulphite and Fe^{3+} to the acidified sea water and allowing it to stand for several hours, or by adding sodium sulphite and Fe^{2+} and allowing the sample to stand for at least 30 minutes. The reductive performance of both of these techniques, which are in current use at DFR, is shown in Figure 2(a) and (b). In general, for samples > 100 litres, the Fe^{3+}/SO_3^{2-} method is preferred because it generates less iron hydroxide which, therefore, facilitates filtration.

The comparative efficacy of these techniques is demonstrated in Table 3(a) and (b), which also shows comparison with a third technique - that of ashing a sample of sea water by repeated evaporation to dryness with nitric acid followed by dissolution and coprecipitation on iron hydroxide under reducing conditions.

2.3 Concentration

Following resolubilisation, the actinides are contained in dilute hydrochloric acid solution with up to 1 g of iron (from a 1000 litre sample). A convenient way to remove this iron is to coprecipitate the actinides onto calcium oxalate at pH ≃ 2 (Scott and Reynolds, 1975). This coprecipitation can be made quantitative providing the following criteria are met:

(i) the actinides are in their lower oxidation states;
(ii) the solution contains at least 100 mg Ca l^{-1}; and
(iii) the pH is adjusted to ≃ 2.

This coprecipitation provides a good preliminary decontamination step from many elements and anions.

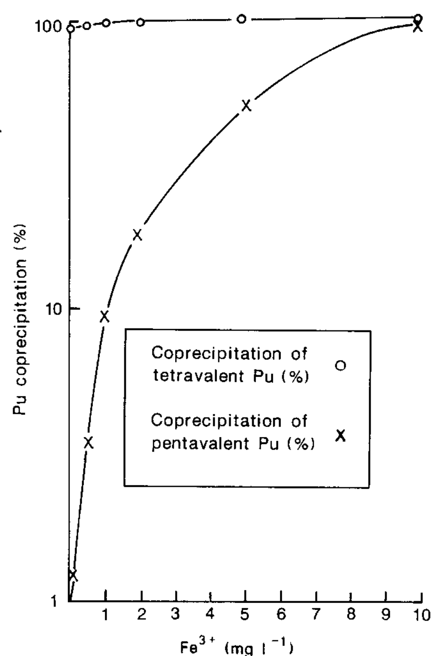

Figure 1 Graph showing the degree of coprecipitation of Pu^{4+} and PuO_2^+ in sea water on varying quantities of $Fe(OH)_3$.

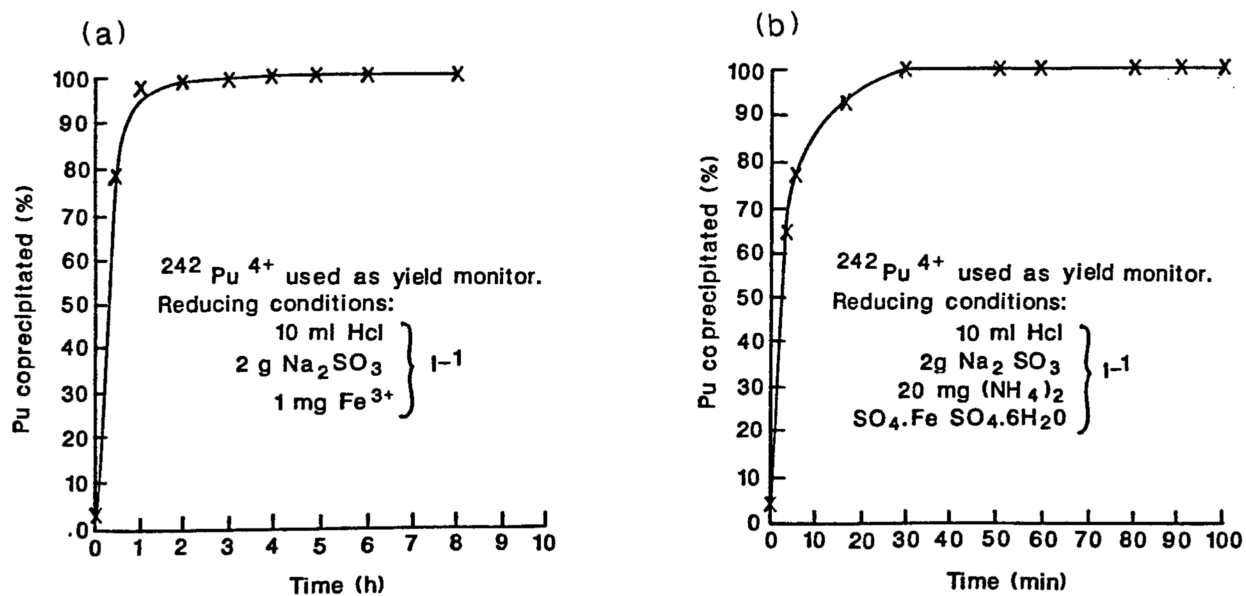

Figure 2 The reduction of $^{236}PuO_2^{2+}$ in sea water with time under reducing conditions: (a) Fe^{3+}/SO_3^{2-}; and (b) Fe^{2+}/SO_3^{2-}.

Table 3. Comparison of three different preconcentration techniques for the determination of: (a) $^{239+240}Pu$; and (b) ^{241}Am in filtered sea water ($\mu Bq\ l^{-1}$)

(a)

Sub-sample	Method I Fe^{3+}/SO_3^{2-}	Method II Fe^{2+}/SO_3^{2-}	Method III $Total/HNO_3$
1	5300 ± 124	5625 ± 144	5318 ± 138
2	5469 ± 138	5723 ± 125	5444 ± 147
3	5346 ± 130	5432 ± 114	5374 ± 134
4	5080 ± 119	5417 ± 116	5583 ± 139
5	5518 ± 131	5427 ± 147	5533 ± 142
6	5427 ± 126	5337 ± 116	5176 ± 133
7	5775 ± 146	5534 ± 117	5093 ± 136
8	5434 ± 109	5188 ± 115	5475 ± 154
9	5260 ± 106	5419 ± 125	5593 ± 137
10	5342 ± 107	5280 ± 128	5358 ± 135
11	5489 ± 113	5484 ± 128	5449 ± 140
Mean ± 1σ s.d.	5404 ± 175	5442 ± 150	5400 ± 159
Median	5427	5427	5444

(b)

Sub-sample	Method I Fe^{3+}/SO_3^{2-}	Method II Fe^{2+}/SO_3^{2-}	Method III $Total/HNO_3$
1	910 ± 29	954 ± 29	1019 ± 35
2	914 ± 29	940 ± 28	996 ± 33
3	957 ± 30	1015 ± 31	941 ± 33
4	933 ± 29	936 ± 29	999 ± 34
5	987 ± 29	923 ± 30	1022 ± 38
6	956 ± 29	951 ± 31	984 ± 33
7	1014 ± 31	993 ± 31	988 ± 34
8	950 ± 28	973 ± 30	1017 ± 32
9	975 ± 29	966 ± 30	997 ± 32
10	927 ± 28	943 ± 30	1006 ± 32
11	1017 ± 32	1018 ± 31	1003 ± 32
Mean ± 1σ s.d.	958 ± 37	965 ± 32	997 ± 22
Median	956	954	999

Errors quoted for the sub-sample measurements are ± 1σ counting propagated errors only.

Error quoted for the mean are the estimate of the imprecision on the replicate samples.

The seawater sample for this study was taken from the shoreline at St Bees, Cumbria. The water was filtered, mixed and then aliquoted in 10 litre portions - 10 litres was considered as a suitably large sample on which to carry out the wet ashing ($TOTAL/HNO_3$) technique.

