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MINISTRY OF AGRICULTURE FISHERIES AND FOOD
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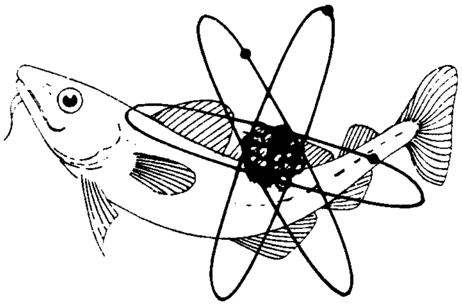
AQUATIC ENVIRONMENT PROTECTION: ANALYTICAL METHODS



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B. R. Harvey and Linda M. Thurston

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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.

H. W. Hill
Director of Fisheries Research
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1. Introduction

The Radioanalytical Groups within the Aquatic Environment Protection Division of the Directorate of Fisheries Research (DFR) routinely analyse a substantial number of radionuclides and determine the range of their concentrations in environmental materials. Gamma-emitting nuclides are usually analysed with a minimum of preparative chemistry, though this depends upon the total quantity and concentration of the nuclide present, whereas alpha-emitting and pure beta-emitting nuclides require detailed separative analytical chemistry. The manner in which this separative chemistry is carried out depends upon the particular nuclide, the presence of other nuclides, their concentrations and the nature of the material. There are no rigorous, absolute standard methods, indeed, none are required because all methodology, is to some extent, continually evolving. Nevertheless, it is useful periodically to draw together the various methods which are in routine use and to discuss their development and applications.

At the present time, environmental radioactivity arising from the presence of neptunium nuclides is only a very small fraction of that due to other transuranium elements, such as plutonium and americium. Hence, there has so far been little to encourage extensive investigations of neptunium radioecology, but its environmental behaviour is now steadily attracting increasing attention as more precise data are sought for computer modelling of the longer-term effects of radioactive waste disposal.

Since the late 1970s, considerable experience has been gained at the DFR in the analysis of neptunium nuclides, often at very low concentrations, in a wide variety of environmental materials. The procedures described in this publication have, therefore, been developed and tested over a considerable period of time with a view to achieving a high degree of decontamination from interfering nuclides and other matrix components which can detract from the required quality and sensitivity of the final measurement.

Neptunium was the first transuranium element to be discovered when, in 1940, McMillan and Abelson (1940) synthesized ^{239}Np ($t_{½}$ = 2.36 d) by the nuclear reaction

$$^{238}\mathrm{U(n,y)}\ ^{239}\mathrm{U} \xrightarrow{\beta^-} {}^{239}\mathrm{Np}$$

At about the same time, Seaborg and his co-workers (Katz and Seaborg, 1957; Seaborg, 1963) produced ^{238}Pu via the intermediary ^{238}Np ($t_{½}$ = 2.12 d) and in 1942, Wahl and Seaborg (1948) prepared ^{237}Np ($t_{½}$ = 2.14 x 10^6 yr) by the reaction

$$^{238}\mathrm{U(n,2n)}\ ^{237}\mathrm{U} \xrightarrow[6.7\ \mathrm{d}]{\beta^-} {}^{237}\mathrm{Np}$$

The half-life of this longest-lived nuclide of the element is too short for it to have survived as a primordial element but it has been detected at a ^{237}Np/^{238}U ratio of about 10^{-12} in uranium ore concentrates, where it is presumably produced by this same reaction. ^{237}Np is also formed in appreciable amounts in nuclear reactors both from the above reaction and from the reaction

$$^{235}\mathrm{U(n,\gamma)}\ ^{236}\mathrm{U(n,\gamma)}\ ^{237}\mathrm{U} \xrightarrow[6.7\ \mathrm{d}]{\beta^-} {}^{237}\mathrm{Np}$$

Furthermore, it also arises as a decay product in the series

$$^{241}\text{Pu} \xrightarrow[14.4\text{ yr}]{\beta^-} {}^{241}\text{Am} \xrightarrow[432\text{ yr}]{\alpha} {}^{237}\text{Np}$$

Not surprisingly, therefore, this nuclide can now be detected in environmental materials as a result of the atmospheric testing of nuclear weapons (Noshkin et al., 1974) and the discharge of low-level aqueous radioactive wastes into the environment from nuclear establishments (Pentreath and Harvey, 1981).

Neptunium has nevertheless been described as the neglected actinide (Thompson, 1982) because relatively few studies have so far been made of its biological, biomedical or environmental behaviour. The chief reason for this lies in the fact that neptunium nuclides are either short-lived beta or X-ray emitters, and of little potential hazard, or very long-lived alpha emitters of low specific activity. Hence, they are of little radiological significance at the concentrations presently found in the environment. In the longer term, however, it has been estimated that ^{237}Np will become one of the most important materials remaining in high-level radioactive wastes from about 10 000 years after disposal (Cohen, 1982).

Reliable analytical procedures for the radiochemical separation and assay of neptunium nuclides are thus clearly important whatever study is made of the element. The procedures are based chiefly on techniques discussed in articles by Hindman, Magnusson and La Chapelle (1949), Magnusson, Hindman and La Chapelle (1949), Moore (1957) and Mikhailov (1973) and have given excellent results in an intercomparison exercise involving the determination of ^{237}Np in a marine sediment (Popplewell and Ham, 1987).

2. Analytical technique

Neptunium is a member of the actinide series of f-transition elements. The fourteen elements comprising the group proper are characterized by the infilling of the 5f electron shell. These 5f electrons have relatively lower binding energies and less effective shielding than the 4f electrons which progressively fill the shell in the formation of the lanthanide series (Bagnall, 1972). The effect of such differences is most noticeable in the early members of the actinide series where it permits the formation of multiple oxidation states and, especially in the case of tetravalent and hexavalent states, an increased tendency to form complex species with a variety of organic and inorganic ligands. Such properties are of considerable benefit in the analytical separations of the actinides, including neptunium (Korkisch, 1969).

The chemical properties most important in the analytical chemistry of neptunium in aqueous solution are thus variable valency (especially IV, V and VI), and covalent bonding of the type Np-X, where X may be oxygen, halogens or groups such as thiocyanate. The stability of these bonds decreases in the order $\text{Np}^{4+} > \text{NpO}_2^{2+} \cong \text{Np}^{3+} > \text{NpO}_2^{+}$. Other analytically important properties include the formation of anionic complexes between Np(IV) and fluoride, chloride or nitrate and in some circumstances, disproportionation of Np(V) to give Np(IV) and Np(VI) (Mikhailov, 1973). At tracer levels, such as those found in environmental samples, co-precipitation of Np(IV) with rare-earth fluorides, from acid solution or with iron hydroxide from slightly alkaline solution, provides an effective means by which the neptunium may be pre-concentrated and separated from environmental matrices. Further purification is then readily achieved by solvent extraction and/or anion exchange procedures, in which oxidation states of the transuranium elements are manipulated to create or destroy complexes of the types described previously, in order to obtain the desired separation of the various elements.

In the environment, the most stable and commonly encountered chemical form of neptunium is the pentavalent oxy-cation NpO_2^+. This highly soluble and mobile species is dominant in well oxidized aqueous systems. However, where conditions are reducing, some reduction to Np^{4+} may occur (Harvey and Kershaw, 1984). Of the thirteen radionuclides of neptunium which are known, only ^{237}Np and ^{239}Np have been found in the environment, the latter, short-lived, beta-emitting nuclide being present in measurable quantities only immediately following nuclear explosions or accidents such as the recent Chernobyl incident. Thus, the procedures described here assume that the long-lived, alpha-emitter ^{237}Np is the determinand normally required. Changes to the procedure required for the analysis of ^{239}Np are considered in Sections 3 and 7. They consist chiefly of changes in the tracers used for determining chemical yield.

A step-by-step laboratory procedure, which includes a detailed explanation of the calculation of results, is provided in the form of an Appendix.

The analytical procedures can be divided into four main sections:

1. preliminary solubilization, and/or preconcentration yield tracer equilibration and separation of transuranics from the bulk of the sample matrix;

2. purification of neptunium from interfering radionuclides and other specific substances;

3. isolation of the neptunium for assay;

4. radiometric assay and analytical quantification.

Seawater samples are best filtered through 0.22 µm or 0.45 µm membrane filters to separate-out suspended particulate matter. The filtrate is acidified to 0.15M HNO_3 and a yield tracer, in the pentavalent state, is added (see Section 3). Ferrous iron is then added, at a rate of 0.2 g l^{-1}, to reduce neptunium to the tetravalent state along with 100 mg l^{-1} of neodymium carrier. After allowing an hour for completion of the reduction, NdF_3 is precipitated by the addition of hydrofluoric acid. Np(IV) co-precipitates quantitatively with the NdF_3 which, after filtering off, is returned to the laboratory for further processing. Np(V) does not co-precipitate under these conditions.

For suspended particulate matter and marine sediments, neptunium radionuclides are extracted with hot *aqua regia* in the presence of a yield tracer, then similarly reduced to the tetravalent state in dilute nitric acid solution and the neptunium co-precipitated as before with NdF_3. If there is a risk that the neptunium may be present in sediments as refractory material then appropriate steps should be taken to bring the sample completely into solution (Bock, 1979). This has not been found necessary in the coastal sediments analysed up to the present time within the DFR.

