DEVELOPMENT AND APPLICATION OF METHODS FOR THE ASSAY OF NEPTUNIUM IN ENVIRONMENTAL MATRICES

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ABSTRACT

Inductively coupled plasma mass-spectrometry (ICP-MS) and neutron activation analysis (NAA) techniques have been investigated as rapid, alternative methods for the analysis of ^{237}Np and other long-lived actinides in environmental matrices. By comparison to the more routine α-spectrometric method, equivalent, if not improved, detection limits for ICP-MS and NAA have been found.

Radiochemical separation and pre-concentration are required for all the methods studied. In this work, anion exchange and TTA solvent extraction of Np^{IV} from hydrochloric acid media were used to separate Np from potential interferences from the naturally occurring nuclides of uranium. The degree of interference was found to vary for each approach and was quite severe in the case of NAA. Analysis by ICP-MS tolerates a lower degree of chemical purification and results in a significant increase in sample throughput. The rapid, mass-scanning facilities of the instrument have allowed multiactinide determination on single samples and have provided important additional information concerning plutonium nuclides in environmental samples. In the absence of suitable certified reference materials, the accuracy and precision of the ICP-MS technique were determined by a series of laboratory intercomparison and replicate analyses. On this basis, the reported measurements of ^{237}Np and plutonium nuclides were considered valid.

The ICP-MS method developed here has been applied to the routine analysis of ^{237}Np and plutonium nuclides in samples of soils and sediments from W.Cumbria, known to be contaminated by discharges from the BNFL fuel re-processing plant at Sellafield. Concentrations ranging from 3.16 to 0.004 Bq kg^{-1} ^{237}Np have been measured with excellent precision. Typically, an exponential decrease of ^{237}Np activity with depth has been found in a number of soil profiles. The pattern is the same as that found for other anthropogenic nuclides in the profiles but, when the effect of profile density variation is considered, it appears that a component of the neptunium is present in a more mobile form and is responsible for a degree of smearing of its distribution down the soil profile.

During the transfer of Sellafield-derived ^{237}Np from the BNFL, through the marine environment to a number of terrestrial sampling locations in W. Cumbria, the activity ratios of ^{237}Np to ^{239,240}Pu, ^{241}Am and ^{137}Cs change in a manner which implies that there is a loss of neptunium from the solid phase. Detailed studies of the chemical association of neptunium in samples of silt and surface soil show that, compared to the other transuranic nuclides studied, a significant proportion of the element is associated with the more sensitive phases the exchangeable and adsorbed components, including carbonate. The organic matter and residual phases are nevertheless found to be significant and merit further study.

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION AND AIMS

This thesis describes the development and application of methods for the analysis of the long-lived, α-emitting, transuranic nuclide ^{237}Np in environmental samples from W. Cumbria, UK. The text can be split into two main sections, one on method development and the other on the practical application of the methods to improve the understanding of neptunium geochemistry.

Neptunium has suffered an obscure existence in the geochemical world, primarily because of its low activity abundance in the environment. This is even true for the W. Cumbrian area, where localized and significant enrichments of transuranic nuclides occur close to the BNFL re-processing plant at Sellafield. There is some concern about ^{237}Np in a radiological context. At present it is of insignificant activity relative to fission product and actinide nuclides in fuel wastes but, in the long term, its long half-life and high environmental cause a significant commitment to man in the intermediate to long term, following disposal of radioactive waste (Cohen, 1983; Kirchner, 1990).

BNFL Sellafield, on the coast of W. Cumbria, has discharged quantities of radioactive waste, under licence, into the Irish Sea for the past 30 years. It is a classic point source of pollution and has afforded the chance for numerous studies of radionuclide behaviour and of the various processes which interact with and modify the discharges. Very few data exist on the behaviour of neptunium nuclides in the environment and of these almost all relate to the marine environment.

The experimental work in this study aims to investigate and apply two very different methods for ^{237}Np assay which are potentially highly sensitive and more rapid than conventional radiometric techniques. Their application to marine and terrestrial samples follows work initiated by Livens (1985) on plutonium geochemistry. By comparing neptunium to fission product and transuranic nuclides, useful information on its mobility and behaviour in the local Cumbrian environment will be obtained.

This first chapter contains a review and discussion of the chemical properties pertinent to its behaviour both during analysis and in the environment. The available literature on neptunium geochemistry has been studied and is reviewed with emphasis on relative elemental behaviour. Chapter 2 contains a description and discussion of the analytical methods available and of those studied here in detail, addressing the problem of ultratrace environmental analysis. Descriptions of the techniques used to acquire ancillary data are also included. Finally, in Chapter 3, the performances of the analytical techniques developed here are assessed and conclusions are drawn on their suitability for environmental assay. The geochemical behaviour of neptunium, as implied from the samples analyzed, is discussed in the context of W. Cumbria.

1.2 THE CHEMISTRY OF NEPTUNIUM

1.2.1. HISTORICAL PERSPECTIVE - THE DISCOVERY OF NEPTUNIUM

The discovery of the first transuranium element by McMillan and Ableson (1940), of mass number 93, placed neptunium, as it was later named, at the gateway of one of the most prolific periods of chemical discovery. Within the next forty years or so, fourteen new elements were discovered, resulting in a 15% increase in the size of the periodic table (Seaborg, 1978).

Early experiments and discussions by Fermi (1934), Segrè (1939) and McMillan (1939) on the recently observed neutron-induced fission of uranium provided a somewhat jittery start to the frantic activity that followed. The experimental work was based on fairly crude, but ingenious, neutron capture studies of uranium salts deposited on simple cigarette papers. The recoiling fission nuclei were caught by successive layers of papers, their penetration a function of energy.

Various reactions (n,α; n,p; n,γ) had been proposed to explain the interactions of various elements with neutrons (Fermi, 1934). The formation of elements with mass >92 was postulated to explain the uncharacteristic behaviour of the species formed when uranium was irradiated with neutrons (Fermi, 1934). However, despite the observation of two non-recoiling components in the irradiated foils (McMillan, 1939; Segrè, 1939) of 23 minute and 2.3 day half-life (one of which had high mass and rare earth like chemical properties) and in spite of the identification of the 23 minute component as a β-emitting uranium nuclide, Segrè (1939) was forced to suggest, "*The necessary conclusion seems to be that the 23 minute uranium decays to a very long-lived 93 and that transuranium elements have not been observed*". This, with hindsight must be one of the most tantalising statements made, with all indications that a new element had been synthesised, yet not quite able to define it.

McMillan and Ableson (1940), stimulated by the earlier conclusions of McMillan (1939) and Segrè (1939) that the 2.3 day product of uranium activation was a rare earth, further investigated this phenomenon. Their eventual discovery and identification of this new element was based on a number of observations:

(i) the 2.3 day component was observed in irradiated uranium salt only and was therefore unlikely to be an energetic fission product nucleus;

(ii) elimination of slow neutrons with cadmium shielding reduced the fission product activity but did not affect the ratio of the 23 minute and 2.3 day components. This suggested a possible generic relationship, which was confirmed by the ingrowth of the 2.3 day component from the freshly isolated 23 minute uranium nuclide;

(iii) the 2.3 day component did not behave consistently as a rare earth, which Segrè (1939) had called it. Much more rigorous investigation of its redox chemistry identified two valence states similar to U^{4+} and UO_2^{2+} (or $U_2O_7^{2-}$). However, the oxidation state potentials differed from uranium and the lower oxidation state was more stable than U^{4+}. This new element indicated the possible existence of a second rare earth like group (McMillan and Ableson, 1940). They also identified the daughter of the β^- and γ-emitting $^{239}93$ as $^{239}94$ which had a long half-life and low β-emission rate.

The observations arise from the following reactions:

$$^{238}\mathrm{U}\ (n,\gamma)\ ^{239}\mathrm{U} \xrightarrow[\text{23 min}]{\beta-} {}^{239}\mathrm{Np} \xrightarrow[\text{2.3 day}]{\beta-} {}^{239}\mathrm{Pu}$$

The intense investigation of the transuranics which quickly followed these observations firmly established neptunium as one of the most interesting elements produced by modern alchemy. However its "glory" was short-lived and obscured by the greater interest in the nuclei of element 94 (plutonium), which were found to be of greater strategic importance (Seaborg, 1978; Katz *et al*, 1986a).

An interesting footnote to illustrate this point is to compare the volumes of material devoted to the chemistries of plutonium and neptunium contained in the recently updated classic text by Katz *et al* (1986a). Plutonium has an impressive 387 pages, neptunium a mere 55.

1.2.2 NUCLEAR PROPERTIES, PREPARATION AND ISOLATION

Many isotopes of neptunium are known with half-lives ranging from <5 minutes to $>10^6$ years. These, together with their principal decays and formation reactions are presented in Table 1.1. Most interest has been shown in the very long-lived ^{237}Np, which, due to its 2 $\times10^6$ year half-life, has been most used to study the chemical behaviour of the element. Its specific activity is thus low enough for it to be handled in appreciable amounts. Wahl and Seaborg (1948) were the first to study the nuclear properties of ^{237}Np. They noted the absence of appreciable fission with slow neutrons (hence excluding this nuclide from accelerated study in strategic research programmes) and assigning it a 3 $\times10^6$ year half-life. Magnusson and LaChapelle (1948) made a more accurate determination and were the first to isolate pure neptunium compounds.

^{237}Np is produced as a by-product of the operation of nuclear reactors (Fahey, 1986) approximately 70% via the route

Table 1.1: The isotopes of Neptunium: Nuclear properties and methods of production (compiled from Lederer and Shirley, 1978). * principle decay modes first, (/) denotes equivalence of decay.

Mass No.	$T_{1/2}$	**Decay***	**Production**
229	4.02 min	α/ E.C.	^{233}U (p, 5n).
230	4.63 min	α, E.C., β^+	^{233}U (p, 4n).
231	48.8 min	E.C., α	^{233}U (d, 4n), ^{235}U (d, 6n), ^{233}U (d, 3n).
232	14.7 min	E.C.	^{235}U (d, 5n), ^{238}U (d, 8n), ^{233}U (d, 3n).
233	36.2 min	E.C., α	^{233}U (d, 2n), ^{235}U (d,4n).
234	4.40 day	E.C., β^+	^{233}U (d, 2n), ^{235}U (d,3n), ^{235}U (p, 2n), ^{233}U (α, p2n).
235	396.1 day	E.C., α	^{235}U (d, 2n), ^{239}Pu daughter (E.C.).
236^m	1.15 x10^5 yr	E.C., β^-	^{235}U (d, n).
236	22.5 hour	E.C., β^-	^{235}U (d, n), ^{235}U (α, 2np).
237	2.14 x10^6 yr	α	^{238}U (n, 2n) ^{237}U (β^-).
238	2.12 day	β^-	^{237}Np (n, γ), ^{238}U (d, 2n), ^{238}U (p, n).
239	2.35 day	β^-	^{238}U (n, γ) ^{239}U (β^-), ^{243}Am daughter, ^{238}U (^3He, p2n).
240^m	7.51 day	β^-, I.T.	^{240}U daughter.
240	67.1 min	β^-	^{238}U (α, pn), ^{238}U (^3He, p2n).
241	16.0 min	β^-	^{238}U (α, p).
242	5.50 min	β^-	^{244}Pu (n, p2n), ^{242}Pu (n, p), ^{242}U daughter.

$$^{238}U\ (n,2n)\ ^{237}U \xrightarrow[6.8\ day]{\beta-} {}^{237}Np$$

and 30% from the two processes

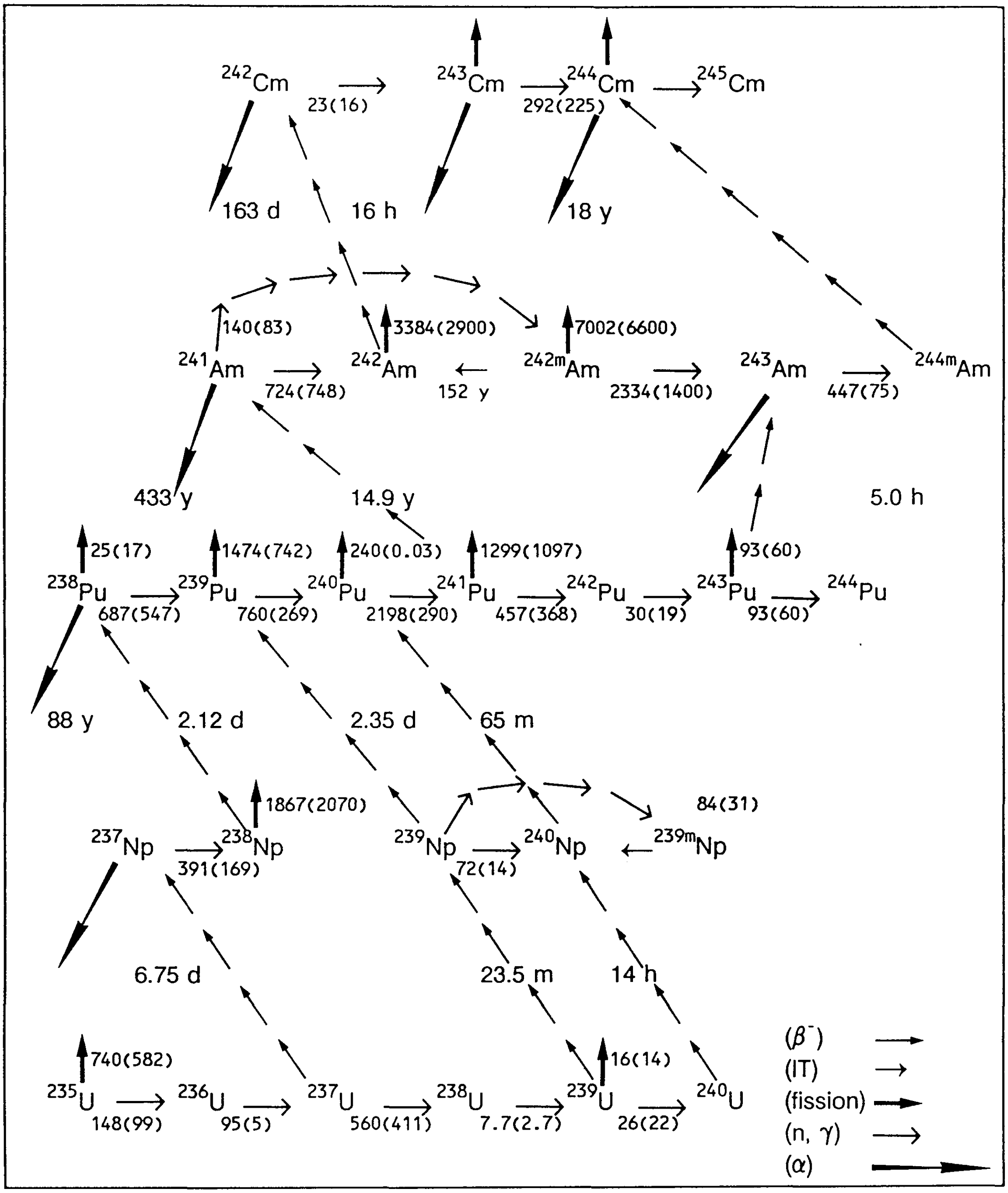
$$^{235}U\ (n,\gamma)\ ^{236}U\ (n,\gamma)\ ^{237}U \xrightarrow[6.8\ day]{\beta-} {}^{237}Np$$

and the decay of ^{241}Pu and ^{241}Am

$$^{241}Pu \xrightarrow[14\ year]{\beta-} {}^{241}Am \xrightarrow[433\ year]{\beta-} {}^{237}Np$$

The schematic diagram (Figure 1.1) summarises the predominant nuclear reactions during the

Figure 1.1: Schematic diagram summarising main neutron reactions during burn-up of nuclear fuel. Reaction cross-sections for LWR (therm. neutrons) shown (Choppin and Rydberg, 1980).



irradiation of nuclear fuel in a reactor. The paths involving nuclides of neptunium are highlighted. The diagram has deliberately been left complex in order to illustrate the generic relationships between the nuclides produced. The exact significance of any of the various routes to ^{237}Np formation will vary depending on the type of fuel and its isotopic composition, both at the start and during burn-up. It is outside the scope of this short description to include more detailed discussion on the physics of reactor burn-up. Excellent references on the subject are a series of early lectures by Tyror (1971) and discussions by Flowers (1983) and Askew *et al* (1983).

The major use of ^{237}Np is in the production of ^{238}Pu through the neutron capture reaction

$$^{237}\mathrm{Np}\ (n,\gamma)\ ^{238}\mathrm{Np} \xrightarrow[2.1\ \mathrm{day}]{\beta^-} {}^{238}\mathrm{Pu}$$

^{238}Pu is used as a power source for remote systems in space vehicles, terrestrial navigation beacons and medical devices (Fahey, 1986). One gramme of ^{238}Pu produces approximately 0.56 W of thermal power, primarily through α-decay (Seaborg, 1978). In general, ^{237}Np is isolated during re-processing. Its behaviour in and recovery from the fuel cycle will be discussed in section 1.3.

1.2.3 NEPTUNIUM IN NATURE

This short section is included purely for completeness. The natural abundances of isotopes of neptunium are insignificant in radiological terms and the half-life of the longest-lived nuclide is too short for it to be a surviving primordial element. However, under certain conditions, it can be observed in natural samples.

The search for neptunium and plutonium nuclides in pitchblende concentrates was initiated by Seaborg and Perlman (1948) in order to ascertain whether, *"useful quantities could be extracted from minerals"*, as alternatives to the low abundance, fissile nuclide ^{235}U. Peppard *et al* (1951; 1952) observed levels of ^{239}Pu in pitchblende concentrate which were similar to those found by Seaborg and Perlman (1948) along with some activity due to ^{237}Np (although this was not accurately quantified). ^{237}Np exists because of its continuous creation as a product of neutron capture by uranium and the observation of ^{239}Pu in these ores must imply the presence of ^{239}Np as an intermediate (see Figure 1.1). Levels were precisely determined by Myers and Linder (1971) by chemical separation of both ^{239}Pu and ^{237}Np from a Katanga pitchblende sample. ^{237}Np was determined by isotope dilution mass spectrometry and ^{239}Pu by α-spectrometry. For a sample containing 40.72% U, they obtained

$$5.45\ \mathrm{x}10^{9}\ \mathrm{atoms}\ ^{237}\mathrm{Np}\ \mathrm{g}^{-1}\mathrm{U}$$

$$7.84\ \mathrm{x}10^{9}\ \mathrm{atoms}\ ^{239}\mathrm{Pu}\ \mathrm{g}^{-1}\mathrm{U}$$

with an overall uncertainty (1σ) of 5%. The production rate constant is a function of the neutron capture cross-section (σ) and the neutron flux (ϕ). The flux itself is a function of the local microscopic environment, eg soil water content, mineral association. The neutrons originate from a number of sources; spontaneous fission of ^{238}U, (α,n) reactions on elements of low atomic number (cf Ra/Be neutron sources) or fission or spallation reactions induced by cosmic rays. Further neutron multiplication by ^{235}U fission may also contribute (Seaborg, 1978).

1.2.4 CHEMICAL PROPERTIES OF NEPTUNIUM

The chemical properties of neptunium will dictate its behaviour in the environment and are utilized in the analytical approach to neptunium assay. It is important to place neptunium in perspective with respect to the other actinides, as in both environmental behaviour and analysis neptunium is in close association with nuclides of uranium, plutonium and americium.

(a) the position of neptunium in the actinide series

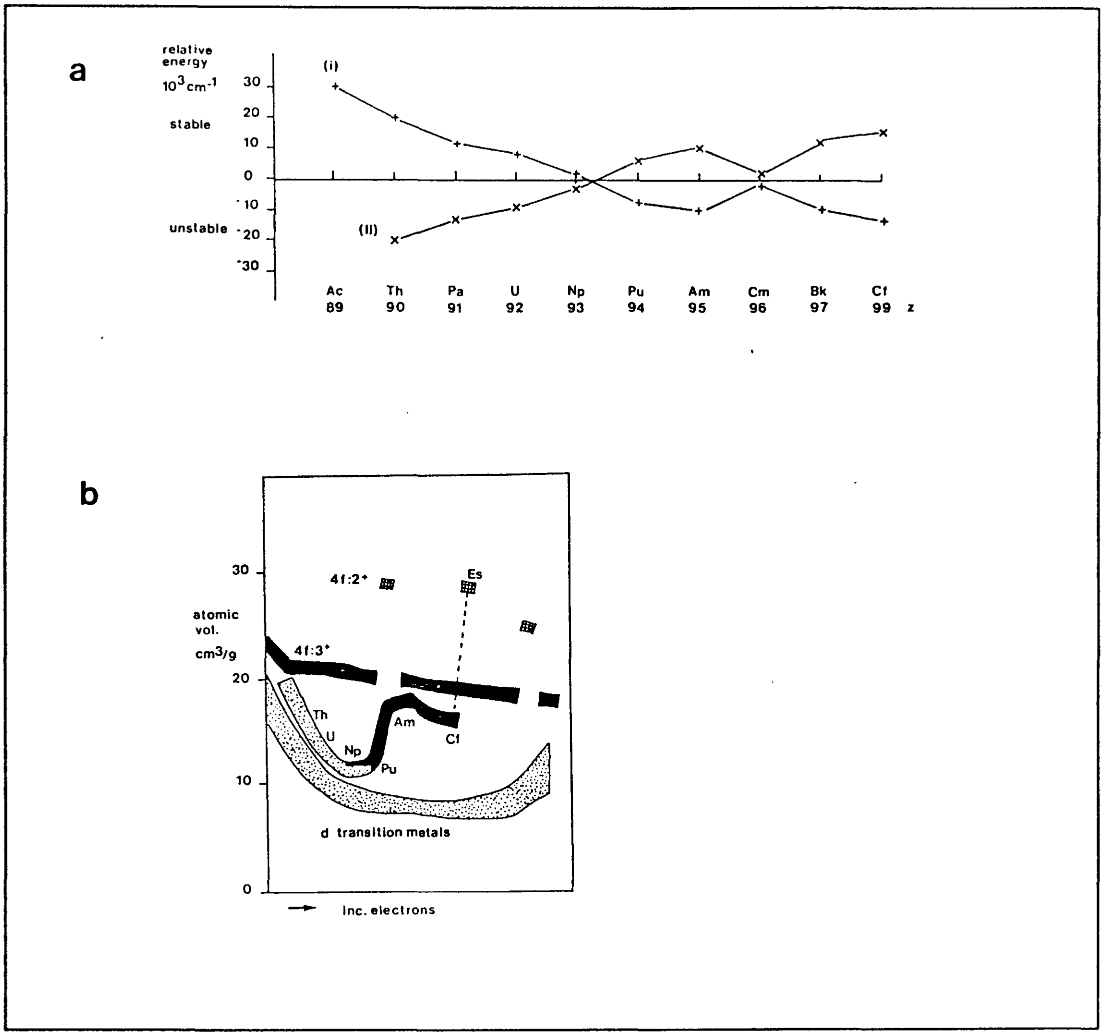
Neptunium is the fifth member of the actinides (abbreviated: An) following naturally occurring actinium, thorium, protactinium and uranium. In 1944, Seaborg (1978) placed the actinides at the foot of the modern periodic table, in an analogous position to the lanthanides (abbreviated: La). The existence of the actinides is possible through the successive filling of the 5f electron shell across the period in a far less regular manner than in the corresponding lanthanides (derived from a consideration of absorption spectra (Katz *et al*, 1986a). At the start of the series, the 6d electrons are energetically favoured compared to the lanthanides (Cotton and Wilkinson, 1980) until, from Th onwards, the 5f shell becomes lower in energy than the 6d. Beyond Np, the 4f and 5f elements strongly resemble each other due to a decrease in the spatial extent of the 5f shells (Lander and Fuger, 1989). This variation can be seen in a number of trends.

The known oxidation states of the actinides are shown in Table 1.2 with the most stable

Table 1.2: The known oxidation states of the actinides up to Lr (most stable states in bold, least stable in parentheses) (adapted from Greenwood and Earnshaw, 1984).

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
					(2)			(2)	(2)	2	2	2	
(3)	(3)	3	3	3	**3**	**3**	**3**	**3**	**3**	**3**	**3**	3	**3**
4	4	4	4	**4**	4	4	4	(4)					
	5	5	**5**	5	5								
		6	6	6	6								
			7	**7**									

Figure 1.2: (a) relative energies of neutral actinides (i) $5f^n7s^2$:$5f^{n-1}6d7s^2$, (ii) $5f^{n-1}6ds^2$:$5f^n7s^2$ (b) atomic vol. v n_e (Huheey, 1975; Cotton & Wilkinson, 1980; Fred, 1986; Lander & Fuger, 1989).



highlighted. Up to neptunium, the most stable state is that involving all valence electrons but, from Np onwards, it becomes lower until, in the second half of the series, the trivalent state becomes dominant. The ionic radii from Ac onwards show a definite contraction across the series, comparable to the "lanthanide contraction" of the 4f series (Cotton and Wilkinson, 1980; Greenwood and Earnshaw, 1984). This trend can be explained by the fact that, although each increase in nuclear charge is balanced by a simultaneous increase in electronic charge, the directional characteristics of the 5f orbitals are less shielding than other orbital types. The nuclear charge has a more pronounced influence on the whole electronic cloud. This is also nicely illustrated in the molar volumes exhibited by actinide-formate compounds (Hauck, 1976). Figure 1.2a and Figure 1.2b very clearly illustrate this variation across the series and show a definite inversion in actinide behaviour, with neptunium at the "pivotal" position.

The ionization energies of the early actinides are lower than for the lanthanides due to the poor penetration of the 5f orbitals into the inner core of electrons and the outer electrons thus will be more effectively shielded from the nuclear charge than for the lanthanides. This can clearly be seen in Figure 1.2a, where the early actinides follow 3d/4d transition metal trends (Huheey, 1975; Lander and Fuger, 1989). Since the outer electrons are less firmly held, they are all available for bonding up to Np and the onset of trivalent character is delayed (Figure 1.2b). The hybrid nature of the actinide series in general is clearly illustrated. Note that the anomalous elements in the lanthanide group, such as Eu and Yb, reflect the increased stability imparted when half-filled shells are possible.

(b) chemical behaviour

Neptunium is a silvery metal, as malleable as uranium, which reacts with air to form a thin oxide coating (Fahey, 1986). The most significant feature of the metal is its unique high solubility in α- and β-phases of Pu metal. It has three different crystalline phases, α-Np(s) being very similar to α-U(s). It also forms intermetallic compounds with Al, Be, Cd and Pd. Like Th, U and Pu, Np forms at least two hydrides (NpH_2 and NpH_3) which are isostructural with their plutonium equivalents and decompose above 300 °C. Oxides of neptunium are obtained by heating hydroxides or nitrides in air and many complex oxides can be formed from NpO_2 (Cotton and Wilkinson, 1980). They may contain 3 to 7 oxygen atoms, depending on reaction proportions and many are similar to the corresponding uranates (Cotton and Wilkinson, 1980; Greenwood and Earnshaw, 1984; Fahey, 1986). Carbides, nitrides, phosphides, silicides, sulphides, selinides, tellurides and arsenides are also known (Zachariasen, 1948; 1949; Dabos *et al*, 1986; Fahey, 1986).

Studies of neptunium-halogen chemistry have been extensive (Greenwood and Earnshaw, 1984; Fahey, 1986). The fluorides are the best characterised in most oxidation states. Chlorides, bromides and iodides have less extensive chemistry. Compounds of mixed alkali/alkaline earth metal oxides and halides have also been prepared (Greenwood and Earnshaw, 1984; Alcock *et al*, 1986). Np^{IV} forms a borohydride, $Np(BH_4)_4$, which is isostructural with the Pu equivalent but not the U equivalent (Banks *et al*, 1980). Sulphates of Np have also been synthesised (Alcock *et al*, 1982). Recent work, initiated by the search to find stable phases to host radioactive waste containing actinide nuclides, has resulted in the synthesis of Np^{IV} Ca monazite (Tabateau *et al*, 1988) via:

$$NpO_2 + CaCO_3 + 2(NH_4)_2HPO_4 \rightarrow CaNp(PO_4)_2 + 3H_2O + CO_2 + 4NH_3$$

The known organometallic chemistry of neptunium is far from extensive compared to the transition metals and other actinides (even plutonium) (Huheey, 1975; Marks, 1982; 1986; Marks and Streitweiser, 1986). This reflects the unavailability of neptunium for experiment rather than an inability to form compounds. Nevertheless, a number of reviews have been published (Marks, 1982; Marks and Streitweiser, 1986). It is interesting to see that for Np (with Th, Pa and

U), hybrid d-block covalency and f-block ionic characteristics are observed for many of the compounds formed. Explanation has already been given above. The range of ligands and oxidation states for which stable compounds have been isolated and characterised is broad, from simple Np^{IV} formates (Hauck, 1976), acetates (Magnusson and LaChapelle, 1948) and acetyl acetates (Allard, 1972) to more complex species containing, pyrometallitic anhydride (Cousson *et al*, 1984; Nectoux *et al*, 1984), bipyridyl (Alcock *et al*, 1984) and cyclopentadienyl/phenylphosphine oxide (Bagnall *et al*, 1986) ligands. As is characteristic of neptunium solid and solution chemistries and of the actinides in general, complexes containing coordinating oxygen atoms or highly localized electron systems predominate (Huheey, 1975; Marks, 1982; Fahey, 1986).

1.2.5 AQUEOUS CHEMISTRY OF NEPTUNIUM

(a) redox trends

In aqueous solution neptunium exhibits all oxidation states from III to VII inclusive, the stability of each a function of pH and the presence of complexing agents (Fahey, 1986). The behaviour of each oxidation state is similar to that for the other actinides, with allowances made for the series trends discussed earlier. More specific variations in behaviour occur primarily as a result of specific thermodynamic differences.

Np^{III} and Np^{IV} exist as hydrated cations in acid solution. Np^{V} and Np^{VI} are both stable in acid solution as the linear oxygenated species NpO_2^{+} and NpO_2^{2+} and as $NpO_2(OH)_2^{-}$ and NpO_4^{-} in basic solution. Np^{VII} is only observed in basic solution as NpO_5^{-} and in acid it oxidizes water (Burney and Harbour, 1974; Katz *et al*, 1986b).

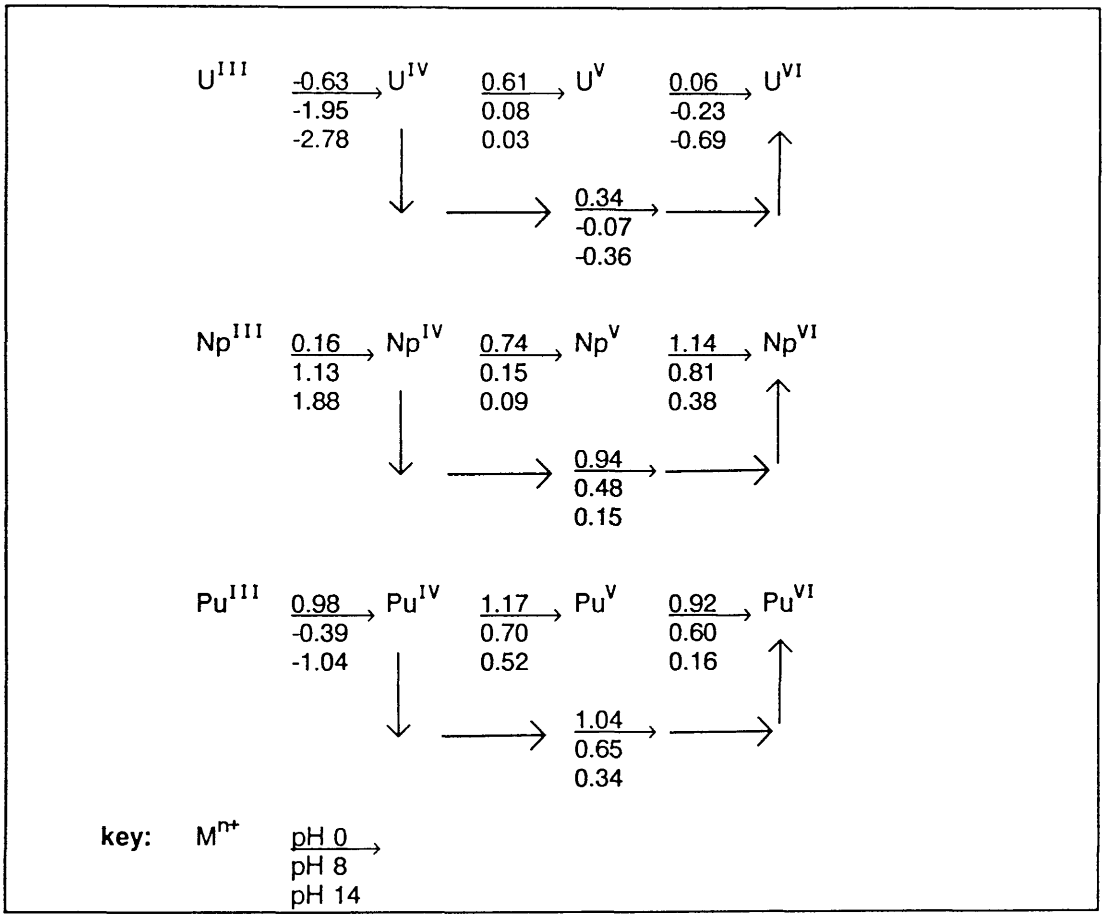
As with the other actinides, neptunium ions interact extensively with water molecules as a function of their charge densities. The interaction is such that it should really be considered an example of complexation with OH^{-}. For the actinides (An) in general, this "hydrolytic" behaviour decreases in the order $An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}$. For Np, the order is $Np^{4+} > Np^{3+} > NpO_2^{2+} > NpO_2^{+}$ due to charge density effects (Katz *et al*, 1986b). The hydrolysis of An^{4+} is the most extensive, with An^{3+} and An^{4+} acting as acids in solution:

$$An(OH_2)_{(x)}^{(n)+} \quad \rightleftharpoons \quad An(OH_2)_{(x-1)}(OH)^{(n-1)+} + H^{+}$$

For Pu^{IV}, this behaviour is very important and has been the subject of much study (Coleman, 1965; Choppin, 1983; Katz *et al*, 1986b). It is of special significance since this oxidation state is most frequently used for chemical separations (see sections 1.3 and 2.2) and the polymeric species which can form through irreversible condensation reactions between the hydrated cations can cause severe difficulties in analytical and fuel process technology. The polymers tend to form when solutions are diluted with water, forming inhomogeneous regions of high pH (Coleman, 1965). Although less extensively studied, analogous Np^{IV} polymerization has been observed in aqueous solution at $[H^+] < 0.3M$ (Burney and Harbour, 1974).

Data on redox potentials are available for Np both in acidic and basic solutions (Patil *et al*, 1978). These have been summarized in Figure 1.3, with U and Pu couples included for comparison. Recently, the temperature and ionic strength dependencies of Np redox couples have been studied (Blanc and Madic, 1984). The IV/ III and VI/ V couples for Pu and Np vary linearly with positive gradients of temperature. The IV/ III gradients are fairly steep and of similar values for both Pu and Np. The VI/ V gradients are lower and values for Pu and Np are significantly different. The variation in the temperature v ΔE (mV) gradient with ionic strength also shows discrepancies between observed and expected behaviour. In the case of IV/ III it is believed that these discrepancies reflect differing hydrolytic tendencies while, for VI/ V, unexplained differences between Pu and Np aquo ions are implicated.

Figure 1.3: The variation in redox potential of aqueous actinides with pH (Choppin, 1983).



Auto oxidation/reduction reactions of Np ions in various oxidation states are important. The extent of reaction is determined by the solution composition . Np^{V} disproportionation occurs via

$$2NpO_2^{+} + 4H^{+} \rightleftharpoons Np^{4+} + NpO_2^{2+} + 2H_2O$$

and is favoured by high $[H^{+}]$ and the presence of strong complexing agents (eg $K_{1MHClO_4} = 10^{-7}$, $K_{1MH_2SO_4} = 10^{-2}$). Much less important reactions are also seen such as

$$2Np^{IV} \rightleftharpoons Np^{III} + Np^{V}$$

$$3Np^{IV} \rightleftharpoons 2Np^{III} + Np^{VI}$$

Other reactions observed in alkali include

$$Np^{V} + Np^{VII} \rightleftharpoons 2Np^{VI}$$

$$Np^{IV} + Np^{VI} \rightleftharpoons 2Np^{V}$$

Equilibria are reached rapidly for electron transfer between IV+III oxidation states and between VI+V oxidation states but are much slower when Np-O bond cleavage is involved (Burney and Harbour, 1974; Fahey, 1986). A summary of redox reactions of neptunium is given in Table 1.3. The IV/ VI reaction depends on [Np] and $[H^{+}]$ with the possibility of two mechanisms in operation. One involves oxygen transfer, the other inter-species hydrogen transfer (Fahey, 1986). The IV/ V exchange rate depends predominantly on $[H^{+}]$, with one mechanism for high concentrations via an activated complex and another for low acid concentrations. V/ VI exchange occurs through a bridging complex. The presence of Cl^{-} can act as a catalyst, by bridging between Np^{III} and Np^{IV} species.

(b) complex formation

The tendency for neptunium ions to complex with different ligands in aqueous media is crucial in understanding and attempting to predict the behaviour of Np in (a) the environment, (b) industrial processes and (c) its analysis. Whilst this will be considered in some detail under "chemical properties", more specific examples will be covered in the sections on analytical procedures to follow.