The calcium oxalate is destroyed by ashing and, following dissolution in a few millilitres of dilute hydrochloric acid, the actinides are concentrated by coprecipitation with 5 mg Fe as $Fe(OH)_3$. This precipitate, dissolved in a few drops of hydrochloric acid and subsequently evaporated to dryness, provides a starting material of almost constant composition for the small-scale anion exchange separation and purification of the elements. Table 4 shows which of the main elements present at this stage of the analytical procedure form anionic complexes with > 6M HCl and 8M HNO_3.

Table 4. Illustration of the ability of some elements to form anionic complexes in two different media

Ion	> 6M HCl	8M HNO_3
Pu^{4+}	Yes	Yes
Am^{3+}	No	No
Cm^{3+}	No	No
Th^{4+}	No	Yes
UO^{2+}	Yes	No
Fe^{3+}	Yes	No

Table 5. Passage of Am through an anion exchange column in the chloride form

Volume (ml) of 9M HCl/0.35M HNO_3	Am (%)
1 (sample)	5
2 (wash)	75
3 "	17
4 "	2
5 "	1
6 "	0
7 "	0
8 "	0

2.4 Purification of plutonium

The purification of plutonium is carried out by anion exchange (Wong, 1971) making use of the multiplicity of its valence states. Plutonium is maintained in its tetravalent state in 9M HCl/0.35M HNO_3 solution in which it forms an anionic complex ($PuCl_6^{2-}$). This complex is strongly adsorbed by the ion exchange resin, whereas americium and curium, being trivalent, do not form anionic complexes in this medium and in consequence pass through the column. The pattern of the passage of americium through the column is given in Table 5. Thorium, although tetravalent, does not form an anionic complex in hydrochloric acid and accompanies the americium. The ferric iron carrier, on the other hand, does form an anionic complex in this medium and so is adsorbed onto the resin.

The column is washed with 8M HNO_3 to remove the ferric iron (and incidentally uranium) - ferric iron being released because it does not form an anionic complex in nitric acid. After thoroughly removing nitrate from the column with 11.3M HCl, the plutonium is eluted with 11.3M HCl which is 0.1M with respect to ammonium iodide. The iodide ion in strong hydrochloric acid reduces the plutonium from its tetravalent to its trivalent state. In its trivalent state, plutonium does not form an anionic complex and thus is released from the column. The elution of the plutonium is given in Table 6.

2.5 Purification of americium

Following the previous stages, americium and curium are contained in a small volume of strong hydrochloric acid. Most of the thorium and lanthanide-type elements originally in the sample will be present, together

Table 6. Elution of Pu from an anion exchange column as Pu^{3+}

Volume (ml) of 11.3M HCl/0.1M NH_4I	Pu (%)
1	0
2	8
3	76
4	14
5	2
6	0
7	0
8	0

Table 7. Passage of Am through an anion exchange column in the nitrate form

Volume (ml) of 8M HNO_3	Am (%)
1 (sample)	3
2 (wash)	56
3 "	33
4 "	7
5 "	1
6 "	0

with perhaps traces of plutonium and possibly other elements. After ensuring the complete removal of chloride by evaporation with excess nitric acid, the sample is dissolved in 8M HNO_3 and passed through an anion exchange column. In this medium, thorium and plutonium (both tetravalent) form anionic nitrate complexes and are adsorbed by the resin, whereas trivalent americium and curium do not form complexes and thus pass through the column. The passage of americium through the column is given in Table 7.

Traces of many elements, such as the transition elements, can be eliminated by coprecipitating the americium with 5 mg Bi as $BiPO_4$ from an acid solution (approximately pH 1.5). This stage may not always be necessary in sea water analyses; however, it is included here because even traces of these other elements will degrade the alpha spectrum, and because it presents the americium in a suitable form for the next stage of the process, which is the removal of the lanthanide-type elements.

The bismuth phosphate precipitate is dissolved in a small volume of 4M NH_4SCN solution with the addition of a few milligrams of hydrazine hydrochloride; it is then applied to an anion exchange column. The function of the hydrazine hydrochloride is to provide a source of a small quantity of acid without the concomitant dilution of the thiocyanate, and to ensure that any cerium present is in the trivalent oxidation state. The thiocyanate complexes of americium and curium are more strongly adsorbed by the anion resin than those of the lanthanides which are consequently washed through the column with a further 20 ml of 4M NH_4SCN solution. The passage of the lanthanides through the column is illustrated by the behaviour of ^{144}Ce and is given in Table 8.

Following elution with 1M HCl (Table 9), the americium and curium are adsorbed onto a cation exchange column from which, following washing with 1M HCl to remove excess thiocyanate, they are eluted with 6M HCl (Table 10).

2.6 Source preparation

The 'weightless' source is the ideal to which all analysts strive in the analyses for alpha-emitting nuclides. Although other physical techniques such as thermal volatilisation or evaporation are available, electrodeposition, because of its simplicity and reproducibility, is the technique which is used by the majority of analysts. Full details of the electrodeposition technique in current use at this laboratory are given in

Table 8. Removal of lanthanide elements from an anion exchange resin in thiocyanate solution

Volume (ml) of 4M NH_4SCN		^{144}Ce (%)
1	(sample)	0
2	(wash)	0
3	"	0.4
4	"	4.2
5	"	12.6
6	"	19.7
7	"	20.6
8	"	16.3
9	"	11.2
10	"	6.8
11	"	3.8
12	"	2.0
13	"	1.1
14	"	0.6
15+16	"	0.4
17+18	"	0.1
19+20	"	0.1

Table 9. Elution of Am from a thiocyanate column

Volume (ml) of 1M HCl	Am (%)
1	0.7
2	26.2
3	41.8
4	17.6
5	8.1
6	3.4
7	1.2
8	0.5
9	0.3
10	0.2

Table 10. Elution of Am from a cation exchange column

Volume (ml) of 6M HCl	Am (%)
1	0
2	10.6
3	58.5
4	23.2
5	5.9
6	1.3
7	0.3
8	0.1
9	0
10	0

Appendix A5.1, Step 14. The apparatus used is shown in Figure 3 and the performance of the electrodeposition is given in Table 11. Many recipes for electrodeposition of actinides are published in the literature: see, for example, Puphal and Olsen (1972); Talvitie (1972); Kressin (1977); and Hallstadius (1984).

Although more quantitative deposition can be obtained (for example, using an ammonium sulphate medium), in our experience, a higher quality source is produced with the ammonium oxalate medium and we have, therefore, made a deliberate choice to sacrifice 5-10% of yield in favour of enhanced quality.

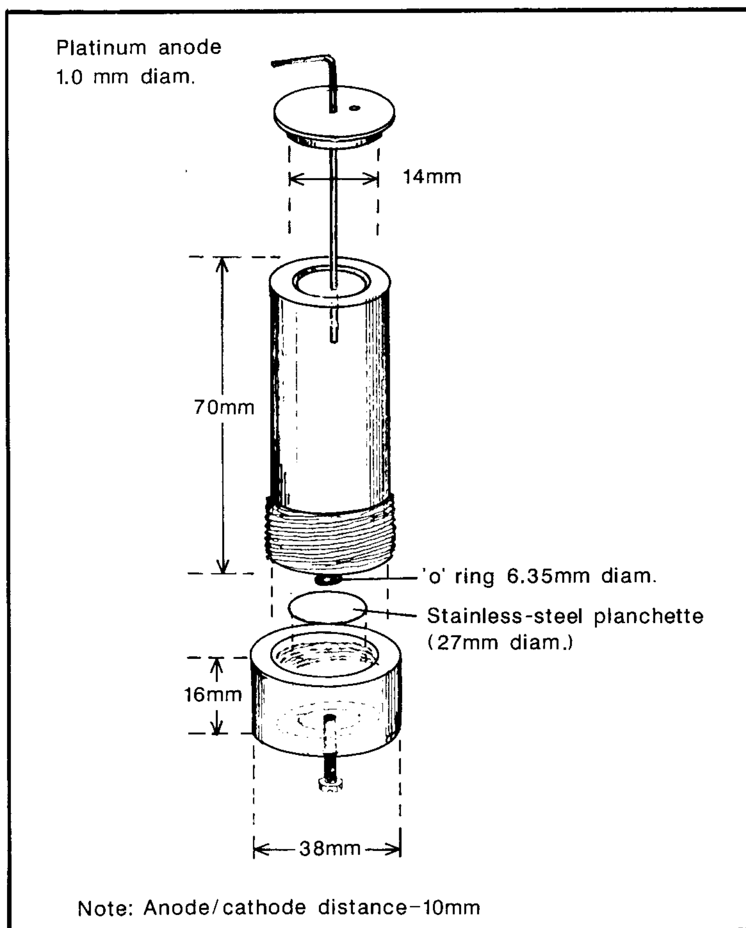

Figure 3 The electrodeposition cell.