Samples of biological origin are first dried and then ashed at 450 ± 25°C to remove the bulk of organic matter. The ash is taken up in nitric acid and, after adding a yield tracer, the sample is evaporated to dryness to remove any remaining carbonaceous matter. The residue is dissolved in 3-4M HNO_3 and neptunium co-precipitated with NdF_3 as before, after reduction to the tetravalent state.

The acid-fluoride co-precipitation provides a substantial measure of decontamination from the major inorganic components of all the matrices. It also eliminates many beta-emitting fission and activation products, plus uranium in the hexavalent state. Elements which co-precipitate with the neptunium include trivalent lanthanides, trivalent and tetravalent actinides and pentavalent protactinium. Subsequent analytical stages are designed specifically to remove these elements.

Before further purification of the neptunium can be undertaken, the NdF_3 precipitate must be brought into solution. This is most easily achieved by boiling with a mixture of nitric and boric acids. Two reactions appear to take place, represented by the following equations:

$$4NdF_3 + 3H_3BO_3 + 12HNO_3 \rightarrow 3H[BF_4] + 4Nd(NO_3)_3 + 9H_2O \qquad \ldots\ldots (1)$$

$$NdF_3 + H_3BO_3 + 3HNO_3 \rightarrow Nd(NO_3)_3 + 3H_2O + BF_3 \qquad \ldots\ldots (2)$$

Though BF_3 is volatile, little fluoride is removed in this way unless the mixture is evaporated repeatedly with, for example, perchloric acid (B.P. 200°C). With only nitric acid present, therefore, the formation of the soluble fluorborate complex is the major route by which the NdF_3 is solubilized.

Various options are available for the further purification of the neptunium, but whichever option is chosen it is useful first of all to precipitate $Nd(OH)_3$ by making the solution alkaline with ammonia. Both Np(IV) and Np(V) are quantitatively co-precipitated whilst the fluorborate remains largely in solution; the Np(IV) is also oxidized to Np(V) on standing in the alkaline conditions. The hydroxide precipitate can then be redissolved in whichever acid strength and type are required for the following stage. From the point of view of decontamination, it was found that one of the most attractive procedures at this point is to extract Np(IV) into a solution of 0.5M thenoyl-trifluoracetone (TTA) in xylene from a 2M HCl solution (Moore, 1957, 1958). Ferrous iron is added to reduce Np(V) to Np(IV) and the solution is saturated with boric acid to ensure that fluoride ions do not interfere with the neptunium extraction. The neptunium extracts quantitatively into the organic phase and can be selectively back-extracted into 8M HNO_3. Table 1 gives the basic performance of the solvent extraction process and greater detail can be found, for example, in Stary (1964). When carried out as described, this solvent extraction gives a very valuable level of decontamination, particularly from uranium and protactinium, both of which have nuclides that may interfere with the alpha spectrometric assay of ^{237}Np and neither of which is especially well separated from neptunium by ion exchange.

To complete the purification, an anion exchange separation is then carried out in order to ensure the highest possible purity of neptunium for radiometric assay. The 8M HNO_3 back-extract from the solvent extraction is passed, without further treatment, through a small (8 mm x 0.6 mm) column of BioRad AG 1 x 4 (100-200 mesh). Figure 1 shows the performance of this ion exchange procedure. The column is prepared in

Table 1 Solvent extraction of metal ions by TTA/xylene

Oxidation species present in 2M HCl	Extraction into 0.5M TTA/xylene	Back-extraction into 8M HNO_3
NpV	Not extracted	-
NpIV	Quantitative extraction	Quantitative back-extraction
PuIV	Not extracted in absence of NO_3^- ions	Quantitative back-extraction
Trivalent actinides	Not extracted	-
Trivalent lanthanides	Not extracted	-
PaV	Extraction almost quantitative	Not back-extracted
PaIV	Some extraction	Not back-extracted
UVI	Not extracted	-
UIV	Some extraction	Not known
ThIV	Not extracted below pH 1	-
FeIII	Quantitative extraction	Not back-extracted

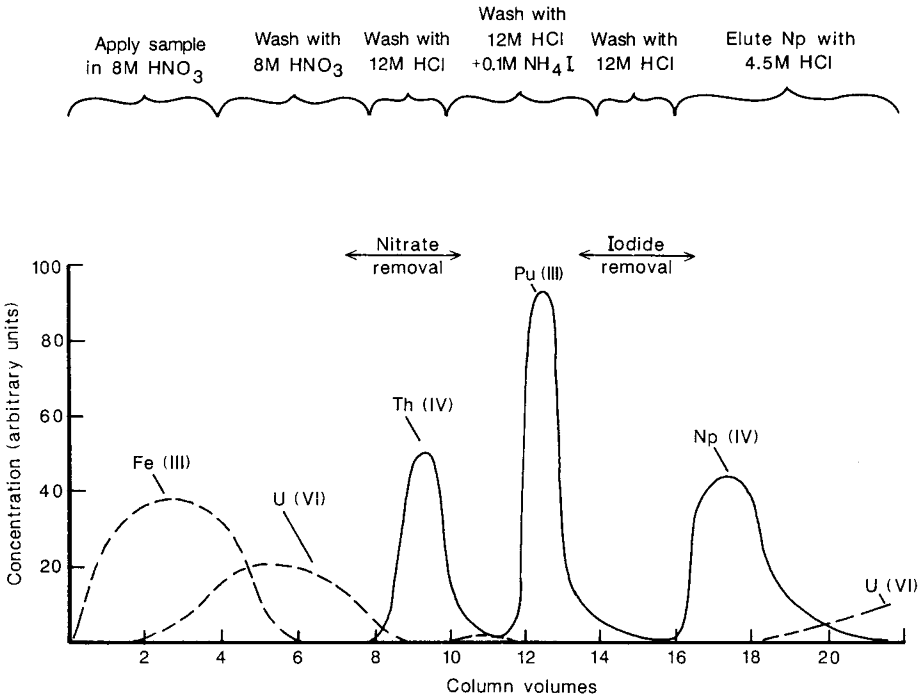

Figure 1. Separation of Np by anion exchange (BioRad AG 1 x 4, 100-200 mesh).

the nitrate form and, on applying the 8M HNO_3 sample solution to the column, neptunium, plutonium and thorium are strongly retained as nitrate complexes (D_v = 4000, 8000 and 500 respectively). Information on the determination of volume distribution coefficient (D_v) is given by Samuelson (1963). Small amounts of iron - Fe(III) and Fe(II) - are not retained but, as the figure demonstrates, U(VI) is retarded by the column ($D_v \simeq 20$) and not completely removed during the washing of the column with 8M HNO_3. When the eluant is changed to 12M HCl, the D_v for U(VI) as a chloro-complex rises to about 1000, while those for Np(IV) and Pu(IV) remain very high. Thorium, however, forms no chloro-complex and is immediately eluted in the 12M HCl wash. In order to separate any remaining plutonium nuclides from the neptunium, use is made of the fact that Pu(IV) is rapidly reduced to Pu(III) in 12M HCl containing iodine ions whereas Np(IV), which is not reduced by the mild reducing agent, remains unaffected. This is because the standard electrode potential (reduction potential) of the Pu^{4+}/Pu^{3+} couple is 0.982V and that of the Np^{4+}/Np^{3+} couple is 0.155V. Finally, the Np(IV) is eluted by lowering the HCl strength to 4.5M. Figure 2 shows that the D_v for the Np(IV) chloro-complex is reduced to about 2, thus allowing easy elution. It also shows that the D_v for the U(VI) chloro-complex is reduced to about 60, and if any uranium is still present some leakage can occur towards the end of the neptunium elution. Fortunately, any iron that has remained on the column to this stage is still firmly held at the molarity of HCl used for the neptunium elution.

The eluate containing the neptunium is collected in a quartz beaker (to reduce uranium contamination) and evaporated to dryness. The residue is then evaporated to dryness twice with high purity HNO_3 to destroy organic residues from the ion exchange material and to volatilize any remaining iodine. The residue is finally taken up in an ammonium oxalate/hydrochloric acid mixture and the neptunium electrodeposited onto a 25 mm stainless-steel planchette at 1 A cm^{-2} for 2 h, at pH 2-3.

After neutralizing the solution with ammonia, the power is disconnected and the planchette removed, washed and flamed to fix the deposit to the stainless-steel disc. The source is then ready for radiometric assay.

The radiochemical separations are shown schematically in Figure 3a and b and full laboratory working details are given in the Appendix, together with practical notes for the analyst.

3. Yield tracers

The mass of neptunium present in samples of environmental materials taken for analysis is likely to be exceedingly small even in the case of the long-lived nuclide ^{237}Np, for which 27 mBq has a mass of only 10^{-9} g and ^{239}Np of similar activity would have a mass of only 3×10^{-17} g. Thus, during complex radiochemical separation it is unlikely that all the neptunium will be recovered, and some means of determining the fraction of neptunium actually assayed must be provided if accurate results are to be obtained.