The water molecules in the primary coordination sphere of Np are labile (Patil *et al*, 1978) and reactions are predominantly electrostatic in nature, rates being dominated by diffusion-controlled mechanisms (Choppin, 1983). In aqueous solutions in the absence of competing ligands, neptunium ions can be described as having a strongly coordinated inner sphere of water

Table 1.3: Examples of redox reactions of neptunium (from Fahey, 1986).

reaction	**reagent**	**solution**	**temp. (°C)**	**rate**
$Np^{IV} \rightarrow Np^{III}$	electrolysis			rapid
$Np^{IV} \rightarrow Np^{V}$	NO_3^-	HNO_3	25	slow
			100	moderate
	$HClO_4$		25	v.slow
			100	rapid
$Np^{IV} \rightarrow Np^{VI}$	Ce^{IV}	HNO_3, H_2SO_4	25	v.rapid
	$MnO_4^- + H^+$	HNO_3, H_2SO_4	25	v.rapid
$Np^{V} \rightarrow Np^{IV}$	Fe^{2+}	H_2SO_4	25	v.rapid
	I^-	5M HCl	25	40 min.
			100	1-2 min.
	NH_2OH	1M H^+		v.slow
$Np^{V} \rightarrow Np^{VI}$	Ce^{IV}	HNO_3, H_2SO_4	25	v.rapid
$Np^{VI} \rightarrow Np^{IV}$	Fe^{2+}	H_2SO_4	25	v.rapid
$Np^{VI} \rightarrow Np^{V}$	Cl^-	Pt catalyst	25	slow
	NH_2OH	1M H^+	25	v.rapid
	NO_2^-	1M HNO_3	25	instantaneous

molecules. $Np^{n+}(aq)$ should strictly be represented as: $Np(H_2O)_8^{3+}$, $Np(H_2O)_8^{4+}$, $NpO_2(H_2O)_6^{+}$, $NpO_2(H_2O)_6^{2+}$. The reaction mechanisms can be envisaged to involve stepwise competition between negatively charged complexing ligands (A^-) and the inner and/or outer coordination spheres of associated water molecules. The strength (ionic potential, pK_a etc.) and steric effects define the extent to which water molecules are abstracted, eg

$$Np(H_2O)_8^{4+} + A^- \rightleftharpoons NpA(H_2O)_7^{3+} + H_2O$$

Variations in the complexing ability of Np ions are due to differences in the charge density (or ionic potential). Np^V, Np^{VI} and Np^{VII} have a strong tendency to complex, as can be seen from their existence in solid and aqueous phases as highly stable oxyanions. This affects the overall complexing ability, which follows the order $Np^{4+} > Np^{3+} > NpO_2^{3+} > NpO_2^{2+} > NpO_2^{+}$ (Patil *et al*, 1978; Katz *et al*, 1986b). There are few data on complexes of III and VII states because of their poor stability in solution (Patil *et al*, 1978). Most interest has been focused on the complexes of Np^{IV}, which is extensively used in analytical procedures (Mikhailov, 1971; Burney and Harbour, 1974) and Np^{V}, which is much more stable than U^{V} and Pu^{V} (Katz *et al*, 1986b).

Hydroxide complexes have already been mentioned. The interaction of water molecules and the acidity of Np ions in aqueous solution lead to the complex polymerization reactions described previously. Relative to the other actinides, Np^{IV} hydrolysis occurs in the sequence $Th^{IV} < U^{IV} > Np^{IV} < Pu^{IV}$ while for Np^{VI}, the trend is $U^{VI} > Np^{VI} > Pu^{VI}$. It is surprising that, for the V oxidation state, Np is more acidic than Pu (Patil *et al*, 1978).

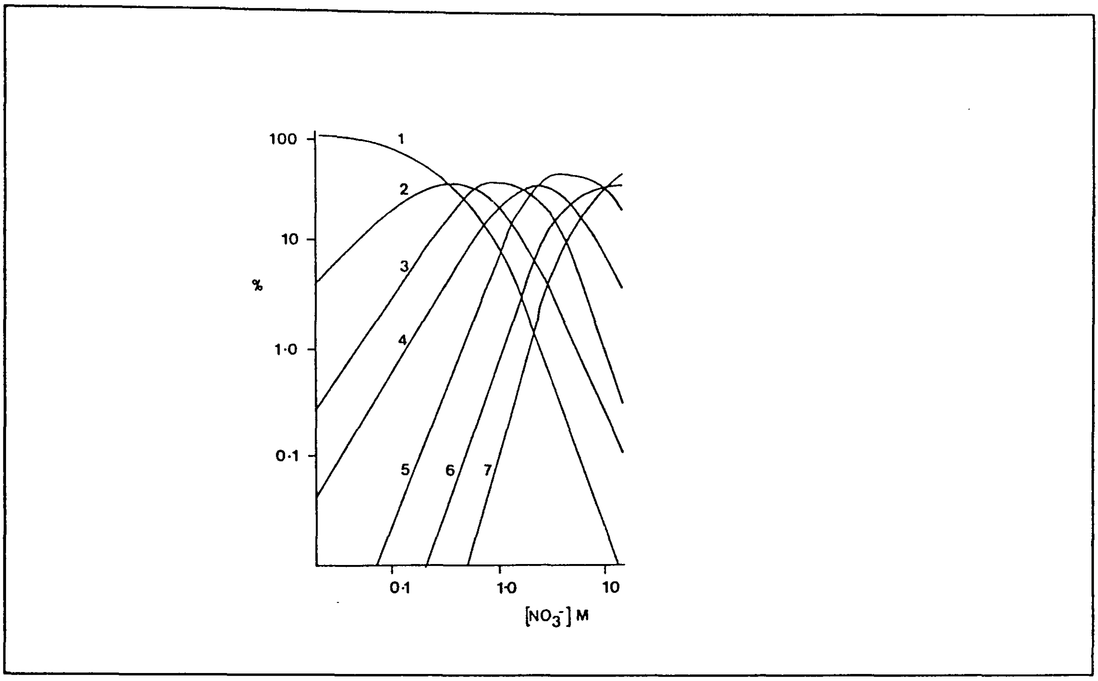
Strong Np-fluoride complexes of inner sphere type are observed for $Np^{IV,V,VI}$ (Kasar *et al*, 1984). A comparison of the stability constants of actinide fluoro-complexes shows the order: $Th^{IV} < U^{IV} > Np^{IV} \approx Pu^{IV}$ and $U^{VI} > Np^{VI} > Pu^{VI}$ with $Np^{IV} > Np^{V} \approx Np^{VI}$. Similarity to Pu^{IV} complexation has been noted and, from consideration of Pu chemistry and thermodynamic constants, the fluoride complexes formed are likely to be NpF^{3+}, Np^{2+}, NpO_2F and NpO_2F^+ (Cleveland, 1970; Patil *et al*, 1978). Chloride complexes are observed for Np^{III}, Np^{IV}, Np^{V}(very weak) and Np^{VI}. They are in general weaker than the corresponding fluorides and have a similar order of complexation (Patil *et al*, 1978). The species formed (by analogy with Pu and considering the stepwise association constants) are for Np^{III} as $NpCl^{2+}$ and $NpCl_2^+$ and for Np^{IV} as $NpCl^{3+}$ to $NpCl_6^{2-}$ inclusive. Although no data are available for higher complexes in strong hydrochloric acid solutions (used extensively in analysis), the species present must include high proportions of $NpCl_5^-$ and $NpCl_6^{2-}$ to explain the observed anion exchange behaviour (Cleveland, 1970; Burney and Harbour, 1974). Using the same reasoning as above, species expected for Np^{V} are likely to be NpO_2Cl or possibly $NpO_2Cl_2^-$ and for Np^{VI} a complex equilibrium between

$$NpO_2^+ \rightleftharpoons NpO_2Cl \rightleftharpoons NpO_2Cl_2 \rightleftharpoons NpO_2Cl_3^- \rightleftharpoons NpO_2Cl_4^-$$

Again the tri and tetrachloro species predominate at higher chloride concentrations.

Bromide complexes of neptunium are reported for Np^{III} (as $NpBr^{2+}$ and $NpBr_2^+$), of similar stability to Pu equivalents (Cleveland, 1970) and Np^{IV} as $NpBr^{3+}$ and $NpBr_2^+$. The stability of $AnBr^{3+}$ follows the order Th< U> Np< Pu (Patel *et al*, 1978). Nitrate complexes of Np, as with U and Pu, are important in process technology and in analytical methodology (Greenwood and Earnshaw, 1984). Complexes of IV, V and VI have been studied in great detail (Mikhailov, 1971; Burney and Harbour, 1974). They are generally more stable than the corresponding chloride complexes for all oxidation states. For Np^{IV}, as with Pu^{IV}, the hexanitrato complex dominates at high $[HNO_3]$. Compositional changes in Np-nitrate species are clearly shown in Figure 1.4. Np^{V} is unlikely to be stable in high nitric acid concentrations, due to the possibility of disproportionation, as described above, and to its low complexing ability in general. Np^{VI}, again by analogy with Pu, is likely to exist in $NpO_2(NO_3)_3^-$ and $NpO_2(NO_3)_4^{2-}$ forms in nitric acid

Figure 1.4: Np^{IV} speciation in HNO_3: (1)Np^{4+}, (2)$Np(NO_3)^{3+}$, (3)$Np(NO_3)_2^{2+}$, (4)$Np(NO_3)_3^{+}$, (5)$Np(NO_3)_4$, (6)$Np(NO_3)_5^{-}$, (7)$Np(NO_3)_6^{2-}$ (Mikhailov, 1971).



and is strongly retained on anion exchange resins (Cleveland, 1970; Mikhailov, 1971; Burney and Harbour, 1974; Fahey, 1986).

Complexes with environmentally important ligands such as sulphate and carbonate have been studied in some detail (Patil *et al*, 1978; Billon, 1981; Kasar *et al*, 1984; Nitsche, 1987). Sulphate complexes are strong for Np^{IV}, with successive addition of SO_4^{2-} ligands as the sulphate concentration increases, in a manner similar to the chloride and nitrate systems described above. Np^{III}, Np^{V} and Np^{VI} are also known to form complexes, but of varying stability (Patil *et al*, 1978; Kasar *et al*, 1984). They are similar to, if not slightly more stable than, those of U, but are weaker than for Pu. For carbonate complexes, the data are rather vague. Np^{IV} presumably forms a series of CO_3^{2-} complexes as a function of ligand concentration. Highly soluble $Np(OH)_4CO_3^{2-}$ has been observed (Patil *et al*, 1978) and soluble Np^{V} carbonates in neutral to alkaline pH have been studied (Billon, 1981; Nitsche, 1987).

Strong phosphate complexes of neptunium ions are observed for:

Np^{III} as $Np(H_2PO_4)^{2+}$, $Np(H_2PO_4)_2^{+}$ and $Np(H_2PO_4)$
Np^{V} as $NpO_2(HPO_4)^{-}$ and $NpO_2(H_2PO_4)$
Np^{VI} as $NpO_2(HPO_4)$ and $NpO_2(H_2PO_4)^{+}$ (Patil *et al*, 1978)

No reports of Np^{IV} phosphate complexes were found (Patil *et al*, 1978). This is particularly surprising when one considers the extensive Pu^{IV}-phosphate system (Cleveland, 1970). It might be expected that Np^{IV} would, by analogy, exist as complexes of the composition $Np(HPO_4)^{2+}$ to $Np(HPO_4)_5^{6-}$ inclusive.

Miscellaneous inorganic complexes of neptunium are observed (Patil *et al*, 1978). Thiocyanates (SCN^-) of Np^{IV} and Np^V have been reported, the Np^{IV} SCN system showing the familiar multistep ligand association up to $Np(SCN)_3^+$ (Musikas and Marteau, 1977). Cyanates (Musikas and Marteau, 1978), iodides, iodates and sulphites of Np^{IV}, Np^V and Np^{VI} are also known.

Complexes of neptunium aquo ions and organic ligands, from simple formates and oxalates to complex polycarboxylates and chelates, are numerous. They tend to be highly stable compared to the more simple inorganic systems described above. Ligands which are strong enough to exclude the inner sphere solvent molecules contain oxygen, phosphorus and nitrogen atoms or molecules containing highly localized electron systems. Electrostatic and steric considerations are important, particularly with the multidentate ligands in chelate systems, to determine the coordination around the central neptunium atom (Choppin, 1983). A brief description will be included here to show the wide range of systems observed. Most development has been in the synthesis of coordinating organic species for analytical and purification purposes and these will be discussed further in later sections.

Mono carboxylate complexes of Np^{IV}, Np^V and Np^{VI} have been observed with acetate, propionate, glycolate, salicylate, amino- and chloro-carboxylates and pyridine acetate ligands (Patil *et al*, 1978). For the tetravalent actinides, the trend in stability is $U < Np < Pu$ and, for the hexavalent actinides, $U > Np > Pu$. Dicarboxylate and polycarboxylate complexes (Patil *et al*, 1978; Cacei *et al*, 1987) show the highest association constants observed (in particular for oxalate). This is seen for all Np aquo ions, the complexes all being of inner sphere type.

Chelate complexes are formed with a large number of systems. The β-diketones (acetylacetone (HAA), thenolytrifluoroacetone (HTTA)) are very important (De *et al*, 1970). Other chelating ligands include hydroxyquionline, tropolones, sulphonic acids and EDTA (De *et al*, 1970; Mikhailov, 1971; Patil *et al*, 1978). A qualitative summary of the relative complexing abilities of ligands for aquo ions of neptunium is given in Table 1.4.

This short discussion has covered the main chemical features of neptunium. While it is obvious that the element shows the same general properties exhibited by the other actinides such as multiple valency and coordination chemistry dominated by electrostatic behaviour, it has a number of very specific features which distinguish it from both its immediate neighbours and the rest of the actinides. On the whole, it is chemically the most interesting yet one of the least understood of the actinide elements.

Table 1.4: The relative complexing ability of ligands for different oxidation states of Np in aqueous systems (Mikhailov, 1971; Burney and Harbour, 1974)

Np^{III}	$Br^- < Cl^-$
Np^{IV}	$ClO_4^- < Cl^- < NO_3^- < SO_4^- \approx CH_3COO^- < F^- < C_2O_4^- < OH^- < EDTA^{4-} < DTPA^{5-} < OX^-$
Np^{V}	$ClO_4^- < Cl^- < NO_3^- < SCN^- < Ac^- < NTA^- < SO_3^- \approx HIBA^- \approx TART^{2-} < HCO_3^- < TTA^- < HPO_4^{2-} < CITR^{3-} < C_2O_4^{2-} \approx HAA^- < OH^- < DTPA^{5-} < EDTA^{4-}$
Np^{VI}	$ClO_4^- < NO_3^- < Cl^- < SCN^- < SO_4^- < CH_3COO^- < F^- < C_2O_4^- < HPO_4^{2-} < CO_3^{2-}$
Key:	OX^- = 8-hydroxyquinolate, $EDTA^{4-}$ = ethylenediamine tetraacetate, $DTPA^{5-}$ = diethylenediamine pentaacetate, Ac^- = acetate, NTA^- = nitrilo triacetate, $HIBA^-$ = hydroxy isobutyrate, $TART^{2-}$ = tartrate, TTA^- = thenolytrifluro acetonate, HAA^- = acetylacetonate, $CITR^{3-}$ = citrate.

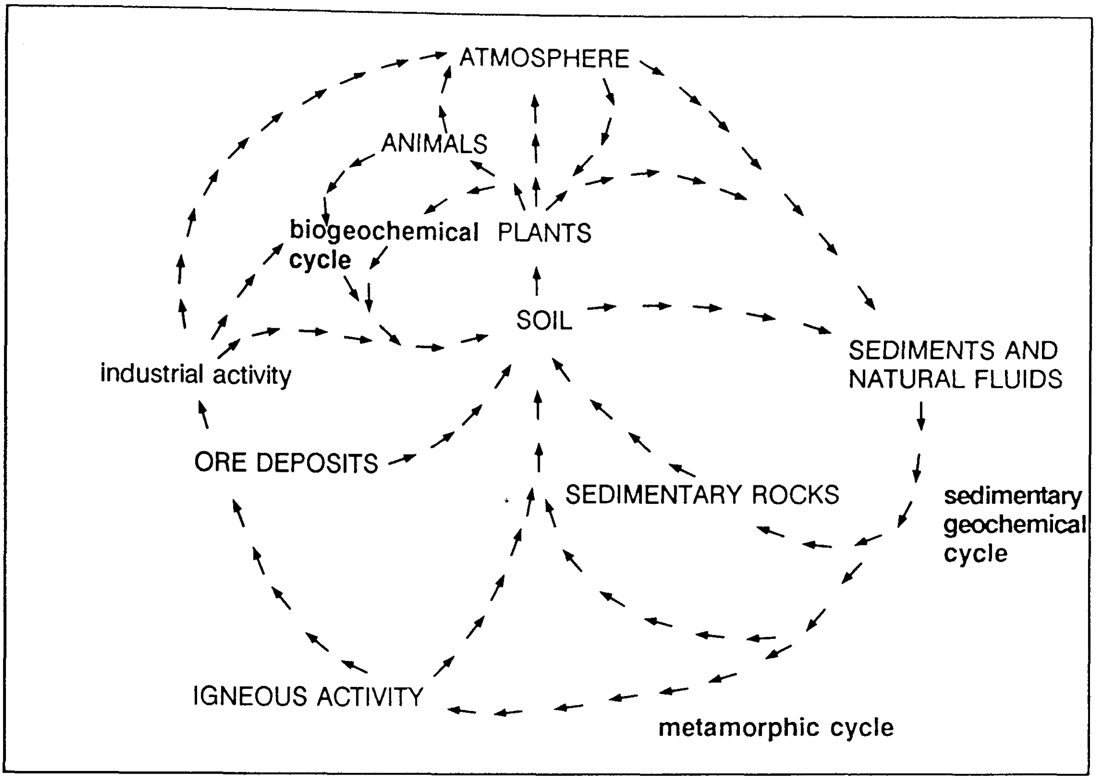
1.3 THE ENVIRONMENTAL BEHAVIOUR OF NEPTUNIUM

1.3.1 INTRODUCTION

Figure 1.5 summarises sources, sinks and transfer processes operating on the elements in the environment and illustrates the complex interrelationships between the processes (Adriano, 1986). The significance of actinide releases from industrial activity is, in the short and intermediate term determined by the pollutant's interactions within the biogeochemical and sedimentary geochemical cycles. Only in the disposal of long-lived active wastes will igneous and metamorphic cycles become important.

The speciation of the element will be the most important factor determining its fate in these processes. This feature is probably one of the least understood and most intensively studied problems in general geochemistry and more specifically when considering the environmental behaviour and fate of radionuclides (Myttenaere, 1983; Murray *et al*, 1984). The monograph

Figure 1.5: Summary of elemental cycling at the earth's surface (Jenkins & Jones, 1980).



edited by Bertrand *et al* (1986), is an excellent discussion of this subject, particularly in relation to trace elements but with obvious implications for transuranic elements.

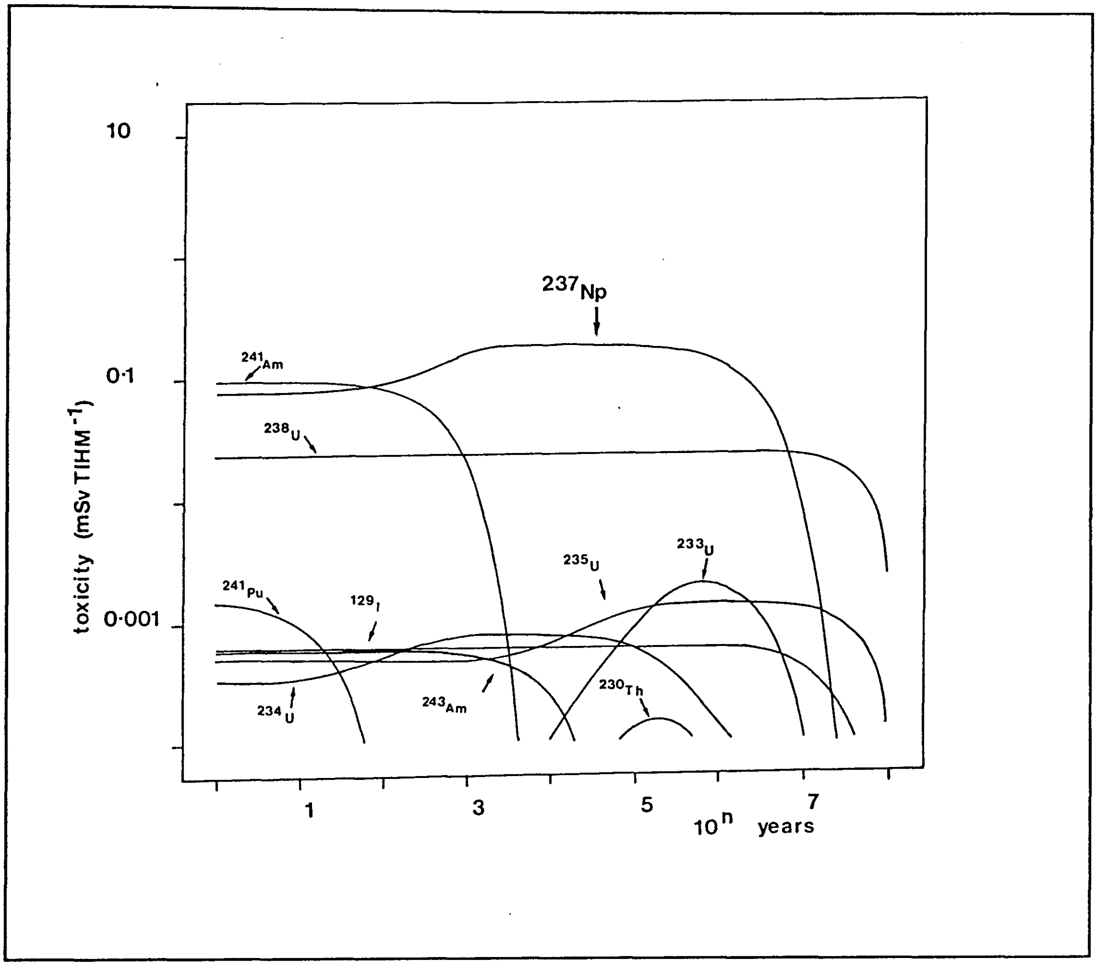
As mentioned previously, it is very clear that neptunium is the least studied of the transuranium elements in the environment (Coughtrey *et al*, 1984). This can be attributed to analytical difficulties, the low abundance of the long-lived ^{237}Np nuclide and the short half-life of ^{239}Np which precludes its use as a tracer in detailed studies. The data which are available are fragmented in nature and ancillary to more detailed considerations of Pu and Am nuclides. They are generally restricted to work carried out in close proximity to contamination sources or to laboratory experiments. Where important areas have not been studied, tentative predictions can be made through the relationship of Np to the more fully understood nuclides of U, Pu and Am. However, from the discussion in the preceding section 1.2, the unique chemical behaviour of neptunium means that such comparisons may also have severe limitations and must be made with caution.

This review of neptunium behaviour considers the sources of neptunium and the interaction of these sources with the environment. Both the terrestrial and aquatic environments will be considered together with studies carried out to assess the relevant aspects of long-term radioactive waste disposal.

1.3.2 THE IMPORTANCE OF NEPTUNIUM IN THE LONG-TERM DISPOSAL OF RADIOACTIVE WASTES

It has been predicted (Baxter, 1982; Cohen, 1982; 1983; Aarkrog, 1986) that ^{237}Np will be the most significant component of high-level radioactive waste at the 10^6 year post-disposal time point (see Figure 1.6). Kirchner (1990) has recently developed a new hazard index which includes a much more comprehensive treatment of environmental transport and dose to man. Detailed considerations are given to the nuclide composition of the waste and underground transport via sorption and desorption processes. Pathways to man directly through drinking water or through transfer via food chains are also considered. This has been highlighted as of particular importance post Chernobyl (O'Neill, 1989). Further emphasis is also placed on the radiotoxicity of the nuclides and radioactive decay and consequences of daughter nuclides introduced via parents (eg ^{241}Pu/ ^{241}Am/ ^{237}Np decay series).

Figure 1.6: Nuclide toxicity (mSv TIHM^{-1}) with time of release (from Kirchner, 1990).



1.3.3 THEORETICAL SPECIATION AND EXPECTED BEHAVIOUR OF NEPTUNIUM IN THE ENVIRONMENT

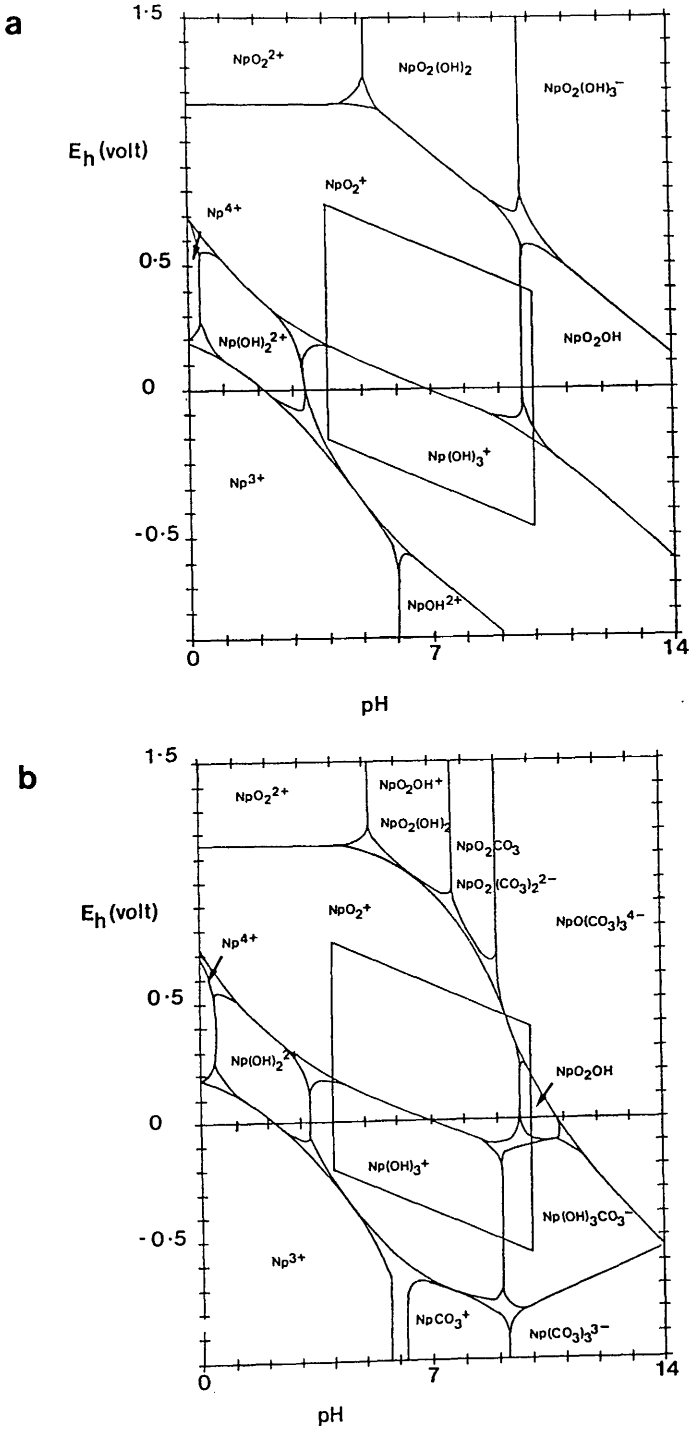
The solution chemistry of the actinides strongly influences their environmental behaviour, since water is the most abundant and important reagent for the mediation of geochemical reactions (Krauskopf, 1979; 1986). The chemical composition of natural solutions dictates the type, extent and rates of possible reactions. The concentration of a species in solution is influenced by pH, E_h, cation exchange capacity, type and amounts of solid phases, complexing ligands and competing ions.

The solution chemistry of Np has already been considered in some detail in section 1.2. The actinides in general exhibit a wide range of oxidation states and their solution chemistry is typically that of hard ions (ie strongly polarising/ complexing, eg Allard *et al*, 1984). The extent of complex formation is a function of the net residual charge on the central ion, ie $An^{IV} > An^{VI} > An^{III} > An^{V}$ and general trends between actinide ions of the same oxidation state are governed by the actinide contraction (Greenwood and Earnshaw, 1984). From an understanding of the complex chemistry of neptunium, it is possible to predict the speciation and behaviour of the element under the conditions expected in the environment.

Groundwaters are characterized by a number of important features. The pH dictates to a large extent the solubility of compounds and degree of complexation with, for example, carbonate and sulphate anions and mineral surfaces. The potential of the system to oxidize or reduce species (E_h) is primarily determined by the O_2 concentration. Anion and cation contents are very variable depending on the surrounding solid and solution phase compounds. Major anions of importance include OH^-, Cl^-, F^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-} and protonated anions. Cations such as Ca^{2+}, Mg^{2+}, Na^+ and K^+ are important in terms of competition for surface exchange sites. Organic matter is a poorly understood component of natural systems but tends to be highly reactive towards metals (Krauskopf, 1979), behaviour being very difficult to predict.

Allard *et al* (1980), Jensen (1980) and Allard *et al* (1984) have illustrated the effect of some of these parameters on the expected speciation of neptunium. Figure 1.7a and Figure 1.7b shows the E_h versus pH stability of aqueous Np species in both the absence (Figure 1.7a) and presence (Figure 1.7b) of CO_3^{2-}. The calculations are based on laboratory-derived data and must be treated with caution when translated to "real" field conditions. The superimposed box delineates the redox conditions observed in nature (Baas Becking *et al*, 1960). Allard *et al* (1980) predict that, at neutral pH, Np^V should be the dominant species in acidic, oxidizing environments, whilst Np^{IV} is expected where reducing conditions are found. However, it is interesting to note that, when compared to Pu, the stability region for Np^V is more extensive than for Pu^V, suggesting that reduced forms of Pu are expected to dominate in nearly all environmental conditions. The effect of carbonate on the predicted speciation is not so clear. It does little to change the stability regions of NpO_2^+ and $Np(OH)_3^+$, but does introduce a stable zone for the Np^{IV} species $Np(OH)_3CO_3^-$.

Figure 1.7: E_h v pH diagrams for Np (a) P_{CO2} = 0 atm (b) P_{CO2} = $10^{-3.5}$ atm. Limits for natural environment superimposed (Jensen, 1980).



Thus, under oxidizing to slightly reducing conditions, Np^V is expected to be the dominant species in acidic and slightly alkaline solutions with Np^{IV} occurring where reducing conditions prevail. Pimpl (1988) however, has evaluated Np speciation in soils and concludes that thermodynamic considerations used previously incorrectly define Np^{IV} stability regions and that Np^V almost exclusively dominates. This contrasts the situation for Pu in which Livens (1985) implies that the plutonium in samples of W. Cumbrian soils is in reduced oxidation state(s). The expected predominance of the pentavalent oxidation state has important implications. The low stability constants of the ion and its ability to form soluble carbonate complexes (Billon, 1981) suggest that it should be very mobile under surface geochemical conditions.

Perhaps the least considered aspect of actinide geochemistry is that of the role of microorganisms. Microbial effects are potentially great (Brady, 1974; Krauskopf, 1979; Wildung and Garland, 1980). A number of potential transformations include indirect mechanisms resulting from metal interaction with microbial metabolites or microbially induced redox changes (Pennders *et al*, 1986). Direct changes may involve alkylation and alteration of valence state through microbial redox reactions. Immobilization by incorporation into microbial tissues and the release of metals on the decomposition of organic residue are also important. Microbial activity has long been known to be responsible for the redox potential gradient observed in aquatic sediments (Krauskopf, 1979; Pimpl, 1988). This activity has been shown to be a significant factor in the kinetic control of Mn oxidation and trace metal and radionuclide binding in lacustrine sediments (Kepkay, 1986). Microbial activity was reported to enhance ^{241}Am binding by a factor of 5.

The major importance of organic matter on trace element cycling has already been mentioned. For the actinides it has similar significance (Choppin, 1988). The material is complex in composition and of a polyelectrolyte nature and varies widely in functionality and concentration. Bulman (1978; 1987) identifies important actinide-complexing functional groups and natural organic matter components as being hydroxamates, citric acid, acetic acids, carboxylates and benzene polyphenolic groups. In the case of the predicted Np^V species, Lieser and Muhlenweg (1988a, 1988b) suggest that humic and fulvic acids may only be important complexing agents in the case of low concentrations of major competing anions.

1.3.4 SOURCES OF NEPTUNIUM IN THE ENVIRONMENT

The various nuclear reactions responsible for the production of nuclides of neptunium have been summarized in section 1.2.2. Of these only the nuclides ^{239}Np and ^{237}Np are of environmental significance. The presence of ^{237}Np in uranium ore concentrates has been shown and the presence of ^{239}Np has been inferred from ^{239}Pu abundances (section 1.2.2). The main sources responsible for the introduction of neptunium nuclides into the environment are the above-ground testing of atomic weapons and discharges related to the processing of nuclear fuels (Facer, 1980; Perkins and Thomas, 1980). Accidents with nuclear weapons and power sources are significant inputs for Pu nuclides only and there are no reports of quantities of neptunium nuclides being released at Thule, Palomares or from the SNAP-9A burn-up in 1964 (Hardy *et al*, 1973; Facer, 1980; Holm ,1981; Pentreath, 1988).

(a) weapons fallout

Data on the production and dispersal of fallout radionuclides (predominantly Pu and fission products) has been discussed in both a world-wide context (Hardy *et al*, 1973; Carter and Moghissi, 1977; Carter, 1979; Facer, 1980; Perkins and Thomas, 1980; Pentreath, 1988) and in relation to the UK (Pierson and Cambray, 1965; Pierson *et al*, 1982). The suite and abundance of nuclides generated by a weapons device differs considerably from that produced in nuclear fuel. Neutron fluxes and temperatures are very much higher and produce a greater abundance of the heavier nuclides (Fields *et al*, 1956; Diamond *et al*, 1960; Kruger, 1971; Perkins and Thomas, 1980).

The dispersal of the generated nuclides and weapons debris is controlled by the size of the weapon, its detonation height, prevailing climatic conditions and the height of the troposphere (Carter and Moghissi, 1977; Perkins and Thomas, 1980). Basically, the larger the device the greater the likelihood of penetration of the tropopause and injection into the stratosphere, resulting in global dispersal. Smaller devices produce debris whose distribution is controlled by the more variable climatic features in the troposphere and consequently is concentrated much closer to the detonation point. The matrix of the debris comprises a mixture of varying proportions of fused or partly fused terrigenous silicate minerals, oxides of aluminium and iron derived from the weapons casing and support and contaminated dusts which acted as nucleating centres for condensing materials immediately after detonnation (Pentreath, 1988).

The activity abundance of ^{239}Np in fresh fallout debris is 30 to 40 times that of ^{140}Ba (the major fission product) (Perkins and Thomas, 1980) and may constitute up to 75% of the β-activity close to the detonation point for up to 4 days after the event (Thompson, 1982). In the case of ^{237}Np, there are a limited number of analyses reported in the literature and these have been summarized in Table 1.5. Noshkin (1980) reports data for water samples from Enewetak in the Pacific Ocean for 1972. The values were determined by mass-spectrometry and activity levels were found to be <0.2% of the observed ^{239,240}Pu activities. A series of α-spectrometric determinations of ^{237}Np in soils and sediments from Japan (Sakanoue, 1987; 1988) indicated that the abundances were 0.21 to 0.22% of the ^{239,240}Pu activities in the Hiroshima area, but the information supplied was not sufficient to be able to give an estimation of total inventories.

Table 1.5: Literature reports of ^{237}Np activity concentrations in environmental samples contaminated by weapons test debris.

	Activity Concentration	Reference/ Comments
Enewetak Atoll (1972)		
Lagoon water (unfiltered)	2.15 ±0.48 μBq l^{-1}	Noshkin (1980)
MIKE, KOA crater water	16.7 ±8.2 μBq l^{-1}	Noshkin (1980)
open ocean, to east	0.48 ±0.11 μBq l^{-1}	Noshkin (1980)
Bikini Atoll		
Soil	≈ 1 Bq kg^{-1}	Sakanoue (1987; 1988)
Hemp palm	≈ 3 Bq kg^{-1}	Sakanoue (1987; 1988)
Sediment	1.7 Bq kg^{-1}	Holm (1981), ^{237}Np/Pu-α 5.6 x10^{-4}
Japanese soil and sediments (early '80s)	0.015-0.002 Bq kg^{-1}	Sakanoue (1987; 1988)
Surface soil close to Hiroshima epicentre	0.0011-0.0015 Bq kg^{-1}	Sakanoue (1987; 1988)
Thule sediment	< 0.5 x10^{-3} Bq kg^{-1}	Holm (1981), ^{237}Np/Pu-α <3 x10^{-6}
Fallout soil	2.26 x10^{-3} Bq kg^{-1}	Efurd *et al* (1982; 1984)

Estimates of the total amount of ^{237}Np released from weapons testing have been made (Holm, 1981; Efurd *et al*, 1982; 1984). By mass, the levels of ^{237}Np and ^{239}Pu should be comparable since the ratio of the (n, 2n) : (n, γ) reactions on ^{238}U in weapons devices is in the range 0.5 to 1.0 (Holm, 1981). Efurd *et al* (1982) determined the ^{237}Np/ ^{239}Pu atom ratio in soils which had been identified as being contaminated by weapons fallout. The value obtained was 0.70 ±0.20 and the activity concentration ratio was 6.46 ±1.85 x10^{-3}; for ^{240}Pu/ ^{239}Pu a value of 0.18 ±0.001 was observed. By assuming that 1.6 x10^{4} TBq of ^{239,240}Pu had been produced from weapons testing (note that Pentreath (1988) estimates 1.3 x10^{4} TBq) and that the ^{240}Pu/ ^{239}Pu ratio is as quoted above, Efurd *et al* (1982) thus predicted that 2,940 ±750 kg of ^{237}Np had been produced by weapons testing.

Holm (1981) predicts that the integrated fallout activity ratio of ^{237}Np/ ^{239,240}Pu should be 3.6 x10^{-3}. Measurements of dry Swedish lichens from 1961 to 1979 show a ^{237}Np maximum concentration in the 1965 to 1966 period which corresponds to the USSR and USA tests between 1961 and 1962. Inventories integrated over the time period give values of (110 ±15) x10^{-3} Bq m^{-2} for ^{237}Np and 4 Bq m^{-2} for ^{239,240}Pu. The measured activity ratio was (2.7 ±0.4) x10^{-3}.