Table 11. Electrodeposition from ammonium oxalate solution at pH 2 and a constant current of 200 mA

Time elapsed (h)	Deposition (%)	
	Pu	Am
0.5	1	2
1.0	41	44
1.5	76	79
2.0	89	92
2.5	92	96

The electrodepositional operation can be quickened by increasing the current density but we have chosen to avoid this because the extra heat evolved would require the use of a more complex, cooled electrodeposition cell with an associated increase in cost.

The radiochemical separations are shown schematically in Figure 4 and full laboratory working details are given in the Appendix, together with practical notes for the analyst.

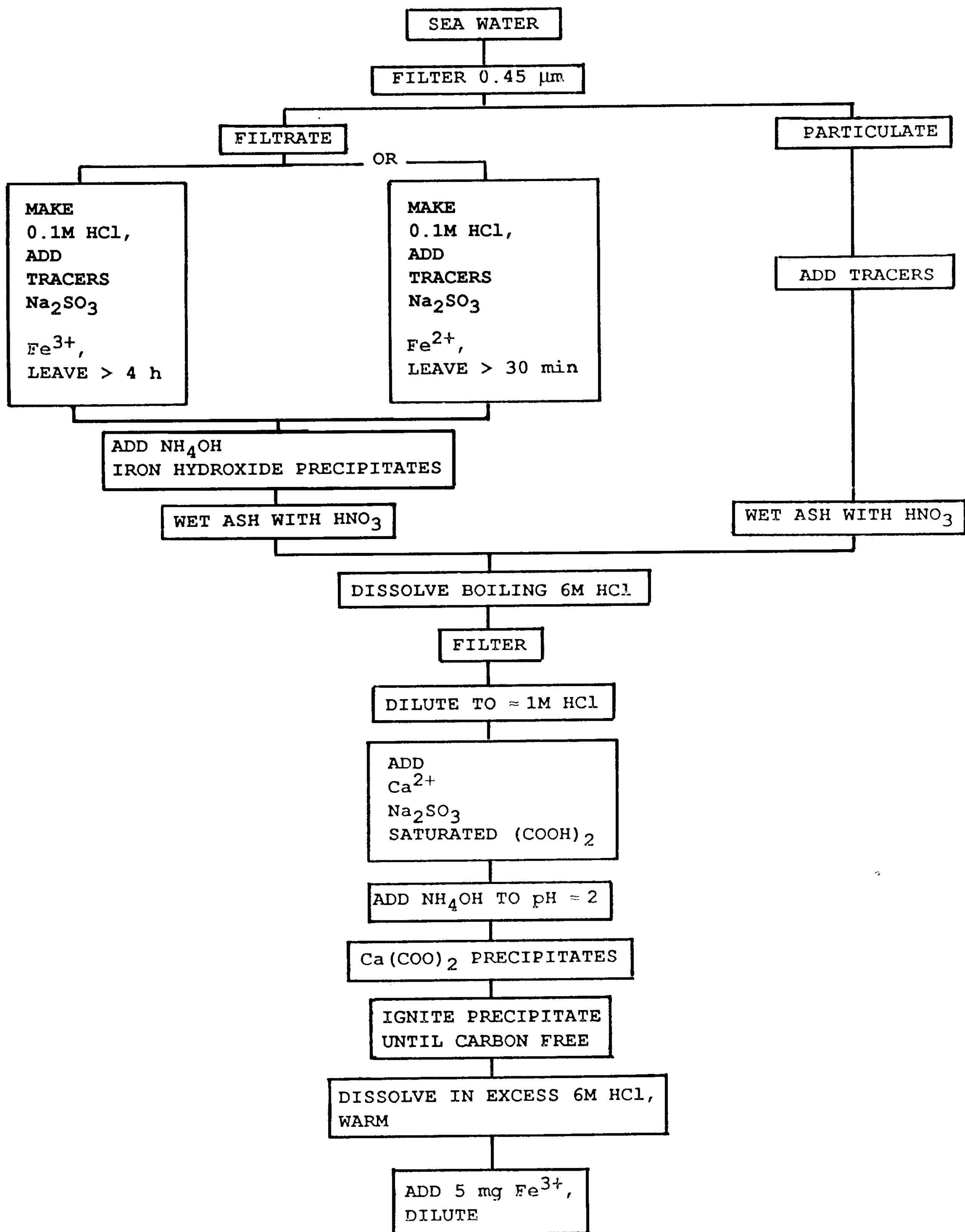

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Figure 4 Schematic diagram of the analytical method.