Yield tracers for use in the radiochemical analysis of actinide elements have been discussed by Harvey and Lovett (1984). In the case of neptunium the choice is very restricted. Ideally, the tracer and determinand should be capable of being assayed together by the same measuring technique (isotope dilution analysis) but for the alpha

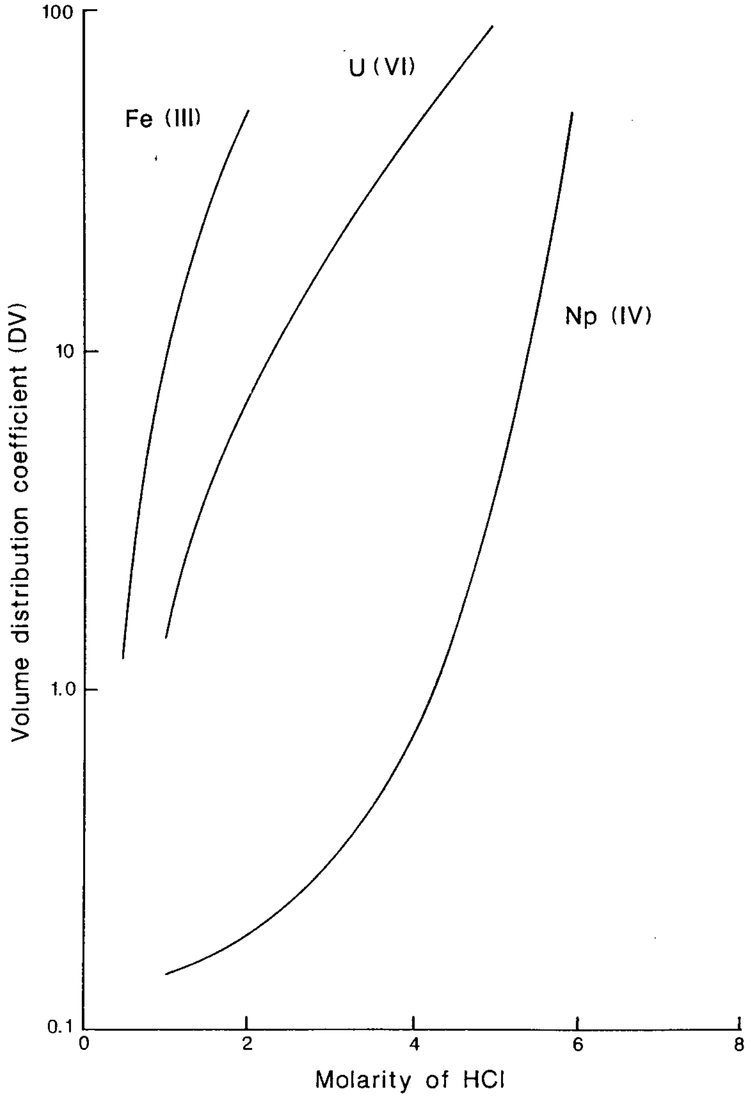

Figure 2. Volume distribution coefficients of Np(IV), U(VI) and Fe(III) between BioRad AG 1 x 4 (100-200 mesh) and HCl.

emitter, ^{237}Np, no other suitable alpha-emitting nuclide is available. Thus, the beta emitter ^{239}Np is commonly used instead, but its short half-life and the need to assay the two nuclides by separate counting techniques are distinct disadvantages. Apart from the need for frequent preparation of fresh batches of yield tracer (see Appendix, Section A3 for details of its preparation from ^{243}Am), there is a need to calibrate each alpha counter used and to prepare standards for each batch of ^{239}Np. Should ^{239}Np be required as the determinand the roles can be reversed, but consideration then needs to be given to the calibration of the beta counter (see Section 6).

Recently, the neutron deficient nuclide ^{235}Np ($t_{1/2}$ = 396 d), which decays by electron capture, has been shown to be a useful additional choice as a yield tracer. It offers the following advantages:

1. it can be added to water samples prior to field or ship-board preconcentration of transuranics without decaying to unacceptably low levels before analysis has been completed;

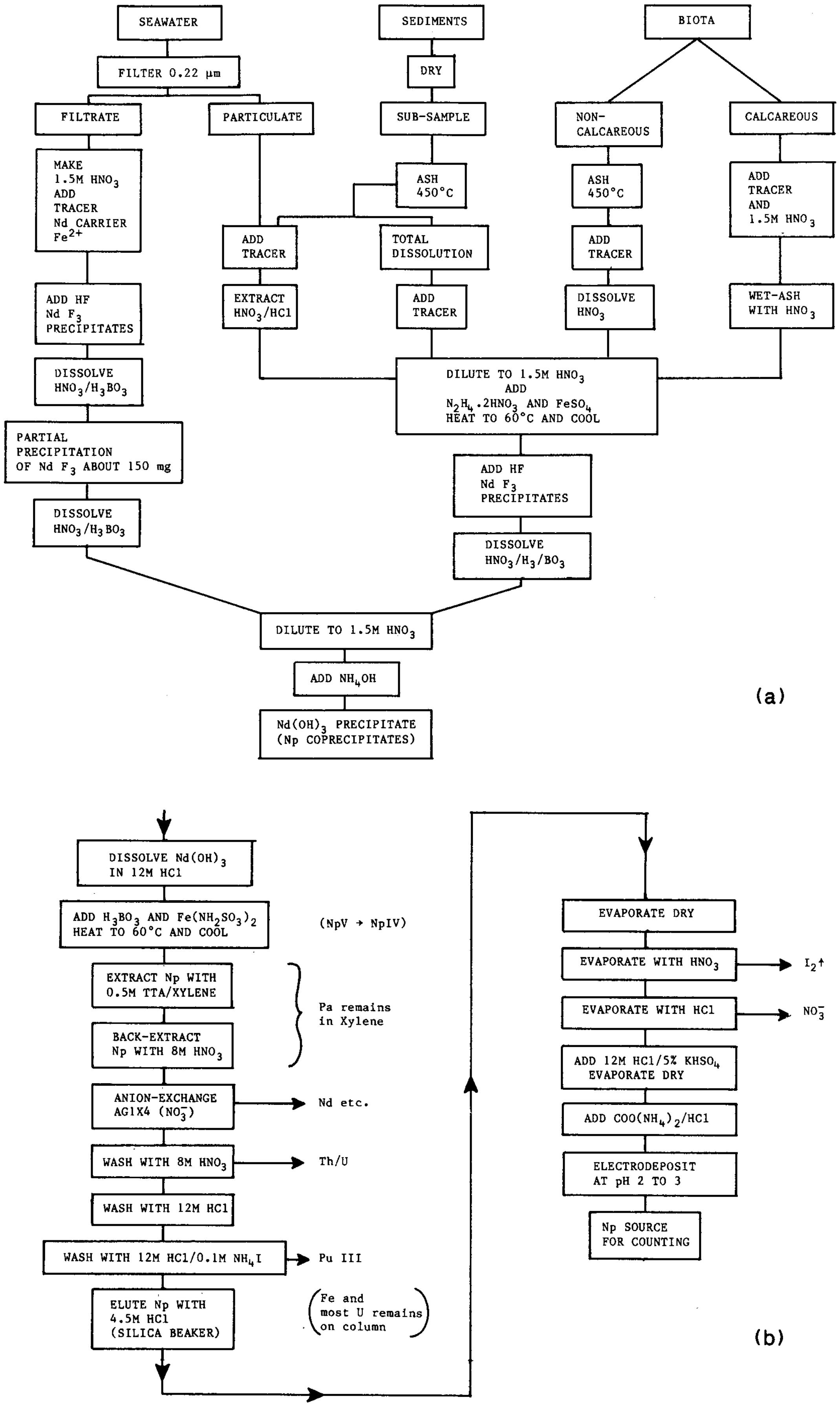

Figure 3. Radiochemical separation (schematic): (a) preliminary treatment of samples; (b) purification and source preparation.

2. the risk of contaminating the sample with ^{239}Pu, as may happen with ^{239}Np, is avoided (^{239}Pu is the daughter of ^{239}Np);

3. it permits the determination of both ^{237}Np and ^{239}Np on the same aliquot of sample.

There are drawbacks, however, to the use of this tracer; it must be assayed by a relatively expensive X-ray spectrometer and some corrections for spectral interferences in the X-ray measurements are necessary. For further details on the use of this nuclide as a yield tracer, reference should be made to Harvey and Sutton (1987).

4. Radiometric assay

As stated previously it is assumed that, for the present scheme, environmental materials are to be analysed either for ^{237}Np or for ^{239}Np. The latter short-lived, beta-emitting nuclide is most likely to appear in the environment as a result of a nuclear explosion (Freiling and Ballou, 1962; Ballou, 1963) or, as more recently demonstrated, from a nuclear accident such as that which occurred at Chernobyl in 1986. The decay of ^{239}Np is accompanied by the emission of gamma rays (0.106-0.49 MeV) and these can be used both to characterise and to measure the nuclide directly in environmental samples if sufficient ^{239}Np is present. Beta counting may, however, be the more satisfactory way to determine ^{239}Np in many cases because of better detection efficiency and the inherently lower background associated with this mode of counting.