To compare the two determinations, ^{237}Np/ ^{239,240}Pu activity ratios can be calculated from the data of Efurd *et al* (1982) to be (4.69 ±1.2) x10^{-3} with the uncertainty being derived from the uncertainty on the ^{237}Np measurements. Although of the same order of magnitude, this figure is significantly different from the value of (2.7 ±0.4) x10^{-3} reported by Holm (1981), yet surprisingly it is much closer to the theoretical value estimated by that author. The discrepancy may have explanation in geographical variation of weapons fallout deposition. Perkins and Thomas (1980) present data for the latitudinal variation in ^{240}Pu/ ^{239}Pu atomic abundance data which show fairly constant values over the Northern and Southern Hemispheres. At fairly low latitudes in the Northern Hemisphere, however, there is a distinct "dip" which is attributed to higher deposition of atypical test debris from the Nevada Ranges. A lowering of this atom ratio would result in a rise in the ^{237}Np/ ^{239,240}Pu activity ratio and the observed discrepancy between the Swedish data, collected at 62°N, and the American data, from samples collected at an estimated 41°N, may thus reflect a subtle variation in source terms.

The production of ^{237}Np from ^{241}Pu and ^{241}Am has already been identified as an additional source of neptunium to the environment. Activity yields of ^{241}Pu from weapons devices can be up to 60 times those of ^{239}Pu (Perkins and Thomas, 1980). Pentreath (1988) estimates a total production of 1.7 x10^{5} TBq of ^{241}Pu which will eventually produce 5.5 x10^{3} TBq of ^{241}Am, peaking in the year 2037. Holm (1981) calculates that this secondary supply of ^{237}Np in 1981 accounted for 0.05% of ^{237}Np from global fallout.

(b) releases from laboratories and the processing of nuclear fuels

A number of laboratory and industrial sites routinely discharge radionuclides to the environment. The releases are primarily confined to the immediate aquatic environment (Holm, 1981; Pentreath, 1985; 1988; Camplin and Aarkrog, 1989). Data on neptunium nuclides are again very fragmented, with the most complete record being from the BNFL Sellafield fuel reprocessing plant. Although some mention of absolute levels will be made here, the nature of the available data relative to the objectives of this particular study warrant the more detailed consideration given in the separate section which follows this.

Thompson (1982), Coughtrey *et al* (1984) and Pentreath (1988) report some Np data from sites in the USA. Sawmill Creek, which receives discharges from the Argonne National Laboratory, is one locality where activity is discharged to a freshwater environment. Concentrations of ^{237}Np decrease down-river from 7.0 to 0.2 mBq l^{-1}. The solution : solid activity ratios were in the range 114 : 1 to 48 : 1, although true K_d values could not be presented. ^{239}Np from the Hanford plutonium plant has been traced in the Savannah and Columbia Rivers (Noshkin, 1972; Coughtrey *et al*, 1984; Pentreath, 1988). This neptunium could still be traced 350 miles downstream. Whilst it had a strong affinity for sediments, approximately 40% passed through water treatment plants 30 to 40 miles from the plant (Thompson, 1982).

The various nuclear facilities of the Indian subcontinent are concentrated around Bombay. Discharges to the coastal waters off Bombay include contributions from research reactors, radionuclide laboratories and fuel reprocessing sites. Varying amounts of fission product and plutonium nuclides are observed in the local environment (Patel and Patel, 1985). Holm (1981) reports the analysis of two sediments from the area. The levels of ^{237}Np were 43 and 33 mBq kg^{-1}, with ^{237}Np/ ^{239,240}Pu activity ratios of 0.0012 and 0.0016 respectively.

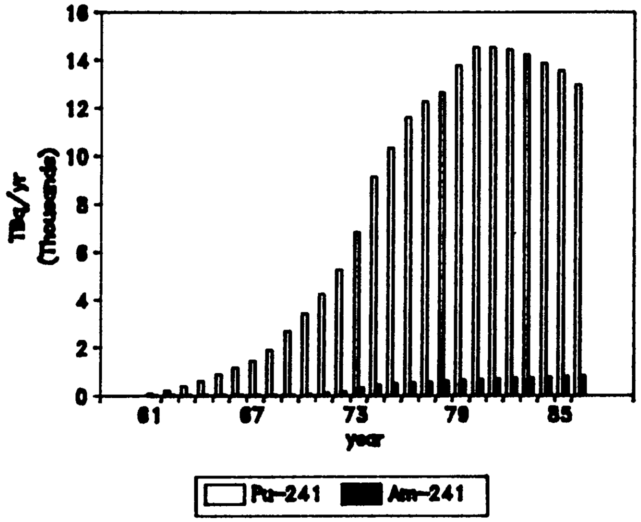
The Cap de la Hague reprocessing facility near Cherbourg, France has routinely discharged radionuclides since 1966 (Pentreath, 1988). Documented discharge data and local monitoring of sediments, marine biota and coastal lichens are available for ^{239,240}Pu, ^{238}Pu, ^{241}Am and ^{244}Cm (Guegueniat *et al*, 1981; Calmet and Guegueniat, 1985). However, no discharge data for ^{237}Np are available. Pentreath *et al* (1986a) present data for the concentrations of ^{237}Np in filtered seawater samples from around the coast of Britain. Maximum levels of 4 mBq l^{-1} in the

Table 1.6: Measurements of marine sediments, waters and biota contaminated by discharges from the Cap de la Hague reprocessing plant data in mBq kg^{-1} (wet) unless otherwise stated. + May and Pinte (1984),* Germain *et al* (1987).

Sample	^{237}Np	^{239,240}Pu	^{241}Am	^{237}Np/^{239,240}Pu
Seawater*(1983)	8 x10^{-2} mBq l^{-1}	NA	NA	NA
Seawater^{+}(1985)	2.7 mBq l^{-1}	NA	NA	NA
Suspended sediment (1985)$^{+}$	9.1 x10^{3}	NA	NA	NA
Fucus serratus* (1983)	3.6 ±0.3	652 ±63	629 ±36	0.006
Nucella Lapillus^{*+}(1984)				
shell	2.3 ±0.2	118 ±33	334 ±45	0.020
flesh	7.2 ±2.3	77 ±11	240 ±25	0.094
Patella^{*+}(1984)				
shell	6.2 ±0.5	183 ±35	401 ±50	0.034
flesh	9.6 ±2.6	100 ±13	240 ±25	0.096
Mytilus edulis^{*+}(1980)				
shell	5.7 ±1.3	96 ±22	104 ±19	0.055
flesh	2.0 ±0.5	74 ±9	74 ±11	0.027

Irish Sea are seen to decrease to $<5 \times 10^{-6}$ Bq l^{-1} at the S.W. and N.E. ends of the English Channel. Midway through the Channel, levels rise to 1.0×10^{-5} and 1.4×10^{-5} Bq l^{-1} close to the Cherbourg peninsula. This is an obvious effect of local discharges. Data from Gueguenait *et al* (1981) report that maximum plutonium discharges occurred in the winter of 1974-1975 (0.6 TBq) and that in subsequent years there was a significant reduction to approximately 0.22 TBq year^{-1} and some variation in the ^{238}Pu/ ^{239,240}Pu activity ratio. Whether the same sort of fluctuation was observed for ^{237}Np is uncertain. Table 1.6 summarizes data from May and Pinte (1986) and Germain *et al* (1987) for a limited number of ^{237}Np analyses of environmental samples from the French coast of the Channel. From these and the values quoted above it is obvious that whilst the discharge data are absent, levels in the local area around Cap de la Hague are very low, especially in comparison with Sellafield.

Figure 1.8: Cummulative total activity released from BNFL Sellafield for ^{241}Pu and ^{241}Am including contribution from Pu decay (BNFL, 1977-1988; Day & Cross, 1981; Cambray, 1982).



Detailed discharge data are provided for Sellafield in yearly discharge and monitoring reports (BNFL, 1978-1988) for liquid effluents and aerial releases. For ^{237}Np, the data are restricted to annual totals from 1978 to present. No mention of ^{239}Np is made but it is unlikely to be present due to its half-life and the several months of cooling to which the fuel is subjected before processing. Yearly discharges are all <1 TBq but fluctuate considerably between years. Since 1978, 3.4 TBq of ^{237}Np has been discharged. This is likely to be a serious underestimate of the total releases though, since releases of the other transuranic nuclides peaked in the mid 1970's. The erratic nature of the published discharges and the absence of any synchronous behaviour with other actinides means that it is not possible to make a projected estimate to earlier periods. Day and Cross (1981) calculated the rate of accumulation in the Irish Sea of ^{241}Am from the decay of ^{241}Pu, which is discharged in significant amounts from Sellafield and has a 14.4 year half-life. By estimating past ^{241}Pu discharges from total Pu-α's back to 1960, the ingrowth activity can be calculated by equating decay constants for a yearly decay period (Kruger, 1971; Day and Cross, 1981). The peak ingrowth activity for ^{241}Am (including contribution from discharges) will occur in 2059. The same calculation was performed for ingrowth of ^{237}Np from ^{241}Am and reveals that the time of maximum ingrowth will occur in 7296. In 1986 this decay-produced component contributed only 0.1% to the total cumulative ^{237}Np discharges since 1978. Figure 1.8 illustrates the cumulative properties of the combination of known (and easily predicted) discharges and the decay/ingrowth effects for the ^{241}Pu/ ^{241}Am decay chain.

(c) the physico-chemical nature and behaviour of neptunium in sellafield discharges released into the marine environment

The levels and routes taken by neptunium during the processing of nuclear fuels are dependent on the type of fuel and on the chemical response of neptunium to the conditions used to dissolve and retrieve the important residues such as fissionable ^{235}U and ^{239}Pu and to a lesser extent ^{238}U (Allardice *et al*, 1983; Farmer, 1983). The behaviour of Np under these conditions has been predicted (Rees and Ship, 1983; Drake, 1987). Table 1.7 shows the amounts of ^{237}Np present in spent fuel from different reactor types. The fraction attributed to ^{241}Pu and ^{241}Am decay is also included. For all fuel types mentioned, > 50% of the ^{237}Np present is attributed to the initial ^{241}Pu present and < 25% to the initial ^{241}Am and ^{237}Np.

BNFL Sellafield is primarily concerned with the processing of spent Magnox fuels and holds >2,500 tonnes of oxide fuel for processing when the THORP (thermal oxide reprocessing plant) starts operation in the 1990's (BNFL, 1985b; 1986b). A schematic diagram of the basic flowsheet for Magnox processing is shown in Figure 1.9. with the sources of waste generation indicated.

Separation of the U and Pu in stripped and dissolved fuel rods is through solvent extraction from nitric acid media. The original BUTEX process used dibutoxy-diethylether solvent but has since

Table 1.7: The levels of ^{237}Np produced in burnt fuel from reactors of different type (Rees and Ship, 1981). Levels are pre-reprocessing

(a) amounts generated for 1 GW(e)-year of electricity.

Reactor	Rating (MW/t)	Amount of ^{237}Np		Amount of ^{241}Am	
		(Bq)	(kg)	(Bq)	(kg)
Magnox	3.16	2.9×10^{11}	7.7	9.9×10^{14}	8.4
AGR	14.66	1.3×10^{11}	5.1	8.4×19^{14}	7.1
LWR	38.3	2.1×19^{11}	8.1	1.1×10^{15}	9.0

(b) percentage proportion of ^{237}Np due to :

Fuel type	^{237}Np	^{241}Am	^{241}Pu
Magnox	23	26	51
AGR	16	21	63
LWR	18	20	62

been superseded by cheaper and more effective tri-n-butylphosphate (odourless kerosene diluent) PUREX system (BNFL, 1985b). Dissolution of the fuel can produce Np in the IV, V and VI oxidation states (see section 1.2 and Drake, 1987), the exact proportions being dependant on the amount of HNO_2 present from the radiolysis of the nitric acid (Rees and Ship, 1983). In practice, the Np^{V} and Np^{VI} states dominate (Rees and Ship, 1983; Drake, 1987). If the $[HNO_2]$ is high, then Np^{V} dominates and follows the high active waste, ie

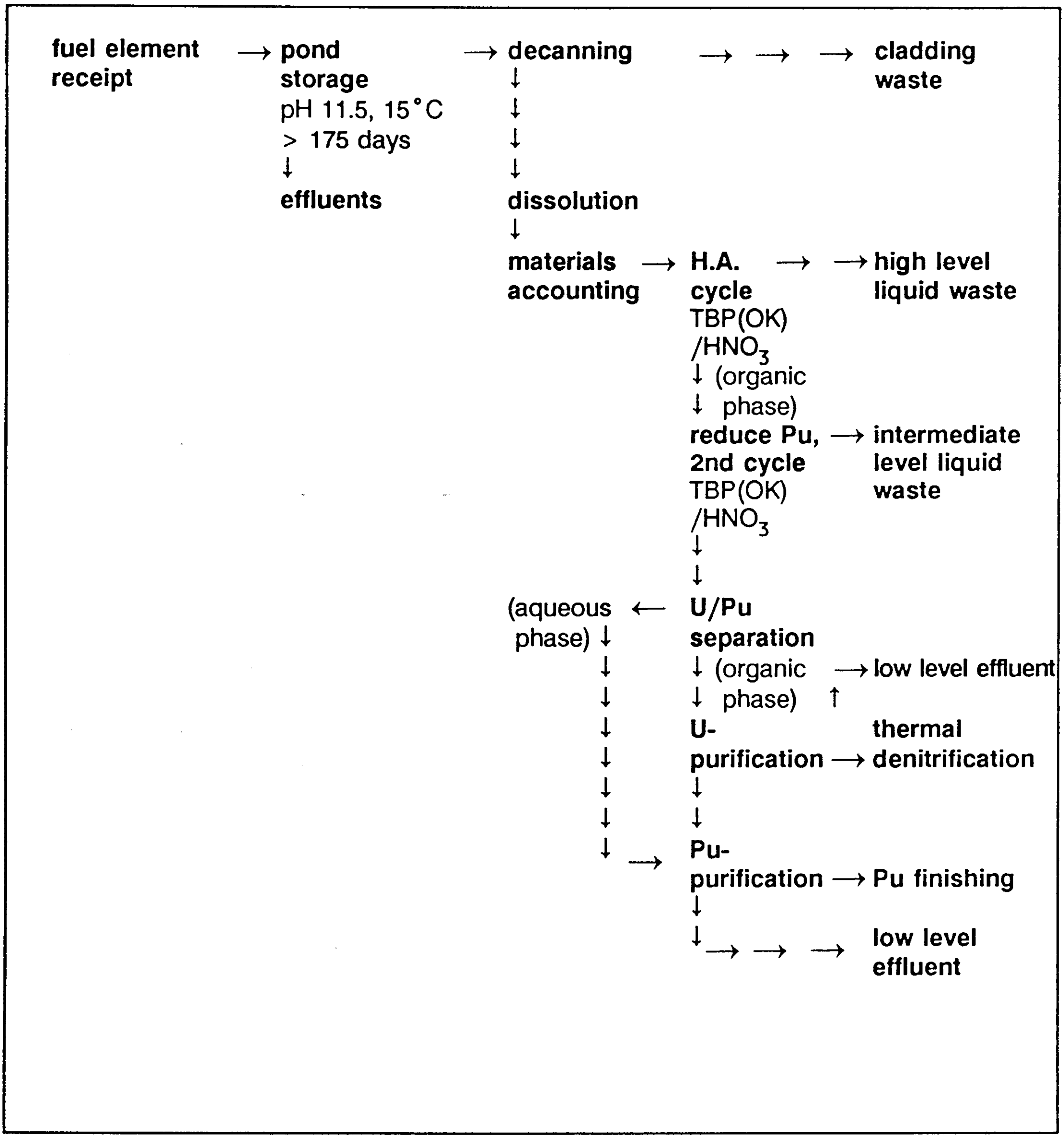
$$2NpO_2^{+} + HNO_3 + H^{+} \rightleftharpoons 2NpO_2^{2+} + HNO_2 + H_2O$$

The equilibrium is further complicated by Np^{V} disproportionation which is favoured by high acid concentrations and the presence of strong complexing agents (see section 1.2), via

$$2NpO_2^{+} + 4H^{+} \rightleftharpoons Np^{4+} + NpO_2^{2+} + 2H_2O$$

The solvent's affinity for the different oxidation states of Np is $Np^{IV} > Np^{VI} >> Np^{V}$ (see section 1.2) and thus in the first extraction step Np is likely to be split. 50 to 80% of the Np has been reported to follow the U/Pu fraction at the first step (Rees and Ship, 1983). The removal of Np^{IV} will further disrupt the V/VI equilibrium and the resulting oxidation of Np^{V} to Np^{VI} (again as a function of the nitric and nitrous acid concentrations). The reduction of Pu from IV to III is accomplished with Fe^{II} ions (see Figure 1.9). Since the conversion between III/IV and V/VI are faster than those involving actinide-oxygen bond cleavage and the equilibria above are present, this step is likely to increase the abundance of Np^{V} species. A high percentage of the Np will

Figure 1.9: Basic Magnox flow sheet (BNFL, 1986b).



therefore follow Pu into the aqueous phase. Drake (1987) compares the observed partitioning of ^{237}Np in a typical fuel processing scheme with its predicted distribution. Approximately 10% of the input Np is found (as predicted) in the aqueous wastes from the first solvent extraction, 18 to 58% follows Pu in the aqueous phase at the U/Pu separation step (54% predicted), 32 to 72% follows through to the Pu purification stage (36% predicted) whilst approximately 0.1% is found in the U fraction. Thus it is likely that the bulk of the ^{237}Np present in the initial process feed will follow through to the high level wastes (which are currently stored at Sellafield). A variable, but low, fraction will be found in the low level effluents from pond storage and U/Pu purification stages.

The liquid discharges to the marine environment are derived from the processes described above and indicated for Sellafield in Figure 1.9. Before discharge, the effluents are neutralized with ammonia which precipitates a mixed metal oxide floc, primarily iron from the ferrous sulphamate reductant (Hamilton, 1981; Pentreath *et al*, 1983; 1986b). The speciation of the released Np has been studied (Pentreath *et al*, 1983; 1986b). The pond waters are slightly oxidising and periodically discharged to sea, whilst the sea tank effluents are mildly reducing with organic residues and significant amounts of iron and are discharged twice a day (Kershaw *et al*, 1986). The resultant speciation for the transuranic nuclides showed 60% of the Np (99% for Pu and Am) to be particle-associated in the sea tank fluids and 12% (89-99% for Pu and Am) particle-associated in the pond waters. Considering these observations with the discharge levels from each source, it is concluded that only 1% of the Pu discharges and 50% of the Np will be released in the oxidised form (V and VI states) into the Irish Sea (Pentreath *et al*, 1983; 1986b).

The Irish Sea is a highly complex, coastal shelf system in which water movement, sediment transport and bioturbation are important and studies on the behaviour of radionuclides, particularly the transuranics and fission products, are extensive (Pentreath, 1985). It is worth considering aspects of the behaviour of the more intensively studied transuranics in order to understand the environment into which Np is released.

The discharged liquid wastes retain their integrity for up to 3 to 4 days but during that time much of the particle-active Pu and Am is removed. Approximately 95% of the total Pu discharged is associated with the sediments of the Irish Sea bed (Dyer, 1986) and its distribution closely follows that of the fine-grained sediment (Woodhead, 1988). The bulk K_d values obtained for Pu and Am have been found to be consistently 10^5 and 10^6 respectively (Pentreath *et al*, 1986c) for suspended particulate matter. There is a considerable difference between the K_d values for the oxidation states of Pu (Nelson and Lovett, 1978; Lovett and Nelson, 1981). The III/IV (reduced forms) and V/VI (oxidized forms) have general values of 10^6 and 10^4 respectively and it has been observed that 75% of the Pu in solution and $<10\%$ on the solid phase are in the oxidized forms. This considerable difference in particle association for the different forms of Pu has prompted much discussion of the "mobility" of Pu in the marine environment and of the marine sediments as a sink for Pu. Release may be through changes in oxidation state or through the dissolution of host phases within the sediment (eg reduction of Mn and Fe oxides, oxidation of organic matter). There is some controversy as to whether or not this is observed in the environment for Pu. Dissolved Pu above the sediment/ water interface has been observed to be in the oxidised form. In interstitial waters, dissolved Pu was greatly lowered in concentration and found to be in the reduced state (Nelson and Lovett, 1981). The solid phase Pu was found to be reduced. It was concluded that the pore water Pu simply represented Pu released from the sediments and that the sediments actively reduced the Pu in the discharges (Nelson and Lovett, 1981; Penrose *et al*, 1987). Sholkovitz (1983) reviewed the area of plutonium geochemistry in great detail and concluded that the evidence both for and against Pu remobilization was far from satisfactory. In the shallow coastal environments, evidence was circumstantial but for some deep sea sediments it did occur. Further arguments for the observed enhancement of Pu at the sediment/ water interface invoke a mechanism of physical sedimentation of a water column-derived flux of solid material dominated by biogenic debris and found in both shallow coastal and deep sea environments (Alberts and Orlandini, 1981; Carpenter and Beasley, 1981; Cochran, 1985; Alberts *et al*, 1986). Clearly this question is still to be adequately answered for Pu and the current uncertainty suggests that it is possible that both mechanisms, namely scavenging from the water column followed by accumulation at depth and a seabed-derived, upward flux occur. There is no reason to think that the situation for Np is any simpler.

Physical processes of deposition and sedimentation of contaminated particles have been concluded to be the major influences on Pu transport in the Irish Sea but there appears to be a time lag of 2 to 3 years between discharge events and appearance within the local sediment record (Aston and Stanners, 1981a; 1981b). Particles of high radioactivity derived from original effluents and in some cases thought to represent primary fuel material have been observed in Irish Sea sediments and the Esk estuary (Hamilton, 1981; 1985; Kershaw *et al*, 1986). A survival time of a few months is suggested before they are dissolved. This would imply that there is rapid dispersal of some component of the particulate phase southwards within the Irish Sea which is related to bulk sediment movement rather than to the more dynamic fluid phase (Bradley *et al*, 1988). It is certain that there is a significant migration of particulate material from within the Irish Sea northwards, following the water flow traced by radiocaesium (Hallstadius *et al*, 1987; Bradley *et al*, 1988) to account for the isotopic signatures and transuranic nuclide inventories in the S.W Scottish coastal region (MacKenzie *et al*, 1987; Baxter *et al*, 1989). Due to the high energy environment of the continental shelf system and the accumulation of the actinides in sediments off Sellafield, the rates of such transfer are uncertain (Dyer, 1986).

There exist a number of determinations of the activity concentration of ^{237}Np in seawater and sediments of the Irish Sea (Holm, 1981; Pentreath and Harvey, 1981; Harvey and Kershaw, 1984; Byrne, 1986; Pentreath *et al*, 1986a). This data set has been summarized in Table 1.8 with the exception of those of Harvey and Kershaw (1984) which will be considered later. The Np K_d values quoted for filtered seawater and solids are at least an order of magnitude lower than those observed for Pu (bulk) and are similar to the values for Pu (oxidized) referenced above. The data from Pentreath and Harvey (1981) suggest a decrease in the K_d north from Sellafield and may indicate a change in the oxidation state of the Np. A tentative K_d value can be assigned to the data of Holm (1981), although strictly this must represent equilibrated phases. Nevertheless a value of 1.4 x10^3, although possibly low, is an acceptable order of magnitude estimate (Holm and Fukai, 1986). The value of the ^{237}Np/ ^{239,240}Pu ratio is a useful tracer. Sellafield discharge ratios, over the past 10 years, range between 8.93 x10^{-3} and 76.0 x10^{-3}.

Table 1.8: The activity concentration of ^{237}Np (Bq kg^{-1} ±2σ) in marine samples. + Holm (1981); * Pentreath and Harvey (1981); ** Byrne (1986).

Sample		(^{237}Np/ ^{239,240}Pu)	
seawater (Mar/77)+	1 x10^{-3}	(0.25)	
sediment (Mar/77)+	1.4	(3.44 x10^{-4})	
Newbiggin silt**	4.5	-	
Grange-over-Sands**	0.55	-	
Ravenglass**	6.5	-	
	particulate (dry)	filtered water	K$_d$ ([partic]/[water])
1 off Sellafield (Apr/80)*	19.9 ±0.3	1.44 ±0.04 x10^{-3}	1.4 ±0.04 x10^{4}
2 off Sellafield (Apr/80)*	38.9 ±2.2	1.18 ±0.04 x10^{-3}	3.3 ±0.32 x10^{4}
3 S. of Sellafield (Apr/80)*	3.1 ±0.3	0.76 ±0.01 x10^{-3}	4.1 ±0.4 x10^{3}
4 S. of Sellafield (Apr/80)*	4.4 ±0.7	1.04 ±0.04 x10^{-3}	4.2 ±0.7 x10^{3}
5 N. of Sellafield (Apr/80)*	1.6 ±0.2	0.13 ±0.01 x10^{-3}	1.2 ±0.2 x10^{4}
6 N. of Sellafield (Apr/80)*	2.8 ±0.3	0.46 ±0.01 x10^{-3}	6.1 ±0.7 x10^{3}
7 N. of I.of Man (Apr/80)*	3.4 ±0.4	0.37 ±0.04 x10^{-3}	9.2 ±1.5 x10^{3}
8 North Channel (Apr/80)*	0.19 ±0.07	0.08 ±0.02 x10^{-3}	2.4 ±1.1 x10^{3}

From Table 1.8 it appears that there is a relative enrichment of Np with respect to Pu in seawater and of Pu relative to Np in sediments, emphasising the K$_d$ differences. The ^{237}Np/ ^{239,240}Pu data presented by Duniec *et al* (1984) for seawater to the S.W. and N.E. of Shetland and the S.W. Norwegian Coast suggest an increasing enrichment of Np in the solution phase with increasing distance from Sellafield. These observations suggest that Np exists in a more mobile form in the marine environment than the other transuranium nuclides.

NpO_2^+ is expected to be the stable species in oxidising waters (see section 1.3.3) and has been implied to be the most important component of Sellafield discharges of ^{237}Np (Pentreath *et al*, 1983; 1986b). From the above discussion on redox sensitive behaviour of Pu, the question of Np oxidation state stability must be considered to be of similar significance. The potential of Irish Sea sediments to reduce Np^{V} has been considered by Harvey (1981a; 1981b). On the basis of porewater chemistry and E$_h$/ pH conditions, slow reduction of Np^{V} to more particle-active Np ^{IV} is expected to occur. Further detailed analysis by Harvey and Kershaw (1984) of interstitial waters for both oxidized and reduced forms of Np shows a good correlation between E$_h$ and the % Np^{IV}. Up to 60% of the total Np is as Np^{IV} in regions where the E$_h$ is <100 mV. Measurement of the apparent K$_d$ values showed values an order of magnitude less than those expected from the observed oxidation state distribution. It was suggested that this reflects complexation of Np^{IV} by soluble organic species, a possibility substantiated by the presence of a relatively high percentage of soluble iron. Table 1.9 summarizes the Np and Pu data obtained for the distribution of the nuclides between pore waters and the solid phase. Np

Table 1.9: The distribution of Np and Pu between the solid phase and interstitial waters of Irish Sea sediments (Bq kg^{-1} ±2σ) (data from Harvey and Kershaw, 1984).

overlying water						
^{237}Np	8.5±0.3 x10^{-3}					
^{239,240}Pu	2.2±0.1 x10^{-3}					
	Core section (cm)					
	0-5	5-10	10-15	15-20	20-25	25-30
sediment						
^{237}Np	11.9±0.3	14.4±0.3	6.9±0.2	2.2±0.1	0.9±0.1	0.8±0.1
^{239,240}Pu	1010±40	1670±50	1300±30	594±13	212±4	106±2
interstit. waters (x10^{-3})						
^{237}Np	31.2±1.6	4.6±0.2	2.6±0.1	1.1±0.1	0.85±0.07	0.44±0.09
^{239,240}Pu	5.8±0.2	2.4±0.2	2.6±0.1	0.97±0.09	0.73±0.09	0.67±0.09
[solid]/ [liquid] (x10^{3})						
^{237}Np	0.4±0.1	3.2±0.2	2.7±0.2	2.1±0.2	1.1±0.1	1.1±0.1
^{239,240}Pu	170±9	680±60	500±25	610±60	290±40	160±20

appears to be more mobile under the conditions prevailing in the sediments.

Routine analyses of the marine environment around Sellafield are made by MAFF and the results are published annually (Mitchell, 1973; 1975; 1977a; 1977b; Hetherington, 1976; Hunt, 1979-1988). The few and fragmented data for ^{237}Np in marine biota are summarized in Table 1.10. There is, as expected from a point source, a distinct geographical variation in total body burdens for the same species for both ^{237}Np and ^{239,240}Pu, also reflecting differences in species feeding patterns. The ^{237}Np/ ^{239,240}Pu ratio varies between species over an order of magnitude but is constant over time for particular species groups. Interpretation of this data set is complicated by the restricted discharge data and it would be unwise to attempt to progress further.

If the literature data on Np in the marine environment are sparse relative to the other transuranic nuclides, the abundance of data concerning the terrestrial behaviour of Np is positively barren (Nilsson and Carlsen, 1989). Only one set of measurements relating to the behaviour of ^{237}Np in soils has been published. Sakanoue (1987; 1988) reports an increase in the ^{237}Np/ ^{239,240}Pu ratio with depth in a Japanese soil, implying a degree of greater mobility for Np with respect to Pu. In the local W. Cumbrian environment, a number of studies on the terrestrial behaviour of

Sellafield-derived radionuclides have important implications for ^{237}Np.

Table 1.10: ^{237}Np activity concentrations (Bq kg^{-1} wet) in marine biota (Mitchell, 1973; 1975; 1977a; 1977b; Hetherington, 1976; Hunt 1979-1988).

year/site/sample (observations)	^{237}Np	(^{237}Np/ ^{239,240}Pu)
1984 Sellafield shore		
crab (2)	0.025	0.012
lobster (4)	0.072	0.051
winkle (2)	0.34	0.006
Sellafield off-shore		
plaice (1)	0.00054	0.025
Netherton		
winkle (2)	0.72	0.008
Coulderton		
winkle (2)	0.26	0.005
St Bees		
winkle (2)	0.38	0.006
winkle (1)	0.077	0.004
winkle (1)	0.14	0.004
mussel (1)	0.65	0.010
limpet (1)	0.18	0.004
Ravenglass		
mussel (2)	0.42	0.010
plaice (1)	0.00065	0.021
cod (1)	0.00015	0.013
Morecambe Bay		
shrimp (1)	0.0015	0.019
cockle (1)	0.22	0.045
1985 Sellafield coast		
cod (1)	0.0008	0.007
crab (1)	0.047	0.003
winkles (2)	0.2	0.004
St Bees		
winkles (4)	0.085	0.004
Nethertown		
winkles	0.012	0.004
Ravenglass		
plaice	0.00065	0.04
cod	0.00015	0.006
1986 Sellafield coast		
crabs (3)	0.16	0.08
lobster (3)	0.12	0.1
winkle (4)	0.25	0.0087
Sellafield off-shore		
plaice (1)	0.0005	0.04
cod (1)	0.0003	0.03
1987 Sellafield coast		
crabs (2)	0.015	0.015
lobsters (3)	0.12	0.037
winkle (4)	0.25	0.011
Sellafield off-shore		
plaice (1)	0.0016	0.10
cod (1)	0.0008	0.05
St Bees		
winkle (4)	0.14	0.007

An excess of total inventories for Pu, Am and Cs nuclides is observed above that due to weapons fallout. This excess in samples far removed from direct marine incursion correlates with Na^+ ions and decreases inland from the coast. An on-land transfer mechanism has been invoked to explain this distribution and aspects of this process have been studied over a number of years (Cambray and Eakins, 1982; Pierson *et al*, 1982; Pattenden *et al*, 1985; Walker *et al*, 1986). The enrichment of radionuclides at the sea surface microlayer and experiments at the surf zone imply that a sea spray aerosol is responsible. At a restricted number of sites in W. Cumbria and S.W. Scotland, the direct incursion of estuarine waters is found to be responsible for enhanced levels of Sellafield-derived fission product and actinide nuclides (Livens, 1985; Livens *et al*, 1986; Bonnett *et al*, 1988; Livens and Baxter, 1988a; 1988b; Baxter *et al*, 1989). At one site, the activity of Pu is 100 times the NRPB general derived limit for surface contamination (Livens, 1985). Such sites are observed to be periodically flooded at high tide, with direct deposition of suspended material. Plutonium at these sites is found to be in the reduced oxidation states and strongly associated with organic material in both the coarse and fine particle size fractions (Livens, 1985; Baxter *et al*, 1989).

The interfacial region between the terrestrial and marine environments is the subject of much study. In the UK, the behaviour of Pu and Am has been observed in the Ravenglass Estuary to the south of Sellafield (Aston and Stanners, 1981b; 1982; Assinder *et al*, 1985; Burton, 1986; Hamilton-Taylor *et al*, 1987; Kelly *et al*, 1988; Mudge *et al*, 1988). The estuary was identified as an important point of net accumulation of relatively highly contaminated sediment prior to the mid 1980's when discharges were relatively large containing Pu and Am nuclides and hot particles of primary Sellafield origin (Hamilton, 1981; Aston and Stanners, 1982). Estuaries are complex and extremely dynamic environments with variable gradients of salinity, chlorinity, E_h, pH and microbial activity over the tidal cycles (Bittel, 1984). At low salinities,both in field and laboratory experiments, plutonium was found to be enriched in the dissolved phase in both the oxidized and reduced forms (Assinder *et al*, 1985; Burton, 1986; Hamilton-Taylor *et al*, 1987; Kelly *et al*, 1988). The remobilization has been explained by rapid surface exchange reactions with competition from major cations and protons for sites on mineral and organic surfaces. Complexation by HCO_3^- and colloidal organic matter was also important (Mudge *et al*, 1988). Salinity/ pH levels and the total sediment concentration influenced the total Pu concentration. In the light of its observed mobility and some redox sensitivity as revealed above, Np behaviour in these environments is potentially one of the most interesting aspects of the element's geochemistry (Bittel, 1984).

(d) the availability and uptake of neptunium by marine biota

Levels of ^{237}Np in marine biota from the Irish Sea and English Channel have been presented above (see Table 1.6 and Table 1.10). Pentreath (1981) and Scoppa (1984) summarized earlier studies in which a surface adsorption mechanism for Np uptake is proposed. Analyses of echinoderm body walls, digestive glands and gonads (Pentreath and Harvey, 1981) indicate that ^{237}Np is accumulated by the species and not adsorbed through the test. Fowler and Aston (1982) used $^{235}NpO_2^+$ to follow the accumulation of Np by zooplankton. Surface adsorption was significant and the proportion of Np ingested was poorly assimilated, with >95% of the input returned after 30 hours. Similar behaviour was reported for Pu and Am (Pentreath, 1981). Germain *et al* (1987) recently studied the uptake of Np^V by polychaete worms and cockles. Different uptake mechanisms were proposed for the different species. The polychaete worm concentration factor after 13 days was only 2 and was constant after 6 days. Cockles showed whole organism concentration factors of 30 to 40, mainly due to uptake in or on the shell. Overall uptake was appreciably lower than for Pu and Am.

(e) the potential impact of the chernobyl accident on ^{237}Np inventories

Following the accident at the Chernobyl number 4 reactor, USSR on 26/4/86, significant quantities of the reactor core inventory were released to the atmosphere and dispersed around the world (Devell *et al*, 1986; Smith and Charlesby, 1988). The more volatile components, ^{131}I, ^{134}Cs and ^{137}Cs, were the most significant nuclides in terms of total worldwide deposition (Aoyama *et al*, 1986; Clark, 1986; Fry *et al*, 1986; Hoheneimer *et al*, 1986; Thomas and Martin, 1986; Webb *et al*, 1986; Ballestra *et al*, 1987; Clark and Smith, 1988). It was estimated (Devell *et al*, 1986) from the measured deposition that the reactor had been in operation for approximately 400 days and that the core inventory of actinide nuclides would have been fairly high. The presence of trace quantities of ^{239,240}Pu in fallout from Chernobyl has been indicated by a number of authors (Ballestra *et al*, 1986; Whitehead *et al*, 1988). In only one report (Thomas and Martin, 1986) was the probability of release of ^{237}Np from Chernobyl implied. Measurements of the activity of air over Paris indicated the presence of trace ^{237}U. This is the short-lived (6.75 day) parent of ^{237}Np (see section 1.2) and would imply some activity due to ^{237}Np, although this could not be detected in samples from Monaco (Whitehead *et al*, 1988). It is certain that any Chernobyl-derived ^{237}Np deposited in Cumbrian soils was negligable.

1.3.5 LABORATORY STUDIES ON THE ENVIRONMENTAL BEHAVIOUR OF NEPTUNIUM

A large number of laboratory-based studies have been performed in an attempt to elucidate the features and properties of the mechanisms responsible for controlling the behaviour and distribution of Np in the environment. This section summarizes the available literature on "non-environmental" observations of Np geochemistry from a wide range of sources. The work involves studies of sorption and desorption mechanisms for simple and complex solid phases of synthetic and natural origin, crushed rock column leaching studies and field and laboratory trials of plant uptake and translocation. The common feature of these groupings is that they are observations from artificial environments and as such the results must be treated with caution when applying them to the real environment. Nevertheless, some behaviourial trends observed in these studies are seen to agree with the limited observations from nature.

The subject of the relevance of laboratory-based studies, particularly in determining distribution coefficient data for radionuclides, has been reviewed by Onishi *et al* (1981) and Choppin and Morse (1987). The data produced so far have been concluded to be lacking in experimental consistency with respect to reaction kinetics, specific surface areas of solid phases, solid : solution ratios and nuclide concentration. This aspect is of particular relevance for Np and the actinides in general (see section 1.2).