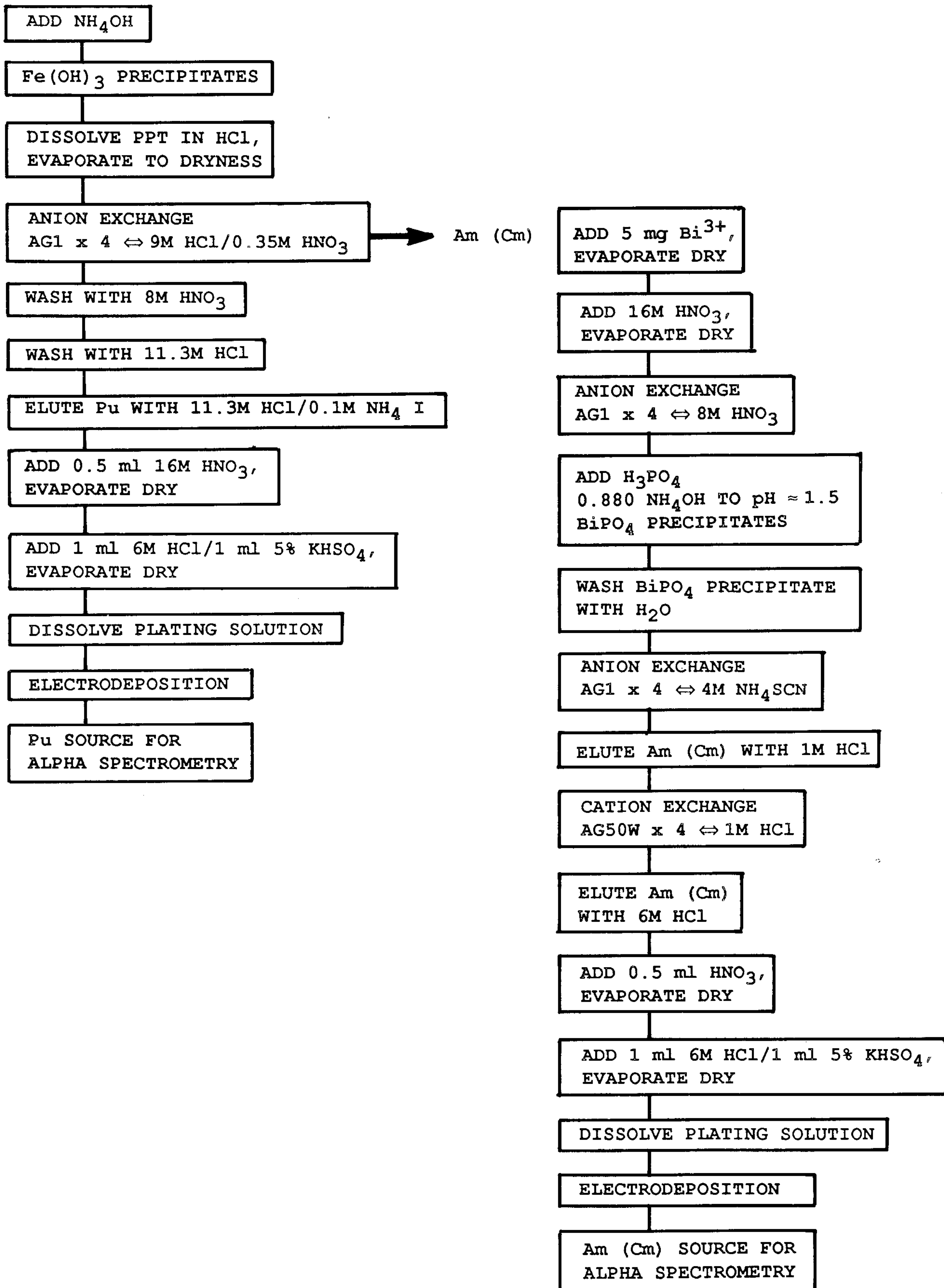

Figure 4 continued.

3. Yield tracers

In any analysis where sub-microgram quantities of the determinand are to be isolated and quantified from large amounts of matrix material, by a complex series of chemical manipulations, the need for a reliable chemical recovery measurement is obvious. As noted in Section 2, ^{236}Pu, ^{242}Pu and ^{243}Am are all available in isotopically pure forms and can be used as yield tracers for the determination of plutonium and americium nuclides. It is generally considered that in most chemical manipulations there is no chemical differentiation between americium and curium. However, we have found that this cannot be assumed and that any procedures adopted must be carefully checked. The techniques described here do not significantly discriminate against curium relative to americium, as is given in Table 12 and, in consequence, the ^{243}Am tracer is also suitable as a simultaneous tracer for curium isotopes. As yet, none of these yield monitors appears in the environment in sufficient quantity to prejudice its use for this purpose, but one must always be mindful of this possibility.

Table 12. Mean Am/Cm ratio, initially and after one and two complete analytical cycles

	Mean Am/Cm ratio
Initially	1.242 ± 0.034
After 1 cycle	1.230 ± 0.040
After 2 cycles	1.239 ± 0.028

Errors quoted are ± 1σ errors.
Each ratio is a mean of four separate determinations.

Considerable care is needed if success is to be assured in the application of these tracers as yield monitors. The spectral quality of an alpha spectrum is very easily degraded by a number of factors including poor source quality and inadequate instrumentation. (Spectral interferences are discussed in more detail in Sub-section 5.2.) Such spectral degradation may often impair the resolution of alpha peaks, one from another, with the result that analytical uncertainties are increased, but it is clear that the analyst should aim to produce sources of the highest possible quality (see Sub-section 2.6). As far as is practicable, the analyst should also attempt to match the amount of tracer added to the amount of determinand nuclide(s) present in the sample. Thus, because of the relative alpha energies of the tracer and the determinands, it is important to avoid overspiking when ^{236}Pu is used as a yield monitor in the analysis of ^{238}Pu and $^{239/240}Pu$. The converse is true when ^{242}Pu is used as a yield monitor in this analysis or when ^{243}Am is used in the analysis of ^{241}Am. Nothing is gained by adding excess yield monitor, as it can be demonstrated that counting statistics are optimised when the number of counts recorded for yield monitor and determinand are approximately equal. It is, therefore, the practice at DFR to try to add a quantity of yield monitor activity similar to that expected for the most abundant determinand nuclide in the sample.

It is also the custom at DFR to purify enough tracer (by ion exchange procedures) to meet the requirements for normal use for approximately 3 years. All tracers are calibrated at yearly intervals against standard solutions of ^{241}Am and ^{238}Pu which are readily available from establishments such as Amersham International plc. The tracers themselves are available from, or can be made by, Isotopes Division, AERE, Harwell.

4. Radiometric assay

The prepared sources are counted on silicon surface barrier detectors (150 mm^2 active surface area) linked to routed multi-channel analysers. Typical spectra obtained for plutonium, americium and curium analyses are shown in Table 13(a) and (b) respectively.

The size of sample is chosen in such a way that it will contain approximately 4, 0.4, 0.04, 0.004 or 0.0004 Bq of the principal determinand nuclide. [These activity levels were chosen so that a 1σ precision or better than 5% could be obtained in a reasonable ($\ngtr$ 6 weeks) counting time for all except the very lowest level samples.] Counters are dedicated to counting 4-0.4, 0.04 and 0.004-0.0004 Bq level samples to avoid the risk of contaminating very low background detectors.

Table 13(a). An alpha spectrum of a Pu source from an English Channel sample

Time (min)	Counts recorded								
29686	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	1	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	1	0	
	0	0	0	0	0	1	0	0	
	0	0	0	1	0	0	0	0	
	0	0	0	0	1	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	1	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	1	0	0	0	0	1	0	1	
	1	1	1	3	5	2	16	18	} ^{242}Pu
	34	48	113	136	243	340	412	549	
	596	693	635	507	305	83	20	3	
	0	0	0	1	1	0	0	1	
	2	2	1	1	1	3	1	4	} $^{239+240}Pu$
	5	9	18	37	53	100	119	191	
	228	297	311	361	316	213	90	22	
	3	0	1	0	0	0	0	2	
	0	4	3	7	8	19	32	59	} ^{238}Pu
	67	92	132	169	209	209	228	213	
	122	46	8	1	0	0	0	0	
	0	0	0	0	0	0	0	1	
	0	0	0	1	0	2	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	1	0	0	0	0	1	0	0	
	0	0	1	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	

Table 13(b). An alpha spectrum of an Am source from an English Channel sample

Time (min)									
14185	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	1	
	0	0	0	0	0	0	0	0	
	1	0	1	0	0	0	0	1	
	0	0	1	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	2	0	0	0	
	2	0	0	2	3	4	7	17	
	12	18	27	48	52	91	141	172	^{243}Am
	238	210	152	85	34	28	22	24	
	20	10	6	5	5	9	6	17	
	16	25	46	70	97	138	146	200	^{241}Am
	220	224	127	79	54	40	16	14	
	7	1	0	0	0	1	0	0	
	0	0	0	2	2	0	1	2	
	2	0	8	13	29	27	55	64	$^{243+244}Cm$
	74	110	125	107	93	33	8	0	
	0	0	0	0	0	0	0	0	
	0	0	1	0	0	1	0	0	
	0	0	1	2	1	3	1	6	^{242}Cm
	11	8	16	15	19	12	8	3	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	1	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	0	0	0	0	0	0	
	0	0	1	0	0	0	0	0	

5. Sources of error

5.1 Sample collection and preliminary treatment

Errors can occur at any stage in an analytical procedure, from the collection of the sample to the calculation and presentation of the final data. Some are predictable and can be taken into account and thus minimised by the careful analyst. Others, less predictable, can pass unnoticed for considerable periods of time causing systematic bias in the data produced. Errors such as these are quite likely to occur in sample collection and pretreatment. Two such sources of error have been identified in Sub-section 2.1.

Another well known source of error is adsorption of chemical species onto container walls. Acidification of a sample is often carried out to prevent this but frequently this only diminishes the extent of adsorption. Table 14 illustrates this point and shows the extent of adsorption of ^{241}Am from filtered sea water onto the walls of 25-litre polythene containers for sea water at normal pH and acidified to pH 1. Clearly, if tracer addition is not carried out immediately after filtration, a differential loss of determinand can result; if the container is not thoroughly rinsed with strong acid, a serious loss in yield can occur.