This helps the analyst in two ways, as illustrated in the results of the experiment shown in Figure 4. A 25 mm stainless-steel planchette on

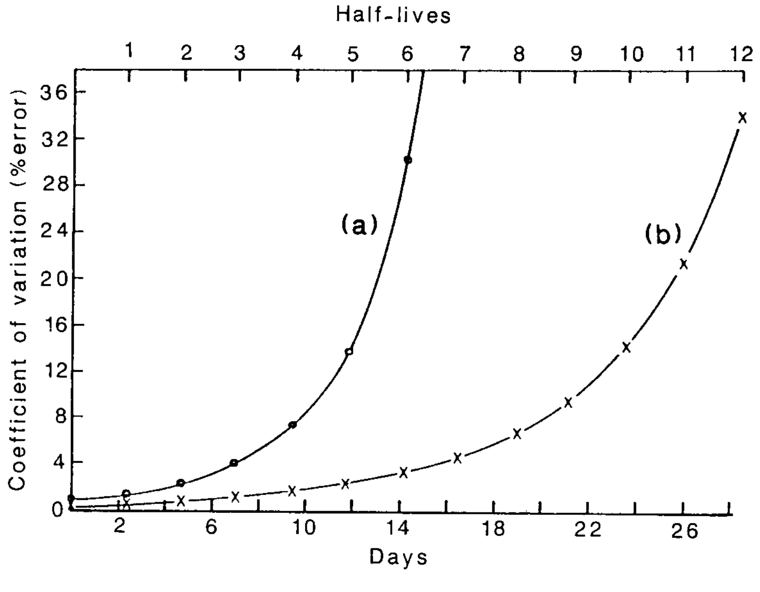

Figure 4. Counting errors associated with (a) gamma and (b) beta counting of ^{239}Np.

which about 75 Bq of ^{239}Np had been deposited was gamma counted on a 75 mm NaI(Tl) crystal (plot A) that had a background count of

194 ct min^{-1} and efficiency of 18% in the appropriate gate, and then beta counted on a Tracerlab SH-4 gas-flow Geiger counter with a background count of 0.2 ct min^{-1} and efficiency of 35% (plot B). As can be seen, the beta counter offered not only better precision for a given counting period, but also allowed the short-lived yield tracer to be measured reliably for appreciably longer. Beta counting thus gives the analyst more time to carry out the separations or to rectify errors in the analysis.

^{237}Np decays by emitting alpha particles and gives rise to a daughter product ^{233}Pa ($t_{½}$ = 27.0 d), which is a beta emitter. A low-energy gamma photon (29.2 KeV) is emitted during the decay of ^{237}Np, but by far the most efficient mode of detection of the nuclide is alpha spectrometry; for example using a 15 mm diameter silicon surface barrier detector, such as the Ortec BA 19-150-100 model, connected via a pre-amplifier and router to 256 channels of a multichannel analyser.

If both ^{237}Np and ^{239}Np are to be determined on the same sample the analyst may proceed in one of two ways; the simplest way is to split the sample into two aliquots just prior to adding the yield tracer. Neptunium is then separated from the unspiked sample and the ratio of ^{237}Np to ^{239}Np is determined. An accurately known amount of ^{239}Np or ^{237}Np tracer is added to the second aliquot and neptunium is separated as before. This provides a chemical yield and, hence, the ability to calculate the amount of both nuclides present in conjunction with the isotopic ratio determined in the first aliquot. An alternative, but more complex, procedure involves the use of ^{235}Np (see Section 3) which can be assayed independently of both determinands.

5. Sources of error

Several sources of error need to be considered in the radiochemical analysis of neptunium nuclides; the more important ones are discussed below.

5.1 Analytical errors

One of the obvious sources of analytical error is the contamination which can occur from the re-use of apparatus which has been inadequately cleaned. Separating funnels in which aqueous and organic phases are mixed present cleaning problems, and it has been found that as much as 0.1% carry-over of material from one sample to the next may occur in Perspex plating cells, despite rigorous cleaning with acids (Harvey, Lovett and Boggis, 1987). Unfortunately, the processing of reagent blanks, however regularly carried out, does not always uncover such errors.

Another error, which is much more difficult to detect, may arise if total chemical equilibration of the yield tracer with the determinand nuclide is not achieved. Care is, therefore, needed to ensure that the sample neptunium is released from complexes and that adequate steps are taken to ensure that both tracer and determinand nuclides are in the same oxidation state before radiochemical separation commences.

5.2 Interfering substances

Both matrix and spectral interferences can occur in the radiochemical analysis. Matrix interferences occur when purification procedures are inadequate, allowing unwanted components of the sample or processing chemicals to become deposited on the counting source in sufficient quantity to increase significantly the thickness of the electrodeposited layer. This causes degradation of the alpha spectrum, as shown in Figure 5. In severe cases of such matrix interference, adjacent alpha peaks may partially merge. Iron is a common cause of such matrix interference because it can be present as a contaminant in all but the very purest grades of nitric and hydrochloric acids, and because of the ubiquitous nature of iron rust in most chemical laboratories.

Spectral interferences can cause severe errors in the radiometric assay of ^{237}Np. The worst problem comes from the persistence of uranium throughout the purification stages, or its re-introduction into the sample by acid-leaching of glassware during the preparation of the sample for electro-deposition. The main alpha energy of ^{234}U is 4.768 MeV, while that of ^{237}Np is 4.781 MeV. The spectra of the two nuclides cannot therefore be resolved and, in practice, a correction may be needed for the presence of ^{234}U in the ^{237}Np spectrum. This is most readily achieved by measuring the amount of ^{238}U present (4.195 MeV) and using this to determine the contribution of ^{234}U in the ^{237}Np peak. A second, though less likely, interfering nuclide is ^{231}Pa whose closest alpha energy is 4.727 MeV. This nuclide, which occurs in nature as part of the 4n+3 series, has other alpha groups extending up to 5.049 MeV. Its spectrum is therefore partially resolved from the ^{237}Np peak and this at least allows its presence to be detected. Other possible interfering nuclides are ^{230}Th (4.682 MeV) and ^{239}Pu (lowest alpha group 5.099 MeV), the latter being present both as a component of the original sample in many instances and as a decay product from the ^{239}Np. With good quality sources the ^{239}Pu is completely resolved from the ^{237}Np peak and causes no problem, but tailing can create some interference if source quality is poor.

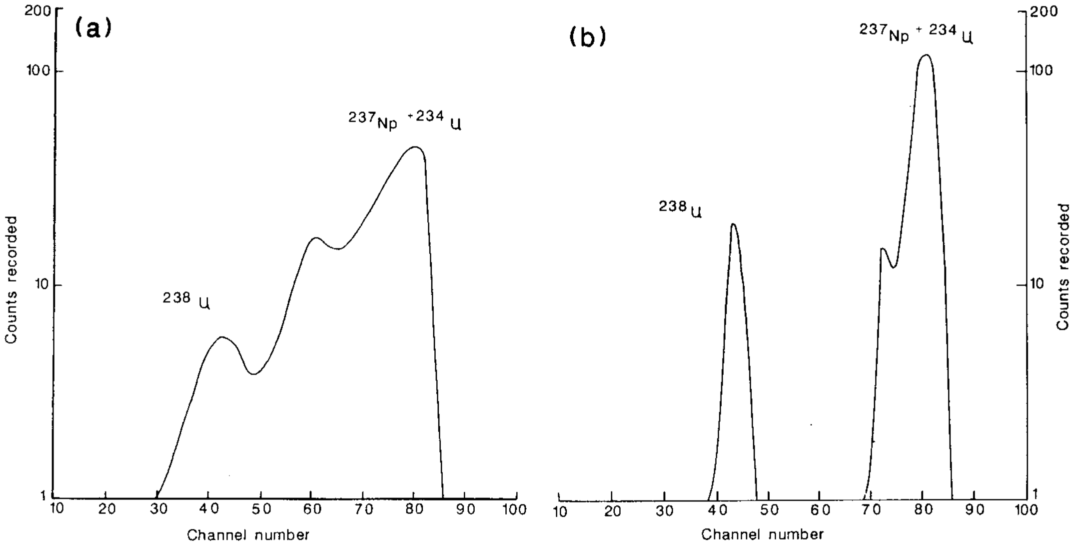

Figure 5. Degradation of an alpha spectrum by extraneous material deposited on the source: (a) poor-quality source; (b) good-quality source.

Interferences can also occur in the beta counting of ^{239}Np. For example, detectors with thin windows will respond to the alpha particles emitted by ^{237}Np. This may be prevented by placing an absorber (10 mg cm^{-2}) between the source and detector. A potential source of interference exists with the ^{233}Pa daughter of ^{237}Np. The beta-emitting nuclide ($t_{1/2}$ = 27 d) is eliminated during radiochemical separation but grows back in (eventually to equilibrium) with any ^{237}Np present. The beta-max energies of ^{233}Pa are 0.568 MeV (5%), 0.257 MeV (58%) and 0.145 MeV (37%) and, hence, the 10 mg cm^{-2} absorber used to eliminate interference from alpha particles will also absorb almost 90% of the beta radiation from the ^{233}Pa. In practice, therefore, it can be disregarded as a source of error in the beta counting.

If ^{239}Np is to be determined by gamma spectrometric analysis directly in environmental matrices, spectral interferences must always be considered likely. However, the lines at 0.278 MeV and 0.228 MeV offer the best chance of detecting and estimating the nuclide in most cases.