(a) adsorption/ desorption studies

The importance of clay minerals and oxides of Fe and Mn in supplying surface sites for the exchange and fixation of trace elements is well documented (see for example: Means *et al*, 1978; Chester and Aston, 1981; Evans *et al*, 1983; Boust and Joron, 1985; Tessier *et al*, 1985; Music and Ristic, 1988; Lang and Wolfrum, 1989). It is of still greater significance in the case of authigenic mineral formation in soils and sediments, when the freshly precipitated solid phases are more highly reactive to the solution phase (Krauskopf, 1979). Scavenging of metals in marine environments is controlled by a number of mechanisms influenced by both chemical and biological factors (Jannasch *et al*, 1988). Hence the interaction of actinide nuclides with such systems has been studied in great detail.

The sorption of Pu^{IV} and Pu^{V} on goethite shows a higher affinity for the IV state, while only reduced species are found in the solid phase (Sanchez *et al*, 1985). Dissolved organic carbon both reduces the Pu and inhibits adsorption and, in the case of carbonate, the sorption of both oxidation states is retarded. Following directly from this work, a series of experiments was performed with a variety of mineral surfaces and the PuO_2^+ and NpO_2^+ species (Keeny-Kenicutt and Morse, 1985; Choppin and Morse, 1987). The carbonate phases of aragonite and calcite were found to adsorb NpO_2^+ rapidly (<30 minutes), with goethite being of lesser importance. Clays and Mn oxides exhibited only slight (20%) sorption. The presence of organic matter did not retard sorption on to aragonite, implying that the Np had not been reduced and the affinity of the carbonate phase for the pentavalent oxidation state was high. The reverse reactions indicated a chemisorption (ie non reversible) mechanism in the case of aragonite that near total reversible desorption for goethite. The identical experiments performed on PuO_2^+ revealed a very different behaviour from Np. Sorption rates were greatly reduced and, unlike Np, were affected by the aqueous phase composition (seawater v distilled water). Carbonate phases were of lowest importance for sorption. The reversibility of Pu^{V} sorption on goethite decreased with time, suggesting a rate-controlled mechanism involving the reduction of Pu on the mineral surface. The exclusion of light during the Pu reactions reduced the sorption rate. In a separate experiment the effect of oxidation by UV light on a pH-dependent redox reaction between Np^{IV}

and Np^V was studied (Pentreath *et al*, 1986a). As pH increased, the percentage of Np^V was also found to increase.

Righetto *et al* (1988) studied sorption of Np^V relative to Th^{IV} and Am^{III} on alumina colloid phases, the effect of dissolved carbonate was to depress sorption for all nuclides and the degree of sorption was in the order V< IV< III. Humic acids increased Np sorption at lower pH and decreased net sorption at higher pH.

A series of diffusion and distribution experiments was performed with Np^V tracer on a number of mineral and deep sea sediment types (Aston *et al*, 1983; Higgo *et al*, 1986; Van Dalen and Wijkstra, 1986; Higgo *et al*, 1988). Inspite of the wide variety of experimental conditions, all distribution coefficients measured were of the order of 10^3, commonly 1 to 2 orders of magnitude lower than those of the Pu and Am tracers. The results also compare favourably with experimental determinations on shallow coastal sediments (Fowler and Aston, 1982; Germain *et al*, 1987). In most situations sorption was reversible but in some anoxic sediments the increase in the apparent K_d was attributed to significant reduction of the Np tracer (Higgo *et al*, 1988) as predicted by Harvey (1981a; 1981b). Only Aston *et al* (1983) studied the time-dependence on apparent K_d. It was suggested that, even after 50 days, equilibrium was not attained.

From the discussion above, it is apparent that carbonate is an important influence on Np distribution and that K_d values correlate strongly with % carbonate in all cases. Although it was not a linear relationship (Germain *et al*, 1987), sequential leaching studies on experimental samples reveal a much more significant association of Np with "carbonate" than for any other transuranic (Aston *et al*, 1983).

(b) behaviour in studies of groundwater/ rock interactions

The experiments described here concern work related to the remote disposal of radioactive waste and to the behaviour of Np under the conditions predicted close to the repository. Some studies contain material which may be considered to be part of section (a) above but has been left here since it is specifically related to remote disposal.

The speciation of Np in samples of oxic groundwaters of varied composition has been studied by Cleveland *et al* (1983a; 1983b; 1983c) and Nash *et al* (1988). Neptunium showed the least variability in behaviour compared to other transuranic nuclides. High solubility (approximately 86%) in most cases was attributed to the Np^V species, although in some waters Np^{VI} may be stable. Insoluble Np was in the IV oxidation state. Nagasaki *et al* (1988) observed that, under oxic conditions, Np existed as positively charged and neutral species in acid / neutral solutions and, in alkaline pH, negatively charged species dominated (this was enhanced in the presence of carbonate). Increased ionic strength shifted the stability fields of the cationic and neutral species to higher pH.

Leaching of borosilicate glass doped with Np tracer and the diffusion of the leachate through solid and crushed igneous, metamorphic and sedimentary rocks constitute much of the experimental work in this area. The experiments by Bidoglio *et al* (1984; 1987; 1988) found that >97% of the released Np was concentrated in the first few centimetres of the columns and that the distribution did not alter even after 187 days equilibration. Carbonate competition for sorption was observed and the species involved deduced to be NpO_2^+ and $NpO_2(CO_3)^-$. Under anoxic conditions, sorption decreased, presumably due to Np reduction. The transport with naturally occurring organic colloids was used to explain the breakthrough of Np in columns using a natural bicarbonate ground water and was aided by increased ionic strength. Lieser and Muhlenweg (1988a; 1988b) performed a similar series of experiments using carbonate and argillic sediments with neutral groundwaters under oxic and anoxic conditions. High sorption under anoxic conditions was due to Np^{IV} formation. This was concentrated at the top of the columns partly as a result of Np^{IV} colloid formation and filtration, although the authors did not consider Np^{IV} sorption mechanisms. Under oxic conditions, relatively weak, reversible sorption was attributed to high proportions of negatively charged Np^V carbonate complexes. Seitz *et al* (1979) found that limestone retarded the migration of Np^V to a greater extent than sandstone, which allowed up to 70% of the input Np to pass through at a similar flow rate.

Studies of a similar nature to those above have been performed with highly concentrated brine solutions in order to simulate conditions in salt dome hosts for active wastes. Np (with Tc) was not effectively sorbed by pressed salt columns although Pu and Am were strongly held (Offerman and Bidoglio, 1988). Bidoglio and De Plano (1986) passed a brine leachate containing Np^V as NpO_2^+ and NpO_2Cl through a soil column. Complexation effects of high $[Mg^{2+}]$ were suggested to explain Np sorption retardation. Retardation factors and apparent column K_d for oxic and anoxic conditions were similar to the above experiments. In the case of the anoxic column, the observed increase in sorption was thought to be due to changes in mineral surfaces rather than the reduction to Np^{IV}. Unfortunately, no indication of E_h conditions was given.

Flow through crushed rock and mineral columns has been studied by Ittner *et al* (1988), Nakayama *et al* (1988), Torstenfelt *et al* (1988) and Thompson (1989). Np^V colloid formation and hydrolysis was used to explain the retardation at high pH and was also affected by Fe^{II} and the presence of phosphate and oxide minerals. Migration through whole rock was controlled by the presence of fissures and high surface area, micaceous minerals (Ittner *et al*, 1988; Torstenfelt *et al*, 1988). Np^V was concluded to be reduced by some basaltic and granitic rocks to explain the fairly rapid sorption observed (Bondietti and Francis, 1979). After >7 days, >75% of the sorbed Np was in the IV oxidation state. In contrast, shale rocks, which also significantly sorbed

Np, could not be shown to contain Np in the IV oxidation state.

(c) laboratory and field studies of water-soil-plant translocation and uptake

The soil environment is complex and extremely heterogenous. Levels of organic matter are generally higher than for other sedimentary environments and soil water chemistries variable over both macro and micro scales. Microbial mediation is an important factor in establishing the redox conditions (Brady, 1974; Pimpl, 1988).

Routson *et al* (1977) studied the distribution of Np between a neutral, sandy silt from an arid region and a clay-rich soil from a humid region and the effect of Ca^{2+} and Na^{+} on Np sorption on these soils. Competition from both Na and Ca for sorption sites was observed to reduce Np sorption, although slope analysis indicated that the mechanism was not through simple ion exchange. A series of experiments by Nishita *et al* (1981a) determined the pH variation in the "extractability" of various actinides, including Np, from a wide variety of soil types. The pH range from 1.5 to 12.5 was studied except in the case of a calcareous soil for which the pH range >7 was investigated. For the mineral soils, the behaviour showed a similar pattern, although the magnitude varied between nuclides. Extractability was initially high at low pH and decreased to a minimum in the pH 6 to 8 region. Above pH 8, extractability increased to a peak and fell off. The calcareous sample decreased in extractability with increasing pH and at pH 8.3 showed the lowest extractability of all soils. For the organic-rich soil, pH 2.1 to 4.1 showed increased extractability which became fairly constant up to pH 8, at which point it increased considerably. Below pH 9, this soil showed the lowest % extractability of all soils. Some correlation with Fe, Al and Mn was observed and Np extractability was generally greater than for the other actinides studied (Pu, Am and Cm) at pH <6. Above this, relative extractability varied with soil type. The distribution coefficients for Np in each soil were commonly 1 to 2 orders lower than those for Pu. The conclusions were that the initial decrease in extractability was a result of a change from exchange controlled sorption to immobilization of hydrolysis products or colloid material on the solid phase. Increased extractability above pH 8 was explained by solubilization of organic material which may have contributed at low pH also. However, the poor extractability of nuclides from organic soils casts doubt on this conclusion. The correlation with Fe, Al and Mn suggests that sorption by and solubilization of sesquioxide phases may also be important. Sheppard *et al* (1979) also observed poor sorption of Np^{V} in soils and that the sorbed Np was distributed over a wide range of particle sizes. The "bioavailability" of Np added to acidic and calcareous soils and left to equilibrate for 2 years in the open has been studied in terms of the extractability by demineralised water and ammonium acetate (Colle and Morello, 1986). In both cases, 30% of the amended total was released by these reagents.

The importance of organic matter complexation has already been indicated in section 1.3.3. For natural waters, sediment and mineral surface sorption of Pu and Am has been severely retarded

The importance of organic matter complexation has already been indicated in section 1.3.3. For natural waters, sediment and mineral surface sorption of Pu and Am has been severely retarded by the presence of organic material (Nelson *et al*, 1985; Nakayama and Nelson, 1988; Moulin *et al*, 1989). In soils, stable, soluble organic complexes with Pu, Am and Eu are not formed to any great extent. Humic acids were found to complex much more strongly than carbonate and oxide species, with the added organic matter essentially locking up the nuclides (Cleveland and Rees, 1979; Maes and Cremers, 1986). Aksoyoglu *et al* (1986) studied the effects of humic acids on the adsorption of ^{237}Np from natural waters on to clay minerals. For single minerals soluble Np organic complexes were thought to be responsible for the reduced uptake and the decrease in K_d with time. For a mixed clay (Molasse), the sorption was complex and it appeared that multiple mechanisms were in operation. These interesting results were not interpreted by the authors and may be related to surface "activation" by the humic acids.

A series of lysimeter and pot experiments have been carried out to assess the relative uptakes of Np and other actinides by plants commonly grown in the USA and Europe for human consumption (Schriekheise and Cline, 1980; 1981; Romney *et al*, 1981; Schulz and Ruggeri, 1981; Garten and Tucker, 1986). Soils were spiked with solutions of the nuclides in the nitrate form and sown with barley, wheat, peas, soy beans and tomatoes. The crops were subject to normal cultivation practices and harvested. Relative uptake was similar for a wide range of species and soil conditions and were generally in the order Np> Am/Cm> Pu. Concentration factors for whole plants were 10^{-1} to 10^{-4} for Np compared to 10^{-5} to 10^{-7} for Pu but in the case of the fruit or seed parts only, the values were 10 to 100 times lower although the same trends were followed. Uptake was found to be consistently greater for acidic as opposed to neutral or basic soils (Garten and Tucker, 1986), possibly correlated to the higher adsorption of nuclides in the soil as pH increased (Nishita *et al*, 1981a; 1981b; Colle and Morello, 1986).

The correlation between plant uptake and extractability from the studies described above (Nishita *et al*, 1981a) was found to be illustrated by a high correlation (0.72-0.94) for Np extracted with calcium chloride and ammonium acetate reagents (Nishita *et al*, 1981b) but with a somewhat erratic pattern for water. Concentration ratios were again highest for Np. The fate of Np in plant systems has been studied in hydroponically grown plants of bush bean, alfalfa, wheat and soy beans (Cataldo *et al*, 1987). In the roots, the majority (>70%) of the Np was found in the insoluble phase, whilst in the shoots >60% is soluble, implying some form of chemical stabilization on uptake. Only 6 to 14% is associated with the pellet fraction. The observed distribution was consistent with that of Pu. Fractionation of the soluble components by ultrafiltration revealed that Np was associated with a broad range of molecular weight fractions and that the low weight fraction (<5000 MW) contained nearly 50% of the soluble fraction. For Pu, the distribution was different, with only 2 to 10% in the <5000 MW fraction implying that some physiological differentiation between actinides can occur.

CHAPTER 2

METHODS

"The ICP mass spectrometer is neither a "black box" nor a field instrument; elemental analysis methods using ICP-MS are still far from routine."

Riddel *et al* (1988)

2.1 THE APPROACH TO ENVIRONMENTAL TRACE ANALYSIS OF ^{237}Np

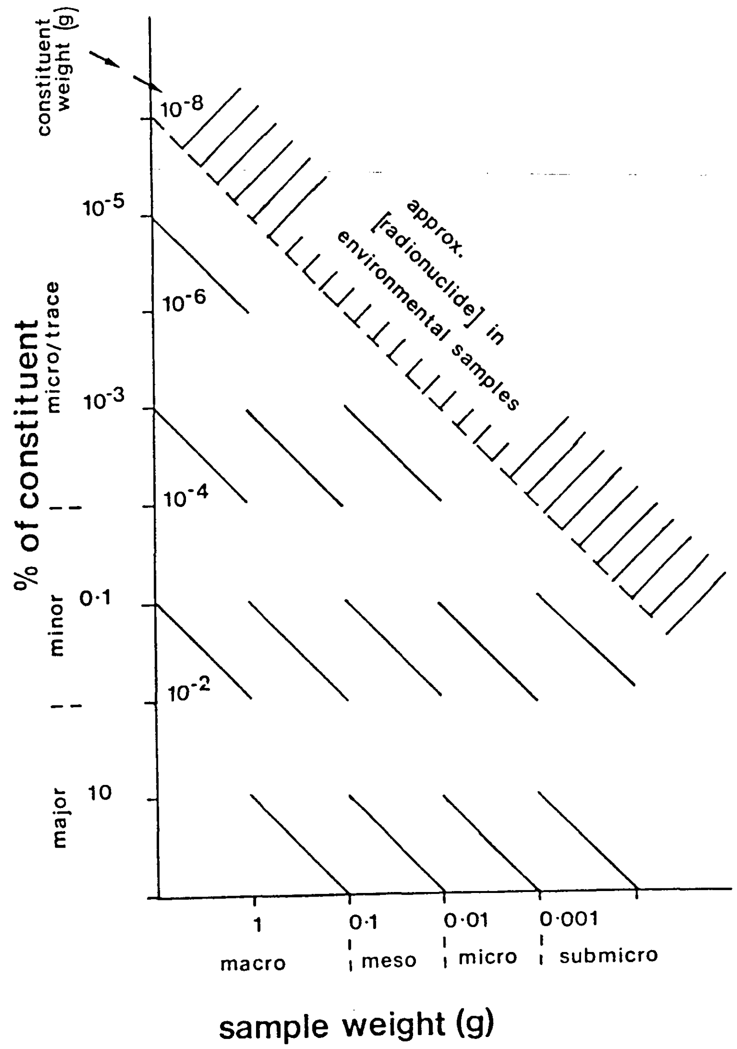
The analysis of ^{237}Np in environmental matrices is a complex problem from many aspects, all of which profoundly influence the practical approach to its assay. In Chapter One, neptunium has already been shown to be the "poor man" of the actinide family in spite of being the first transuranic to be discovered.

As in general chemistry, studies of its analysis have taken second place to various other nuclides, particularly plutonium. Consequently there is a comparative scarcity of data. This leads directly to a further problem with the actinides in general, but particularly the transuranium elements. Within nuclear technology research, the analytical requirements are far from demanding. They have in general been developed for the fairly rapid assay of fuel rods, process solutions and highly active wastes from nuclear power programmes or targets used in the search for new elements. The abundances of the nuclide(s) sought are thus far higher than expected in the environment and the matrices in which they are contained are generally far simpler and, in some instances, well characterized. As a direct consequence, the methods of analysis available are often partially tested and unrefined in nature and use equipment of a highly novel type. Routine environmental radiochemical analysis has, until recently, not stimulated much interest and has been beset with technical difficulties.

The ideal approach to environmental actinide analysis is derived directly from the experiences of standard approaches to trace and ultratrace analysis. Figure 2.1 is a useful illustration showing the classification of analytical methods on the basis of analyte concentration. The requirements of methods for ^{237}Np assay fall, in concentration terms, into the category of ultratrace analysis. The ^{237}Np distribution in the environment will reflect its origin from a point source, either, from effluent, aerial discharges or from weapons devices. The direct result is that the levels that are observed will vary from a maximum at or near the source to essentially zero at some distance away. Consequently the methods chosen for development and application must be able to cope with a wide dynamic range often spanning three or four orders of magnitude. Samples may be such that the analyte is at trace levels in a moderately sized sample, a major component in a small mass or the concentration of the analyte as a particular chemical species. Some form of sample pretreatment followed by dissolution and chemical processing will be required before assay. The sample matrix must also be considered, as it more often than not will affect the assay in an undefined and unpredictable manner.

An ideal method should thus adapt or be easily adaptable to cope with a wide range of analyte concentrations in a wide range of matrices. Figure 2.2 is a schematic diagram summarizing the key stages involved in most types of environmental analysis. The determination starts with the receipt of a sample and ends with some additional information about the sample even if that

Figure 2.1: Classification of analytical methods on the basis of sample size and analyte concentration. Region of interest for environmental radioanalysis shown (Hamilton, 1980; Eakins, 1984).



information is that the analyte concentration is below the detection limit of the technique!

2.1.1 SENSITIVITY AND DETECTION

For the analysis of a particular nuclide, the method chosen must be of adequate sensitivity and selectivity for the analyte in complex matrices. The signal corresponding to the determinand must be easily distinguishable from spurious background noise. Hamilton (1980) defines the sensitivity (γ) of a method as:

$$\gamma = dI/dCs$$

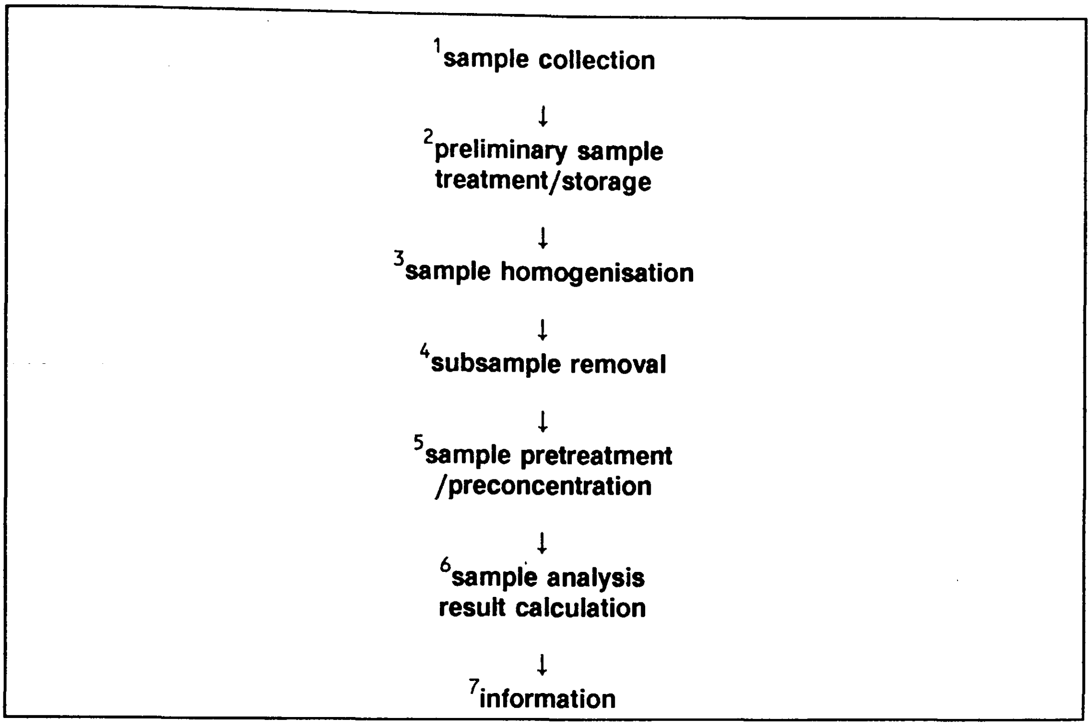
where I = signal intensity, C = analyte concentration and s = standard deviation of signal measurement. The limit of detection occurs when the sample and background signals cannot be distinguished. For quantification purposes, the detection limit is usually defined as 3σ above background (see Currie, 1968) and is the criterion used for the work described in this study. In the case of α-spectrometry, the detector background is essentially zero or very low and generally due to contamination of the counting chamber or detector surface. Livens (1985) concluded that such a theoretically non random situation could be accounted for by assuming normal distribution and using the 3σ value as above or another predetermined limit.

2.1.2 SAMPLE COLLECTION AND PREPARATION

The distribution of a component within the environment reflects both its source and of the chemical, physical and biological processes which interact with it during its residence in the environment. The nature of sampling and sample pretreatment prior to analysis will be dictated not only by the distribution of the component but also by the requirements of the survey. Sampling is without doubt the most crucial process in any trace determination and a logical sampling strategy must be adopted and adhered to at the start of any study if the results are to provide any meaning. It is also the most seriously abused aspect of environmental work, yet it is the one most likely to influence the final result due to the large uncertainty which can arise during sample collection. It is certainly one of the more strongly debated aspects (Anders, 1977; Anders and Kim, 1977; Hamilton, 1980).

The act of removing a sample from the environment can cause changes in the distribution and nature of the components. Obvious examples are in the sampling of material from anoxic environments, where the sudden change in redox conditions may have serious implications for analyte speciation, particularly in the case of aqueous phases. In general, environmental radioanalysis for anthropogenic nuclides does not suffer the same potential contamination problems found for trace metal analysis in respect to sampling equipment and sample containers (Hamilton, 1980; Grasshoff, 1983). However, Harvey *et al* (1987) report "memory effects" from the repeated use of sampling devices for low-level transuranic analysis of marine samples. It would seem prudent that the same approach used in trace analysis should be used. Continued monitoring of laboratory results over a long period of time may be the only way that this type of contamination is identified.

Figure 2.2: A schematic summary of the key stages in environmental analysis (Philips, 1981).



a) Soils

Simple soils comprise a mixture of mineral and biological components at varying stages of degradation and alteration. Primary and secondary minerals, living organisms and residues and anthropogenic inputs are all present and complex reactions are in progress (Brady, 1974; Hamilton, 1980; Berrow, 1988). Total soil profiles may be collected as a complete soil pedon or sectioned at predetermined depth intervals for physicochemical studies or mapping (Berrow, 1988). Survey of topsoil can be accomplished rapidly by the collection of at least 25 random soil cores from within the site to give a suitably representative sample (Parkinson and Horrill, 1984). Parkinson and Horrill (1984) found that, in their study of field variability of samples analyzed for $^{239,240}Pu$, 23 to 44 samples per site would be required to achieve 95% confidence within 10% of the mean result.

b) Unconsolidated sediments

Sediments sampled from lakes and marine systems require the use of specialized coring devices and grabs of which a wide range are available (Reeves and Brooks, 1978; Grasshoff, 1983). In some cases the exact location of the sampling point may be difficult to identify accurately due to the depth of overlying water. Often the pore water content or sediment stratigraphy may be disrupted or contaminated during coring and transport processes (Barnes and Cochran, 1988). The effects of this can often be minimised by immediate sample freezing and the removal of the outer few cm prior to analysis but this necessitates the use of specialized facilities. McKay and

Baxter (1985) found that even relatively low drying oven temperatures were enough to affect the geochemical distribution of Cs on the solid phase of marine sediments.

c) Water samples

Samples may be collected by a wide variety of automatic bottle systems (Grasshoff, 1983). Often they are multiply arranged and may be remote controlled. In the case of large volumes of sea water, continuous pumping devices may be used (IAEA, 1970). It is the storage of collected samples and not sample homogeneity which is the main problem in sampling for water analysis. Adsorption onto container walls or leaching of ions from the container material may be an important interference. In general, polythene is the most robust and contamination-free material (Hamilton, 1980). Acidification of samples to pH 1.5 by the addition of AnalaR acids is the most frequently used method to reduce this problem.

d) Biological materials

The general procedure that, once the representative sample population has been identified, all material should be washed free from solid matter is a highly survey-dependent approach. For plant transfer coefficient determination, where the physiological processes involved in assimilation of elements or nuclides are to be studied it is important to analyze soil or sediment free matter or at least check for contamination (Berrow, 1988). If however, radiological consequences are being investigated, it is more realistic to collect the sample and process it in a similar way to that used by the consumer. Plant material may be stored in fridges or washed and then dried at 105°C before processing. Animal material should be deep frozen before analysis although γ-irradiation may be a viable alternative (IAEA, 1970). Freeze-drying allows samples to be stored at room temperature before processing (Hamilton, 1980) and has been described as one of the best methods for sediment and biological samples (IAEA, 1970).

e) Laboratory procedures

Subsequent to the collection of samples in the field, the first stage of laboratory work involves sample homogenisation and subsampling of the material. For most samples, this may be before or after drying, depending on the study aims. Soils and sediments usually require sieving and grinding. The extent of grinding will be dictated by the heterogeneity of the sample and the concentration of the analyte in the sample. This dictates the minimum workable sample size for the method of analysis employed (Hamilton, 1980). A number of expressions for the deviation of results using samples of various weights with a constant analyte concentration are described in some detail by Hamilton (1980).

For the analysis of stable trace elements, much attention has been paid to the problem of the design and construction of laboratories to minimise sample contamination (Hamilton, 1980; Moody, 1982). Scrubbed air and double distilled water supplies constructed from low trace element materials (generally plastics) are required. Benches and laminar flow cupboards should be designated for particular manipulations or the treatment of particular concentration ranges. Laboratory clothing should also be of a low particle generation type. These considerations are crucial when measuring trace elements but are of less importance for anthropogenic nuclides where the main concern is likely to be cross contamination of materials rather than primary contamination from surrounding materials. On the other hand, it is possible that a laboratory which routinely analyses relatively active samples will suffer from a high blank. A few simple procedural rules have been followed throughout this study. They include the designation of high and low activity glassware and separate glassware for manipulations involving activated samples, routine blank analyses, analysis of samples in ascending order of activity and segregation of dusty manipulations from the main laboratory. In all, they represent a compromise between the principles outlined for more routine trace analysis, the ALARA system of radiological protection and the common sense approach to working in a shared radiochemical laboratory.

2.1.3 STANDARDISATION AND TRACEABILITY

Christmas (1984) defines the use of standards in the determination of an unknown quantity by a particular method. The idea of "*traceability*" for any analysis through a hierarchical structure of standards to a single primary standard is evolved. Hutchinson (1988) outlines the primary objectives of such standards. They include testing and development of analytical procedures, testing of technical competence, interlaboratory comparison and the demonstration of reliable data output. In the case of ^{237}Np, there is an acute lack of such standards. The following discussion considers this problem in more detail.

The accuracy and precision of determinations in environmental analysis can be quantified by relating the analytical method to either a primary standard of matrix comparable to the sample matrix analyzed or the interlaboratory comparison of homogenised, common matrix material. For both approaches, the material may be sampled directly from the environment or may involve the spiking of material which is blank for the analyte concerned (Sill and Hindman, 1974). The standardisation of either material ideally involves multiple measurements by a number of different methods in a number of laboratories, with strict attention paid to sample homogenisation (Hutchinson, 1988; Roetlands, 1989).

A number of different types of standard reference materials (SRM's) are available for routine geochemical analysis. They have recently been reviewed by Roetlands (1989). The list reflects the greatly increased demand for such material since the 1950's and 1960's, as much more rapid and refined instrumental methods of analysis were developed (Boumans and Roetlands, 1989). The wide range of matrices available to the geological community is quite remarkable and similar diversity is found for other SRM groups. For environmental radioanalysis, the picture is far from satisfactory. Inn (1987) summarises international initiatives from over a decade ago (1976 and 1977) which aimed to provide a wide range of low-level radioactivity SRM's for natural and anthropogenic α, β and γ-emitting nuclides. Bortels and Hutchinson (1984) again emphasised the need for such materials and since then both the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS), and the IAEA have instituted extensive programmes of interlaboratory comparison and SRM production (Bojanowski, 1987; Inn, 1987). The results have been very slow in release, partially attributed to the restricted number of laboratories involved, problems intrinsic to the analysis of environmental samples and skill required by the analysts for the determinations required (Inn *et al*, 1984; Volchock and Feiner, 1984; Bojanowski, 1987).

A search through the catalogues of SRM suppliers reveals that, at the present time (1990), only the IAEA, Vienna and NIST, USA produce low-level environmental radioactivity SRM's. Table 2.1 lists all available soil and sediment SRM materials and the certified nuclides present. There are few data for the transuranic nuclides in general and none for ^{237}Np. This presents an obvious problem in the validation of the methods developed in this study and questions the reliability of published data. One recent NRPB-organised intercomparison exercise (Popplewell and Ham, 1987) circulated a sample of Ravenglass silt for the determination of ^{237}Np. The standard of analysis by those laboratories which returned results was concluded to be very good. The sample was prepared by grinding, seiving and hommogenising before circulating to participating laboratories. A total of nine laboratories returned measurements. In one case the determination of ^{237}Np was by neutron activation analysis, in all other cases quantification was by α-spectrometry. Details of radichemical separations used, varied in each case but generally involved techniques such as coprecipitation, anion exchange and solvent extraction. The short-lived ^{239}Np nuclide was used to correct for chemical losses in most procedures. The mean value was 6.2 ±0.1 Bq kg^{-1} (standard error on the mean), with one laboratory not achieving the required sensitivity. To date this material is the closest to a SRM in the world. Attempts to obtain samples of the material from the distributor were unsuccessful as to were requests to a number of the participating laboratories (Byrne, 1988a; 1988b; Hislop, 1988; Harvey, 1989). A 2g portion of the Silt was finally obtained from the IAEA, Monaco laboratory, together with two α -spectrometry sources prepared from the sample (Ballestra, 1988; Noshkin, 1989). Their use in the validation of the methods developed in this study will be described later.

2.2 THE PRECONCENTRATION OF SAMPLES FOR ^{237}Np ANALYSIS

The general approach to the analysis of trace and ultratrace levels of elements in environmental matrices has been discussed in terms of sampling, sample preparation and analytical quality

Table 2.1: Currently available, non-biological, natural matrix standard reference materials for radionuclide assay. Certified nuclides are also included (IAEA, 1988; NBS, 1988).* reference material, activities approximate, not certified.

supplier		**certified nuclides**
National Bureau of Standards, USA		
SRM 4350B	Colombia River Sediment (Sep-81)	^{60}Co, ^{137}Cs, ^{152}Eu, ^{154}Eu, ^{226}Ra, ^{238}Pu, ^{239,240}Pu, ^{241}Am.
SRM 4353	Rocky Flats Soil 1 (Dec-80)	^{40}K, ^{90}Sr, ^{137}Cs, ^{226}Ra, ^{228}Ac, ^{228}Th, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, ^{239,240}Pu, ^{241}Am.
SRM 4355	Peruvian Soil (blank) (Jun-82)	^{137}Cs, ^{228}Th, ^{230}Th, ^{232}Th, ^{239,240}Pu, ^{241}Am.
SRM 4354	Freshwater Lake (Nov-86)	^{60}Co, ^{90}Sr, ^{137}Cs, ^{228}Th, ^{232}Th, ^{235}U, ^{238}U, ^{238}Pu, ^{239,240}Pu, ^{241}Am.
RM 45B	River Sediment (Mar-78)*	
IAEA, Vienna		
SL 1	Lake Sediment	U, Th (ppm)
SL 2	Lake Sediment (Jan-86)	^{40}K, ^{137}Cs
SL 3	Lake Sediment	U, Th (ppm)
Soil 6	Soil (Jan-83)	^{90}Sr, ^{137}Cs, ^{226}Ra, ^{239}Pu
Soil 7	Soil	U, Th (ppm)
SD-N-1/2	Marine Sediment (Jan-85)	^{40}K, ^{210}Pb, ^{226}Ra, ^{230}Th, ^{232}Th, ^{234}U, ^{238}U
SD-N-2	Marine Sediment (Jan-85)	^{40}K, ^{137}Cs, ^{232}Th, ^{239,240}Pu

control (see section 2.1). This section will review procedures specific to ^{237}Np assay and how they relate to the problems considered in this study.

There are a vast number of actinide preseparation and preconcentration methods which can be used for neptunium assay. The basis of such techniques is to isolate the desired nuclide from both bulk matrix and other actinide nuclides which would otherwise interfere in its determination.

In contrast, there are only a few detection systems of adequate sensitivity for routine application to ^{237}Np assay.

In the monograph on Np radiochemistry, Mikhailov (1971) presents a useful approach to understanding Np radioanalysis. A series of fundamental analytical reactions are proposed. These are summarized in Table 2.2. Assuming that they are of high enough selectivity, they form the basis of an analytical scheme. For the actinides in general, the formation of covalent bonds with oxygen, halogens and thiocyanate are characteristic reactions in aqueous chemistry. For Np, the stability of bonding follows the order $Np^{IV} > Np^{III} \approx Np^{VI} > Np^{V}$ (see section 1.2). Reactions 1, 2, 4, 5, 6, 8, 9, 10, 15, 16, 17 (Table 2.2) are usually applied in analysis, whilst numbers 7 and 12 usually interfere. Any analytical scheme tends to consist of a combination of two or more reactions or separation methods to achieve the required purity for analysis (eg. Mikhailov, 1971; Burney and Harbour, 1974; Hamilton, 1980).

Table 2.2: Fundamental analytical reactions of neptunium (From Mikhailov, 1971).

Reaction number	**valence state**	**reaction**	**application in analysis**
1	IV	formation of simple bonds	Y
2	VI	with O-atoms of reagent	Y
3	III	" "	N
4	V	" "	Y
5	IV, V, VI	formation of cyclic bonds with O-atoms of reagent	Y
6	IV, V, VI	formation of cyclic bonds with O and N-atoms of reagent	Y
7	IV	formation of hydrolytic polymers	N
8	IV	formation of anionic nitrate complexes	Y
9	IV	formation of anionic chloride complexes	Y
10	IV, VI	complexation with F^-	Y
11	IV, VI	complexation with other anions	Y
12	V	disproportionation	N
13	III	oxidation to IV	N
14	IV	oxidation to V	N
15	V	oxidation to VI	Y
16	VI	reduction to V	Y
17	V	reduction to IV	Y
18	IV	reduction to III	N
19	VI	oxidation to VII	N

2.2.1 SAMPLE DISSOLUTION

The release of the analyte into the solution phase is the first requirement of any analytical scheme subsequent to sample collection, preparation and subsampling. This can be achieved in a number of ways, the method used depending on the type of sample and nature of the analyte host phase.

For biological materials a combination of wet ashing with strong oxidizing agents such as H_2SO_4/H_2O_2, $HClO_4/HNO_3$, HCl/HNO_3, HCl-NaOH or dry ashing in a muffle furnace at 500-550°C usually suffices (Burney and Harbour, 1974). If not successful, additional treatments usually applied to soils and sediments may be included.

Soils and sediments are likely to contain neptunium and other transuranic contamination in non-primary mineral phases. It is advantageous to avoid total dissolution of the bulk matrix in order to minimise the extent of chemical and radiochemical purification required to minimise potential interferences with the determination. In most situations, a simple acid leach using HCl, HNO_3 or more aggressive combinations of HCl and HNO_3 are sufficient to release all of the analytes, particularly if the contamination is derived from aqueous discharges (Popplewell and Ham, 1987). In so doing 30-50% of the total weight of a soil sample can be released into solution (Krey and Bogen, 1987). Partial dissolution of the primary silicate minerals can be performed using HNO_3 and small amounts of HF or HCl/HNO_3 in a 3:1 ratio (*aqua regia*) (Dolezal *et al*, 1966). These steps are reported to be sufficient to release all fallout actinides from soils and sediments (Krey and Bogen, 1987). However, in some cases, particularly close to weapons test sites, more rigorous dissolution is often required.

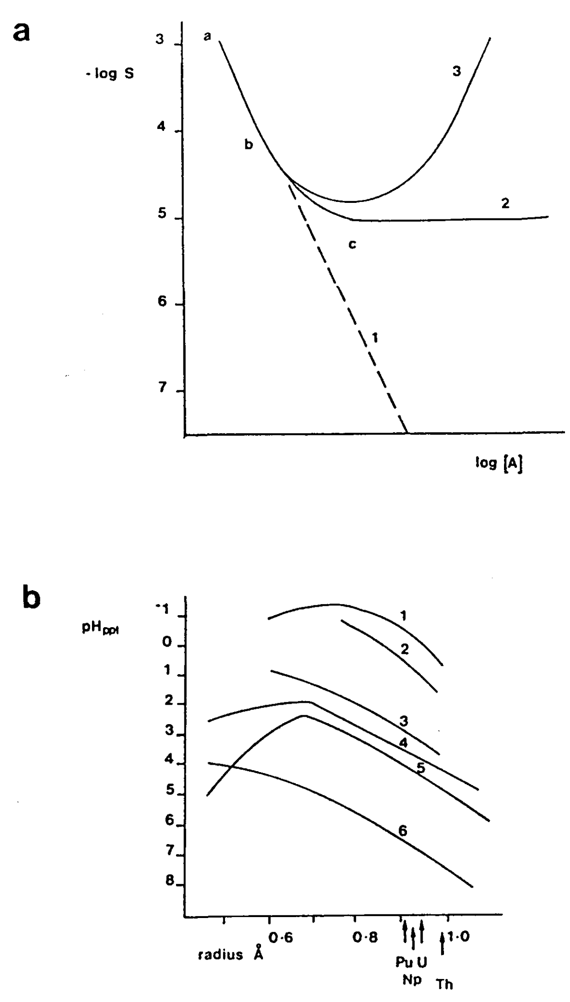
Complete dissolution with HF or fusion with bisulphate, pyrosulphate, borates, hydroxides, peroxides, carbonates and fluorides can be used to produce acid-soluble residues (Dolezal *et al*, 1966; Reeves and Brooks, 1978). Such approaches were found to release an additional 8% of the total $^{239,240}Pu$ from NBS Rocky Flats Soil 1 (Hutchinson *et al*, 1988). It was assumed that this represented contamination contained within fused silica and primary bomb material close to the detonation point (Krey and Bogen, 1987).