Table 14. Percentage of ^{241}Am remaining in solution in sea water at normal pH (pH 8) and sea water acidified to pH 1 with HCl

Time (weeks)	^{241}Am (%) remaining in solution	
	pH 8	pH 1
0	100	100
1	69	97
2	46	94
4	-	88
6	-	83
8	-	78
10	-	73

5.2 Analytical errors

Probably the major source of error in any radiochemical technique lies in the possible lack of chemical equilibration between the tracer and determinand. In aqueous samples this stems from two primary causes:

(i) the determinand may be present as a complexed chemical species and, unless the chemical treatment is sufficiently rigorous to break down this complex, the uncomplexed tracer cannot possibly equilibrate with it;

(ii) the determinand may be in a different oxidation state from that of the tracer (see Sub-section 2.2).

Spectral interference between peaks in an alpha spectrum increases the uncertainty of the analyses and, where such interference becomes severe, it may be impossible to obtain the correct answer for a given nuclide. Spectral degradation occurs on the low-energy side of the peak such that nuclides of higher energy will, to a greater or lesser extent, interfere with the measurement of those of lower energy. The extent of the interference depends upon the degree of spectral degradation, the proximity of the relevant peaks and the relative amounts of the various nuclides present.

Table 3(a) and (b) gives the results of concentration by coprecipitation versus an unequivocal chemical ashing technique. The results indicate that complete chemical equilibration has been achieved for Pu (analysis of variance [ANOVA] shows no significant difference between the three methods at $P < 0.1$); however, for americium, for reasons which we cannot as yet explain, equilibration may not have been complete for the coprecipitation techniques (ANOVA for methods I and II versus method III shows a significant difference at $P < 0.1$ although there is no significant difference at $P < 0.02$).

Biased data can also be produced if contamination is introduced. There are two main mechanisms for this:

(i) methodological contamination, through purely random events such as analysing high- and low-level samples together and prejudicing the low-level samples; or

(ii) deliberate but unplanned contamination from, for example, injudicious use of tracers (see Section 3).

6. Method performance

6.1 Decontamination

The major nuclides likely to interfere alpha-spectrometrically with the determination of plutonium, americium and curium are shown in Figure 5(a) and (b).

Experimental decontamination factors (shown in Table 15) have been determined by adding relatively large amounts (≃ 350 Bq) of an alpha-emitting nuclide of the interfering element to an acid extract of sediment containing 0.02 Bq of tracer, then determining the quantity of the added isotopes on the final sources.

Table 15. Experimental decontamination factors

Interfering element	Decontamination factor	
	Pu analysis	Am analysis
Am	10^5	-
Pu	-	10^5
U	3×10^5	10^5
Th	10^4	2×10^4
Po	5×10^5	10^5
Ra	8×10^3	2×10^5
Bi	8×10^4	8×10^4
Rn	3×10^4	3×10^4

6.2 Chemical recovery

Typical chemical recoveries from recent cruises are shown in Table 16 for a range of sample volumes. It would be considered to be unsatisfactory if average recoveries were to fall below 60%.

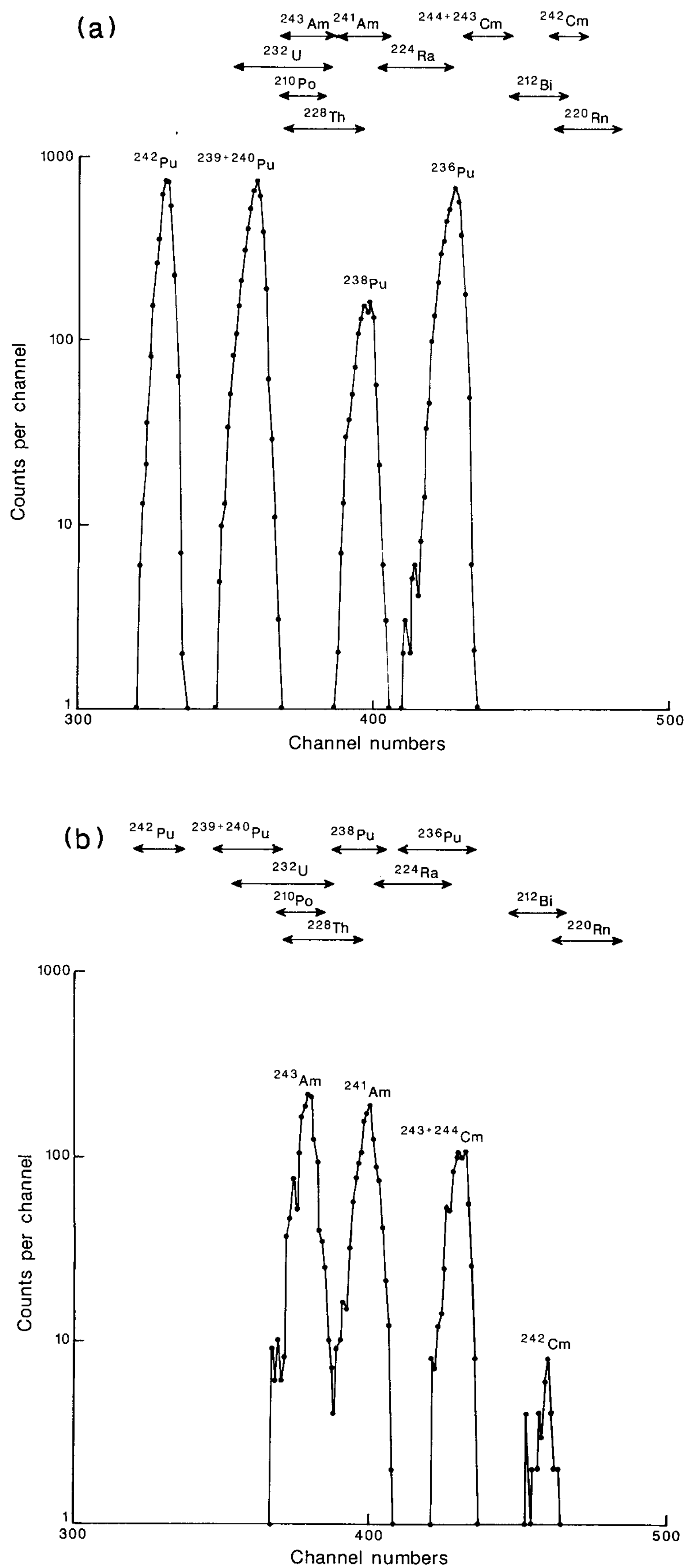

Figure 5 Plutonium spectra (a) and americium spectra (b) showing the position of the most likely interfering nuclides.

Table 16. Average recoveries for a range of sample sizes from three recent cruises

Volume (l)	No. of samples	Pu			Am		
		Mean	Median	Range	Mean	Median	Range
600	21	75	76	63-84	72	72	55-81
100	16	74	75	64-81	64	66	42-77
10	9	86	86	79-90	79	81	67-85

7. Quality assurance (QA)

Steps are taken to assure the continuing quality of the data in three main ways:

(a) Good housekeeping

Samples are divided into levels, in such a way that the main determinand activity is equivalent to one of five levels (4, 0.4, 0.04, 0.004 or 0.0004 Bq) in the total sample. Laboratory areas, apparatus and reagents are dedicated to each of the five levels. Where appropriate, equipment is not re-used. For example, some research samples cost many hundreds of pounds to collect and it would be economic nonsense to prejudice the analysis by re-using apparatus, costing a few pounds, which might be contaminated.

(b) Blanks and quality control (QC)

Blank and QC analyses are carried out with each batch of samples to assure the continuing precision of the analytical data. Some 12% of the analytical effort is devoted to blank and QC determinations. A summary of the appropriate QC data for a 5-year period is given in Table 17(a-c). Americium figures can only be compared directly between levels; they cannot be compared between years, because of the incremental increase in the ^{241}Am value due to grow-in from the ^{241}Pu parent.