5.3 Instrument calibration errors

The fact that the yield tracer and determinand nuclide must be assayed by different counting methods prevents the use of true isotope dilution analysis in the case of those neptunium nuclides which are most likely to occur in environmental samples (Harvey and Lovett, 1984). Thus, unlike isotope dilution analysis where the absolute efficiency of the detection system need not be known, both alpha and beta detectors (and/or X-ray detector if ^{235}Np is used as a yield tracer) must be individually calibrated using known standard sources of the appropriate nuclide. Therefore, it is not difficult to appreciate that, for the highest quality analysis, great care is needed in these calibrations because of the cumulative nature of errors, whatever their cause.

6. **Decontamination factors**

Decontamination factors for the analytical scheme were determined either by addition of known amounts of specific nuclides to samples of sediment, which were then subjected to the analytical separation, or by calculation from known naturally-occurring concentrations in various samples that were analysed for their ^{237}Np content. Nuclides for which good decontamination is particularly important are included in Table 2.

Table 2 Decontamination factors (alpha emitters)

Nuclide	Decontamination factor
^{230}Th	$> 3 \times 10^5$
^{230}Pa	$> 2 \times 10^4$
^{234}U	$> 5 \times 10^4$
$^{239/240}$Pu	$> 10^3$

Decontamination factors for beta-emitting radionuclides were not determined individually. However, sources counted after the ^{239}Np tracer had been allowed to decay for a month were never found to show beta activity significantly above that of the background.

7. Quantification of results

In order to quantify the analytical results, the radiometric counting data from the extracted neptunium nuclides must be compared with those from known standards of the respective nuclides counted in the same equipment.

Alpha counters may be calibrated using electrodeposited sources from known amounts of ^{237}Np. Since the electrodeposition process is not totally quantitative, it was found to be most satisfactory to take a standard solution containing, for example, 10 Bq of ^{237}Np and electrodeposit the neptunium onto a source. Then, the aqueous residue can be evaporated to dryness with nitric acid and re-prepared for electrodeposition. A secondary source is then also prepared, and both are counted in the silicon surface barrier detector to give counting statistics better than ± 1% (1 standard deviation). More than 99.5% of the ^{237}Np present in the standard is normally deposited onto the two sources, and together they provide an acceptable calibration of the detector. The standardization should, of course, be carried out at least in duplicate. These duplicates should agree within the limits of the collective counting errors, and from the results the absolute counting efficiency of the detector for ^{237}Np can be ascertained.

If, as is likely in most cases, ^{237}Np is the determinand and ^{239}Np is being used as the yield tracer, the absolute counting efficiency of the beta counter need not be known. Instead, for each batch of ^{239}Np tracer prepared from the ^{243}Am parent, duplicate standards are prepared and electrodeposited as for the ^{237}Np standard. The activity of the ^{239}Np standard solution is then calculated per unit weight of solution. Thus, knowing the weight of ^{239}Np solution added to each sample, the neptunium recovery can be determined by counting the electrodeposited sources and relating the counts obtained, in each case, to that which would have been expected had all the ^{239}Np in the known amount of added tracer solution been present on the source. This is taken to be the fractional recovery of neptunium from the sample.

Should ^{239}Np be required as a determinand following radiochemical separation, then arrangements must be made to calibrate the beta counter. This is not something which can be done with great accuracy. For most purposes it is sufficient to 'milk off' the ^{239}Np from a known quantity of its ^{243}Am parent, with which it is in equilibrium (at least seven half-lives are needed for > 99% grow-in). The procedure described in the Appendix is suitable as long as appropriate care is taken to ensure that quantitative recovery is achieved. The efficiency of the detector for ^{239}Np can thus be determined. An alternative procedure is to calibrate the detector with other radionuclides which are available as certified standard solutions from, for example, Amersham International. This approach is only satisfactory for thin window gas-flow beta detectors operated in the Geiger region, where the variation of sensitivity with energy is low. The ^{239}Np beta spectrum is complex - 0.332 MeV (28%), 0.393 MeV (13%), 0.437 MeV (48%), 0.0654 MeV (4%), 0.713 MeV (7%). Probably the best compromise is to use ^{59}Fe ($t_{½}$ = 44.56 d) which is available as a standardized solution and has the following beta spectrum - 0.273 MeV (48.5%), 0.475 MeV (51.2%), 1.573 MeV (0.3%). It can also be electrodeposited quantitatively on to stainless-steel planchettes from a suitable medium (Maletskos and Irvine, 1956).

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Appendix - Laboratory procedures

A1 Reagents

Analytical grade reagents are suitable unless otherwise stated. Prepared reagents should be stored in polythene bottles unless otherwise stated.

A1.1 Water

Distilled water or deionized water should be used throughout.

A1.2 4.5M hydrochloric acid

Dilute 390 ml of HCl (sp.gr. 1.18) to 1 litre with distilled water.

A1.3 8M nitric acid

Dilute 500 ml of HNO_3 (sp.gr. 1.42) to 1 litre with distilled water.

A1.4 4M nitric acid

Dilute 250 ml of HNO_3 (sp.gr. 1.42) to 1 litre with distilled water.

A1.5 1.5M nitric acid

Dilute 94 ml of HNO_3 (sp.gr. 1.42) to 1 litre with distilled water.

A1.6 12% ammonium fluoride

Dissolve 120 g of NH_4F in 1 litre of distilled water.

A1.7 Neodymium carrier

Dissolve 11.7 g of Nd_2O_3 in 70 ml of 8M HNO_3 and make up to 100 ml with 8M HNO_3.

A1.8 1M hydrazine nitrate $N_2H_4.2HNO_3$

Dissolve 14 ml of concentrated HNO_3 to 200 ml with distilled water. Add slowly, and with stirring, 10 ml of hydrazine hydrate ($NH_2.NH_2.H_2O$). Make up to 400 ml with distilled water and store in a well-stoppered glass bottle.

NOTE: Considerable heat is generated during the reaction.

A1.9 Ferrous sulphamate $Fe(NH_2SO_3)_2$

Place 80 ml of distilled water in a 250 ml glass beaker and cover with a watch glass. Boil well for about 5 minutes to expel air, and allow to cool. Add 20 g of sulphamic acid (NH_2SO_3H) and when this has dissolved add 6 g of iron powder. Warm the mixture to 50-60°C (sulphamic acid may decompose above 60°C). When the majority of the iron has dissolved, filter through a Whatman No.541 filter paper supported in a glass funnel and make up the filtrate to 100 ml with boiled distilled water. Store in a well-stoppered glass bottle in a refrigerator. Under these conditions the solution is stable for about 2 weeks.

A1.10 12M hydrochloric acid/0.1M ammonium iodide

Immediately prior to use, add 0.15 g of NH_4I to 10 ml of HCl. Stir to dissolve and use immediately.

A1.11 Plating solution

Dissolve 24 g of ammonium oxalate $(COONH_4)_2.2H_2O$ in 700 ml of distilled water; add 16 ml of concentrated HCl and make up to 1 litre.

A1.12 Radionuclide standards

Standardized solutions of ^{237}Np are available from Amersham International plc., Little Chalfont, Buckinghamshire, England HP7 9NA.

A2 Hazards

In addition to observing normal standards of safety in the chemical laboratory, particular care is needed when handling hydrofluoric acid. HF burn jelly should be available in case of accidental spillage of hydrofluoric acid on to the skin.

The handling of radionuclides in analytical laboratories is now governed by the Ionizing Radiations Regulations 1985 (Great Britain - Parliament, 1985), to which reference should be made before using the radioactive tracers and standards recommended in this booklet.

A3 Preparation of ^{239}Np yield tracer

^{239}Np is produced from the decay of ^{243}Am in the following way:

$$^{243}\text{Am} \xrightarrow[(t_{1/2}\ 7380\ \text{yr})]{\alpha} {}^{239}\text{Np} \xrightarrow[(t_{1/2}\ 2.36\text{d})]{\beta} {}^{239}\text{Pu} \xrightarrow[(t_{1/2}\ 2.41 \times 10^4\ \text{yr})]{\alpha} {}^{235}\text{U}$$

The neptunium daughter-product grows in with a half life of 2.36 days and may conveniently be separated from the parent by anion exchange. It should be noted that the ^{239}Np decays to ^{239}Pu, a fact which must be recognized if plutonium radionuclides are also to be determined on the same sample.

A3.1 Procedure

Transfer not more than 2000 Bq (0.05 µCi) of ^{243}Am from the stock solution into a 10 ml polythene bottle in concentrated hydrochloric acid (1 ml). This amount of ^{243}Am may then be transferred to an unclassified radiochemical laboratory for regular separation of the ^{239}Np daughter.

Prepare a small column of BioRad AG 1 x 4 (100-200 mesh) anion exchange resin 50 mm x 6 mm in a glass Pasteur pipette and condition it by passing 2 ml of concentrated HCl through the resin bed. Pass the ^{243}Am solution in concentrated HCl through the column and collect the raffinate in the 10 ml polythene storage bottle. This contains the ^{243}Am. Wash the column with 5 x 1 ml portions of concentrated HCl and retain these washings for subsequent recovery of ^{243}Am.

Elute the ^{239}Np with 5 ml of 1M HCl, collecting the eluate in a 25 ml glass beaker. Add 1 ml of concentrated HNO3 and evaporate to dryness.

Repeat the evaporation to dryness with a further 1 ml of concentrated HNO_3 plus 1 drop of 100 volume H_2O_2 to ensure that the ^{239}Np is present as Np(V). Add 5 ml of 1.5M HNO_3 to dissolve the residue and transfer to a 10 ml polythene bottle for use as a yield tracer.