2.2.2 COPRECIPITATION AND PRECIPITATION METHODS

These approaches are the classic methods of actinide separation and were used for many years during the first experiments to isolate the actinides (McMillan and Ableson, 1940; Wahl and Seaborg, 1948). The levels of radiochemical purity obtained were adequate for these preliminary studies under chemically controlled conditions. However, in the analysis of environmental samples, higher degrees of separation and preconcentration are required and, as such, this type of separation is often used as a preliminary group "clean up" step in the overall analytical scheme (Reeves and Brooks, 1978). In general, coprecipitation is a very useful technique for isolating trace amounts of elements from large volumes of solution. It tends to be more complete but is less selective than other methods (Burney and Harbour, 1974). A "carrier" is used to scavenge the trace constituents through a number of possible mechanisms. These may include the mechanical inclusion of foreign ions within the bulk precipitate, adsorption on freshly prepared surface sites or more selective solid solution formation of ions of suitable charge and radius with the precipitate mass (Reeves and Brooks, 1978).

Solubility of sparingly soluble actinide salts is described schematically in Figure 2.3a. The solubility of a compound with a simple ionic bond is described by (1). Curve (2) shows the behaviour of An^{4+} and AnO_2^+ present in solution as undissociated molecules (eg. An fluorides, hydroxides and some organic solids (Mikhailov, 1971)). Curve (3) describes the solubility of actinide compounds where the central metal atom forms anionic complexes, thus explaining

Figure 2.3: Salt solubilty (a) different compounds: 1 ionic, 2 covalent, 3 anionic complex, (b) pH pptn v ionic radius, M3+: 1 phenylarsonates, 2 phenylphosphates, 3 hydroxides, M4+: 4 8-hydroxyquinolate, 5 phenylarsonates, 6 hydroxides (Mikhailov, 1971).



the solubilities of oxalates and phosphates. The effect of cation radius on pH of precipitation has been shown by Mikhailov (1971) to be a monotonic increase as radius decreases. Figure 2.3b illustrates the situation for M^{3+} and M^{4+}.

A summary of the main inorganic coprecipitation systems applicable to neptunium separation is given in Table 2.3. Fairly good separations can be obtained through the judicious use of various valence states of the actinides, mainly based on La and Ce fluoride "redox cycles" (Mikhailov, 1971). Np^{IV} can also be precipitated with oxalates and peroxides and other tetravalent actinides tend to follow.

Organic reagents find some use as coprecipitators. There exist few data on neptunium, most following from analogy with Pu^{IV}. Np^{IV} and Np^{VI} can be separated from trivalent actinides and lanthanides by zirconium phenylarsonate (Mikhailov, 1971). Np^{IV} and Pu^{IV} hexanitrato species are coprecipitated with nitrates of heavy organo cations such as butylrhodamide, quaternary ammonium bases and benzyl quinolium compounds.

Table 2.3: Common inorganic coprecipitation methods for neptunium isolation (compiled from: Mikhailov, 1971; Burney and Harbour, 1974; Sill, 1980; Singh, 1988).

Reagent	**oxidation state**	**comments**
MOH (M = Fe^{III}, Al^{III})	III, IV, V, VI	Fe^{III}, La^{III}, Th^{IV}, Pu^{IV} follow, not quantitative for U^{VI} and Np^{V}
LaF_3 (mineral acids)	IV	$Pu^{III,IV}$, Th^{IV}, REE^{III} follow (U decontamination from H_2SO_4)
MPO_4 (M = Zr or Bi)	IV	Ln^{IV} and An^{IV} follow
$BaSO_4$	IV	An^{IV}, Ce and Be follow
$KLa(SO_4)_2$	IV	An^{IV} follow
Na uranyl acetate	VI	
K uranyl carbonate	V, VI	

2.2.3 LIQUID-LIQUID EXTRACTION OF NEPTUNIUM

The use of the preferential distribution of neptunium complexes between two immiscible organic and aqueous phases is one of the most rapid methods for neptunium isolation and purification. Liquid-liquid extraction (or solvent extraction) has long been used for the isolation of the actinides, particularly in process technology (Katz *et al*, 1986a). Solvent extraction of Np can be performed with a diverse range of organic reagents from a mixture of aqueous phases. the systems involved can be categorised by the nature of the extraction mechanism involved (Reeves and Brooks, 1978). These comprise

(i) Chelating reagents, which form extractable complexes by replacing coordinated water around the central ion, eg β-diketones,

(ii) Ion association systems, where uncharged, extractable compounds are formed by electrostatic attraction, eg, organophosphates and amines,

(iii) Mixtures of extractants which have a higher extraction ability for species of interest than when used separately. This is known as the *synergistic effect* or *synergism.*

(a) Neptunium/chelate systems

(i) The β-diketones have been used extensively in Np solvent extraction. Thenoyltrifluoroacetone (TTA) is the most commonly used and was designed to provide strong extraction for many ions from acid solutions (Poskanzer and Foreman, 1961). Extraction is very pH dependent and resolution very sharp. A number of summaries of extraction conditions for metal ions have been published (Poskanzer and Foreman, 1961; Morrison and Freiser, 1966; De *et al*, 1970; Stary and Freiser, 1978).

TTA is slightly soluble in water and highly soluble in organic solvents. It exists in three structural forms through keto-enol tautomerism (keto, enol and keto hydrate). The enol form complexes through dissociation of the OH group, the greatest dissociation occurring at stronger acid concentrations than for the other β-diketones (Stary, 1964). In benzene, 11% of the TTA is in the keto form, the remainder in the enol form (Poskanser and Forman, 1961). The extraction mechanism is proposed to be:

$$M^{z+}(aq) + zHTTA(org) \rightleftharpoons (MTTA_z)(org) + zH^+$$

Each TTA molecule coordinates to the central metal ion through the double bonded oxygen atom and the dissociated OH group. At low pH, less than 2.5% of the TTA is soluble in the aqueous phase, the solubility increasing with salt content. At pH 8, approximately 50% of the TTA is soluble in the aqueous phase and, by pH 9 or above, cleavage of the molecule into trifluoroacetone and acetylthiophene occurs (Poskanser and Foreman, 1961). Np extraction parameters are summarized in Table 2.4a. Table 2.4b shows the variation in extraction coefficient with ion type for the system 0.5M TTA(xylene)/HNO_3, whilst Figure 2.4 graphically illustrates the pH effect on TTA extraction. The expected trend for actinide complexation is followed. The An^{4+} ions are more strongly complexed and extracted than the other oxidation states. The equilibrium constants for Pu^{IV} are greater than for Np^{IV} (Ramanujan *et al*, 1978) and decrease as acidity increases. This is explained by changes in the "salting out" parameter which influences the solubility of $Np(TTA)_4$ in aqueous and organic phases.

Ramanujan *et al* (1978) discuss the problems associated with obtaining distribution coefficient data for Np^{IV} and Pu^{IV} which allow valid cross-comparison between TTA-aqueous extraction systems. The differences are generally accounted for by the complexing abilities of the inorganic species, competing with TTA for Np ion complexation. These effects can be accounted for in a more refined treatment of the equilibrium distribution expressions. In an early study by Moore (1957), Np^{IV} (with Pu^{IV}) was extracted from 0.5M HCl with 0.5M TTA(xylene). The optimum equilibration time was found to be 10-15 minutes to give >99% recovery from <1.0M HCl. Up to 1M HNO_3 could be tolerated in the HCl phase without affecting extraction. Quantitative recovery could also be obtained from 1M HNO_3, although HCl media were recommended to reduce the possibility of ferric iron formation and simultaneous extraction. Fakhi *et al*, (1988) studied the extraction of Np^{IV} in the TTA (benzene)/ NO_3^- system. They observed that at pH< 0.5 Np^{IV} is present and that at pH >1.0 hydrolysis becomes a significant interference. Decontamination by a factor of 10^3 from Pu can be achieved if it is selectively

Table 2.4: Solvent extraction of neptunium by HTTA: (a) conditions of extraction for different oxidation states (Stary, 1964; De *et al*, 1966), (b) extraction coefficients into 0.5M HTTA(xylene) (Burney and Harbour, 1974).

(a)

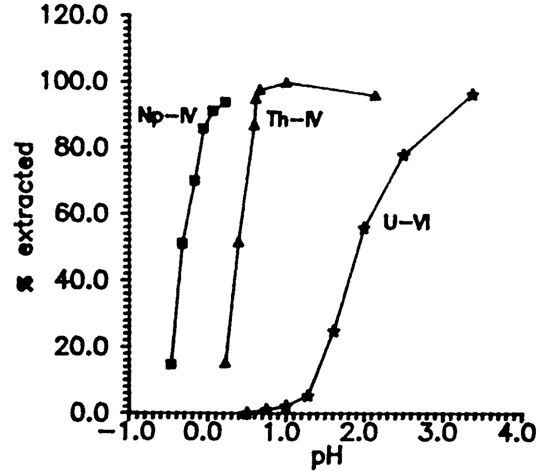
oxidation state	**conditions**	**comments**
IV	0.5M HTTA (benzene or xylene) pH 0.5 (HCl or HNO_3)	quantitative, Pu^{IV} follows
V	0.01M HTTA (isobutyl alcohol) pH 7-9	quantitative, polar solvents only

(b)

ion		**molarity (HNO_3)**	**extraction coeff. (25°C)**
Np	III	1.0	$< 3 \times 10^{-3}$
	IV	1.0/ 8.0	$10^{4}/ < 5 \times 10^{-4}$
	V	0.8	$< 5 \times 10^{-4}$
	VI	0.8	$< 10^{-3}$
Pu	III	1.0	10^{-6}
	IV	1.0/ 0.8	$10^{4}/ 10^{-2}$
	V	1.0	10^{-4}
	VI	1.0	4×10^{-3}
U	VI	1.0	3×10^{-5}

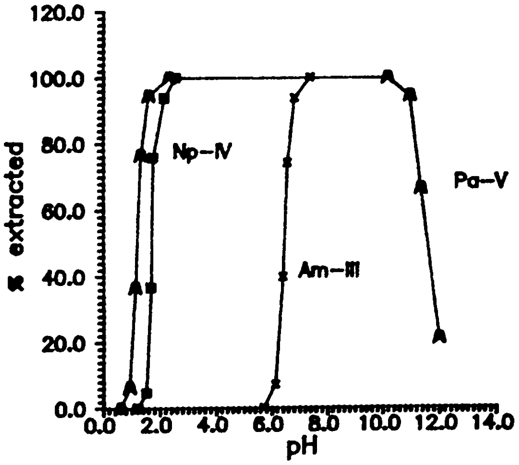
reduced with NH_4I to Pu^{III}. Np is quantitatively removed from the organic phase with 8M HNO_3 whilst iron remains as a bright red organic complex.

Figure 2.4: The effect of pH on the extraction of ions by HTTA(benzene) (Stary, 1964).



(ii) 8-hydroxyquinoline is a bidentate chelating agent which forms complexes with many metal ions through OH and N group coordination. Although its use is restricted for neptunium (De *et al*, 1970), complexes of the form $Np^{IV}(C_9H_6NO)_4$ and $H[Np^VO_2(C_9H_6NO)_2]$ are observed

Figure 2.5: The effect of pH on the extraction of ions by 8-hydroxyquinoline($CHCl_3$) (Burney & Harbour, 1974).



(Burney and Harbour, 1974). The variation in extraction with pH is shown in Figure 2.5. Only 30-70% of Np^V is extracted by 0.1 M 8-hydroxyquinoline in organic solvents such as isoamyl alcohol, but it is not extracted when solvents such as chloroform and benzene are used (Stary, 1964).

(iii) 1 nitroso-2-napthol has been used to extract Np^V from a 1% solution in polar solvents such as isoamyl alcohol or n-butyl alcohol at pH 9-11 (Stary, 1964; De *et al*, 1970). It is likely that, since Pu^{IV} can be extracted at pH 2 with methyl isobutyl ketone (MIBK) solvent, Np^{IV} will follow.

Other chelating agents which have had limited application for Np separation include 4-benzoyl-3-methyl-1-phenyl-pyrazolin-5-one (Np^{IV} from 1-4M HNO_3 or 1-6M HCl, but not Np^V or Np^{VI}) (Burney and Harbour, 1974). By further analogy with Pu, n-benzolylphenyl-hydroxylamine (from 3M HNO_3) and acetyl acetone (chloroform or benzene, at pH 4-7) may also have application to Np^{IV} extraction (Stary, 1964; Burney and Harbour, 1974), although there is no evidence of their use in the literature. One very recent development is the use of polyethylene glycol (PEG) to extract tri and tetravalent actinide complexes with anions of unsaturated heteropolytungstates (Molochnikova *et al*, 1988) and $arsenazo_{III}$ (Shkinev *et al*, 1985). This works most favourably for trivalent actinides, but tetravalent actinides (Np, Pu) can be extracted nearly quantitatively at higher polytungstate concentrations. Penta and hexavalent oxidation states are hardly extracted.

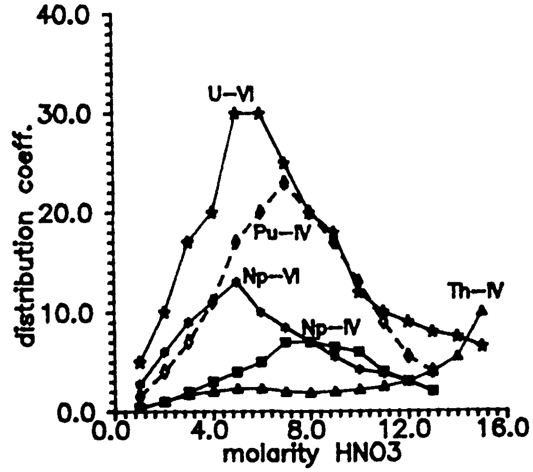
(b) Neptunium-ion association systems

(i) tri-n-butyl phosphate

TBP is a non-ionizing solvent which forms organic soluble coordination complexes with metal salts. It is widely used in large scale fuel processing schemes such as the PUREX process (Katz *et al*, 1986a; Schulz and Horwitz, 1986). Its domination in the fuel industry reflects high selectivity for U and Pu, good chemical and radiation stability and ease of recycling (De *et al*, 1970). It has, however, only restricted application to neptunium analysis. Much information is nevertheless available for TBP/HNO_3 or HCl systems (Burney and Harbour, 1974; Schulz and Horwitz, 1986). Complexes of the form $M(NO_3)_4.2TBP$ are easily formed and extractions are affected by nitrate concentration, the presence of complexing ions (SO_4^{2-}, F^-, PO_3^{4-}), the presence of salting agents, TBP concentration, reagent purity and mixing time.

Table 2.5 lists extraction data for a number of actinide ions including neptunium. Figure 2.6 shows the variation in distribution coefficient with nitric acid concentration for tetra and hexavalent actinides. The order of oxidation state extractability is $An^{IV} > An^{VI} >> An^{III} > An^V$, Within the An^{IV} group the order is Pu> Np> U> Th and, within the An^{VI} group, the order is U> Np> Pu (Coleman, 1965; Burney and Harbour, 1974). For neptunium, the extraction reactions

Figure 2.6: The effect of [HNO_3] on actinide extraction by TBP(kerosene) (Coleman, 1965; Burney & Harbour, 1974).



involved are:

Np^{IV}: $Np^{4+}(aq) + 4NO_3^-(aq) + 2TBP(org) \rightleftharpoons [Np(NO_3)_4.\ 2TBP](org)$

Np^{VI}: $NpO_2^{2+}(aq) + 2NO_3^-(aq) + 2TBP(org) \rightleftharpoons [NpO_2(NO_3)_2.2TBP](org)$

Np^V: $NpO_2^+(aq) + NO_3^-(aq) + TBP(org) \rightleftharpoons [NpO_2(NO_3).TBP](org)$

Table 2.5: Actinide extraction coefficient data for the system TBP-HNO_3 (Burney and Harbour, 1974).

ion		molarity (HNO_3)	% TBP	extraction coefficient (25°C)
Am	III	4.0	30	0.013
Pu	III	5.0	20	0.012
	IV	5.0	20	16.6
	V	5.0	20	2.7
Np	IV	4.0	30	3.0
	VI	4.0	30	12.0
U	IV	4.0	25	10.0
	VI	4.0	25	23.0

Transport coefficients and data relating to the mechanisms of actinide extraction from these systems have been recently reported (Marx *et al*, 1984; Friehmett *et al*, 1987). The principal rate-determining step for extraction would appear to be diffusion within the organic layer. There was no observed hindrance of transport at the boundary between the organic and aqueous phases. For analytical procedures, extraction is complete with 5 minutes equilibration. HCl systems follow the same trend, but extraction maxima are not so sharp. For $HClO_4$ aqueous phases, distribution coefficients are much lower (Burney and Harbour, 1974).

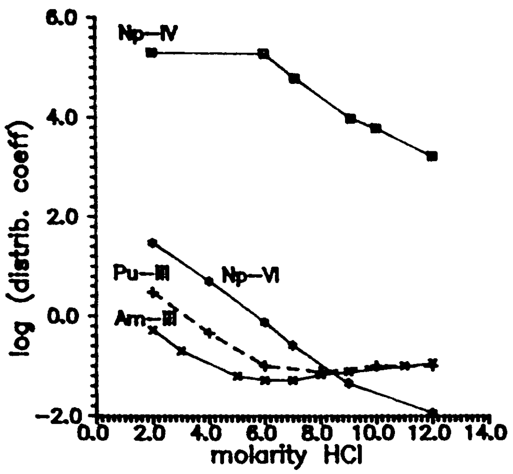
(ii) other organophosphorus compounds

A wide range of other organophosphorus-containing solvents have also been identified as being useful components in actinide separation schemes (Schulz and Horwitz, 1986; Myasoedov, 1987). Their development and use has been restricted to small research projects, in marked contrast to the intensive work conducted by large research teams during the 1960's as actinide purification processes were being developed (Schulz and Horwitz, 1986). The current status of neptunium solvent extraction in particular is greatly improved from the initial observations by Burney and Harbour (1974) that *"few separation methods for Np have been defined"*.

The organophosphorus compounds have the highest extraction capacity and radiation stability of reagents used for actinide separation (Myasoedov, 1987). Concentration factors can be 20-100, but the reagents tend not to have high selectivity. The extraction properties are a function of a number of factors (Burney and Harbour, 1974; Myasoedov, 1987) including the electronegativities of substituent groups, length, degree of branching and number of alkyl groups on the PO_4 centre. Coleman (1965) and Burney and Harbour (1974) describe data showing that the extracting power increases with the number of C-P bonds. This correlates with the basicity of the phosphoryl oxygen. For the butyl series, the following order was observed: phosphate ($(RO_3)PO$) < phosphonate ($R(RO_2)PO$) < phosphinate ($R_2(RO)PO$) < phosphine oxide (R_3PO).

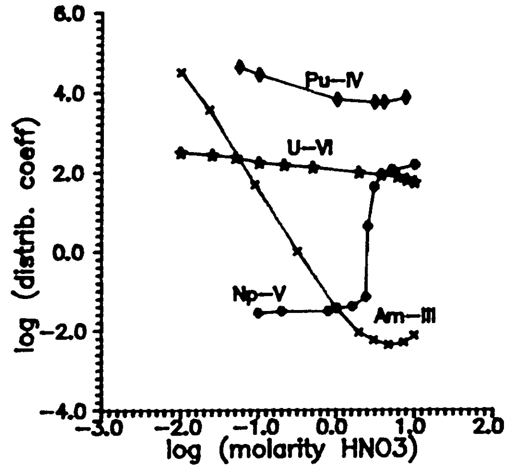
Mono(2-ethylhexyl)orthophosphoric acid (H_2MEHP) has been used to extract An^{IV} from HCl media (Peppard *et al*, 1959; Marhol, 1966). Np isolation was achieved by extraction from 12M HCl and multiple back-extraction to remove Pu and U. Np^{IV} was removed by scrubbing with TBP. Figure 2.7 shows the acidity dependence of actinide extraction for 0.48M H_2MEHP as a function of HCl concentration. High HCl concentration favours Np and Pu separation from other actinides. At 2M HCl, the equilibrium constants are 2×10^5 (Np^{IV}), 30 (Np^{VI}), 6×10^2 (U^{VI}), 3 (Pu^{III}) (Marhol, 1966). It is uncertain as to whether the extraction mechanism is through ion exchange or discrete chelation/ion association (Peppard *et al*, 1959). This may be due to the tendency of H_2MEHP to show different degrees of association in different solvents (De *et al*, 1970).

Figure 2.7: The effect of [HCl] on actinide extraction by H_2MEHP(toluene) (Peppard *et al*, 1959).



Bis-2-ethylhexylorthophosphoric acid (HDEHP) exists as a dimer in most organic liquids and has greater stability and lower aqueous solubility than its close relation dibutyl phosphoric acid (HDBP) (De *et al*, 1970). The HDBP/HCl/HNO_3/H_2O systems have been considered by Butler (1965), Marhol (1966), Burney and Harbour (1974) and Lebedev and Myasoedov (1984). The

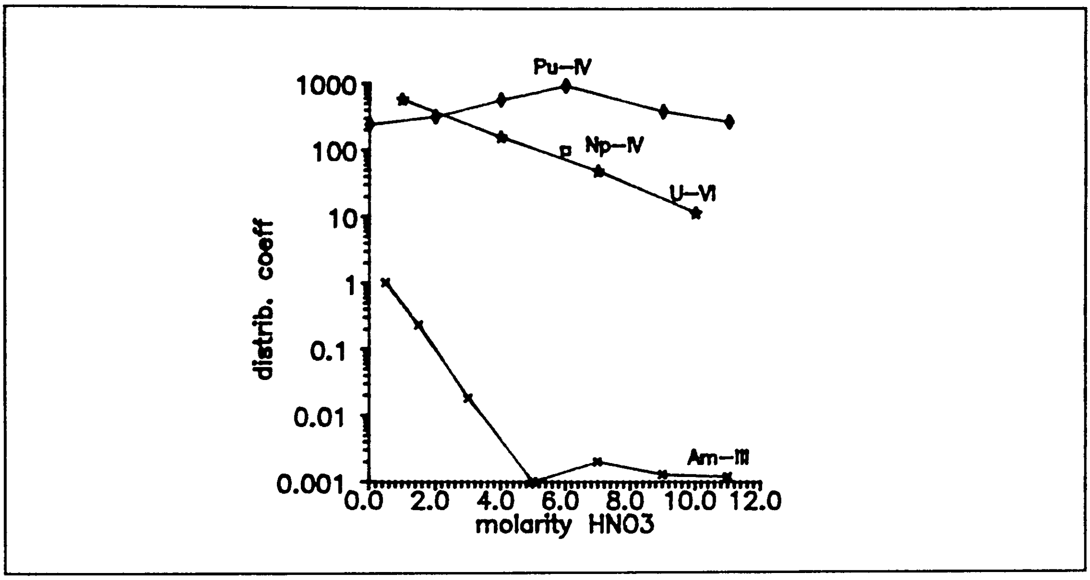
Figure 2.8: The effect of [HNO_3] on actinide extraction by HDEHP(isooctane) (Burney & Harbour, 1974).



variation in actinide extraction by HDEHP with acidity is shown in Figure 2.8. The inflexion in the case of Np^V/HNO_3 is due to Np^V disproportionating to Np^{IV} and Np^{VI}, the tetravalent species being more extractable. Np^{VI} is quantitatively extracted from 0.5M HCl/1.5M HDEHP(toluene) (De *et al*, 1970). HDEHP is currently under investigation as a system for the separation of actinides from highly active wastes (Mannone *et al*, 1984; Musikas, 1987) and in extraction chromatography separations (see section 2.2.5) (Jemli and Billon, 1983).

Tri-n-octylphosphine oxide (TOPO) extraction of Np^{IV} is similar to that for Pu^{IV} (De *et al*, 1970). Maximum extraction occurs from 1M and 8M HNO_3 and is enhanced significantly when nitric acid is replaced by neutral nitrate salts. Figure 2.9 shows the behaviour of Pu and U oxidation states in the system 0.1M $TOPO/HNO_3$ (Coleman, 1965). The data from De *et al* (1970) have been superimposed. Pu^{IV} is extracted as $Pu(NO_3)_4.2TOPO$ (De *et al*, 1970), which is the expected structure for the Np^{IV} species formed. Np^V is ≈50% extracted from 2-8M HNO_3 with 0.3M TOPO.

Figure 2.9: The effect of $[HNO_3]$ on actinde extraction by TOPO(cyclohexane) (Coleman, 1965; Burney & Harbour, 1974).



The following two reagents (DHDECMP and CMPO) are examples of recent developments in bidentate organophosphorus extraction chemistry (Schulz and Horwitz, 1987). They have been studied as possible reagents for the isolation of actinides from highly active wastes in an attempt to reduce the volume of material requiring secure and expensive containment (Musikas, 1987). They are superior to the diphosphonate and diphosphinates in their ability to extract An^{III}, An^{IV} and An^{VI} ions.

Heugen *et al*, (1984) studied the extraction of Pu^{IV}, Np^{IV} and Am^{III} using dihexyl N,Ndiethylcarbamylmethylenephosphonate (DHDECMP) (diethylbenzene). Equilibrium with nitric acid is established rapidly (≈30 seconds) and the distribution coefficients are found to increase with the concentration of both the nitric acid and DHDECMP. In 3M HNO_3 the distribution ratios observed are 221 (Np^{IV}), 101 (Pu^{IV}) and 2.2 (Am^{III}). The generalized extraction reaction was found to be:

$$M^{n+}(aq) + nNO_3^-(aq) + xDHDECMP(org) \rightleftharpoons M(NO_3)_n.xDHDECMP(org)$$

x =2 and n =4 for Np and Pu and x =3 and n =3 for Am. Back-extraction can be performed using weak solutions of nitric acid.

Octylphenyl-N,N-diisobutylcarbamolymethylphosphine oxide (CMPO) is the most intensively investigated of the new breed of organophosphorus compounds. The main advantages lie in its low aqueous solubility, high chemical and radiation resistance, high solubility in organic solvents and high affinity and capacity for tri, tetra and pentavalent actinides. Aqueous phases used are HCl and HNO_3. One particular application has been the **TRUEX** process (**TR**ans **U**ranium **EX**traction). The specific details are described by Schulz and Horwitz (1987) and Baker (1988). The organic phase used is 0.2-0.25M CMPO/ 1.0-1.4M TBP in a paraffinic solvent. The TBP is present to allow a high organic phase loading with actinides and prevent a third phase forming. The choice of solvent is important. The distribution ratios are found to decrease in the order: normal paraffinic hydrocarbons> aromatics> chlorocarbons. Over 99.9% of An^{III}, An^{IV} and An^{VI} are extracted along with Ln^{III} and variable amounts of fission products from a 1M HNO_3 aqueous phase. Trivalent lanthanides and actinides can be stripped with 0.1M HNO_3, tetravalent actinides and any residual trivalent species remain. $Na_2CO_3(aq)$ is used to clear any An^{IV} and degradation products of TBP and CMPO.

(c) high molecular weight amines

High molecular weight amines have long been used in liquid-liquid extractions. Their action is observed to be similar to anion exchange by virtue of the formation of organic-soluble ion association complexes. Thus they have been termed liquid anion exchangers (De *et al*, 1970). The process is summarized below:

$$R_3N(org) + H^+(aq) + A^-(aq) \rightleftharpoons R_3NH^+A^-(org)$$

$$R_3NH^+A^-(org) + B^-(aq) \rightleftharpoons R_3NH^+B^-(org) + A^-(aq)$$

The use of these compounds combines many of the advantages of both ion exchange and solvent extraction. However, emulsion formation can be a problem (De *et al*, 1970). They are excellent extractants for tetravalent Np and Pu ions and have advantages over organophosphorus compounds due to their greater resistance to radiolysis and hydrolysis in radioactive solutions (Burney and Harbour, 1974). The extraction order for the oxidation states of Np is IV> VI>> V and for the different amines is ammonium salts> tertiary> secondary> primary (Coleman, 1965). They are usually dissolved in organic solvents such as xylene, benzene or chloroform, with a small amount of long chain aliphatic alcohol to prevent third phase formation (Burney and Harbour, 1974).

Of the primary amines, Primene JM-T (a mixture of primary amines in the C_{18-22} range) has been used for the isolation of tetravalent Np and Pu from sulphuric acid media. The extraction of Np is greater than for Pu (De *et al*, 1970). This method has been applied to Pu analysis in bone by Singh (1987) but not to Np.

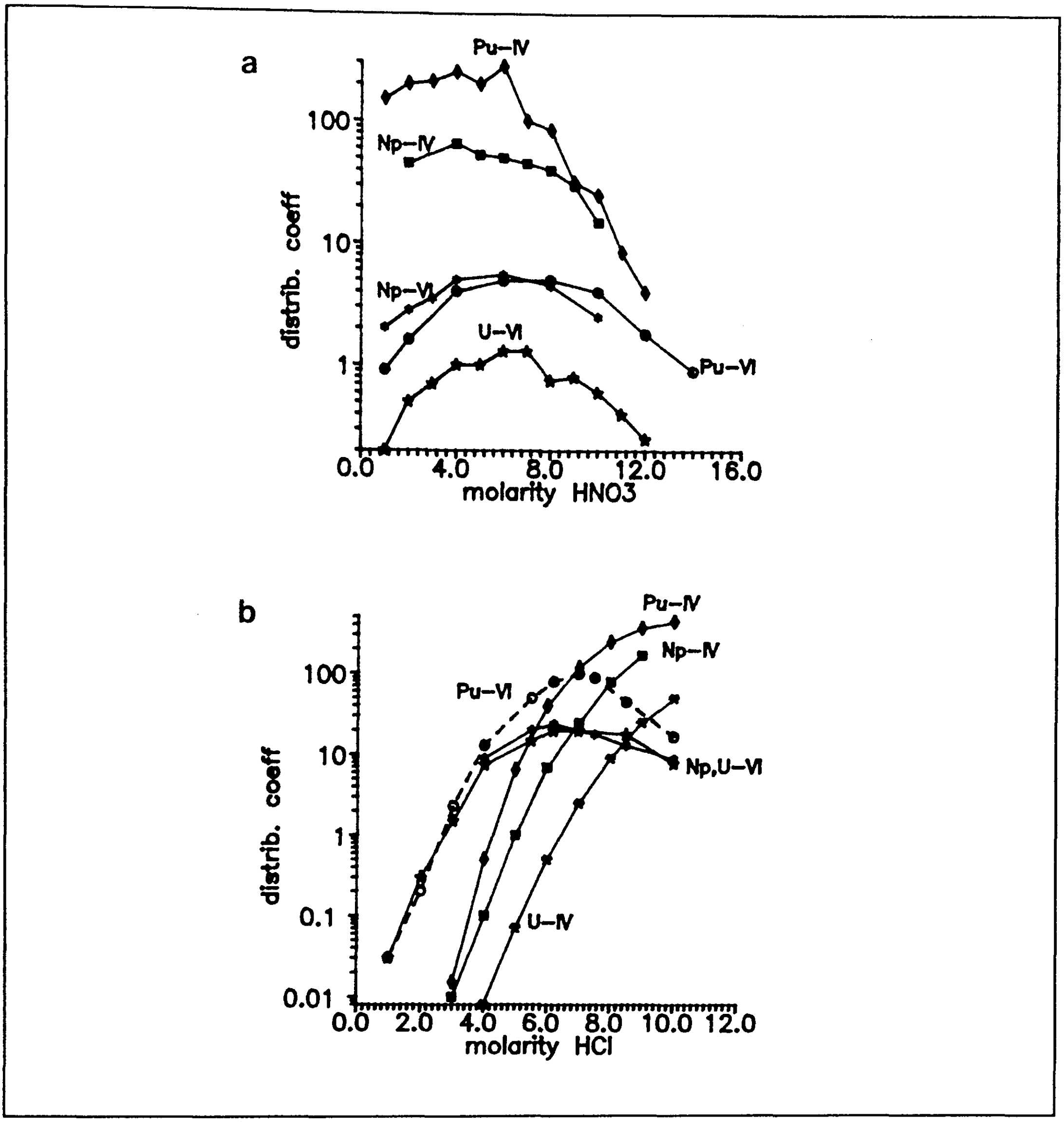
The secondary amines have generally lower application in actinide solvent extraction chemistry and are not used in environmental analysis (Singh, 1987; 1988). The secondary amine mixture, Amine 9D-178, has limited application for Pu (De *et al*, 1970) and perhaps some potential for Np.

Tertiary amines have been studied most intensively. Tri-n-octylamine (TOA) has useful distribution coefficients in both HCl and HNO_3 systems (Coleman, 1965). Tetravalent actinide ions are extracted in a two amine molecule complex (Coleman, 1965; Burney and Harbour, 1974). Figure 2.10 shows the variation in extraction of actinides with TOA from varying HCl and HNO_3 concentrations.

Tri-iso-octylamine (TIOA) has been used for rapid separation of actinides, including Np, in bioassay (Butler, 1965; 1968). HCl and HNO_3 media were used. The diagrams in Figure 2.11 show customary extraction versus concentration behaviour. In 8M HCl, 98% of Np^{V} is extracted as opposed to 40% for Pu^{IV} and 0% for Am^{III}. In 4M HNO_3, 20% Np^{V} and 96% Pu^{IV} are removed with 10% TIOA(xylene) (Butler, 1965). Other TIOA-based systems include 2M HNO_3-ferrous sulphamate/0.3M TIOA(xylene) for quantitative extraction of Np^{IV} (De *et al*, 1970). Sill (1966) used 5% TIOA(xylene) to milk $^{239}Np^{VI}$ from ^{243}Am parent in conc.HCl to prepare a suitable spiking solution.

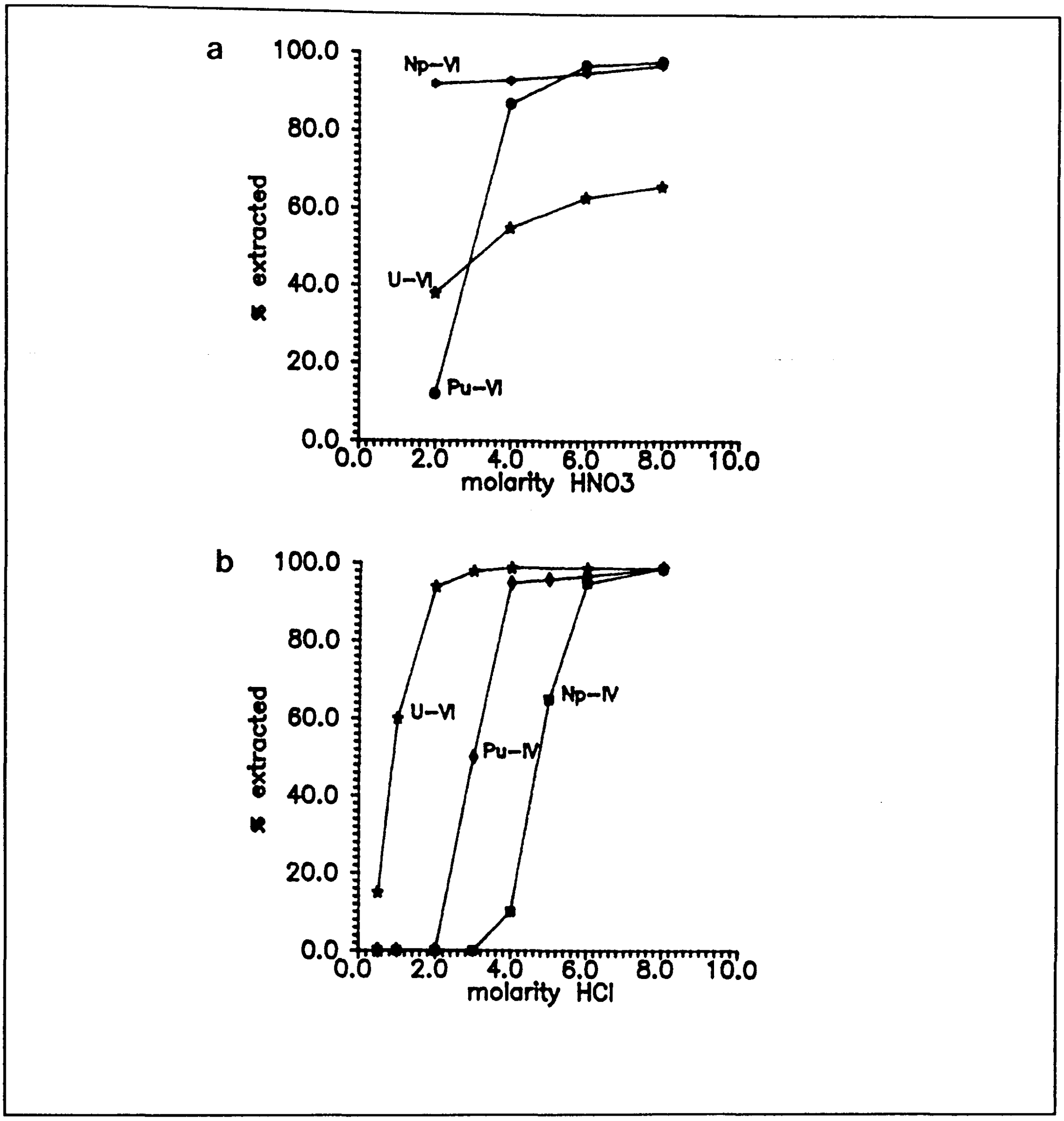
Trilaurylamine (TLA) has been used to extract tetra and hexavalent Np from nitric acid (Burney and Harbour, 1974). Singh *et al* (1984), Singh (1987) reports its use in the system 10M HCl-(2-4)M HNO_3/ 20% TLA(xylene) to determine Th, U and Pu in tissue and faeces. From 4M HNO_3, Th and Pu (or 2M for Pu only) are extracted, presumably as An^{IV} species. U and Pu, as presumably An^{VI} and An^{IV}, are extracted from 10M HCl. These systems in principle could be applied to Np also, with the tetra and hexavalent oxidation states behaving in an analogous manner to Pu and U.