Blank samples are rarely found to contain more than 0.1% of the appropriate level of sample activity.

(c) Intercomparisons

Repetitive analysis of a QC sample provides an excellent demonstration of the precision with which the analytical procedure can be carried out. However, it provides no indication as to how accurate the result may be relative to the true value for the determinand concentration in the sample. This can only be demonstrated by applying the technique to an appropriate environmental matrix with a certified determinand concentration. For sea water, no such matrix standard exists and intercomparison exercises provide the best alternative means of demonstrating the validity of an analytical procedure. By such intercomparison exercises (Whitehead, 1986) (where DFR is laboratory no. 10) the method described in this report has been shown to give very reliable results even at 'fall-out' concentrations of Pu and Am in sea water. These, incidentally, have the added advantage of subjecting the analytical procedure used to peer review.

Table 17. Comparison of QC data over a 5-year period and at 5 orders of magnitude (Bq ml^{-1}) for: (a) $^{239+240}Pu$; (b) ^{238}Pu; and (c) ^{241}Am

(a)

Total no. of Bq in sample analysed	1983	1984	1985	1986	1987
4	0.273 (9)	0.273 (14)	0.275 (6)	0.272 (19)	0.276 (6)
0.4	0.270 (12)	0.270 (12)	0.268 (5)	0.275 (9)	0.275 (6)
0.04	0.280 (11)	0.280 (12)	0.276 (9)	0.282 (8)	0.277 (8)
0.004	0.271 (10)	0.280 (12)	0.280 (14)	0.288 (15)	0.279 (6)
0.0004	NA	0.269 (11)	0.277 (2)	0.296 (1)	0.265 (6)

(b)

4	0.0604 (9)	0.0592 (14)	0.0600 (6)	0.0585 (19)	0.0587 (6)
0.4	0.0598 (12)	0.0592 (12)	0.0558 (5)	0.0593 (9)	0.0588 (6)
0.04	0.0613 (11)	0.0596 (12)	0.0608 (9)	0.0618 (8)	0.0590 (8)
0.004	0.0622 (10)	0.0609 (12)	0.0599 (14)	0.0627 (15)	0.0605 (6)
0.0004	NA	0.0583 (6)	0.0566 (2)	0.0500 (1)	0.0537 (6)

(c)

4	0.506 (8)	0.518 (15)	0.529 (8)	0.540 (16)	0.543 (5)
0.4	0.500 (12)	0.516 (12)	0.528 (6)	0.539 (9)	0.543 (9)
0.04	0.508 (10)	0.512 (12)	0.526 (6)	0.554 (8)	0.541 (3)
0.004	0.512 (10)	0.520 (12)	0.537 (10)	0.551 (13)	0.532 (4)
0.0004	NA	0.514 (6)	0.546 (3)	NA	0.504 (6)

( ) - denotes the number of separate determinations.

The QC sample is a marine sediment extract diluted to the appropriate level.

For Pu nuclides, a two-way ANOVA of these data shows no 'levels' effect nor 'between years' effect at $P < 0.1$.

For ^{241}Am, a two-way ANOVA carried out between levels shows no significant difference at $P < 0.1$ for any one of the years.

For ^{241}Am data, figures can only be compared between levels <u>not</u> years, as no allowance has been made for grow-in from the ^{241}Pu parent.

NA - No analyses undertaken.

Disclaimer: The reference to proprietary products in this report should not be construed as an official endorsement of these products, nor is any criticism implied of similar products which have not been mentioned.

8. References

BOGGIS, S. J. and LOVETT, M. B., in preparation. The determination of plutonium-241 in environmental materials. To be published in the Aquatic Environment Protection: Analytical Methods series. MAFF, Directorate of Fisheries Research, Lowestoft.

COLEMAN, G. H., 1965. 'The Radiochemistry of Plutonium'. USAEC, Oak Ridge, Tennessee, NAS-NS 3058, 184 pp.

HALLSTADIUS, L., 1984. A method for the electrodeposition of actinides. Nucl. Instrum. Meth. Phys. Res., 223: 266-267.

HARVEY, B. R. and LOVETT, M. B., 1984. The use of yield tracers for the determination of alpha-emitting actinides in the marine environment. Nucl. Instrum. Meth. Phys. Res., 223: 224-234.

HARVEY, B. R., LOVETT, M. B. and BOGGIS, S. J., 1987. Some experiences in controlling contamination of environmental materials during sampling and processing for low-level actinide analysis. J. Radioanalyt. Nucl. Chem. Art., 115: 357-368.

INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION, 1983. Radionuclide transformations. Energy and intensity of emissions. Annals ICRP, 11-13. Pergamon Press, Oxford, 1250 pp. (ICRP Publ. (38)).

KERSHAW, P. J., PENTREATH, R. J., HARVEY, B. R., LOVETT, M. B. and BOGGIS, S. J., 1986. Apparent distribution coefficients of transuranium elements in UK coastal waters. pp.277-287. In: 'Application of Distribution Coefficients to Radiological Assessment Models', T. H. Sibley, and C. Myttenaere (Eds.). Elsevier Applied Science Publishers, London and New York, 430 pp.

KRESSIN, I. K., 1977. Electrodeposition of plutonium and americium for high resolution α-spectrometry. Analyt. Chem., 49: 842-845.

ORLANDINI, K. A., PENROSE, W. R. and NELSON, D. M., 1986. Pu(V) as the stable form of oxidised plutonium in natural waters. Mar. Chem., 18: 49-57.

PENTREATH, R. J., 1988. Sources of artificial radionuclides in the marine environment. pp.12-34. In: 'Radionuclides: a Tool for Oceanography', J. C. Guary, P. Guegueniat and R. J. Pentreath (Eds.). Elsevier Applied Science Publishers, London and New York, 461 pp.

PENTREATH, R. J., HARVEY, B. R. and LOVETT, M. B., 1985. Chemical speciation of transuranium nuclides discharged into the marine environment. pp.312-325. In: 'Speciation of Fission and Activation Products in the Environment', R. A. Bulman and J. R. Cooper (Eds.). Elsevier Applied Science Publishers, London and New York, 437 pp.

PUPHAL, K. W. and OLSEN, D. R., 1972. Electrodeposition of alpha-emitting nuclides from a mixed oxalate-chloride electrolyte. Analyt. Chem., 44: 284-289.

SCOTT, T. G. and REYNOLDS, S. A., 1975. Determination of plutonium in environmental samples. Part II: Procedures. Radiochem. Radioanalyt. Lett., 23: 275-281.

SEABORG, G. T., KATZ, J. J. and MANNING, W. M. (Editors), 1949. 'The Trans-uranium Elements'. Research Papers, Vol. 14, Parts 1 and 2. McGraw-Hill Book Co. Inc., New York, Toronto and London. Reproduced by University Microfilms International, Ann Arbor, Michigan and London, England, 859 pp.

SHOLKOVITZ, E. R., 1983. The geochemistry of plutonium in fresh and marine water environments. Earth Sci. Rev., 19: 95-161.

TALVITIE, N. A., 1972. Electrodeposition of actinides for alpha spectrometric determination. Analyt. Chem., 44: 280-283.

WHITEHEAD, N. E., 1986. Results of intercalibration exercises on low-level radionuclide measurements by the CRESP participating laboratories. CRESP Task Group Meeting, Neuchatel, Switzerland, June 1986, 8 pp. (unpublished mimeograph).

WONG, K. M., 1971. Radiochemical determination of plutonium in seawater, sediments and marine organisms. Analyt. Chim. Acta, 50: 355-364.

Appendix - Laboratory procedures

A1. Reagents

Analytical grade reagents are suitable unless otherwise stated. Reagents can be stored in polythene bottles unless alternative container materials are specified. Distilled or deionized water should be used throughout.