Weigh out, accurately, two portions of about 0.5 g each of this solution into 25 ml beakers and prepare sources for counting as described in Section A5. Retain the plating residue and return to the 25 ml beaker; evaporate to dryness with 1 ml of concentrated nitric acid and repeat steps 1-10 of Section A5. Count the four sources as standards and use them to calculate the recovery of the ^{239}Np yield tracer in the samples, as described in Section A6.

A4 Apparatus

(1) Centrifuges capable of accepting 50 ml tubes and 1 litre polythene containers are required.

(2) An alpha spectrometer plus a silicon surface barrier detector, mounted in a demountable vacuum chamber connected to a rotary vacuum pump, are needed to count the alpha particle emissions from ^{237}Np.

(3) A beta counter designed for 1- or 2-inch diameter planchettes and of the gas-flow proportional, or gas-flow Geiger type, is ideal for the assay of ^{239}Np. A scaler and timer are also required. End window beta counters may also be used.

(4) Filtration apparatus made from glass is unsuitable for use where HF is employed. Units made from acid-resistant plastics such as polycarbonate are available from various manufacturers.

A5. Detailed practical procedures

Step	Experimental procedure	Notes
	<u>Preliminary treatment of samples of seawater</u>	
1	Collect a known volume of seawater.	a. About 50-200 litres are usually required.
2	Filter through a 0.22 µm membrane filter to remove suspended particulate matter.	b. Set aside the membranes for suspended particulate analysis (1 membrane for 50 litre sample).
3	Add an appropriate (known) amount of a suitable yield tracer.	c. See main text (Section 3 for choice of yield tracer.
4	Add 50 ml of concentrated HNO_3 per litre of sample and mix well.	
5	Add 100 mg of Nd carrier per litre of sample.	

A5 Continued

Step	Experimental procedure	Notes
6	Add 0.2 g of ferrous iron per litre of sample.	d. As a solution of ferrous sulphate or ferrous ammonium sulphate in 1M H_2SO_4.
7	Mix well and leave for 0.5-1 h.	e. Fe^{2+} reduces Np(V) to Np(IV) during this time period at room temperature.
8	Add 10 ml of 40% HF per litre of sample, mix well and leave for 10 minutes.	f. See notes on hazards in handling HF solutions (Section A2).
9	Filter-off the NdF_3 precipitate through a 0.22 μm membrane filter and retain the filter for Np purification steps.	g. Np(IV) coprecipitates quantitatively with the NdF_3 from the acid solution.
10	Place the filter membranes containing the NdF_3 precipitate in the bottom of a 2 litre beaker. Add 100 ml of concentrated HNO_3, boil to destroy the cellulose membranes.	h. The NdF_3 from each 50 litres of water should have been collected on one filter.
11	Add 1 g of H_3BO_3 for each filter membrane present and evaporate to low bulk.	i. The H_3BO_3 helps to solubilize the NdF_3 by forming a fluorborate complex.
12	Add a further 50 ml of HNO_3 and repeat the evaporation to low bulk until all organic residues from the membranes are destroyed.	j. If taken completely dry, the rare earth fluoride may become difficult to dissolve.
13	Dilute to about 1 litre with 1.5M HNO_3, then warm on a hot plate to about 60°C and stir in the minimum amount of H_3BO_3 needed to dissolve all the NdF_3 precipitate.	k. Stoichiometrically 0.32 g of the H_3BO_3 are needed for each 1 g of Nd present.
14	Add 50 ml of hydrazine nitrate solution and 0.1 g of ferrous sulphate. Maintain at 60°C for 10 minutes, then cool.	l. This is to reduce Np(V) to Np(IV).
15	When cool, place the beaker on a magnetic stirring table. Put a 2-inch PTFE-covered magnetic stirrer in the 2 litre beaker and stir the solution.	
16	Add a 12% W/V aqueous solution of NH_4F slowly until a small permanent precipitate of NdF_3 forms.	m. The aim is to coprecipitate the Np(IV) on about 150 mg of NdF_3.

A5 Continued

Step	Experimental procedure	Notes
17	Centrifuge-off the precipitate and repeat the partial precipitation if necessary (steps 11 to 17) until no more than 150 mg NdF_3 is obtained as a precipitate.	
18	Proceed to step 5 of the purification stage.	
	Preliminary treatment of samples of sediment	
1	Dry the sample to constant weight either by freeze drying or by oven drying at 110°C.	a. Freeze drying gives a more easily handled dry sample than that of oven drying if appreciable amounts of clay are present.
2	Homogenize the dry sample until all the material will pass through a 63 μm sieve.	
3	Cone and quarter the sieved sample to give a sub-sample of suitable size.	
4	Ash the sub-sample in a muffle furnace at 450 ± 25°C for at least 6 h.	b. Aluminium trays make ideal containers for muffle-ashing.
5	Cool the sample in a desiccator.	
6	Weigh out portions of the ashed sample material large enough to provide sufficient of the required neptunium nuclide for analysis.	
7	Place the weighed sample (up to 30 g dry) in a 500 ml Pyrex glass beaker, add 30 ml of distilled water followed by an appropriate amount of yield tracer solution and slurry the mixture.	c. See main text (Section 3) for choice of yield tracer.
8	Add 30 ml each of concentrated HNO_3 and HCl. Cover the beaker with a watch-glass cover and simmer on a hotplate for several hours.	d. For the majority of marine sediments, Np is not matrix-bound or present as refractory oxides. However, if any portion of the Np is suspected of being present in a non-leachable form then the sample should be brought completely into solution by fusion methods as discussed in main text (Section 2)(see Bock, 1979).

A5 Continued

Step	Experimental procedure	Notes
9	Cool somewhat, then centrifuge or filter to separate the phases. Retain the solution for further treatment.	
10	Re-extract the solid residue with HNO_3 + HCl (30 ml portions of each) twice more to ensure thorough removal of the neptunium.	
11	Repeat the phase separations and combine all the extract solutions together in the 500 ml beaker.	
12	Evaporate the acid extract to low bulk on a hotplate to remove the bulk of the acids present.	e. Evaporate until crystallization occurs. Do not take to dryness.
13	Add 4M HNO_3 to make the volume up to about 300 ml.	
14	Proceed to the first purification step.	
	Preliminary treatment of biological materials (except calcareous shell)	
1	Dry the sample to constant weight either by freeze drying or by oven drying at 110°C	
2	Homogenize by grinding or other suitable method.	
3	Sub-sample as appropriate to provide suitably-sized samples for the analysis.	
4	Muffle-ash at 450-500°C to remove bulk of organic matter present.	a. This can often conveniently be done in a 500 ml or 1 litre Pyrex beaker.
5	Add an appropriate quantity of a suitable yield tracer plus 100 ml of concentrated HNO_3.	b. See main text (Section 3) for choice of yield tracer.
6	Evaporate slowly to very low bulk to oxidize any remaining organic matter. Repeat with further 50 ml portions of HNO_3 until no further oxidation takes place and the residue is free from organic matter.	

A5 Continued

Step	Experimental procedure	Notes
7	Add about 300 ml of 4M HNO_3 and warm to dissolve the inorganic residue.	
8	Filter-off any insoluble residues through a 0.22 µm membrane filter and proceed to the first step of the purification procedure.	
	Preliminary treatment of calcareous shell	
1	Place an appropriate quantity of the dry shell sample in a 500 ml beaker.	a. Use a larger beaker if there is risk that effervescence will cause spillage.
2	Add 5 ml of 1.5M HNO_3 per 1 g of shell and an appropriate quantity of a suitable yield tracer.	
3	When effervescence ceases, add concentrated HNO_3 equal in volume to that of the 1.5M HNO_3 in step 2. Boil to destroy organic matter.	
4	Evaporate to very low bulk and repeat the evaporation with further quantities of HNO_3, if necessary, to destroy organic residues.	
5	Add 300 ml of 4M HNO_3 and warm to dissolve the inorganic matter.	
6	Filter off any insoluble residue through a 0.22 µm membrane filter and proceed to the first step of the purification procedure.	
	Purification	
1	To the sample of about 300 ml in 1.5 to 4M HNO_3, add 100 mg of Nd carrier, 20 ml of hydrazine nitrate and 0.1 g of ferrous sulphate.	
2	Heat the mixture in a 500 ml beaker to 60°C on a hotplate for 10 minutes. Let the mixture cool.	a. To reduce Np(V) to Np(IV).
3	Transfer to a 1 litre open-necked centrifuge bottle and add 10 ml of 40% HF to precipitate NDF_3.	