Figure 2.10: The effect of (a) $[HNO_3]$ and (b) [HCl] on actinide extraction by TOA (Coleman, 1965; De *et al*, 1970).



Quaternary ammonium reagents have received limited application in neptunium separation. Singh (1987) mentions methyltricapryl ammonium chloride (Aliquat-336) as a reagent for extracting Pu^{IV} from 8.5M HNO_3. Presumably Np^{IV} would behave in a similar manner. Swarup (1977) describes the extraction of An^{IV} and An^{VI} species from nitric acid using tetraheptyl ammonium nitrate (THAN) in Solvesso-100 (an aromatic diluent). The order of extraction was $Pu^{IV} > Np^{IV} > Th^{IV} > Pu^{VI} \geq Np^{VI} > U^{VI}$, the maximum extraction occurring at approximately 1M HNO_3 (see Figure 2.12). A linear dependence of the extraction coefficient on THAN concentration and the observed gradient imply an extraction mechanism for An^{IV} involving a $[(C_7H_{15})_4N]_2An(NO_3)_2$ complex and for An^{VI} a $[(C_7H_{15})_4N]AnO_2(NO_3)_2$ complex. Data for the extraction of An^{IV} and An^{VI} by a number of quaternary ammonium salts from nitric and hydrochloric acid solutions are summarized by Coleman (1965).

Figure 2.11: The effect of (a) [HNO$_3$] and (b) [HCl] on actinide extraction by TiOA (Butler, 1968).

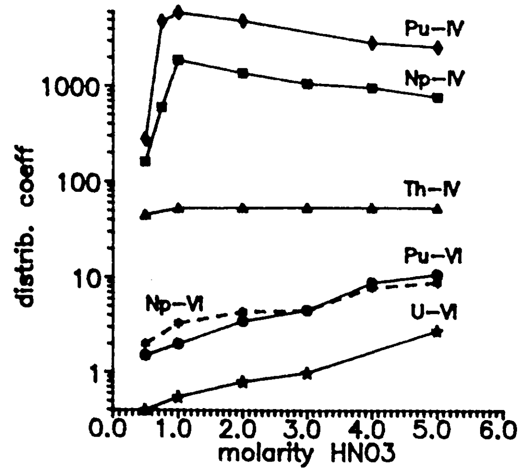


(d) alcohols, ketones, esters and amides

These reagents were superseded by organophosphorus and amine compounds in the 1960's (Coleman, 1965). Their one common characteristic is the presence of a basic oxygen atom, which is able to solvate a proton or metal atom.

Methylisobutyl ketone (hexone) was once used for large scale irradiated fuel processing (Burney and Harbour, 1974). The extraction coefficients of a number of actinides (including neptunium), into hexone at 25°C are given in Table 2.6, the extent of extraction being found to be strongly influenced by the salt content of the aqueous phase. The hexavalent actinides are preferentially extracted, together with Pu^{IV} (Figure 2.13).

Figure 2.12: The effect of [HNO_3] on actinide extraction by THAN(solvesso-100) (Swarup & Patil, 1977).



Diisopropyl ether quantitatively extracts Np, Pu and Am from oxidising solutions. The order of extraction is An^{VI} > An^{V} > An^{IV} > An^{III} and Np^{IV} > Pu^{IV} (Burney and Harbour, 1974). In nitric acid, the distribution coefficients for Pu^{IV} are much greater than for Np^{IV} and for Np^{VI} > Pu^{VI}. Figure 2.14 graphically illustrates this behaviour.

The macro-cyclic ligands (crown ethers) have been the subject of much study since their discovery in the late 1960's (Greenwood and Earnshaw, 1984; Streitweiser and Heathcock, 1985).

Table 2.6: Extraction coefficients for actinide ions into MIBK (Burney and Harbour, 1974).

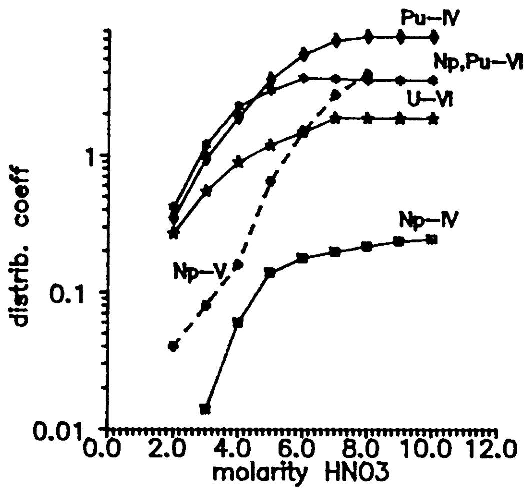
ion		**molarity**		**extraction**
		(NO_3^-)	**(HNO_3)**	**coefficient (25°C)**
Am	III	6.4	0.5	0.0018
Pu	III	11.6	0.5	0.14
	IV	11.6	0.5	1.7
	VI	6.3	0.3	50.0
Np	IV	4.4	0.5	1.5
	V	5.0	0.5	< 0.001
	VI	2.6	0.5	1.7
U	IV	4.4	0.5	2.1
	VI	1.8	0.3	50.0

They are cyclic polymers of ethylene glycol which form an inner, size-specific ring of oxygen atoms and as a result are able to solvate cations strongly (Streitweiser and Heathcock, 1985). The outer shell has hydrocarbon properties, making the complexes soluble in organic solvents. Their complexing abilities for lanthanide and alkaline earth metals are well known (Greenwood and Earnshaw, 1984; Nakagawa *et al*, 1988) and they have had some application to actinide systems.

Godbole *et al* (1986) describe the use of 15-crown-5 and dicyclohexyl-18-crown-6 (DC-18-CW-6) to extract U^{VI}, Np^{IV} and Am^{III} from aqueous thiocyanate and nitric acid media. Figure 2.15 shows the crown ether concentration dependence of the distribution coefficient. The proposed mechanism for Np^{IV} extraction is:

$$Np^{4+}(aq) + 4NO_3^-(aq) + 3(DC\text{-}18\text{-}CW\text{-}6)\ (org) = [Np(NO_3)_4.3(DC\text{-}18\text{-}CW\text{-}6)]\ (org)$$

Figure 2.13: The effect of $[HNO_3]$ on actinide extraction by MIBK (Grindler, 1962).



The N,N-dialkylamides have been used for the extraction of An^{IV} and An^{VI} (Coleman, 1965). Recently, Musikas (1987) discussed the potential advantages of these compounds over traditional TBP technology. In particular, they are completely incinerable and have high fission product decontamination factors. Furthermore, their degradation products do not tend to poison process solutions and U^{VI} back-extraction is easier than with TBP. Their main disadvantage, poor organic solubility, can be overcome by changing substituents on the molecule. For tetravalent species (Th, Np, Pu), at high nitrate concentrations the extraction mechanism involves more than two amides per metal atom. Distribution data for various N,N-dialkyl amides with a number of actinides are listed in Table 2.7, whilst Figure 2.16 shows the extraction of the actinides by N,N-dibutyloctanamide (n-dodecane) from nitric acid.

Figure 2.14: The effect of [HNO_3] on actinide extraction by diisopropylether (Grindler, 1962).

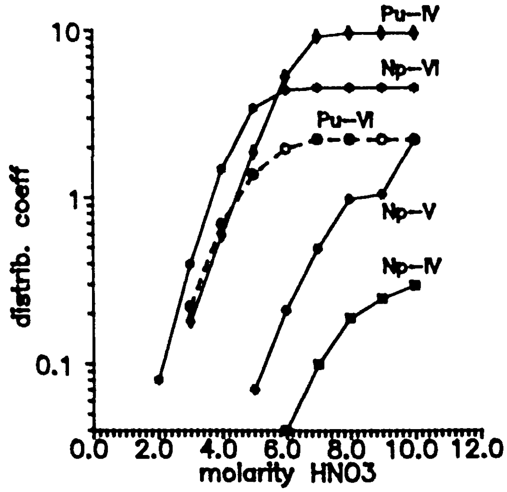
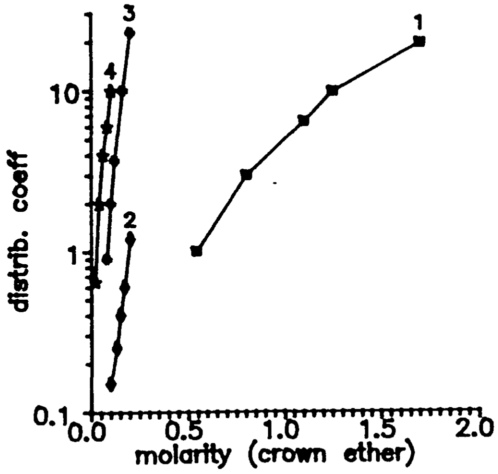


Figure 2.15: Actinide extraction from aqueous thiocyanate+/nitric acid* by crown ethers (Godbole *et al*, 1986) (1, 2) U^{VI}-15-cw-5* in nitrobenzene, dichloroethane, (3) Np^{IV}-DC-18-cw-6$^+$, (4) Am^{III}-15-cw-5*.



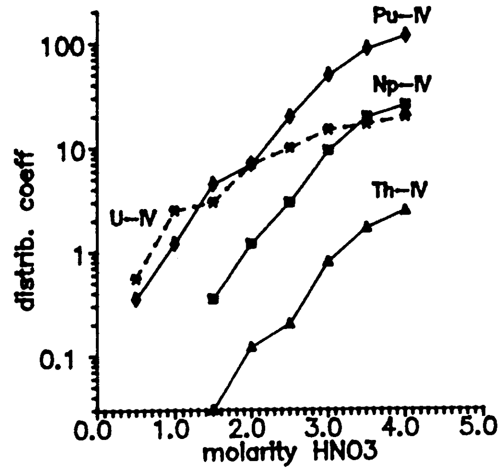
(e) mixed extractants and the synergistic effect

The combination of two or more organic solvents can lead to the enhanced extraction of metal ions to levels far greater than those observed for the single solvents. This phenomenon has long been observed (De *et al*, 1970) and has been termed the *"synergistic effect"* or *"synergism"*. The opposite effect, the reduced uptake of a species by a solvent on addition of a second or third component is termed *"antagonism"* and has been utilized in a few systems (Peppard *et al*, 1959).

Table 2.7: Distribution coefficients for various actinides with N,N-dialkylamides (Coleman, 1965).

	Distribution coefficient [3M (6M) HNO_3]				
Amide	U^{VI}	Np^{IV}	Np^{VI}	Pu^{IV}	Pu^{VI}
N,N-dibutyliso-buylraminde	2.4 (3.3)	0.024 (0.07)	1.2 (-)	0.08 (0.21)	0.23 (-)
N,N-dibutylpival-amide	0.6 (1.4)	- (-)	0.33 (-)	0.0009 (0.005)	0.051 (-)
N,N-dibutylbutyr-amide	5.3 (4.7)	1.0 (2.2)	3.4 (-)	4.0 (8.7)	0.63 (-)
N,N-diisobutylbutyr-amide	5.1 (4.8)	0.62 (1.6)	3.0 (-)	3.5 (7.1)	0.48 (-)
N,N-diisobutyliso-butyramide	2.0 (3.1)	0.007 (0.04)	- (-)	0.057 (0.11)	- (-)

Figure 2.16: The effect of [HNO_3] on actinide extraction by N,N-dibutyloctanamide(n-dodecane) (Coleman, 1965).

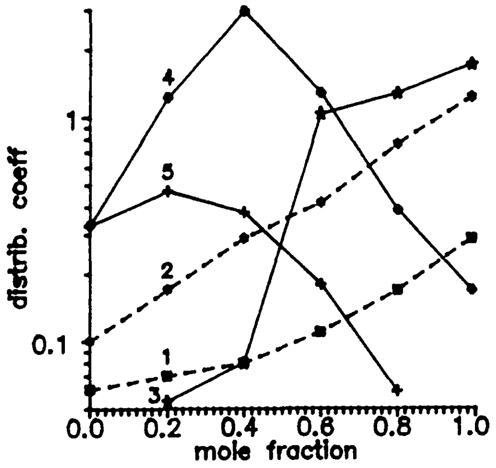


There are few reports of this effect for neptunium extraction systems, but this may just reflect a lack of research interest. Such effects are certainly well known from studies of plutonium and other actinides (Coleman, 1965). The range of properties and combination of extractants in such systems is very diverse. Mathur (1983) has produced an excellent illustration of the various factors influencing such systems for the trivalent lanthanides and actinides. Although trivalent Np and Pu were not considered, they should be very similar.

Np^{IV} has been extracted from a mixture of fission products and trivalent actinides in 0.5M HNO_3 using a mixture of 0.1M 1-phenyl-3-methyl-4-benzoyl-pyrazolon-5 (PMBP) and 0.25M TBP in benzene. Decontamination factors of $>10^3$ were obtained (Burney and Harbour, 1974). Organophosphorus and amine solvent extraction have also been investigated (Burney and Harbour, 1974). Figure 2.17 shows the effect of varying the polarity of diluents on the extraction of Np^{IV} and Np^{VI} into TBP or tetrabutyl ammonium nitrate (TBA) from nitric acid. These observations have been interpreted in terms of complex size, diluent structure and interactions between complex and diluent (Burney and Harbour, 1974).

The synergistic effect of mixtures of TTA/TBP (cyclohexane) on the extraction of Np^{IV} from nitric acid has been investigated by Patil *et al* (1979). The mechanism is complex but can be elucidated by slope analysis of the extraction curves (Mathur, 1983). The effect of complexing of the central metal by aqueous ions must be considered. In $HClO_4$, complexation by ClO_4^- ions is poor, while in nitric acid, NO_3^- moieties are distinctly involved. The equilibrium constant expression must also be modified to correct for weak association of any aqueous soluble TTA with Np^{IV} via:

Figure 2.17: The synergistic effect from nitric acid: TBP, $C_6H_6/CHCl_3$ 1 Np^{IV}, 2 Np^{VI}; TBA, Np^{IV}, 3 CCl_4/C_6H_6, 4 $CHCl_3/\ C_6H_6$, 5 $CHCl_3/\ C_6H_6$ (Burney & Harbour, 1974).



$$Np^{4+}(aq) + HTTA\ (aq) \rightleftharpoons [Np(TTA)]^{3+}(aq) + H^+(aq)$$

This is especially important when the organic solvent used has a low capacity for TTA. The variation of TTA, H^+ and TBP concentrations were studied for systems in which TBP, TBP+TTA and TTA+H^+ concentrations were kept constant. Slope analysis suggested that four TTA^- ions and one TBP molecule were associated with the extracted species. The form of extracted species was therefore likely to be predominantly $Np(TTA)_4.TBP$, with possible contributions from species of the general formula $Np(NO_3)_x(TTA)_{4-x}.TBP_y$. All equilibrium constants were found to be higher in "inert" cyclohexane than in benzene.

There are a number of other systems which have recently been studied and which may have some applicability to neptunium ions. Singh *et al* (1988) extracted Th^{IV} and U^{VI} from chloride media using LIX-26 (alkylated 8-hydroxyquinoline). The presence of sulphate, chloride and thiocyanate at high concentrations reduce extraction. In the presence of dipentylsulphoxide (DPSO), slope analysis revealed the extracted complexes to be $[ThQ_2(DPSO)_2(SCN)_2]$ and $[UO_2Q_2(DPSO)]$ (where Q =LIX-26 anion).

Synergism of TTA with crown ethers for An^{3+} extraction (Nair and Prabhu, 1988) and tri-n-octylphosphine oxide (TOPO) for Ln^{3+} extraction (Favro and Atulla, 1987) has been studied. In both cases, the central mechanism involves the loss of coordinated water molecules and the extraction of $M(TTA)_3$.(n-CE or n-TOPO) species into the organic phase.

For UO_2^{2+}, Jain *et al* (1988) looked at the synergism of lower fatty acid and amines. The extracted complex observed was $UO_2A_2.2HA.2B$ (HA= fatty acid, B= amine). The greatest synergism was obtained for systems using heterocyclic amines.

The use of TBP, hexone, TOPO etc as synergists for TTA etc have been documented. Pai *et al* (1987) have studied the effect of long chain sulphonic acid sulphoxides on the extraction of UO_2^{2+} by 1-phenyl-3-methyl-4-benzoly-pyrazolone (HPMBP). A linear increase in synergistic ability with increasing basicity of the sulphoxides was observed. The optimum number of carbon atoms was 7-8. On the basis of thermodynamic comparisons with TTA systems a steric hindrance effect during the bonding of the sulphoxide to the chelate was used to explain this behaviour.

2.2.4. ION EXCHANGE CHROMATOGRAPHY

Ion exchange is a commonly occurring, natural process which has many applications in chemistry (Amphlett, 1964). The process relies on the exchange between a free species in solution and on immobilized or sorbed onto an inert solid phase. This can be summarized by the equation:

$$A_{RESIN} + B_{SOLN} \rightleftharpoons B_{RESIN} + A_{SOLN}$$

The most commonly used substances in analytical separations are organic polymer-based anionic and cationic resins. They were used extensively in the pioneering days of actinide synthesis, isolation and determination (Choppin and Dinus, 1962) and are still of major importance in separation chemistry (Fritz, 1987). There are a few inorganic ion exchangers that have specialized uses. Their relevance to neptunium separation will be discussed later. Also of interest are the liquid ion exchange materials, based on primary, secondary and tertiary amines, which have already been discussed in the preceding section (2.2.3.). The exchange resins usually comprise a polymerized styrene skeleton, held together by cross-linking between chains. This is accomplished by using divinyl benzene (DVB), the amount of DVB determining the amount of cross-linking (Basset *et al*,1978). A high degree of cross-linking produces brittle, harder and more impervious resins. The cross-linking itself acts as an anchor and inhibits the excessive swelling and dispersion which may be caused by solvation when it is in contact with aqueous solvents or if the nature of the solvent is changed. The result is a sponge-like framework from which the active ion exchange groups protrude. The types of active groups on the resin dictate the exchange nature. The commonly used resins can be split into four main groups:

(i) strong acid cation exchangers. The exchange group is the sulphonic acid moiety, which reacts as below:

$$[\mathrm{RESIN\text{-}SO_3^-}]\mathrm{H^+} + \mathrm{M^+(aq)} \rightleftharpoons [\mathrm{RESIN\text{-}SO_3^-}]\mathrm{M^+} + \mathrm{H^+(aq)}$$

(ii) weak acid cation exchangers. The exchange group used is the carboxylic acid group, ionization occurs only at pH >7 and hence there is little reaction in acid solution;

(iii) strong base anion exchange. The base groups are commonly quaternary ammonium groups and are largely ionized in both hydroxide and salt forms:

$$[\mathrm{RESIN\text{-}NMe_3^+}]\mathrm{Cl^-} + \mathrm{OH^-(aq)} \rightleftharpoons [\mathrm{RESIN\text{-}NMe_3^+}]\mathrm{OH^-} + \mathrm{Cl^-(aq)}$$

As with the strong cation resins, there is little effect on capacity with pH.

(iv) weak base anion exchange. These contain amine groups which are poorly ionized in basic solutions:

$$[\mathrm{RESIN\text{-}NMe_2}] + \mathrm{H_2O} \rightleftharpoons [\mathrm{RESIN\text{-}NHMe_2^+}]\mathrm{OH^-}$$

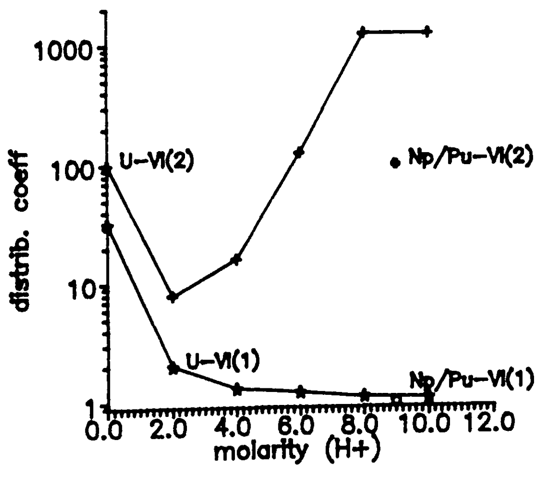
The equilibrium is strongly to the left at pH >7. In acid they behave like strongly basic anion exchange resins.

Equilibria and the exchange of ions in solvents are described by distribution coefficients (K_d). The K_d is defined by the chemical properties of the resin and the nature of the ion. When the resin is used to separate one ion from another, a separation factor (α) may be defined as the ratio of the individual ion K_d (Basset *et al*, 1978). Quantitative separation of the ions is observed for $0.8 > \alpha > 1.2$. Studies of cation exchange equilibria identify *particle* and *film* diffusion controlled mechanisms which influence the equilibrium position and kinetic controls for simple monovalent (Zuyi *et al*, 1987) and divalent actinide (Aimin *et al*, 1987) exchange systems. The mechanisms will be relevant for anion exchange processes also. The nature of the mechanisms involved is determined by the balance of electrostatic charge within the solid and solution phases. The large number of interrelated factors involved results in varying interdiffusion rates and a constantly changing resin composition.

(a) cation exchange of neptunium

The most frequently used cation exchange resins contain strongly acidic sulpho groups (eg Dowex-50, Amberlite IR-120) (Burney and Harbour, 1974; Vobecky, 1986). The distribution coefficients decrease in the order $Np^{IV} > Np^{III} > Np^{VI} > Np^{V}$, but due to the strong complexing ability of Np^{IV} in aqueous solutions, the presence of chloride or nitrate anions generally precludes its use in cation exchange. Cationic forms of Np^{VI} and Np^{V} are the most suitable Np species. However, Np^{VI} is readily reduced by the ion exchange resins to Np^{V} (Burney and Harbour, 1974).

Figure 2.18: The cation exchange behaviour of aqueous actinide ions on Dowex 50-X4: (1) HCl, (2) $HClO_4$ (Coleman, 1965; Burney & Harbour, 1974; Saito, 1978).

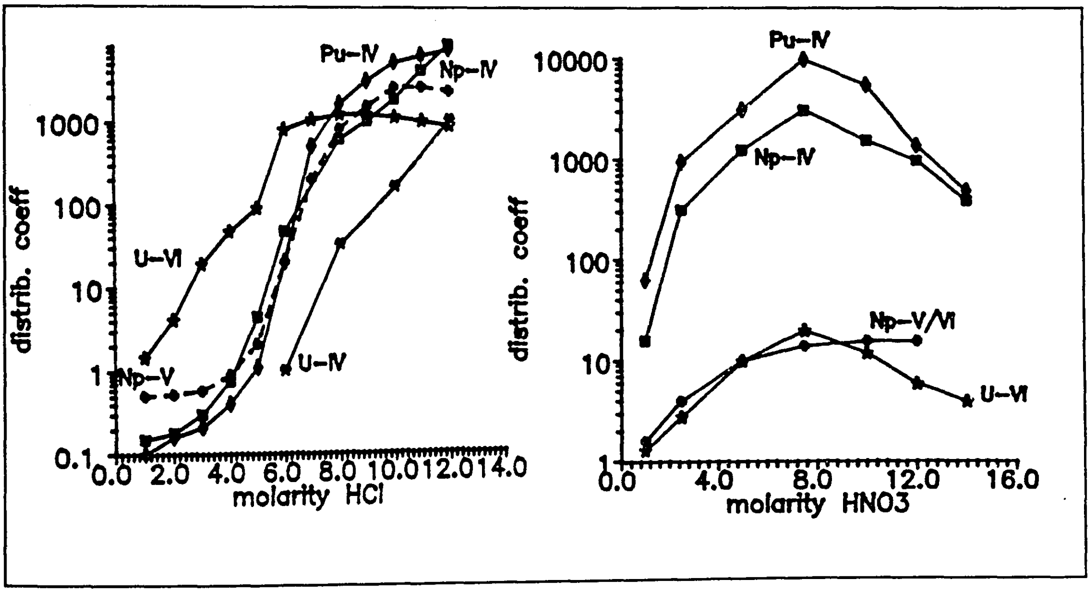


The behaviour of Np ions on cation exchange columns is shown in Figure 2.18. Maximum sorption occurs at high acid concentration and removal is facilitated by lowering acidity, changing the oxidation state on the column or eluting with a strong complexing agent. The effect of complexing anions in the aqueous phase can be seen to decrease the distribution coefficients of the cations.

(b) anion exchange of neptunium

Anion exchange is the most frequently utilized ion exchange method for actinide separations. Strongly basic resins and hydrochloric or nitric acid aqueous media are generally used (Burney and Harbour, 1974; Clanet *et al*, 1972; Veselsky, 1977; Lally and Eakins, 1978; Holm, 1984) . The strongest anionic complexes are formed by Np^{IV} and Np^{VI} with chloride and nitrate anions (see section 1.2.5).

Figure 2.19: The anion exchange behaviour of aqueous actinide ions on Dowex 1X8 (Coleman, 1965; Edginton, 1967; Burney & Harbour, 1974; Saito, 1978; Harvey & Thurston, 1988).



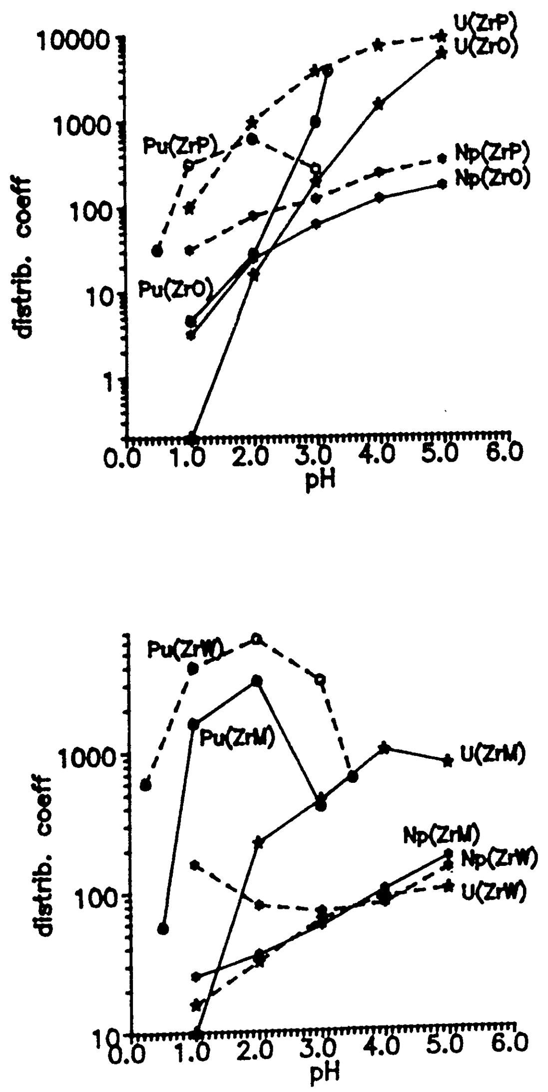
The diagrams in Figure 2.19 illustrate the exchange behaviour of neptunium under a wide range of conditions. Separations are slightly better from nitric acid than from hydrochloric acid. However, the oxidising nature of this reagent towards the organic resin can lead to disruption of the resin bed and, in some cases, can cause explosions. Thus practical application of separations from nitrate media may not be as advantageous as theoretical predictions suggest.

Mixtures of acid and alcohols at elevated temperatures have also been used for both anion and cation exchange of lanthanides and actinides (Usuda, 1987a; 1987b; 1988; Usuda *et al*, 1987). Solutions of up to 95% methanol in HCl or HNO_3 increased distribution coefficients by 6 to 8 times with greatly improved reaction rates. Mixed anion and cation exchange systems have also been developed (Guseva and Tikhomirova, 1988), primarily to investigate the application of less frequently used oxidation states of the actinides for separation procedures. These systems can also be pressurized, but increased elution speed significantly reduced peak resolution.

(c) inorganic ion exchangers

A series of hydrous oxides and acid salts have limited application in the ion exchange of actinides (Amphlett, 1964). They have the advantage of high radiation and oxidation stability at elevated temperatures but are poorly characterised and suffer from poor chemical stability. The hydrous oxides are soluble in acid solution and acid salts are soluble in alkali (Amphlett, 1964).

Figure 2.20: The exchange behaviour of aqueous hexavalent actinide ions on inorganic ion exchange materials (Maek *et al*, 1963)[ZrP,O,M,W = zirconium phosphate, oxide, molybdate & tungstate].



Data from Maek *et al* (1963), reviewed by Marhol (1966), are presented in Figure 2.20 these summarizing the exchange characteristics of Np^{VI} and other hexavalent actinides for a number of inorganic compounds. Hydrous zirconium oxide behaves as an anion exchanger at low pH. Its adsorption ability is reduced with increasing pH. At pH above the isoelectric point, it behaves as a cation exchanger and thus has limited use for actinide ions separations due to problems of hydrolysis and polymerization. Zirconium acid salts act as cation exchangers only. Sorption increases with increasing pH.

The exchange properties of ammonium 12-molybdophosphate (AMP) have been studied for Th, U and Np (Ganzeri-Valetino *et al*, 1972; Burney and Harbour, 1974). The sequence of sorption is $Np^{IV} > Th^{IV} >> U^{VI} > Np^{VI} > Np^{V}$ and using a selection of HCl, HNO_3 and HF solutions, efficient separations can be achieved.

2.2.5 EXTRACTION CHROMATOGRAPHY

Extraction chromatography is a technique which has some important application in the isolation and analysis of both the lanthanide and actinide elements. It was introduced as a technique in the 1950's and can be considered as a hybrid method with characteristics of both conventional ion exchange chromatography and liquid-liquid extraction (Stary, 1976). The basic principle of the method involves the immobilization of a thin film of non-polar organic extractant on an inert supporting material. The elution is performed by a polar mobile phase, as opposed to the mechanism in conventional partition chromatography in which the organic phase is mobile.

The main advantages of this method include its high selectivity, ease of prediction of chromatographic behaviour from liquid-liquid distribution experiments, simple apparatus and small amounts of reagent required and possible re-use of columns. The main disadvantages are the relatively limited number of suitable extractants, the need for fast kinetics, a limited pH range due to the solubility and dissociation of reagents at high or low pH and weak sorption of high polarity solvents (Stary, 1976). A detailed description of the dependence of the distribution ratio on the volume of the stationary phase, on free column volume and on elution volume in defining separation factors is given by Stary (1976). The efficiency of extraction is dependent on the column construction, temperature and reagent concentration in a manner similar to ion exchange chromatography (Stary, 1976; Basset *et al*, 1978).

The application of extraction chromatography to the separation of Np and actinides in general has been described in a few cases (Singh, 1988).

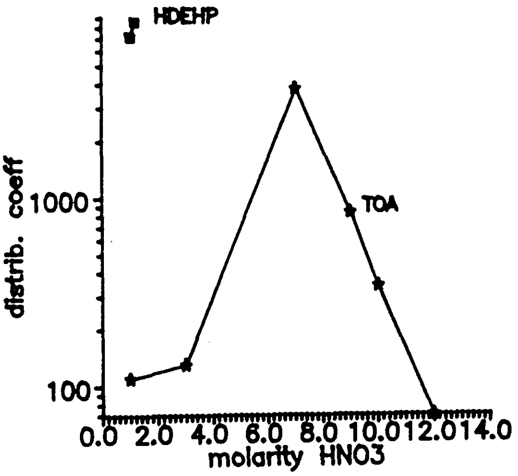
TBP and TLA supported on diatomaceous earths or kieselguhr treated with dichloromethyl silane or polyfluoroethylene have been used to separate U^{IV}, Np^{VI}, Pu^{VI} and fission products from a nitric acid medium. The oxidation states of neptunium were found to elute in the sequence V>

IV> VI as the acid concentration was increased from 0.5M to 2M (Mikhailov, 1971). TTA (xylene) and HF/methylethyl ketone mixtures have been used to separate Np from fission products (Burney and Harbour, 1974).

A microthene column support was used for a number of studies on Th, U, Np and Pu separation from biological and environmental samples and to monitor urine of occupationally exposed workers (Delle Site, 1973; Santori and Testa, 1973; Jemli and Billon, 1983; Testa *et al*, 1987). A wide range of organic phases was used, including TnOA, TBP, HDEHP, DHOA, TOPO and HX-70. The actinides were sorbed and then eluted from the columns using varying acidities of nitric acid and additional combinations of nitric acid with sulphuric, sulphurous, hydrofluoric, iodic and hydrochloric acids and some simple organic reagents. Decontamination factors for neptunium were high under the conditions used (eg $>10^4$ for Np/Am, $>10^2$ for Np/Pu and >30 for Np/U) and separations were achieved much more quickly than for methods which have correspondingly high factors. Horwitz and Bloomquist (1975) used HDEHP and TCMA.Cl/DIPB on Celite to produce a detailed flow sheet for high speed group separation of many elements from irradiated uranium targets. Group separation factors were $>10^3$, but individual element resolution was poorer.

Further applications have recently included the isolation of transplutonium and rare earth elements on TVEX support using TBP, POR and HDEHP as organic phases (Kremliakova *et al*, 1988). Data for the behaviour of Pu^{IV} under these conditions, using nitric acid as the aqueous

Figure 2.21: The behaviour of Pu^{IV} on TVEX containing various organic reagents (Kremliakova *et al*, 1988).



phase, are presented in Figure 2.21. Whilst Np has not been studied directly, the data presented will no doubt have analogous significance for Np^{IV}. TBP on a polystyrene support has been used for preliminary separation of U and Pu from fission products with subsequent separation of Pu from U (Glatz *et al*, 1984). It is likely that the future development of this technique and the separation methods described above will include the use of more highly automated standard chromatographic systems. Examples already exist of the use of HPLC for speciation studies of Np and other actinides in radioactive waste and environmental materials (Apostolidis *et al*, 1987).

2.3 METHODS FOR THE QUANTIFICATION OF ^{237}Np IN ENVIRONMENTAL MATRICES

2.3.1 INTRODUCTION

The discussion in section 2.2 has outlined the principal methods commonly used for actinide separations and the specific reagents available for Np preconcentration and isolation. This section summarises the methods available for neptunium quantification. In particular, the principles underlying those methods which are applicable to environmental assay will be considered.

From section 2.1 it is apparent that the sensitivity and detection limit for any method of assay will determine its suitability for any specific application. In trace analysis, the environmental levels of the analyte are often at concentrations well below the detection limits of the available analytical methods. Consequently some form of preconcentration is required to produce a sample in which the levels of analyte are sufficiently high to be determined. The preconcentration step also serves a second purpose, namely to minimise interferences from the sample. The levels and nature of these interferences exert a profound effect on the "real" detection limits.

Table 2.8 summarises the methods commonly used for ^{237}Np assay. These include chemical and physical methods and techniques dependent on the measurement of the radioactivity of ^{237}Np or of its atomic concentration.

The main characteristic of ^{237}Np is its long half-life (2.14×10^6 years) and correspondingly low specific activity (2.6×10^7 Bq g^{-1}; cf ^{239}Pu = 2.26×10^9 Bq g^{-1}). This, coupled with its low yield in nuclear reactions, means that, for the levels encountered in the environment (see section 1.3), the highly sensitive and versatile radiometric method of α-spectrometry is not necessarily the method of choice. The characteristics of the methods in Table 2.8 show clearly that techniques using neutron activation, mass-spectrometry and α-spectrometry offer the highest sensitivities for ^{237}Np. The other methods are derived from process technology where activities or concentrations are very high (Burney and Harbour, 1974).

Table 2.8: A comparison of published methods for the determination of ^{237}Np.

method	**detection limit/ sensitivity**	**comments**
spectrometry	40 ng ml^{-1} (1.04 Bq ml^{-1})	increased sensitivity with arsenazo III-complex (Burney & Harbour, 1974)
laser induced photo-acoustic spectroscopy	2.37 x10^{3} ng ml^{-1} (61.8 Bq ml^{-1})	Cross & Hooper (1987), Pollard *et al* (1988),Klenze & Kim (1988)
controlled potential coulombetry	>10^{4} ng (> 261 Bq)	Burney & Harbour (1974)
polarography	2 x10^{4} ng g^{-1} (522 Bq ml^{-1})	in presence of Fe, U, Ni and fisson products (Mikhailov, 1971)
mass spectrometry	3.94 x10^{-8} ng (1.03 x10^{-9} Bq)	very pure electroplated source (Efurd *et al*, 1986a; Halverson, 1984)
X-ray fluorescence	200-300 ng (5.2-7.8 Bq)	Burney & Harbour (1974)
neutron activation analysis	100-1 x10^{-4} ng g^{-1} (2.6-2.6 x10^{-6} Bq g^{-1})	sensitivity dominated by neutron flux, post-irradiation chemistry required (Byrne, 1986;May & Pinte, 1986; Germain *et al*, 1987)
luminescence spectrometry	5 ng g^{-1} (0.13 Bq g^{-1})	Fe, U interfere if >10^{-6} g (Novitov *et al*, 1975; 1987)
α-spectrometry	0.5-0.014 ng (0.013-3.7 x10^{-4} Bq)	detection limits for 10^{6} s count, low background (Holm & Nilsson, 1981; Germain *et al*, 1987)

2.3.2 RADIOCHEMICAL YIELD TRACERS FOR ^{237}Np DETERMINATION

All methods for the determination of ^{237}Np involve some form of separation before assay. In most cases, chemical processing is limited and is assumed to be quantitative. However, to develop an adaptable method capable of highly accurate determinations, losses during the chemical processing must be accounted for. The technique of isotope dilution has been used for many years in stable and radiogenic isotopic analysis of geological samples (Moore *et al*, 1973; Faure, 1986; Russ, 1989) and has easy application to radiochemical determinations. For most elements, there are many known isotopes producing characteristic radiation. The addition of a different nuclide to the sample, prior to analysis allows losses during processing to be accounted for, provided that it behaves chemically in an identical way to the determinand (Eakins, 1984). Ideally the added nuclide should be of similar decay character as the determinand and of similar activity to allow simultaneous measurement. The advantage of isotopic dilution is that errors associated with matrix interferences and measurement by more than one detection system may be eliminated.