A1.1 Sodium sulphite solution (20% w/v)

Dissolve 200 g of anhydrous Na_2SO_3 in water and make up to 1 litre. The solution should then be filtered.

A1.2 Ferric iron solution (5 mg Fe^{3+} ml^{-1})

Dissolve 24.2 g of ferric chloride ($FeCl_3.6H_2O$) in 6M HCl and dilute to 1 litre.

A1.3 Calcium solution (25 mg Ca^{2+} ml^{-1})

Dissolve 62.5 g of calcium carbonate ($CaCO_3$) in 3M HCl and dilute to 1 litre.

A1.4 Methyl violet indicator (0.1% w/v)

Dissolve 1 g of methyl violet in 1 litre of water

A1.5 Ion exchange resins

Ion exchange procedures described in this report refer to the use of BioRad AG1 x 4 (100-200 mesh) anion exchanger or BioRad AG50w x 4 (100-200 mesh) cation exchanger. Before use, all resins are washed with 6M HCl (and then water where appropriate). Equilibration is then carried out by passing 5 column volumes of the sample matrix solution through the resin before applying the sample.

Ultra-high-purity acids (such as Aristar grade) are recommended for use in all the ion exchange work.

A1.6 Solution A (9M HCl/0.35M HNO_3)

Mix 180 ml of 11.3M HCl (Aristar) with 5 ml of 16M HNO_3 (Aristar) and dilute to 226 ml with deionized water. This solution should be prepared just prior to use.

A1.7 Hydrochloric acid/ammonium iodide reagent (11.3M HCl/0.1M NH_4I)

Dissolve 1.47 g of NH_4I in 100 ml of 11.3M HCl (Aristar). This solution should be prepared just prior to use.

A1. 8 Ammonium thiocyanate solution (4M NH_4SCN)

Dissolve 304.9 g of NH_4SCN in deionized water and make up to 1 litre. Pass the solution through a column of BioRad AG1 x 4 (100-200 mesh) anion exchange resin to remove traces of iron. This solution must be stored in the dark to retard decomposition.

A1. 9 Potassium hydrogen sulphate (5% w/v)

Dissolve 50 g of $KHSO_4$ in deionized water and make up to 1 litre.

A1.10 Bismuth solution (5 mg Bi^{3+} ml^{-1})

Dissolve 11.6 g of bismuth nitrate [$Bi(NO_3)_3.2H_2O$] in 3M HNO_3 and make up to 1 litre with 3M HNO_3.

A1.11 Electrodeposition solution

Dissolve 24 g of ammonium oxalate [$(COONH_4)_2.H_2O$] in distilled water, add 16 ml of 11.3M HCl and make up to 1 litre.

A1.12 Ferrous iron solution (20 mg ammonium ferrous sulphate ml^{-1})

Dissolve 20 g of ammonium ferrous sulphate [$(NH_4)_2Fe(SO_4)_2.12H_2O$] in 1M H_2SO_4 and make up to 1 litre. The solution should be freshly prepared when required.

A2. Hazards

In addition to observing normal standards of safety in the chemical laboratory, reference should be made to the Ionizing Radiation Regulations (1985) which govern the handling of radionuclides, such as the yield tracers specified in the procedures.

A3. Preparation of yield tracers

After purification by ion exchange, tracers are diluted to a suitable level (~ 4 Bq ml^{-1}) in a 6M HCl medium. These tracers are calibrated at this level by preparing mixed sources using standard ^{238}Pu and ^{241}Am solutions. Appropriate order of magnitude dilutions are made from this calibrated solution and stored in a 6M HCl medium.

A4. Apparatus

1. A centrifuge capable of handling 1-litre sample containers is required for the procedure as specified.

2. Electrodeposition cells (as shown in Figure 3) can be made from Perspex or other suitable material. A power supply capable of delivering a constant direct current of 200 mA per cell is also required.

3. Silicon surface barrier alpha detectors with an active area of 150 mm^2 are suitable. For very-low-level work, it is our policy to purchase these detectors untested to avoid contamination by ^{241}Am (sputtered from the test source).

A5. Practical analytical procedures

A5.1 Ferric iron/sodium sulphite method

Step	Experimental procedure	Notes
1.	The seawater sample is filtered through a 0.45 µm membrane filter. The filter with the particulate material is reserved for subsequent analysis (see Section A5.3).	That which passes through the 0.45 µm filter is defined as being soluble.
2.	To the filtrate add, successively and with thorough mixing, appropriate quantities of ^{236}Pu or ^{242}Pu and ^{243}Am tracers. Then to each litre of filtrate, add 10 ml of 11.3M HCl, 10 ml of Na_2SO_3 solution and 1 mg of Fe^{3+}. Leave for at least 4 h.	
3.	Add, to each litre of filtrate, with thorough mixing, 10 ml of 0.880 ammonia solution. Filter through a 0.45 µm filter and reject the filtrate.	
4.	Transfer the filter to a beaker, add 25 ml of 16M HNO_3 and evaporate under a clock glass to dryness. Add a few ml of 16M HNO_3 and evaporate to dryness.	
5.	Dissolve in ~ 100 ml of boiling 6M HCl. Filter. Reject the filter.	
6.	Dilute the filtrate to 700 ml and add 100 mg of Ca^{2+}, 10 ml of Na_2SO_3 solution and 100 ml of saturated $(COOH)_2$ solution. Adjust the pH to ~ 2 with 0.880 ammonia solution using methyl violet as an indicator. Stand for at least 1 h.	The action of SO_2 can 'fade' the indicator. pH papers are often used.
7.	Filter off the precipitated $Ca(COO)_2$. Reject the filtrate. Transfer the filter to a platinum crucible and ignite until carbon-free.	A pure white residue may not result owing to coprecipitation of small amounts of Fe.
8.	Transfer the ash to a 50 ml centrifuge tube, dissolve in an excess of 6M HCl, then heat in a water bath to expel CO_2. Add 5 mg of Fe^{3+}, dilute to ~ 40 ml, and add a slight excess of 0.880 ammonia solution. Centrifuge and reject the supernate. Dissolve the $Fe(OH)_3$ in a few drops of 6M HCl, dilute to ~ 40 ml, then add a slight excess of 0.880 ammonia solution. Centrifuge and reject the supernate.	

Step	Experimental procedure	Notes
9.	Add a few drops of 6M HCl and evaporate to dryness.	To ensure the correct acid molarity at the next stage.
10.	Dissolve the residue in 2 ml of freshly prepared solution A and apply to the top of an anion exchange column. Wash the test tube and resin column with six successive 1 ml portions of solution A, allowing each to percolate the column before applying the next portion. The raffinate and washings are collected in a 25 ml beaker and reserved for Am determination (see A5.1 Step 15 _et seq_.).	The column is 7 mm x 40 mm BioRad AG1 x 4, 100-200 mesh, with a free volume of approximately 1 ml above the resin.
11.	Wash the resin column successively with 20 ml of 8M HNO_3, 5 ml of 11.3M HCl and 0.5 ml of 11.3M HCl/0.1M NH_4I. Reject the washings.	
12.	Elute the Pu from the resin with five further 1 ml portions of 11.3M HCl/0.1M NH_4I and collect the eluate in a 10 ml beaker.	
13.	Add 0.5 ml of 16M HNO_3, mix well then gently evaporate to dryness. Add 1 ml of 6M HCl and 1 ml of 5% $KHSO_4$ and evaporate to dryness.	
14.	Dissolve in 5 ml of electrodeposition solution and transfer to the electrodeposition cell (see Figure 3). Add 1 drop of 0.880 ammonia solution to adjust the pH to ~ 2. Pass a direct current of 200 mA for 2 h. Add 1 ml of 0.880 ammonia solution, wait one minute then disconnect the current. Remove the stainless-steel tray, rinse gently with water then ethanol and heat to incipient red heat in a flame.	The source is then ready for alpha spectrometry.
15.	<u>Further purification of Am (Cm)</u> To the raffinate and washings from Step A5.10, add 5 mg of Bi^{3+}, then evaporate to dryness. Add 1 ml of 16M HNO_3 and evaporate to dryness.	
16.	Dissolve in 1 ml of 8M HNO_3 and apply to the top of an anion exchange column. Wash the beaker and resin column with five successive 1 ml portions of 8M HNO_3, allowing each to percolate the column before applying the next portion. Collect the raffinate and washings in a 50 ml centrifuge tube.	The column is 7 mm x 40 mm BioRad AG1 x 4, 100-200 mesh, with a free volume of approximately 1 ml above the resin.