A5 Continued

Step	Experimental procedure	Notes
4	Centrifuge-off the precipitate and dissolve it in 20 ml of hot 8M HNO_3 containing 1 g of H_3BO_3.	
5	Dilute to 100 ml with saturated H_3BO_3 solution. Then precipitate $Nd(OH)_3$ by adding 12 ml of NH_4OH solution (0.880 sp.gr.).	
6	Centrifuge-off the $Nd(OH)_3$ precipitate and redissolve it in the minimum of concentrated HCl in a 100 ml beaker.	b. It may be necessary to repeat the hydroxide precipitation from HNO_3/H_3BO_3 solution more than once to remove fluoride from the mixture sufficiently to achieve complete solubility in the HCl.
7	Add 1 ml of saturated H_3BO_3 solution and 1 ml of ferrous sulphamate solution and heat to 60°C for 10 minutes. Let the mixture cool.	c. If ferrous sulphate were to be used, there would be a risk that sulphate complexing could interfere with the extraction of the Np.
8	Transfer to a 100 ml separating funnel fitted with a PTFE tap. Use a further 1 ml of 1M HCl to transfer the remaining material from the beaker to the separating funnel and add 10 ml of 0.5M TTA in xylene.	
9	Fit the stopper and shake the separating funnel vigorously for 10 minutes.	
10	Allow the phases to separate then run off the lower aqueous layer.	
11	Wash the organic phase by shaking with 2 x 1 ml portions of 1M HCl.	
12	Back-extract the Np (+ Pu) with 10 ml of 8M HNO_3 for 10 minutes.	d. Pu is back-extracted with the Np but Pa is retained in the organic phase along with Fe.
13	Prepare a small ion-exchange column of 0.5 cm x 8 cm in a glass Pasteur pipette tube of BioRad AG 1 x 4 anion exchange resin. Convert the resin to the nitrate form by passing 10 ml of 8M HNO_3 through the column.	

A5 Continued

Step	Experimental procedure	Notes
14	Pass the back-extract from step 12 through the ion-exchange column. Then wash the column with 4 further 1 ml portions of 8M HNO_3.	
15	Pass 2 x 1 ml portions of 12M HCl through the column to remove nitrate ions then elute Pu with 4 ml of 12M HCl/0.1 M NH_4I.	e. Pu(IV) is reduced to Pu(III) by the iodide mixture, but the Np is not reduced.
16	Wash out the remaining Pu and NH_4I with 2 x 1 ml portions of 12M HCl.	
17	Elute Np with 6 ml of 4.5M HCl into a 25 ml silica beaker.	f. Any U present on the column begins to elute after about 4 ml have passed. Glass beakers contribute U to the sample when heated with acids at later stages.
	Source preparation	
1	Evaporate the eluate to dryness then add 1 ml of ARISTAR HNO_3 and again evaporate to dryness to remove I_2.	
2	Add 1 ml of ARISTAR HCl and evaporate to dryness to remove nitrate ions. Repeat the process.	
3	Add 0.5 ml of ARISTAR HCl + 1 ml of 5% $KHSO_4$ solution and again evaporate to dryness.	
4	Add 2 ml of ammonium oxalate/HCl plating solution to dissolve the residue. Use a 1 ml polythene spitzer to rinse round the beaker and transfer the solution to the plating cell.	
5	Adjust the plating mixture to pH 3 by adding 2-3 drops of ARISTAR NH_4OH. Check with pH paper.	
6	Insert the cap and anode into the plating cell and apply electrical current of 0.5 to 1 A cm^{-2} of the cathode area for 2 h.	

A5 Continued

Step	Experimental procedure	Notes
7	Add 1 ml of ARISTAR NH_4OH while the current is still flowing. Wait one minute and then remove the anode; pour out this plating solution and remove the stainless-steel disc.	
8	Wash the source with distilled water followed by alcohol, and dry.	
9	Hold the disc in a Bunsen flame for a few seconds to burn off organic residues and fix the deposit more firmly to the disc.	
10	Retain the plated source for radiometrics.	
	Radiometrics	
1	Place a clean planchette in the beta detector and count, for example overnight, to establish the detector background.	a. For a low background counter, up to 1000 minutes is needed to provide an adequate number of counts.
2	Count the duplicate ^{239}Np standards and the sample planchettes, preferably alternatively.	b. If the detector has a thin window, a 10 mg cm^{-2} absorber should be placed between it and the source, to prevent the detector responding to alpha particles or low-energy beta particles.
3	If ^{239}Np is being used as the yield tracer, calculate the recovery as detailed in Section A6.	
4	Transfer the sample planchettes to silicon surface barrier detectors and record the alpha spectrum between 4.0 MeV and 5.2 MeV, until sufficient counts have accumulated in the ^{237}Np region of the spectrum (4.8 MeV) to give the required precision of measurement.	c. With low-level environmental samples this may take up to several weeks.
5	Determine the background count of each silicon surface barrier detector at regular intervals throughout its working life. The background of such detectors is normally very low and the user must allocate time to determining the background of detectors according to the accuracy of results required and the activity of samples being counted.	d. If highly-active or poor-quality sources are placed in the evacuated chambers of these detectors, sputtering can cause a rise in the background of the detector. Such deposits can not normally be removed from the detector surface by cleaning.

A5 Continued

Step	Experimental procedure	Notes
6	Periodically, check the calibration of each alpha detector by counting planchettes containing known amounts of ^{237}Np. From this, the efficiency of each detector can be calculated.	e. See Section A1, step 12 for supplies of standardized solutions of radionuclides.
7	Calculate the amount of ^{237}Np present on each sample planchette and, in conjunction with the chemical yield, determine the concentration of ^{237}Np in the original environmental sample.	f. See Section A6 (Table A1) for typical samples and background spectra.

A6. Calculation of results

A6.1 Chemical yield

Table A1 Beta counting of ^{239}Np in a 25 mm gas flow Geiger counter

Sample 1	Counting date 2	Starting time 3	Count duration (min) 4	Counts recorded 5	Counts per minute 6	Counts per minute less background 7	Decay correction factor (f) 8	Counts per minute at 08.00 h 29.6.84 9	Weight of ^{239}Np tracer solution (g) 10
Background	28.6.84	15.45	900	217	0.241	-	-	-	-
Standard I (1st plating)	29.6.84	08.27	50	10,363	207.26	207.02	1.0107	209.33	0.8343
Sample A	"	09.23	50	14,438	288.76	288.52	1.0223	294.94	1.2909
Standard II (1st plating)	"	10.38	50	9,963	199.26	199.02	1.0380	206.59	0.7617
Sample B	"	11.44	50	14,404	288.08	287.84	1.0521	302.83	1.3397
Standard I (2nd plating)	"	15.07	50	756	15.12	14.88	1.0968	16.32	0.8343
Sample C	"	16.07	50	13,259	265.18	264.94	1.1101	294.10	1.2556
Standard II (2nd plating)	"	17.10	50	154	3.08	2.84	1.1232	3.19	0.7617

Table A1 shows the parameters which must be recorded when counting the ^{239}Np to determine the chemical yield. Columns 1 to 7 are self explanatory. Column 8 is the decay correction factor (f) calculated from the mid-point of each counting period according to the standard formula:

$$f = e^{\frac{0.693t}{t_0}}$$

where t is the difference in time between that given in column 9 and half-way through the counting period (columns 2 and 3);
t_0 is the half-life of the nuclide (in this case ^{239}Np
$t_{½}$ = 56.64 h)
e is the exponential number.

Correct all counts to the chosen time in column 9. The time and date given in column 9 may be any convenient time to which all the measurements can be corrected. From the two standards, calculate the mean activity of the tracer solution:

$$\underset{\text{(tracer solution)}}{\text{ct min}^{-1}\text{ g}^{-1}} = \frac{\underset{\text{(1st plating of standard)}}{P} + \underset{\text{(2nd plating of standard)}}{P}}{\text{weight of tracer solution taken}}$$

where P is the counts per minute of ^{239}Np corrected for decay. Column 10 shows the weight of tracer solution used in each case. Thus in the example, the mean activity of the tracer solution from the two standards is:

$$^{1}/_{2}\left(\frac{209.23 + 16.32}{0.8343} + \frac{206.59 + 3.19}{0.7617}\right)$$

$$= \quad 272.88 \text{ ct min}^{-1}\text{ g}^{-1}$$

From this, calculate the chemical yield (Y) in each sample:

$$Y = \frac{\text{ct min}^{-1}\text{ of }^{239}\text{Np in sample}}{\text{weight of tracer added to sample}} \times \frac{1}{\text{ct min}^{-1}\text{ g}^{-1}\ ^{239}\text{Np tracer}}$$

Thus for sample A:

$$Y = \frac{294.94}{1.2908} \times \frac{1}{272.88} \times \frac{100}{1} = 83.73\%$$

A6.2 Concentration of ^{237}Np

Table A2 Alpha spectrometry of ^{237}Np with the silicon surface barrier detector

a) Background planchette

Channel number	Time (minutes)	Counts recorded								Total counts in gate
1	24301		0	0	0	0	0	0	0	
9		0	0	0	0	0	0	0	0	
17		0	0	0	0	0	0	1	0	^{238}U = 2
25		0	0	0	0	1	0	0	0	
33		0	0	0	0	0	1	0	0	
41		0	0	0	0	0	0	0	0	
49		0	0	0	0	0	0	0	0	
57		0	0	0	0	0	1	0	1	
65		0	0	0	0	1	0	0	0	
73		1	0	0	0	0	0	0	0	
81		0	0	0	0	0	1	0	0	
89		0	0	0	0	0	1	0	1	^{234}U + ^{237}Np = 9
97		0	0	1	0	2	0	1	0	
105		0	0	3	0	2	0	0	1	
113		2	0	0	0	0	0	0	0	
121		0	0	0	0	0	0	0	0	

b) Sample planchette

Channel number	Time (minutes)	Counts recorded								Total counts in gate
1	23128		0	0	0	0	0	2	0	
9		0	1	0	0	0	0	0	0	
17		0	0	0	1	0	1	0	0	^{238}U = 25
25		0	0	2	4	4	4	1	5	
33		2	1	0	0	0	0	0	0	
41		0	0	0	0	0	0	0	0	
49		0	0	0	0	0	0	0	0	
57		0	0	0	0	0	0	0	1	
65		0	1	1	1	0	0	3	2	
73		2	1	4	1	4	6	11	6	^{234}U + ^{237}Np = 578
81		6	7	9	15	15	15	26	25	
89		26	37	38	57	55	48	39	41	
97		17	14	11	16	8	7	2	1	
105		0	1	1	0	2	0	0	0	
113		0	1	1	0	3	0	0	0	
121		0	0	0	0	0	0	0	0	

1. Consider the alpha spectra shown in Table A2. The counting time, in minutes, is given in channel 1. The sample spectrum shows some contamination from uranium, but this can be assessed from the ^{238}U peak and, from this, an appropriate correction made for the contribution of ^{234}U in the ^{237}Np area of the spectrum.