For ^{237}Np assay, the situation is far from satisfactory (Cross and Hooper, 1987). For the more commonly used α-spectrometry determinations, there are no strong α-emitting nuclides suitable as internal tracers (see section 1.2.2). The short-lived, β-emitting ^{239}Np has found most use as a tracer in ^{237}Np chemistry (Sill, 1966; Holm and Nilsson, 1980; Holm, 1984; Harvey and Lovett, 1984; Shinohara *et al*, 1989). However, its short half-life and need for separate assay by γ or β-spectrometry are distinct disadvantages. Standards must be prepared prior to each analysis by milking from secular equilibrium with ^{243}Am or by separation from a solution of irradiated uranium. The absolute efficiency for the detection of both ^{237}Np α-emissions and ^{239}Np γ-photons must be determined. This greatly complicates the procedures and increases the risk of systematic error. However, the decay characteristics of ^{239}Np make it an ideal tracer for the analysis of ^{237}Np by neutron activation (see section 2.3.3).

The 396 day ^{235}Np nuclide has recently been used as a yield monitor for α-spectrometry (Harvey and Sutton, 1987; Harvey and Thurston, 1988). Again there are problems of measurement by more than one detection system and of significant contamination of tracer solutions by ^{237}Np (Whittaker, 1984). For mass-spectrometry, the 10^7 year ^{236m}Np nuclide has potential application (Landrum *et al*, 1969; Efurd *et al*, 1986a). Again the production of standards of adequate purity is very difficult due to ^{237}Np contamination.

The particular uses of yield tracers in the methods developed in this study will be discussed later.

2.3.3 THE DETERMINATION OF ^{237}Np BY NEUTRON ACTIVATION ANALYSIS

The potential advantage of the neutron activation analysis approach over other routine radiometric methods has already been indicated. In theory the conversion of the low specific activity ^{237}Np to a short-lived, β-emitting nuclide should improve analytical sensitivity over methods which are dependent on the measurement of ^{237}Np decay. The added advantage is the less rigorous source preparation requirements of γ-spectrometry compared to α-spectrometry. In principle, the analytical approach is very simple. A sample containing an unknown quantity of ^{237}Np is irradiated in a suitable flux of neutrons together with a standard of known ^{237}Np concentration. The activity induced is described by the familiar activation equation (see for example: Kruger, 1971; De Soete *et al*, 1972; Choppin and Rydberg, 1980; Bowen, 1981) below.

$$A_i = n_i \sigma_i \phi \, (1-e^{-\lambda t})$$

Where A_i = induced activity of radionuclide i, n_i = number of target nuclei in the sample to produce i, σ_i = reaction cross-section (probability) to produce i (cm^2, quoted in terms of *barns*, 1 barn = $10^{-24}cm^2$), ϕ = flux of irradiating neutrons (n cm^{-2} s^{-1}), λ = decay constant of the nuclide produced (s^{-1}) and t = irradiation time (s). The activities produced by reactions of neutrons on the neptunium atoms, primarily by (n, γ) reactions, in both the samples and the standards are compared. If both the irradiation and counting conditions are identical then the ratio of the induced activities is equal to the ratio of the atom abundances in the sample and the standards. The unknown quantity can then be determined. In the case of the activation of a parent nuclide it is obvious that there will be potential for improved sensitivity of radiometric assay if the daughter nuclide produced is of much shorter half-life than the parent nuclide (ignoring, of course, differences in the sensitivities of the radiometric methods used in each case). Such a situation is favoured if $(\lambda n)_{daughter}$ is large, so that the daughter activity comes close to saturation, ie $(\lambda n)_{daughter} \approx n\sigma\phi$ or $\sigma\phi >> \lambda$. In the case of a cross-section of 1 barn and a flux of 10^{13} $ncm^{-2}s^{-1}$ implies that on an activity basis, this approach would have advantage for nuclides with half-lives >> 3,000 yr, offering great potential for ^{237}Np assay.

In published applications of this approach to ^{237}Np assay, the methods rely on pre- and post-irradiation chemical processing and the access to neutron irradiation sources of suitable flux. Consequently, developments of this method have been limited to a few sites with the appropriate facilities. The origin of this technique was for rapid and sensitive assay of ^{237}Np in process solutions and waste material from the nuclear industry. It has had a very limited application to environmental assay primarily because of the specialist facilities required. The following sections include a discussion of the principles of neutron activation analysis as applied to the highly specific case of ^{237}Np determination in theory and in terms of practical approach.

(a) theory of neutron activation analysis (n.a.a.)

The activation equation above indicates that there are many factors which must be assessed in high precision NAA. They are closely related and include the nature and relative importance of various potential neutron reactions with the target-atoms, the neutron flux characteristics of the source and the properties of the reaction cross-sections.

There are a number of potential reaction types involving neutrons impinging on the atomic nucleus (Kruger, 1971; Choppin and Rydberg, 1980) which, due to the absence of charge on the neutron, have no coulombic barrier to overcome. They include,

(i) neutron capture with γ-ray emission, which changes the n : p ratio and produces a nuclide which is unstable with respect to β-decay,

(ii) transmutation of the nucleus in which the chemical identity of the activated nucleus is changed and a charged particle is emitted. The most common reaction is (n, p); others include (n, d), (n, α), (n, t), (n, ^{3}He). In the (n, p) reaction, the product nucleus is generally unstable with respect to β^- decay and decays back to the target nucleus. The (n, α) reaction is more common for the lighter elements and products are unstable with respect to β^-,

(iii) fission, particularly of the heavier nuclides ($z \geq 90$) occurs when the activated nucleus splits into two large fragments and a number of neutrons,

(iv) inelastic scattering, in which the incident neutron imparts a fraction of its energy to the target and escapes. The target can either be raised to a metastable state (n, n') and can then decay by γ-emission, or when the incident neutron is of sufficient energy, emission of a neutron (n, 2n) results and the target is unstable with respect to β^+-decay.

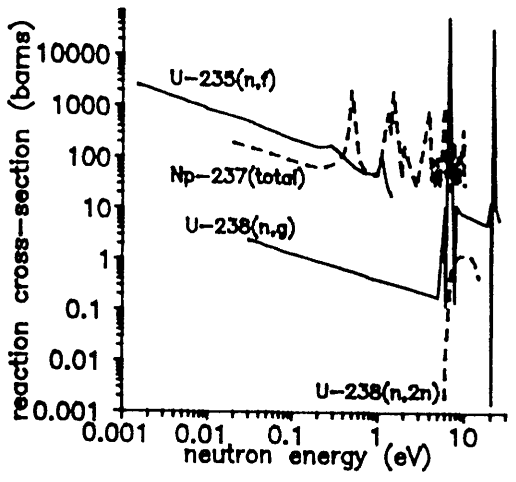
From the above description of possible neutron reaction types, the sensitivity of a particular analytical method using a specific reaction is dependent on the energy of neutrons incident on the target and the response of the target to the specific neutron energy.

The neutron *cross-section* (σ) is defined as the probability that an incident neutron will react with the target nucleus (Kruger, 1971). The total cross-section (σ_T) is the sum of the partial cross-sections due to scattering (σ_S) and absorption (σ_A). Further subdivision of the partial cross-sections takes into account, by simple summation, the cross-sections for the individual reactions:

$$\sigma_T = \sigma_S + \sigma_A = (\sigma_{EL} + \sigma_{INEL}) + (\sigma_{n,\gamma} + \sigma_{n,2n} + \sigma_{n,p} + \sigma_{n,d} + \sigma_{n,\alpha})$$

The cross-sections vary between reactions type and with the energy of the incident neutron. For charged particles there is a threshold energy requirement. There is usually a single energy at which maximum probability occurs for each reaction and thus the total reaction cross-section obscures wide variation in the details of neutron interaction. The dependence of cross-section on incident energy is described by the *excitation function*. The excitation functions for different nuclides including ^{237}Np are shown in Figure 2.22. It can be seen that the cross-sections exhibit rapid changes with energy when the incident neutron energy coincides with energy levels in the nucleus (Askew *et al*, 1983). In the case of particles with a spectrum of energies, such as in a reactor, an integrated reaction cross-section must be considered. The excitation function for ^{237}Np(σ_T) shows strong interactions in the thermal neutron energy region (average energy < 1 eV) in common with other nuclei, which decreases as neutron energy increases. At 0.49 and 1.5 eV and at higher energies strong and discrete interactions are observed. These are *resonances* and are due to the coincidence of neutron energy with an energy level of the

Figure 2.22: Excitation functions for various neutron reactions of U and Np nuclei (Hughes *et al*, 1960; Buckingham *et al*, 1961; Alley *et al*, 1968).



excited compound nucleus (Choppin and Rydberg, 1980).

The *neutron flux* (ϕ) is defined as the product of the total density of neutrons (cm^{-3}) and their average velocity ($cm\ s^{-1}$) (Choppin and Rydberg, 1980). In the case of reactor sources, the flux can be divided into several components:

(i) thermal neutrons, in thermal equilibrium with the surroundings (mean energy = 0.024 eV at room temp.),

(ii) epithermal neutrons, not in thermal equilibrium with the surroundings,

(iii) resonance neutrons, in the 1 eV to 1 keV range,

(iv) intermediate neutrons, in the 1 to 500 keV range,

(v) fast neutrons, with energies >0.5 MeV.

In the average nuclear reactor thermal neutrons are most abundant and most nuclides have high cross-sections in this region. Intermediate neutrons do not show much reactivity, whilst fast neutrons can be used to produce many interesting reactions, particularly in particle accelerators (Choppin and Rydberg, 1980).

It is therefore essential to consider the nature of the reaction and neutron flux characteristics of the source to be used. Some authors suggest that at least three different flux determinations are required for accurate NAA determinations (Verheijke and Jansen, 1988a; 1988b). However it is generally concluded that the single comparator methods are very sensitive approaches (Cornelis *et al*, 1976; Dams *et al*, 1976; Puchelt and Kramar, 1976; Jovanovic *et al*, 1989) and that improvements in the accuracy of determinations by including detailed flux considerations are somewhat reduced by the poor quality of nuclear data available (Giradi *et al*, 1965; Simonitis *et al*, 1982; Caletka *et al*, 1988).

The accuracy of the NAA method is thus primarily determined by the quality of the standard used as a comparator whilst the precision is determined by the counting statistics of the peaks monitored and any differences in the integrated neutron flux to the sample and the standard for which corrections must be made.

(b) application of n.a.a. to ^{237}Np assay

A number of methods have been published for the determination of ^{237}Np by neutron activation analysis in process solutions (Landrum *et al*, 1969; Guay and Pinelli, 1973; Ragahavan *et al*, 1976; Ruf and Friedrich, 1978) and some limited application to environmental samples (Byrne, 1986; May and Pinte, 1986; Germain *et al*, 1987). All involve some form of sample pre-separation, pre- or post-irradiation to remove interferences from nuclides of uranium, to reduce the matrix-induced activity of the sample post-irradiation and to preconcentrate the ^{237}Np from the samples.

The principal reaction observed is

$$^{237}\text{Np}\ (\text{n}, \gamma)\ ^{238}\text{Np} \quad \xrightarrow[2.11\ \text{d}]{\beta-} \quad ^{238}\text{Pu}$$

The reaction cross-section for thermal neutron capture and resonance integral (absorption of resonance neutrons) are high (170 and 600 barns respectively; see Figure 2.22) and the short-lived ^{238}Np produced has a half-life comparable to ^{239}Np, the convenient radiochemical tracer, as well as suitable, intense γ-rays free from spectral overlap (see Table 2.9). These emissions are easily detected by routine γ-spectrometry using Ge and Ge(Li) detectors (see section 2.4.1).

Potential interferences with the reaction and the proposed methods stem from the presence of nuclides of uranium. They can directly interfere with the determination by forming ^{237}Np via:

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

Table 2.9: Nuclear data for nuclides of neptunium used in neutron activation analysis (from Lederer and Shirley, 1978).

nuclide	$T_{1/2}$	**main γ-emissions (keV, % rel.int.)**		
^{238}Np	2.11 days	943	83%	
		1027	100%	
		1030	100%	
^{239}Np	2.35 days	99.5	15.08%	(Pu $K_{\alpha 2}$)
		103.6	23.98%	(Pu $K_{\alpha 1}$)
		106	22.8%	
		117	8.63%	(Pu $K_{\beta 1}$)
		121	2.92%	(Pu $K_{\beta 2}$)
		209	3.4%	
		228	11.8%	
		278	14.1%	

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

The (n, 2n) reaction results, as previously described, from the inelastic scattering of incident neutrons by the target nucleus. The energy requirements of the process are that the incident neutrons should be of sufficient energy such that $E_{incident} > 2 \times E_{neutron\ b.e.}$ in the nucleus (Choppin and Rydberg, 1980). The excitation function for ^{238}U (n, 2n) (Figure 2.22) has a maximum of 1.4 barns in the 10 eV region. This energy corresponds to the crossover between resonance and intermediate neutron energies and as such, the reaction is unlikely to be of significance in highly thermalized fluxes. In the case of the multiple neutron capture on ^{235}U, the capture cross-sections for ^{235}U, ^{236}U and ^{237}U are higher than for ^{238}U (see Table 2.10). However, coupled with the strong fission cross-section (580 barns), the low abundance of the nuclide in naturally occurring uranium suggests that this too is likely to be of negligible importance. Continued neutron capture of the ^{238}Np nuclide is unlikely. It has a negligible capture cross-section and a high fission cross-section (see Table 2.10). Further interferences are possible from single neutron capture on ^{238}U:

$$^{238}U\ (n, \gamma)^{239}U \xrightarrow[23.5\ min]{\beta -} {}^{239}Np$$

This reaction will have potential to interfere in any post-irradiation chemical manipulations using ^{239}Np as a tracer.

Table 2.10: Nuclear data for the neutron reactions of importance in neutron activation analysis of ^{237}Np (from Lederer and Shirley, 1978).

nuclide	$T_{1/2}$	**neutron capture cross-sections (barns)**	
		σ_{TH}	σ_F **(0.025 eV)**
^{235}U	1.62 x10^5 yr	100	580
^{236}U	2.39 x10^7 yr	6.0	0
^{237}U	6.75 d	480	2
^{238}U	4.51 x10^9 yr	2.7	-
^{239}U	23.5 min	22	14
^{237}Np	2.14 x10^6 yr	170	19
^{238}Np	2.11 d	0	2000
^{239}Np	2.35 d	35-25	<1

The conditions used for the published methods of NAA determination of ^{237}Np are summarized in Table 2.11. The "industrial" applications are relatively crude methods with hardly any consideration given to potential interferences. Purification procedures are particularly rough and the majority favour single step solvent extraction separations with TTA. Ruf and Friedrich (1978) do note that ^{239}Np is generated in modest amounts during the irradiation process but since the method does not require post-irradiation chemical treatment, this is not a problem. Ragahavan *et al* (1976) did monitor the effect of adding quantities of Pu and U to the solutions to be irradiated and noted that there was a subsequent increase in the ^{238}Np generated. The arguments regarding flux attenuation are somewhat confusing. In the application of these early methods to environmental assay, greater emphasis is placed on adequate decontamination of the sample from nuclides of uranium. In the methods of May and Pinte (1986) and Germain *et al* (1987), further purification of the sample post-irradiation involves the removal of the 15 hour ^{24}Na, an activation product of ^{27}Al and ^{23}Na (via (n, α) and (n, γ) respectively) using hydrated antimony phosphate (Krishnan and Craper, 1975). This is particularly important for marine samples with low ^{237}Np content. In all published cases, the ^{238}Np generated is determined by γ-spectrometry with or without ^{239}Np tracer.

The method of Byrne (1986) provided preliminary data on the determination of ^{237}Np in Irish Sea sediments. It is this method which was studied here as an alternative approach to routine α-spectrometry and will be briefly summarized.

The method involved a pre-irradiation separation of ^{237}Np from an acid leach of silt material. Reduction with hydroxylamine hydrochloride and anion exchange of Np^{IV} from HCl media was used. It was proposed that some effort should be made to remove uranium from the sample by increasing the anion exchange clean-up by washing with 8M HNO_3, although this was not considered to be crucial. Post-irradiation chemical separation was by a single cycle of TTA

Table 2.11: Published methods for the determination of ^{237}Np by neutron activation analysis.

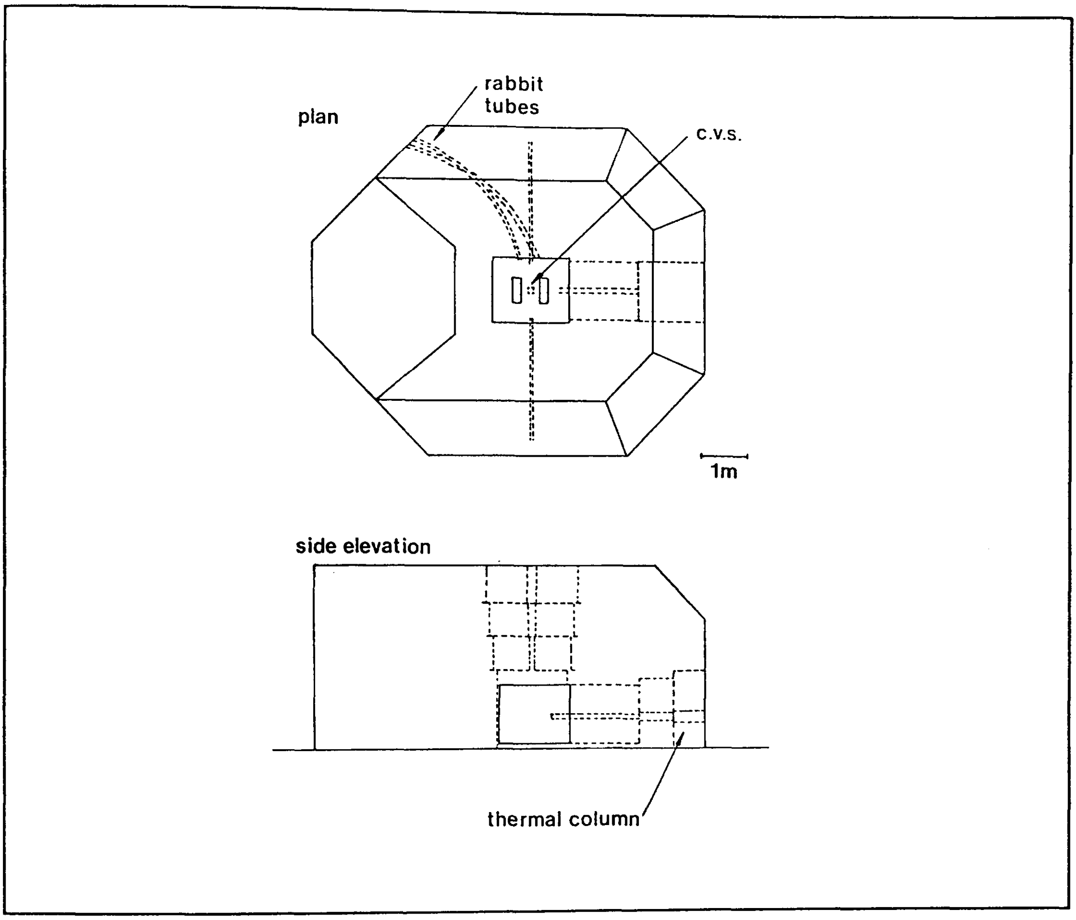
sample type	**chemical treatment**	**irradiation conditions**	**lower limit of detection for ^{237}Np**
^{237}Np in process solutions:			
Landrum *et al* (1969)	not quoted, post irrad. ^{237}Np to trace ^{238}Np	$\phi = 1.5 \times 10^{14}$ ncm^{-2}s^{-1} t_{irr} = 6 hrs	0.007 -0.05 ngml^{-1}
Ragahavan *et al* (1976)	pre and post irrad. chem. ^{239}Np pre ^{237}Np post irrad. tracer	$\phi = 0.001\text{-}0.1 \times 10^{14}$ ncm^{-2}s^{-1} $t_{irr} \leq 1$ hr	
Ruf & Friedrich (1978)	pre and post irrad. chem. ^{239}Np tracer	$\phi = 0.3 \times 10^{14}$ n cm^{-2} s^{-1} t_{irr} = 12-48 hrs + 2 days cooling	1 ng
^{237}Np in ^{238}Pu + ^{239}Pu:			
Guay & Pinelli (1973)	post irradiation chem.	$\phi = 0.8 \times 10^{14}$ ncm^{-2}s^{-1} t_{irr} = 20 hrs	0.1 ng
^{237}Np in marine samples:			
Byrne (1986)	pre and post irrad. chem.	$\phi = 0.02 \times 10^{14}$ ncm^{-2}s^{-1} t_{irr} = 20 hrs	0.004 ngg^{-1}
May & Pinte (1986), Germain *et al* (1987)	extensive pre and post irrad. chem.	$\phi = 2.2 \times 10^{14}$ ncm^{-2}s^{-1} t_{irr} = 14-65 hrs + 2 days cooling	5×10^{-4} ng

solvent extraction from 0.5M HCl. The yields were monitored by ^{239}Np, prepared from irradiated solutions of uranium. The pre-irradiation separations were found to be 90 to 95% efficient, while the post-irradiation separations were quantitative. The method was validated by participation in the one major intercomparison exercise (Popplewell and Ham, 1987). The results obtained by the author agreed well with the published mean.

(c) application of n.a.a. at the S.U.R.R.C.

The facilities for neutron activation analysis at the SURRC comprise the UTR-300 reactor which is a Universities Teaching Reactor, built and commissioned by the Advanced Technology Laboratories Division of American Standard in 1963 (Wilson, 1965). It is a tank-type, light water moderated and graphite reflected thermal reactor (Advanced Technology Laboratories, 1962). An overall plan of the reactor layout is given in Figure 2.23. The fuel elements comprise six assemblies of 13 or 14 plates each containing 22 to 24.5 g of 90% ^{235}U in a UO_2/ Al matrix clad in Al metal. The reactor is controlled by four neutron absorbing, boral control rods and shielded by 2.5 m of concrete. The reactor is started using a Pu/ Be source of 1.4 $\times 10^6$ n s^{-1} to initiate

Figure 2.23: Plan and side elevation of the UTR-300 (Advanced Technology Laboratories, 1962).



the chain reaction. Routine operation involves running at full power of 300 kW for 3 days per week (6 hours per day) and two days per week at lower power. A number of irradiation positions (see Figure 2.23) are available, each with their own characteristic neutron fluxes. They include

(i) the fast transfer "rabbit system", in which small samples can be irradiated for up to 1 hour in polythene capsules. Transfer between sample introduction and irradiation position is via pneumatic tubes with transfer times of 0.5 s.

(ii) the central vertical stringer (CVS) which is used for longer irradiations (> 1 hour) and large samples which can be lowered into the reactor core. Reactor shut down is required before access to the samples is possible.

(iii) the thermal column is situated in the blocks of graphite close to the core. The fluxes are well thermalized, but one position has a fairly high fast neutron flux. Again reactor shut-down is required before sample retrieval.

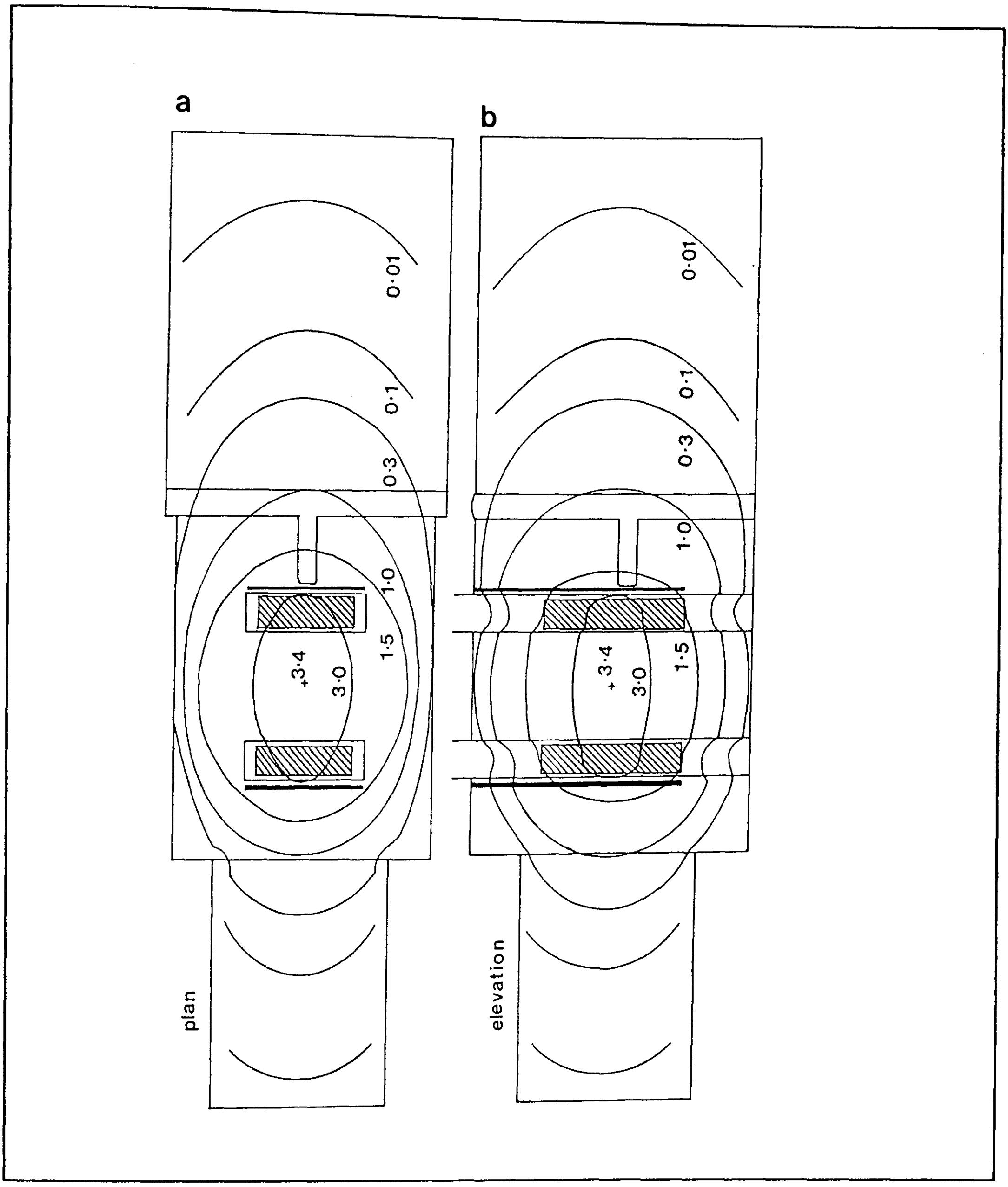
The fluxes available at each of the irradiation positions are given in Table 2.12 for both the original UTR-100 and the post-upgrade UTR-300. The diagrams in Figure 2.24 show the flux distribution in various parts of the reactor.

Table 2.12: Flux characteristics for irradiation facilities in (a) UTR-100 (1963-1969), (b) UTR-300 (1970-present).

irradiation position	**maximum neutron flux** $n\ cm^{-2}\ s^{-1}$	
	(thermal)	**(fast, >2 MeV)**
(a) **UTR-100**, 1963-1969 (Izatt and Scobbie, 1967)		
fast transfer: rabbit 1 (small)	8.4×10^{11}	2.7×10^{10}
rabbit 2 (large)	7.8×10^{11}	8.5×10^{10}
central vertical stringer (cvs)	1.4×10^{12}	4.1×10^{10}
thermal column (maximum)	9.1×10^{11}	2.0×10^{11}
(b) **UTR-300**, 1970-present (SURRC, 1977)		
fast transfer: rabbit 1 (small)	2.5×10^{12}	8.0×10^{10}
rabbit 2 (large)	2.3×10^{12}	2.5×10^{11}
central vertical stringer (cvs)	4.2×10^{12}	1.2×10^{11}
thermal column (maximum)	2.7×10^{12}	6.0×10^{11}

The optimum irradiation position for the activation analysis of ^{237}Np, from the discussion in section 2.3.3 b above, should have the highest thermal neutron flux so that (n, γ) reactions dominate. The lowest fast neutron flux is also desired to minimise potential interferences from (n, 2n) reactions on any ^{235}U in the samples. It is obvious, from the data presented in Table 2.12, that the CVS position is the most suitable facility. In order to assess the capabilities of the UTR-300 CVS position for ^{237}Np, simple calculations were performed to determine the theoretical accumulation of activity with time of an aliquot of ^{237}Np in the UTR-300 (using the maximum

Figure 2.24: Flux distribution in the UTR-300 (a) plan, (b) side elevation (SURRC, 1977).

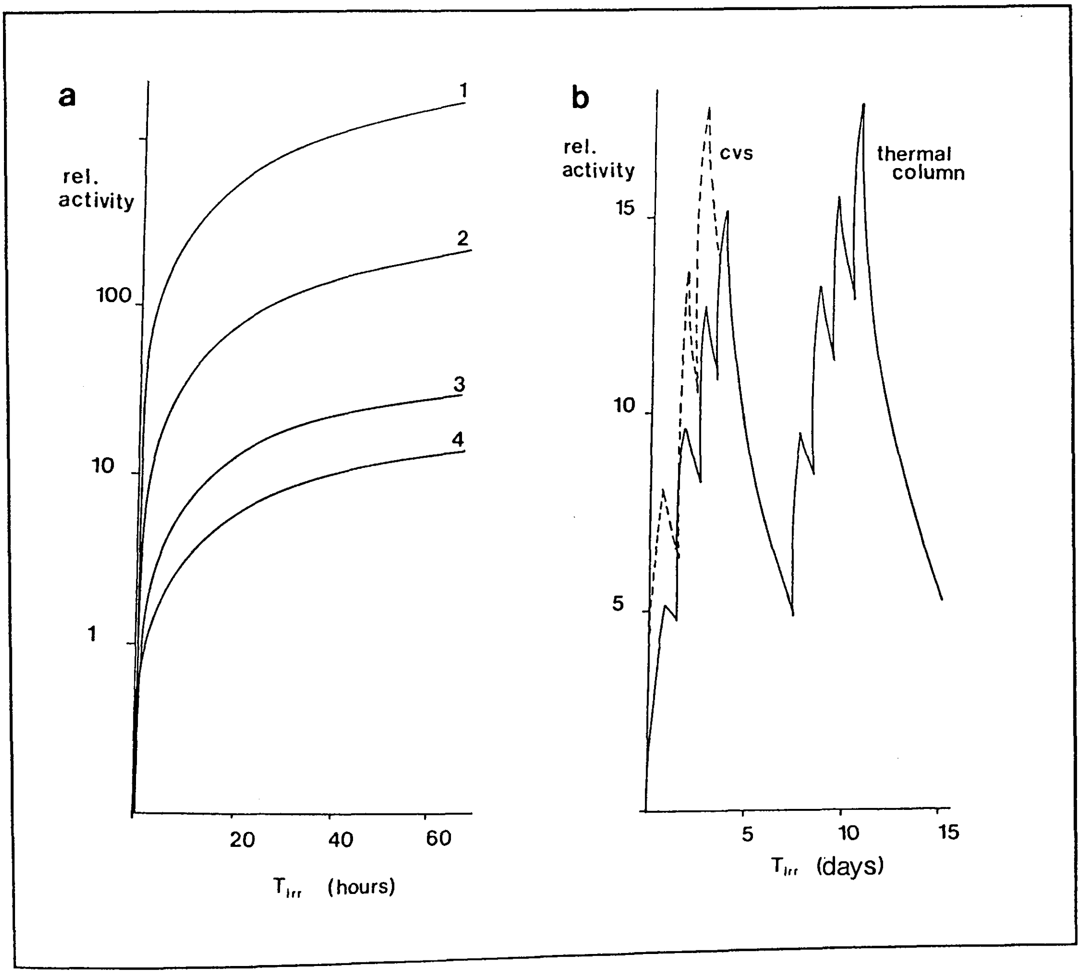


thermal neutron flux available in the UTR-300) and to compare the activation to the methods published previously.

The results are illustrated in Figure 2.25a for irradiation in (i) the 70 MW OSIRIS reactor, CEN-Saclay, France (May and Pinte, 1986; Germain *et al*, 1987), (ii) the FR-2 reactor, Karlsruhe, FRG (Ruf and Friedrich, 1978), (iii) the CVS of the 300 kW UTR-300, SURRC and (iv) the 250 kW TRIGA-MK$_{II}$ reactor, Ljubljana, Yugoslavia (Byrne, 1986). The advantage of the very much higher fluxes in the French and W. German reactors is obvious. The CVS facility at the SURRC does, however, have potential for increased sensitivity over the facility used by Byrne (1986).

For the same irradiation time, the induced activity is calculated to be 2.1 times greater in the UTR-300. The second part of this assessment involves the determination of the optimum irradiation procedure with the options available. Figure 2.25b shows, in greater detail, the relative activation of ^{237}Np under routine operating conditions of the UTR-300 for both the thermal column and the CVS facilities. The saw-toothed pattern is the result of the 6 hours run time per day and overnight cooling during shut-down. The shut-down period of approximately 20 hours is significant compared to the 2.1 day half-life of the ^{238}Np produced. Consecutive 6 hour periods of irradiation in the CVS would appear to be the most effective way of building up the ^{238}Np activity under normal running conditions. Access to the samples from the CVS is only possible after overnight cooling and, for the thermal column, after a weekend shut down. From Figures 2.25a and 2.25b, it is obvious that the induced activation obtained by Byrne (1986) is reached after 2 days of irradiation in the UTR-300 CVS under normal operating conditions. Any further irradiation would significantly improve the sensitivity of the method applied at the SURRC.

Figure 2.25: Relative ^{237}Np activation with irradiation in the UTR-300 (a) compared to thermal fluxes used in published activation methods (b) cvs v thermal column under normal operating conditions.



It was decided that a single 6-hour irradiation in the thermal flux of the CVS would be the most convenient procedure whilst the method was under investigation. This would produce approximately 75% of the ^{238}Np induced by irradiation under the conditions used by Byrne (1986). Adequate ^{238}Np would still be produced to study chemical procedures in detail and to optimise counting conditions.

(d) detection and measurement of γ-emitting nuclides of neptunium

Both the ^{239}Np yield tracer and the induced ^{238}Np are strong γ-emitting nuclides. Data on their decay characteristics have been presented earlier (Table 2.9). Section 2.4.1 describes the general principles and characteristics of the detectors used for the quantification of these nuclides. A number of γ-detectors were available for use in this study, these being a mix of both the older Ge(Li) and newer, hyperpure Ge types. A survey of the detectors was performed using an aliquot of a standard solution of ^{243}Am (Amersham International ltd) which is in secular equilibrium with its daughter, ^{239}Np. With a knowledge of the precise activity in the aliquot, the absolute detection efficiency of the detectors was calculated for the peaks observed between 74 keV and 277 keV. It was the intention to provide a relative series of calibrations in order to choose the most efficient array for counting ^{239}Np yield tracer. The peaks due to ^{238}Np occur close to 1000 keV, towards the lower detection efficiency side of the semiconductor detectors. At this region there is not much difference in detection efficiency between the Ge and Ge(Li) detectors of similar crystal size and consequently the optimum array for ^{239}Np detection was assumed to be adequate, if not optimal, for ^{238}Np. The detectors used and the efficiencies obtained are given in Table 2.13. On the basis of these results, the older Ge(Li)-type detector was considered the most appropriate counting system for this project.

Table 2.13: Absolute efficiency (%) of semiconductor γ-detectors for ^{239}Np and ^{243}Am photons. All data uncertainties <1% at 2σ confidence level.

detector type	**absolute efficiency (%)**				
	74 keV	106keV	209keV	228 keV	277 keV
Ge (Li), 20% rel.eff.	2.53	4.48	4.04	3.83	2.90
Ge (Li), 80 cm^3	7.89	9.18	+	2.90	2.78
Ge (Li), 25 cm^3	4.33	4.26	+	2.45	2.19
L.E.P. Ge	14.07	0.95	BDL	BDL	BDL
R.E. Ge	6.52	4.00	4.05	3.24	2.49
G-X Ge	4.01	2.16	2.42	1.96	1.54

+ low intensity, poor counting statistics

For the detection of short-lived nuclides at low levels, the counting time used is important. In radiometric methods, an increase in the count time has the advantage that, for the long-lived nuclides, more decay particles or photons are observed and the counting statistics improved. With a short-lived nuclide, as the count time is increased, it will start to become significant with respect to the half-life. The count rate observed will be an average of the count rate exhibited by the nuclide. It is not only important to correct for decay during counting, but also to realize that at some point after the start of the count, it will cease to become advantageous to continue counting. This point will depend on the half-life of the nuclide. Heydorn (1980) and Harvey and Thurston (1988) suggest that no gain in precision of low count rates will occur by increasing the counting time beyond 1.8 to 3 half-lives of the nuclide of interest (even when the background is constant). For ^{239}Np this translates to 4.2 to 7.0 days and for ^{238}Np 3.8 to 6.3 days.