Step	Experimental procedure	Notes
17.	Add 5 drops of 14M H_3PO_4 then 3 ml of 0.880 ammonia solution. Cool, add ammonia solution dropwise to adjust the pH to 1.5 using methyl violet as an indicator. Centrifuge and reject the supernate.	
18.	Wash the precipitate with 10 ml of water. Centrifuge and reject the washings.	As much fluid as possible should be removed, with a clean tissue, to minimise dilution of the 4M NH_4SCN.
19.	Add 0.5 ml of 4M NH_4SCN and ~ 10 mg of hydrazine hydrochloride. Mix well to dissolve the $BiPO_4$ then apply to the top of an anion exchange column. Wash the centrifuge tube with two 0.5 ml portions of 4M NH_4SCN, applying each successively to the column. Carefully place on top of the sample ~ 5 mm of anion exchange resin (equilibrated with 4M NH_4SCN). Wash the column with a further 20 ml of 4M NH_4SCN. Reject the raffinate and washings.	The column is 7 mm x 80 mm BioRad AG1 x 4, 100-200 mesh, and must be acid-free before equilibrating with NH_4SCN. A small funnel is affixed to the top of the column.
20.	Elute the Am with ten 1 ml portions of 1M HCl, passing each of these portions from the anion exchange column through a cation exchange column positioned directly below the anion exchange column. Reject the effluent from the cation column.	The column is 7 mm x 40 mm BioRad AG50W x 4, 100-200 mesh, with a free volume of approximately 1 ml above the resin.
21.	Wash the cation column by completely filling the free space five times with 1M HCl. Reject the washings.	
22.	Elute the Am with 10 ml of 6M HCl and collect in a 25 ml beaker. Add 1 ml of 16M HNO_3 to the beaker and evaporate gently to dryness. Add 1 ml of 6M HCl and 1 ml of 5% $KHSO_4$. Evaporate to dryness.	
23.	Proceed as in A5.1 Step 14.	

A5.2 Ferrous iron/sodium sulphite method

Step	Experimental procedure	Notes
1.	The seawater sample is filtered through a 0.45 µm filter. The filter with the particulate material is reserved for subsequent analysis (see Section A5.3).	That which passes through the 0.45 µm filter is defined as being soluble.

Step	Experimental procedure	Notes
2.	To the filtrate add, successively and with thorough mixing, appropriate quantities of ^{236}Pu or ^{242}Pu and ^{243}Am tracers, then to each litre of filtrate, add 10 ml of 11.3M HCl, 10 ml of Na_2SO_3 solution and 20 mg of $(NH_4)_2SO_4.FeSO_4.6H_2O$. Leave for at least 30 min.	
3.	Add to each litre, with thorough mixing, 10 ml of 0.880 ammonia solution. Filter through a 0.45 μm filter. Reject the filtrate.	
4.	Proceed as in A5.1 Step 4 _et seq_.	

A5.3 Treatment of suspended particulate

Step	Experimental procedure	Notes
1.	Transfer the filter and the particulate to a beaker and add appropriate quantities of ^{236}Pu or ^{242}Pu and ^{243}Am, then add 25 ml of 16M HNO_3 and evaporate to dryness under a cover.	
2.	Add a few ml of 16M HNO_3 and again evaporate to dryness under a cover.	
3.	Add 100 ml of 6M HCl and digest by gently boiling for one hour. Filter and reject any insoluble material.	
4.	Dilute the filtrate to ~ 700 ml then add 100 mg of Ca^{2+}, 10 ml of Na_2SO_3 solution and 100 ml of saturated $(COOH)_2$ solution. Adjust the pH to ~ 2 with 0.880 ammonia solution using methyl violet as an indicator. Stand for at least one hour. Centrifuge, and reject the supernate.	The indicator fades in the presence of SO_2. pH papers are a viable alternative.
5.	Dissolve the $Ca(COO)_2$ precipitate in a minimum of hot 6M HCl. Dilute to ~ 200 ml, add 10 ml of saturated $(COOH)_2$ solution and adjust to pH ~ 2 as before. Filter and reject the filtrate.	
6.	Proceed as in A5.1 Step 7 _et seq_.	

A6 Calculation of results

For the determination of the alpha-emitting isotopes of plutonium and americium, it is fortunate that we have suitable alpha-emitting nuclides of these elements available for use as yield monitors. This is the true isotope dilution situation and means that the concentration of the determinand can be obtained from a measurement of the ratio of counts of the

determinand to tracer and an accurate knowledge of the amount of tracer used. The ^{243}Am tracer also acts as a simultaneous tracer for the curium isotopes and, although this is not a true isotope dilution situation, it is valid, since the analytical procedure does not differentiate chemically between americium and curium.

To quantify the amount of determinand, the following information is required from the alpha spectrum:

N_M - the total number of counts in the tracer peak

N_D - the total number of counts in the determinand peak

T - the counting time.

Given this information, it is possible to calculate:

g_M - the gross count rate of tracer $(\frac{N_M}{T})$ and

g_D - the gross count rate of determinand $(\frac{N_D}{T})$.

From regular background counts we know:

b_M - the count rate from background in the tracer peak channels and

b_D - the count rate from background in the determinand peak channels

and from the calibration of the added tracer we also know:

A_M - the activity of the tracer added and

i_M - the isotopic impurity ratio in the tracer

$$\left(\frac{\text{net count rate of determinand in tracer}}{\text{net count rate of tracer}}\right)$$

i_M is used to calculate the count rate of the determinand present in the sample as a result of tracer additions (i_D):

$$i_D = (g_M - b_M)i_M.$$

From the above information, it is possible to calculate the determinand activity (A_D) present in the sample:

$$A_D = A_M.\left(\frac{(g_D - b_D - i_D)}{(g_M - b_M)}\right).\ e^{\lambda t}$$

where t = the time lapse between the date of sample collection and the mid-date of the counting period.

Note: An allowance for decay of the determinand is normally only necessary for isotopes of curium but is taken into account for ^{238}Pu and ^{241}Am if a delay in analysis makes it significant.

As results are normally quoted as Bq kg^{-1} (A_S), it is necessary to allow for the weight of the sample originally taken (W), so we have:

$$A_S = \frac{A_D}{W}.$$

The 1σ errors (E_M for the tracer and E_D for the determinand) associated with counting are given by:

$$E_M(\%) = 100 \sqrt{\frac{N_M + T.b_M}{[N_M - T.b_M]^2}}$$

$$E_D(\%) = 100 \sqrt{\frac{N_D + T(b_D + i_D)}{[N_D - T(b_D + i_D)]^2}}$$

thus, the overall 1σ counting error on any result (E_R) is given by:

$$E_R(\%) = \sqrt{\%E_M^2 + \%E_D^2}$$

Since tracers are usually of high purity, i_D is normally small and since the backgrounds of detectors are also low, the corrections for both of these is often insignificant (except for samples of very low activity). Then the calculation of error can be simplified to:

$$E_R(\%) = 100 \sqrt{\frac{1}{N_M} + \frac{1}{N_D}}$$

A7. Appendix reference

GREAT BRITAIN - PARLIAMENT, 1985. The Ionizing Radiations Regulations 1985. Her Majesty's Stationery Office, London, 83 pp.

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