   From Figure A1:

   $$c = f\ a$$

   where f is a factor relating the count rates of the ^{234}U and ^{238}U peaks.

   If x represents the count rate of the ^{237}Np:

   $$x = b - f\ a \qquad \ldots\ldots\ldots\ldots (1)$$

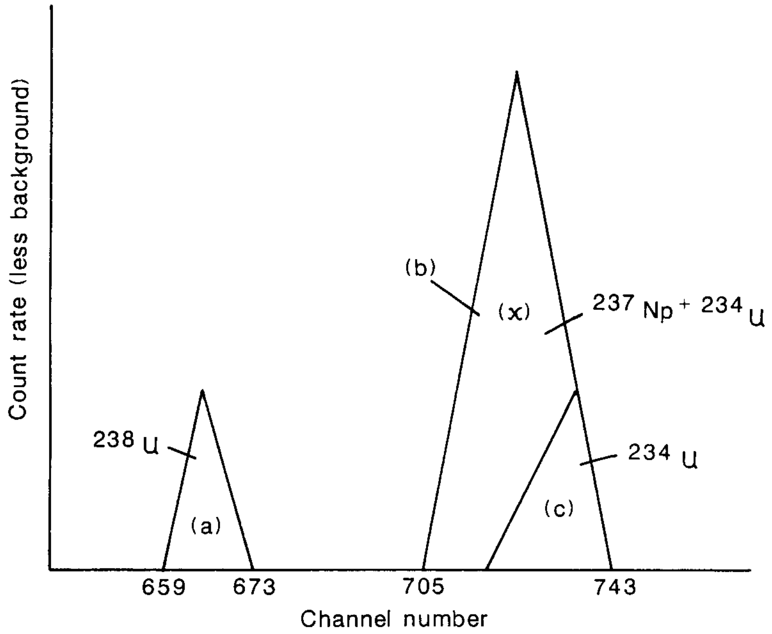

Figure A1. Interference of ^{234}U in the spectrum of ^{237}Np (diagrammatic): χ = (b)-(c).

2. Add the counts in the ^{238}U gate and in the ^{237}Np + ^{234}U gate for both sample and background spectra and calculate counts per minute minus the background (ct min^{-1} - background) for both gates of the sample spectrum.

3. Calculate (ct min^{-1} - background) for the ^{237}Np contribution in the sample (x) according to equation 1 above.

4. Let the counting efficiency of the detector be D (ct min^{-1} Bq^{-1}). The ^{237}Np on the source = $\frac{x}{D}$ Bq.

5. If Y = chemical yield (from sub-Section A6.1) and W = weight of the original sample (kg), then the concentration of ^{237}Np in the original sample (N) is given by:

$$N = \frac{x}{D} \times \frac{1}{Y} \times \frac{1}{w} \text{ Bq kg}^{-1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

For example, if the spectrum in Table A2(b) represents the alpha spectrum of sample A in Table A1, then:

background count rate in ^{238}U gate $= \frac{2}{24,301}$ ct min^{-1}

^{238}U count rate in sample A $= \left(\frac{25}{23,128}\right) - \left(\frac{2}{24,301}\right) =$

0.0010 ct min^{-1} ((a) on Figure A1)

f = 1.12

$\therefore$ ^{234}U count rate = 0.0010 x 1.12 = 0.00112 ct min^{-1} ((c) on Figure A1)

$$b = \frac{578}{23128} - \frac{9}{24301} = 0.02462 \text{ ct min}^{-1}$$

$\therefore$ x = 0.2462 - 0.00112 = 0.02350 ct min^{-1}.

Now D = 15.96 ct min^{-1} Bq^{-1}
Y = 83.73%
W = 84.55 kg.

$$\text{Thus } N = \frac{0.02350}{15.96} \times \frac{100}{83.73} \times \frac{10^6}{94.55} \ \mu\text{Bq kg}^{-1}$$

$$= 18.60 \ \mu\text{Bq kg}^{-1}.$$

A6.3 Precision of the analysis

Clearly, there are a number of imprecisions in a complex analysis of this type. These include, weighing the original sample and the added tracer solution, the calibration of alpha detectors and the radiometric assay of tracer and determinand nuclides. For the determination of neptunium nuclides in environmental samples at low levels, it is likely that imprecisions in counting the samples will be the major source of uncertainty in the analysis. The errors included in the calculations should, therefore, reflect this fact. For a simple discussion of the statistics of radiometric counting refer to Faires and Boswell (1981).

If S = gross count rate, B = background count rate and t_s and t_B are the respective counting times:

$$\sigma_{S-B} = \sqrt{\frac{S}{t_s} + \frac{B}{t_B}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

In the case of the ^{239}Np yield determination, the combined errors of counting two standards and the sample must be taken into account. Thus, the combined counting error for the ^{239}Np standards is given by:

$$\sigma_{std} = \sqrt{\frac{S_1}{t_1} + \frac{B}{t_B} + \frac{S_2}{t_2} + \frac{B}{t_B}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where S_1 and S_2 are the count rates for the two ^{239}Np standards
B is the background count rate
t_1, t_2 and t_B are the respective times for which each was counted in the beta counter.

The error on the beta counting of the yield tracer in the sample is given by:

$$\sigma_z = \sqrt{\frac{Z}{t_z} + \frac{B}{t_B}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where Z is the count rate of the sample
t_z is the time for which the sample was counted for ^{239}Np in the beta counter.

From equation 2 (using the example given in sub-section A6.1):

$$\sigma_{std} = \sqrt{\frac{207.36}{50} + \frac{15.12}{50} + \frac{199.26}{50} + \frac{3.08}{50} + 4\left(\frac{0.24}{900}\right)} = 2.91 \text{ ct min}^{-1}$$

Thus the percentage error on the ^{239}Np standards

$$= \frac{2.91 \times 100 \times 2}{(207.26 + 15.12) + (199.26 + 3.08) - 4(0.24)} = 1.37\%$$

And from equation 3 (for sample A in Table A1):

$$\sigma_z = \sqrt{\frac{288.76}{50} + \frac{0.24}{900}}$$

$$= 2.0 \text{ ct min}^{-1}.$$

Thus, the percentage error on the ^{239}Np content of sample A (in Table A1):

$$= \frac{2.40 \times 100}{(288.76 - 0.24)} = 0.83\%$$

In the alpha spectrometric measurement, errors which arise from the presence of interfering nuclides underneath the ^{237}Np peak must also be included. From Figure A1, the general equation for the error associated with the measurement of x is:

$$\sigma_x = \sqrt{\frac{b}{t} + \frac{2fa}{t}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where a, b, c and x are the respective count rates (less background) for the nuclides as shown in the figure.

From Table A2(a), it is clear that a small but significant background count occurs in each of the gates and the uncertainties of these background count rates must also be included in the error calculation.

Using the example given in sub-section A6.2:

$$\sigma_x = \sqrt{\frac{578}{(23{,}128)^2} + \frac{9}{(24{,}301)^2} + 2f\left(\frac{25}{(23{,}128)^2} + \frac{2}{(24{,}301)^2}\right)}$$

$$= 0.00110 \text{ ct min}^{-1}.$$

Since $x = 0.02350$ ct min^{-1}, then the percentage error on the ^{237}Np count rate

$$= \frac{0.00110 \times 100}{0.02350} = 4.68\%$$

It is now possible to combine the various errors in the radiometric assay of the ^{237}Np content of a sample:

$$\sigma_{\text{total}} = \sqrt{\begin{pmatrix}\text{\% error}\\ \text{on}\\ \text{alpha}\end{pmatrix}^2 + \begin{pmatrix}\text{\% error}\\ \text{sample}\\ \text{recovery}\end{pmatrix}^2 + \begin{pmatrix}\text{\% error}\\ \text{yield tracer}\\ \text{standards}\end{pmatrix}^2}$$

For the example worked in sub-section A6.2:

$$\sigma_{\text{total}} = \sqrt{(4.68)^2 + (0.83)^2 + (1.37)^2}$$

$$= 4.95\%$$

Thus, the ^{237}Np content of the sample
= 28.6 ± 0.9 $\mu Bq\ kg^{-1}$.

A7 Appendix references

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