A simple correction can be made for decay during counting, the governin g equation having been derived by a number of authors (Hoffman and Van Camerik, 1967; Junod, 1974; Heydorn, 1980). The precision of the correction is within 1% for counting times up to 0.7 half-lives (= 34.5 hours for ^{239}Np and 35.5 hours for ^{238}Np) (Heydorn, 1980). In practice, the intensity of the peaks measured was such that good counting statistics were obtained in substantially shorter counting times. The derivation of the formula to account for decay during counting is presented in Appendix A.

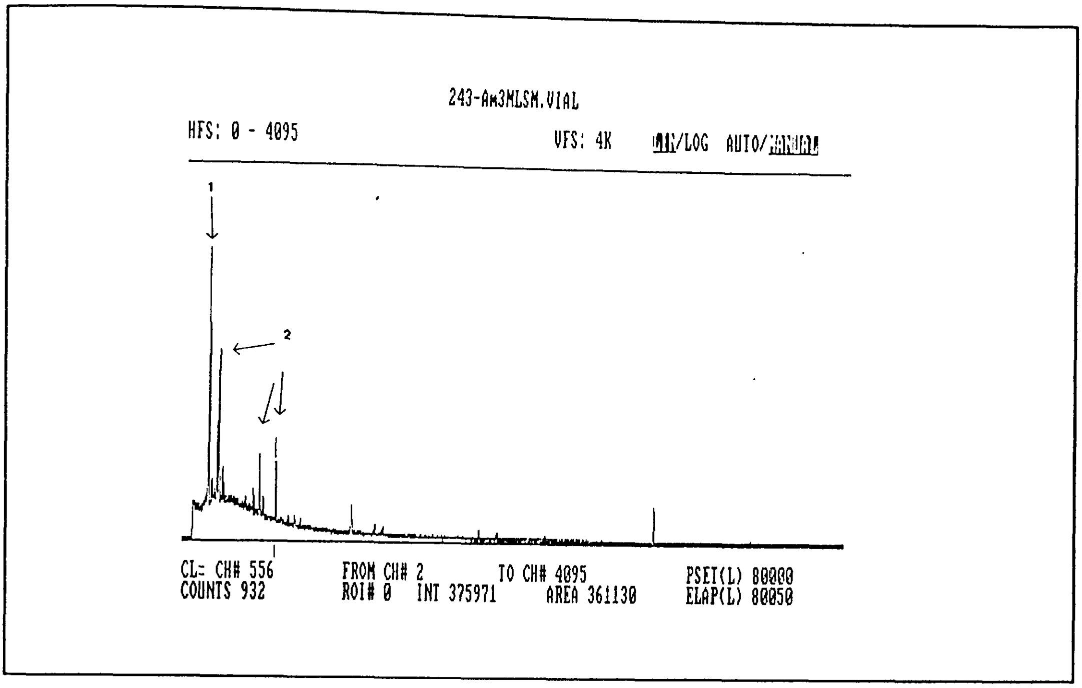
(e) chemical yield determination and counting geometries

The most convenient chemical yield tracer for this study is ^{239}Np (see section 2.3.2) which has a comparable half-life and decay energies far removed (in energy terms) from the induced ^{238}Np. The strong, well resolved emissions at 228 keV (11.8%) and 277 keV (14.1%) were used for all yield calculations. The more abundant 106 keV (22.8%) peak, close to the detector efficiency maximum, is somewhat obscured by strong Pu K_α and K_β lines (see Table 2.9 and Figure 2.26). Due to its short half-life, fresh batches of tracer must be prepared before analysis. Two options are available for its production, one from (n, γ) reactions on ^{238}U as used by Byrne (1986), the other by separation from secular equilibrium with its parent ^{243}Am. It was decided to use the latter route as irradiation of uranium suffered from a number of drawbacks, namely

(i) For dosimetric reasons, it was desired to keep the handling of irradiated materials to a minimum,

(ii) The addition of ^{239}Np from a solution derived from the irradiation of uranium has the potential to introduce quantities of uranium, together with activation and fission products to the sample. It is these nuclides from which Np is required to be separated and this addition would thus appear to be a backwards step,

Figure 2.26: Gamma-spectrum of ^{243}Am (1- 74 keV) and daughter ^{239}Np (2- 106, 227, 228 keV) in secular equilibrium.



(iii) Regular irradiation of quantities of uranium followed by chemical processing is outwith the licence of the SURRC facility.

Despite the possibility of obtaining high activities of tracer by activation, ^{243}Am-derived ^{239}Np is a much more convenient source. The parent has a long half-life (7.4 x10^3 years) and can be efficiently "milked" using a simple chemical procedure, since the chemical properties of Am and Np are very different. The short-lived daughter grows in with a rate proportional to its half-life according to the laws of secular equilibrium (Kruger, 1971).

The chemical procedure outlined by Byrne (1986) involved both a pre- and post-irradiation chemical separations. To obtain quantitative information from the sample, losses during the chemical treatment stages must be accounted for, commonly by isotope dilution (see section 2.3.2).

The pre-irradiation process requires the addition of a known amount of tracer and its assay at the end of processing to give an absolute activity of retrieved tracer. A number of problems arise in this situation. Firstly, as the ^{239}Np is milked from a stock solution, the relationship of A_P = A_D at secular equilibrium cannot be used to determine the ^{239}Np activity added since repeated processing might involve minute losses of the parent, which may become increasingly significant with time. Furthermore the solution would have to be left to re-equilibrate for more than 2 weeks before it re-approached equilibrium. This would be inconvenient for the routine processing of samples as a high activity or a large number of lower activity stock solutions would be required for milking. To overcome this problem, a milked spike was counted in the same geometry and on the same detector as the processed samples for pre- and post-irradiation quantification and an aliquot added to the samples. The differences in the activity observed between the samples post chemical separation and the freshly prepared spike, if the separations were 100% efficient, would then be due to radioactive decay and dilution.

This approach was used to determine the post-irradiation yields and the chemical yields for the determinations involving ICP-MS. In the case of the pre-irradiation separations for the NAA determination and α-spectrometry method, however, the geometries for counting the freshly prepared spike and the pre-irradiation samples differed. To resolve this problem, a geometry correction factor was determined. A 10 ml aliquot of standard ^{243}Am was placed in a 20 ml scintillation vial and counted in order to determine the absolute efficiency of the isolated spike geometry. Prior to irradiation, the ^{239}Np activity in the samples was measured as a 3 ml solution contained in a small 10 ml polythene pot. The absolute efficiency of this geometry was determined by counting an aliquot of the ^{243}Am solution. Due to the radiolysis of aqueous solutions which produces noxious fumes, the irradiation of solutions was avoided. Polythene vials were used as they were inexpensive and of reproducible shape. Also the stable nuclides of silicon found in quartz (^{28}Si, ^{29}Si, ^{30}Si) all have very high thermal neutron cross-sections and activate strongly to ^{31}Si, which is a strong β-emitter of 2.62 hour half-life. Consequently manipulations with irradiated quartz vials are to be treated with caution if adequate cooling time is not given. The polythene used in the construction of the vials chosen was found to be free of any major contaminants. The one drawback was that the 20°C temperature rise in the reactor during irradiation and the interaction of the neutrons with the vials deformed the polythene and made it somewhat brittle. For irradiations longer than 6 hours, the careful use of quartz vials would be recommended.

Dried down solutions produced very variable counting geometries due to the deposition of traces of material on the walls of the vials. Carrier salts to dry down the solution evenly were avoided so as not to introduce nuclei which activated strongly in the reactor. Counting the purified solutions as a calibrated volume before drying under an infrared lamp proved most

Table 2.14: ^{239}Np geometry correction factors used in the calculation of ^{237}Np pre-irradiation chemical recovery.

energy	**absolute efficiency (%)**			**correction factor**	
	scint. vial	poly. pot		(vial/pot)	
	(10 ml)	(3 ml)	(5ml)	(3ml)	(5 ml)
227 keV	3.83 ±0.05	4.85 ±0.11	4.04 ±0.09	1.27 ±0.03	1.06 ±0.03
277 keV	2.90 ±0.04	3.88 ±0.07	3.35 ±0.06	1.34 ±0.03	1.16 ±0.03

convenient. The absolute efficiencies and geometry calibration factors (simply the ratio of absolute efficiencies) for the NAA method are presented in Table 2.14. Correction factors for the post-irradiation separation were not required as it was convenient to count the processed samples as 10 ml solutions in the 20 ml scintillation vials. In all calibration measurements the standard ^{243}Am solution used was 78.44 ±0.74 Bq ml^{-1} (Amersham International ltd).

The production of the ^{239}Np tracer solution is based on a single cycle of TTA solvent extraction (see Byrne, 1986 and section 2.2.3). A solution of ^{243}Am was obtained from E.Hamilton and R.Clifton, then of I.M.E.R., Plymouth, nominally 4 kBq in activity but not standardized. The accuracy of the solution was not important for the tracer generation as the efficiency determinations were all relative. 800 Bq aliquots of the solution were placed in 10 ml solutions of 0.5 M HCl containing 0.5 g of hydroxylamine hydrochloride ($NH_2OH.HCl$, BDH AnalaR). ^{239}Np was extracted with 10 ml of 0.2 M TTA (toluene) by mixing using a disposable pasteur pipette, for 10 to 15 minutes. The solutions were centrifuged to separate the layers and the upper organic layer carefully drawn off and placed in a second container. The Np was rapidly back-extracted with 10 ml 8 M HNO_3, the phases separated by centrifugation and the 8 M HNO_3 pipetted off and counted. Weighed aliquots of the spike were then added to the samples.

The aqueous spike can be cleaned by repeated drying with conc. HNO_3. An example of the γ-spectrum of the ^{243}Am and ^{239}Np in secular equilibrium is given in Figure 2.26.

(f) studies on the chemical separation procedures for ^{237}Np assay

A number of experiments were performed to test the separation procedures of the method proposed by Byrne (1986), as summarized in Figure 2.27.

Aliquots of ^{243}Am were added to four 5 to 10 g portions of acid-washed sand and treated as samples for the steps 2 to 5 in Figure 2.27. The separations were excellent and no Am or Np was extracted at the Fe removal step using MIBK. Recoveries from the pre-irradiation separations were found to be >85%, with no reduction in recovery observed when it was decided to include a wash of 8M HNO_3 during the anion exchange to effect a better decontamination from uranium and iron. The post-irradiation separation was tested in a similar way, with the additional step of back-extracting the Np from the TTA phase with 8M HNO_3. Separation of Am from Np was 100%. All the added ^{243}Am was observed in the aqueous waste from the solvent extraction, the ^{239}Np present being accountable for by ingrowth. The total chemical efficiency for this step was found to be >95%.

5 g aliquots of Ravenglass silt and gley (0 to 5 cm) samples were processed according to the method of Byrne (1986). The Ravenglass silt sample was used throughout to study method

Figure 2.27: A schematic summary of the analytical procedure of Byrne (1986) used for the determination of ^{237}Np by neutron activation analysis.

^{1}**ash sediment**
(550 °C)
↓

^{2}**leach**
(conc. HCl, ^{239}Np tracer)
↓

^{3}**reduce Np**
(→ Np^{IV} with $NH_2OH.HCl$)
↓

^{4}**solvent extraction**
(remove Fe with MIBK)
↓

^{5}**anion exchange**
(9M HCl, Dowex 1x4)
→ sample on in 9M HCl, wash
→ 8M HNO_3 wash (optional)
→ 5M HCl wash, Np removal, retain, measure ^{239}Np and seal in vial

↓
^{6}**irradiate in reactor with standard**
↓

^{7}**retrieve residues**
(conc. HNO_3, ^{239}Np tracer)
↓

^{8}**reduce Np**
(→ Np^{IV} with $NH_2OH.HCl$)
↓

^{9}**solvent extraction**
(Np^{IV} with TTA)
↓

^{10}**back extract**
(Np ^{IV} with 8M HNO_3)
↓

^{11}**measure ^{238}Np and ^{239}Np in sample and standard** development. Its homogeneity was checked by γ-spectrometry of approximately 12 g subsamples in efficiency-calibrated 10 ml geometries. The results for ^{137}Cs (661 keV) and ^{241}Am (60 keV) are in good agreement, indicating that the homogeneity of the sediment at this sample size was good (see Table 2.15). The pre-irradiation processing of these samples gave recoveries >75% and took 2 to 3 days to reach the end of the pre-irradiation steps. The samples and standards were dried in polythene vials and packed together using aluminium foil as secondary containment. Short (1 to 2 cm) pieces of high-purity iron wire were coiled around the base of the vials. These were used to correct for differences in neutron flux between the samples and their standards. The reaction followed was multiple (n, γ) on ^{56}Fe, ^{57}Fe and ^{58}Fe to give ^{59}Fe with a half-life of 45 days. Despite the close packing of samples, flux variations of up to 20% were found over the order of 10 cm.

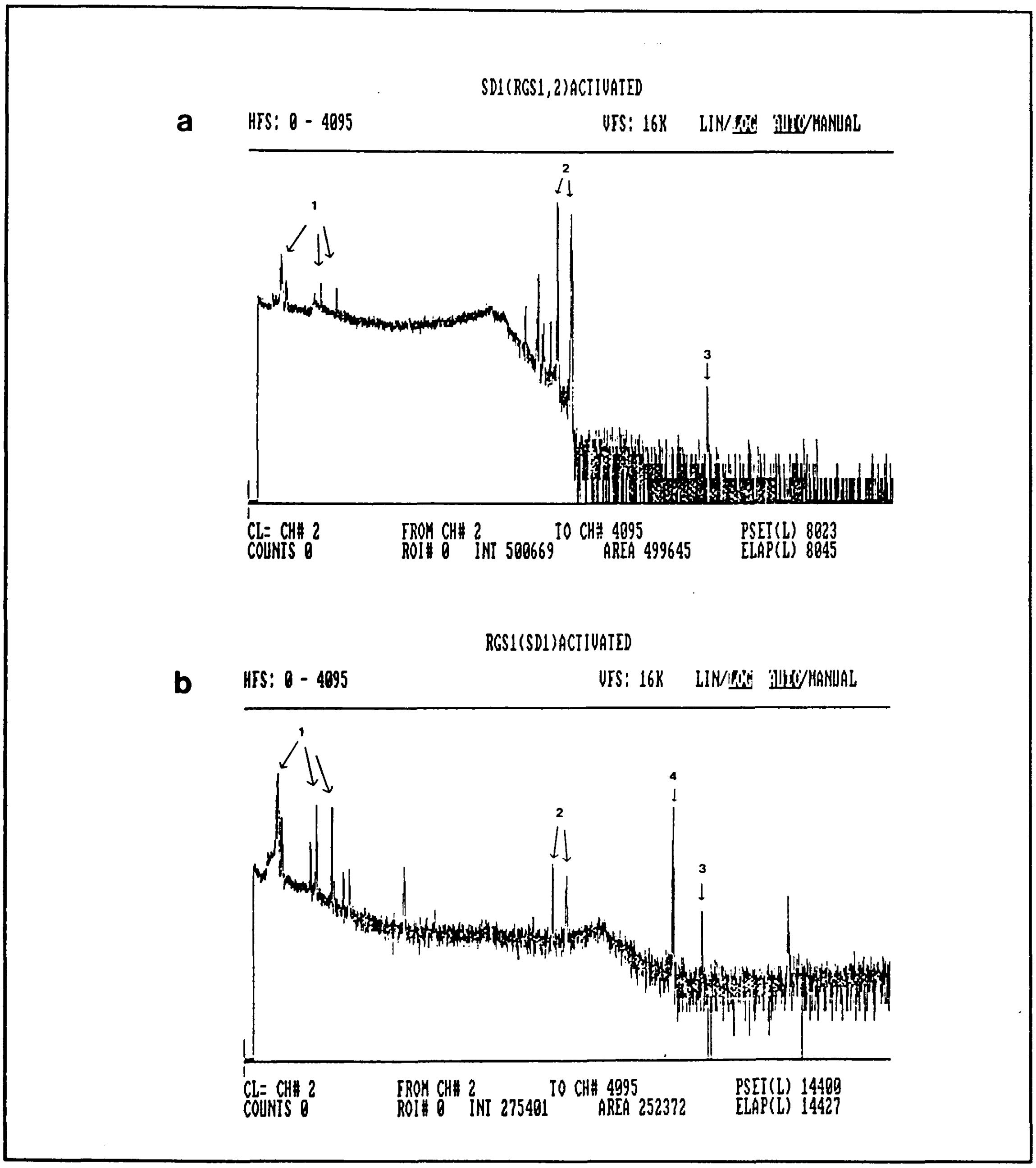
Following irradiation, all manipulations were carried out in a designated controlled area, for which an approved system of work is required. After 6 hours irradiation and overnight cooling in the CVS, the irradiated samples were transferred to the laboratory in lead pots so that the dose rate did not exceed the recommended 7.5 μSv hour^{-1} (ICRP,1977) at the exterior surface. All subsequent manipulations were performed behind lead shielding. The Al foil used for packing was the most active material, due to the high thermal neutron cross-sections of ^{27}Al and ^{23}Na. This foil was removed and discarded in the active waste bin. The vials and flux monitors were wiped and placed in clean polythene bags. At this stage, the dose rate from the clean materials did not exceed 7.5 μSv hour^{-1}. The vials were cut open and the samples leached from the pot with conc.HNO_3. The leached vials were counted to check for any traces of ^{238}Np and then discarded. Following the post-irradiation separation, the intensities of the ^{238}Np and ^{239}Np γ-rays were counted on top of the Ge(Li) system identified in the preliminary survey. The Fe flux monitors were counted 2 to 3 days after irradiation on detectors such that the dead-time did not exceed 2%.

Table 2.15: Homogeneity test of bulk Ravenglass silt sample.

sample	**weight (g)**	**activity concentration (Bq g^{-1} ±2σ)**	
		^{137}Cs	^{241}Am
1	12.04	0.91 ±0.06	1.17 ±0.18
2	12.48	0.73 ±0.06	1.18 ±0.18
3	12.99	0.77 ±0.06	1.22 ±0.18
4	13.10	0.80 ±0.06	1.26 ±0.20
5	12.32	0.78 ±0.06	1.25 ±0.20

The calculation of the final concentration of ^{237}Np in the original sample must take into account many factors, including decay corrections during counting and chemical separation, variations in neutron flux and differences in counting geometries. The details of the calculation are important in terms of the propagation of uncertainties but will not be detailed here. The calculation procedure for this method is, however, described in full in Appendix B.

Figure 2.28: Examples of the γ-spectra of irradiated ^{237}Np fractions (a) standard , (b) purified sample of Ravenglass silt [1- Np-239: 106, 227, 277 keV; 2- Np-238: 984, 1028 keV; 3- K-40: 1460 keV; 4- Na-24: 1368 keV].



Examples of the γ-spectra from activated samples and standards are shown in Figure 2.28. The peaks from ^{238}Np and ^{239}Np are well resolved and interference-free. ^{24}Na at 1368 and 2745 keV and ^{82}Br with a large number of peaks between 554 and 1474 keV are the main potential interferences. Br_2 is easily volatilized from the sample by repeated drying with conc.HNO_3. ^{24}Na interference is restricted to increasing the background continuum due to Compton scattering.

Following the method described by Byrne (1986), a number of observations and problems were observed. The efficiency of the pre-irradiation extraction of the samples was found to be approximately 75% for silt and soil samples. However, it was surprising to find that, in the case of the post-irradiation chemical separations, the apparent chemical recoveries ranged between 675% and 2,250% !! Further studies on a number of samples of silt between 5 and 50 g without tracer ^{239}Np showed the presence of ^{239}Np in the post-irradiation, purified samples. The activity levels were very variable and showed no obvious correlation with the weight of sample used. A range of between 2 and 100 times the absolute activity of the induced ^{238}Np was found. It was concluded that this interference was due to variable traces of ^{238}U passing through the separation steps and being activated to produce ^{239}Np via

$$^{238}U\ (n,\gamma)^{239}U \xrightarrow[23\ \text{min}]{\beta^-} {}^{239}Np$$

Pentreath and Harvey (1981) observed that significant traces of uranium were found to interfere with ^{237}Np determination by α-spectrometry. The source was analytical grade reagents, in particular conc.HCl. A series of blank experiments was run to determine whether such a contamination source existed here. Blank runs taken to different stages of the analysis showed that no detectable contamination could be attributed to the polythene vials used for irradiation, the concentrated AnalaR acids, the organic solvents or any glassware used in the analysis. The aluminium foil used as secondary containment during irradiation was found to contain appreciable amounts of ^{239}Np post-irradiation. Contamination of the sample leached from the vial by a small (< 1mm) flake of foil, may have contributed to the inconsistent chemical recovery. Careful manipulation of the sample vials during the leaching step and the removal of all Al foil sticking to the external surface was required to remove this problem. The procedure was rendered more difficult by the need to perform the "decanning" and leaching steps using tweezers and scalpels. Stubborn flakes of foil could be removed with hot conc.HCl and demineralised water.

Surprisingly, the Dowex 1x4 anion exchange resin initially used was found to contain significant quantities of uranium. Whether this was a result of contamination at the point of manufacture or in the laboratory was uncertain. The former source was considered most likely, since the containment and physical appearance of the resin was very different from a fresh batch of the same resin found to be free of uranium. However, the contamination observed was found to account for only 0.25% to 4.0% of the ^{239}Np levels. It could be successfully removed from the contaminated resin with a pre-conditioning wash with 1.2M HCl, but resisted washing with 8M HNO_3. With the new resin batch and a batch of Dowex 1 x8, the uranium contamination problem was still found to be present despite washing through with up to 100 column volumes of 8M HNO_3. These observations conform with the expected behaviour of uranium under the acid conditions used. The oxidation state of U is expected to be hexavalent under these conditions (see section 2.2.4). This is somewhat confusing since, by comparing the redox potentials of the actinides in section 1.2, the reduction step used to take Np^{V} to Np^{IV} should be capable of reducing U^{VI} to U^{IV}. The anion exchange behaviour of U^{IV} is similar to other tetravalent actinides in HCl. As [HCl] increases, the U^{IV} sorbs to the anion column, presumably as a negatively charged chloro complex. If U^{IV} is prevalent under the conditions used for Np separation, then the 8M HNO_3 column wash will not remove the species unless it is capable of oxidising U^{IV} to U^{VI}. From the anion exchange data described in section 2.2.4, the distribution coefficient of U^{VI} is <10 in 8M HNO_3 and for Np^{IV} $>10^3$. Consequently, a small fraction of uranium will remain on the ion exchange resin and should in theory be reduced to negligible levels with repeated washing. The data for anion resin distribution for U,Np and Pu from HCl solutions indicate that all the IV and VI oxidation states have very low distribution coefficients at low acidity and should therefore be eluted from the resin with 1.2M HCl. The use of 5M HCl to elute Np^{IV} will obviously result in a portion of any U^{VI} following. The exact interpretation of the behaviour observed on the basis of the data available is a problem.

At this point of the study, an additional wash of 9M HCl at the pre Np-elution stage was included. It did not have any apparent effect on uranium decontamination but did improve the chemical recoveries for Np. To attempt to remove the uranium interference, a single cycle of TTA solvent extraction from 0.5M HCl, in the same manner as the post-irradiation separation, was performed on the Np fraction from the anion exchange step. The organic-extracted fraction was found to contain only ^{238}Np and no induced ^{239}Np, whilst the aqueous waste contained significant amounts of ^{239}Np and no ^{238}Np. This observation served to answer the question as to whether or not the other nuclides of uranium could produce significant quantities of ^{237}Np under the irradiation conditions used via (i) multiple (n, γ) on ^{235}U, (ii) (n, 2n) on ^{238}U. Theoretical considerations earlier suggested that this was unlikely to be important. The observation above implies that, whilst nuclides of uranium are present in the aqueous wastes (generating ^{239}Np), the potential ^{237}Np (and hence ^{238}Np) generating reactions are not a problem here. This modification was included in a batch of analyses of Ravenglass silt. The pre-irradiation chemical separation gave lower recoveries than previously (50%). However, post-irradiation separations exhibited recoveries between 98% and 166%. Obviously there was some improvement, but the uranium interference was still significant. A second series of samples was run with two cycles of TTA solvent extraction. Pre-irradiation recoveries ranged from 40% to

60%. In all cases, the post-irradiation chemical yields were between 65% and 83%, suggesting that the uranium interference had been removed. Two samples were processed without adding ^{239}Np tracer and no induced ^{239}Np was observed in the post-irradiation analysis. The results from the study of ^{237}Np assay by NAA are summarized and discussed in Chapter 3.

2.3.4 THE DETERMINATION OF ^{237}Np BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

(a) the application of mass-based techniques to ^{237}Np assay

The determination of the mass abundance of long-lived nuclides, such as ^{237}Np, ^{99}Tc and ^{129}I, should have some advantage in sensitivity over conventional radiometric methods of analysis (Halverson, 1984; Hislop *et al*, 1987). The change in species detected from decay products to atomic masses changes the nature of both the information obtained and the approach to method interferences. In conventional radiometric methods, the main interference is the coincidence of decay products and for mass-spectrometry the existence of more than one chemical species of the same mass (*isobars*) and isotopic overlap. The former problem may be approached through chemical purification. The latter is an instrumental problem and is determined by the resolution and peak tailing features of the mass spectrometer (Baxter *et al*, 1987; Russ, 1989). In the case of the mass-based determination of ^{237}Np, there are no potential isobars, but the high natural abundance of ^{238}U and low levels of neptunium expected, means that there is potential for isotopic interference through peak overlap.

A large number of different mass-spectrometric devices are available for the determination of suitably long-lived nuclides (Koppenaal, 1988). They include the standard geochemical techniques of thermal ionization mass-spectrometry (TIMS) and the less precise but more versatile spark-source mass-spectrometry (SSMS). More recent developments of plasma source mass-spectrometry systems such as inductively coupled plasma mass-spectrometry (ICP-MS), microwave-induced plasma (MIP-MS) and glow discharge sources (GD-MS) have heralded a change in the status and versatility of the technique in environmental analysis, with important implications for the long-lived nuclides. A future development, which holds great potential for radionuclide studies, is the use of resonance ionization mass-spectrometry (RIMS), which has already found some application in this field (Young *et al*, 1979; Hurst, 1981; Donohoue and Young, 1983; Houston, 1986; Baxter *et al*, 1987; Rimke *et al*, 1987; Fasset and Travis, 1988; Trautman *et al*, 1988; Walker, 1988; Towrie *et al*, 1989).

The development of mass-spectrometric measurement of ^{237}Np in this study revolved around the commisioning at the SURRC of an ICP-MS (PQ1, VG Elemental) instrument in 1988 and the investigation of its potential as an alternative to a NAA approach for environmental assay. There are surprisingly few determinations of ^{237}Np by mass-spectrometry. Landrum *et al* (1965) used

TIMS as an alternative approach to NAA for ^{237}Np at the sub-nanogram level. The sample was evaporated on to a Ta filament and thermally ionized using a double element approach. The mass region between 235 and 238 was scanned and ^{237}Np quantified by isotope dilution using the long-lived ^{235}Np and ^{236}Np. There were problems of ^{237}Np in the standards, which increased the uncertainty of the determination. A much more refined approach was more recently presented by Efurd *et al* (1982; 1984; 1986a; 1986b). Samples of soil material and human tissues were analyzed by this method. An excellent description and discussion of the procedures is given in Efurd *et al* (1986a). The samples are rigorously purified by solvent extraction and anion exchange steps and are electroplated on to a single filament. Quantification is by isotope dilution with ^{236}Np. There are a number of interfering elements with this procedure, mainly transition elements, which modify the signal intensity and stability. Detection limits were quoted at 1 $\times 10^{5}$ atoms (3.9 $\times 10^{-8}$ ng or 1 $\times 10^{-9}$ Bq) with a precision of 0.15% (2σ).

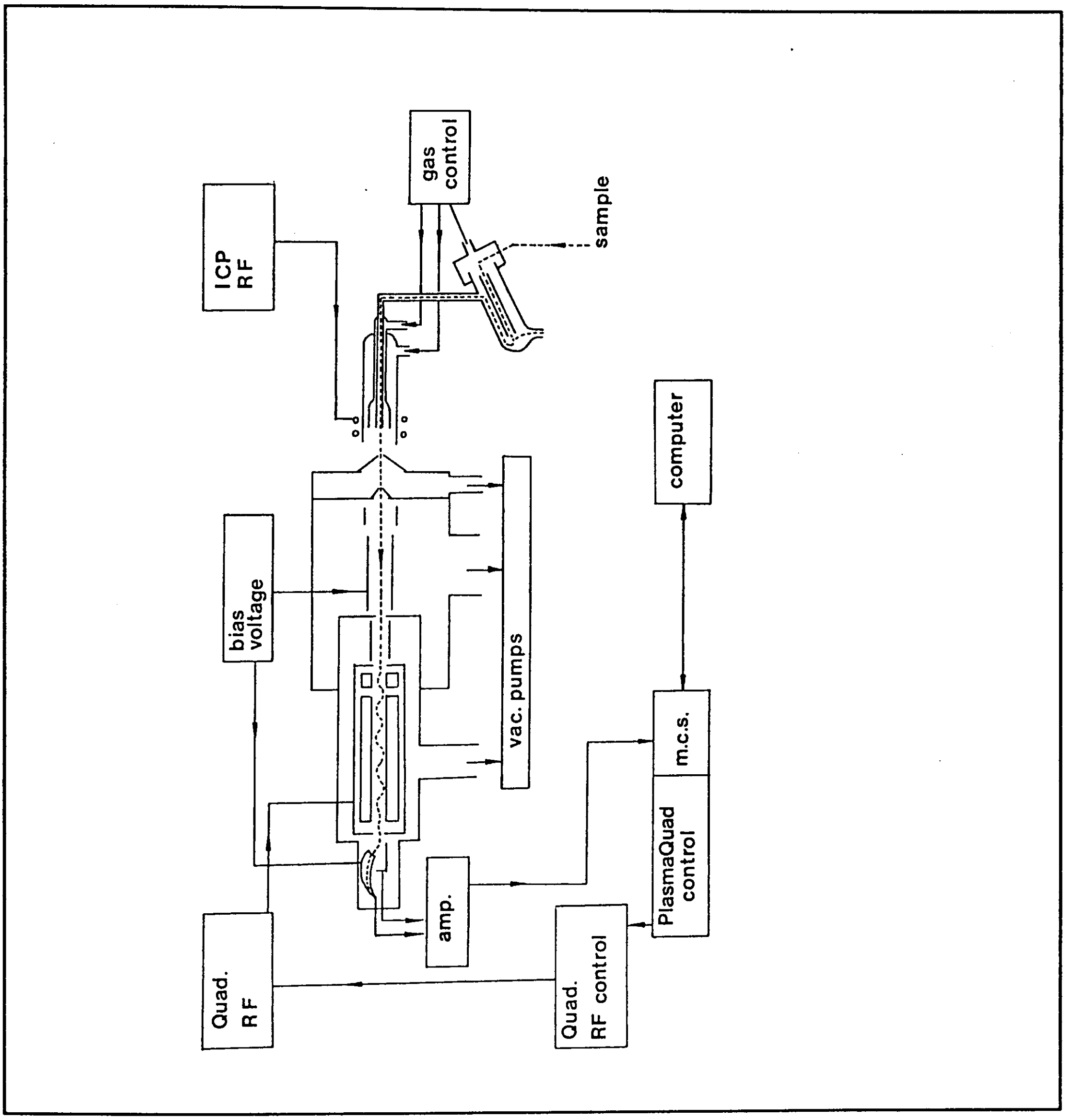
(b) description of the ICP-MS instrumentation and principles of operation

ICP-MS is a relatively recent technique which has provided a rapid, multielement analytical capability with very low detection limits and few of the problems of conventional optical techniques (Pickford and Brown, 1986). Since the production of the first commercial instrument in 1978, it has found widespread application in many branches of analysis (Gray, 1989). Its power derives from the synergistic combination of the high ionizing power of conventional argon ICP sources, used successfully for two decades in optical systems (Walsh and Howie, 1986; Meyer, 1987), with the precise and rapid mass analysis of the quadrupole mass-spectrometer systems used in routine organic analysis (Gurka *et al*, 1988). The "Achilles Heel" of its development was the ability of the system to sample efficiently the high yield of ions in the ICP at atmospheric pressure and transmit those ions to a mass analysis system at very high vacuum. The work of Gray (1975) was fundamental to the initial development by indicating that useful analytical data could be obtained from solutions sampled by plasmas at atmospheric pressure. The rapid development which followed resulted in the release of the first commercial machine by SCIEX, Canada in 1978 after much development by Houk (Houk *et al*, 1980; Houk, 1986). Interesting and detailed discussions of the development of the technique are included in the reviews by Gray and Date (1983), Gray (1985), Houk and Thompson (1988) and Gray (1989).

As far as radionuclide assay is concerned, the first applications of ICP-MS were to the determination of Th and U in geological samples (Gray and Date, 1983; Boomer and Powell, 1987; Kantipulty *et al*, 1988; Riddle *et al*, 1988; Russ, 1989). Hislop *et al* (1987) and later Brown *et al* (1987) produced critical assessments of the capabilities of the technique for long-lived radionuclides. It was concluded that currently available ICP-MS units would have advantages in sensitivity over radiometric methods for radionuclides with half-lives $>10^{6}$ years.

In view of the limited studies on actinide determination by ICP-MS, it is worth describing in some detail the features of the instrumentation, since there are many characteristics which influence the performance and behaviour of the machine and which must be appreciated in order to develop and apply the technique to specific problems. Figure 2.29 is a schematic diagram of the VG PlasmaQuad instrument used in this study. It can be divided into four sections: (i) sample introduction, (ii) ICP torch/ ion generator, (iii) plasma/ mass-spectrometer interface and (iv) quadrupole mass analyzer. Each feature will be described in turn below. The horizontally mounted torch is the same as that used for optical systems in a vertical configuration. The ions generated are fed into a mass analyzer through sampling and skimmer cones lying in front of an array of lenses, which focus the ion beam. The large pressure difference between the torch

Figure 2.29: A schematic diagram of the VG PlasmaQuad (PQ1) used in this study (VG Isotopes, 1988).

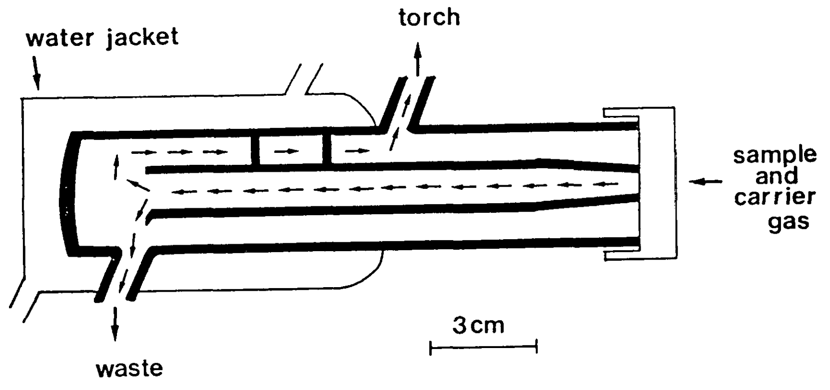


and the analyzer is obtained through a combination of rotary and diffusion pumps. The ion detection system comprises an electron multiplier and amplifier. The whole system is controlled by a central microprocessor which allows the data acquisition parameters and the quantification procedures to be defined.

(i) sample introduction

The most commonly used method of introducing a sample into the plasma is via the aspiration and nebulization of aqueous media. The particles generated should be less than 10 µm (ideally 3µm) in diameter (Houk and Thompson, 1988). Most samples are introduced in the form of aqueous solution although organic liquids can be used (Hutton, 1986). Pneumatic nebulization is the most frequently used technique for aerosol generation and is performed by a high velocity jet of gas disrupting the flow of sample. Different configurations of the two incident fluids are available to cope with either relatively high solid loading or to produce very stable aerosol flow. Ultrasonic nebulization is also known and can have up to 3 to 10 times greater aerosol generation efficiency (Olivares and Houk, 1986). The aerosol then passes into the spray chamber where condensation of the larger droplets occurs and a more uniform aerosol is produced with droplets of <10 µm diameter. A diagram of the aerosol flow through a standard spray chamber is shown in Figure 2.30. This selection step allows only 1 to 2% of the aspirated sample to be introduced into the plasma. Increased sample introduction can be achieved using a recirculating spray chamber, which can allow up to 30 minutes of measurement on 1 ml of solution (Gray and Date, 1983). The spray chamber is jacketed with a water cooling system, which is used to lower the water loading in the aerosol in order to reduce plasma cooling. It also reduces oxide levels, improves ion sensitivity and reduces thermal buffering of the plasma (Hutton and Eaton, 1986; Long and Browner, 1988). Other methods of sample introduction to

Figure 2.30: Diagram of spray chamber (double pass, Scott-type) used on the PQ1 showing aerosol flow.

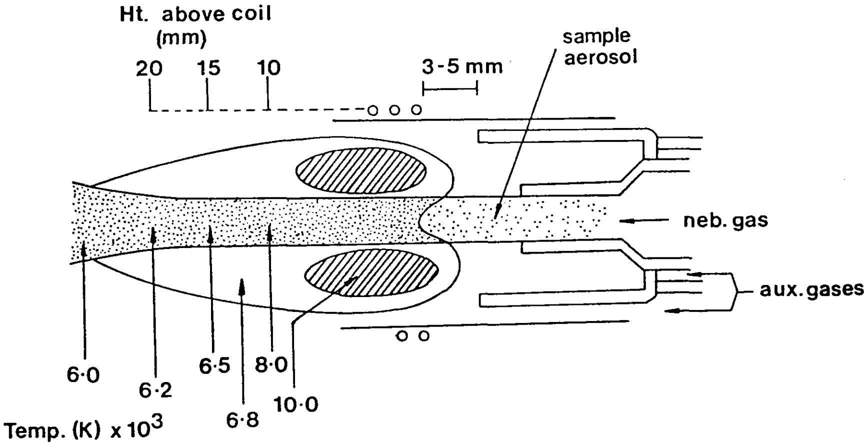


the plasma include: sparking, laser ablation, slurry nebulization and electrothermal vaporization, although many of these are at the developmental stage only (Gray and Date, 1983; Gregoire, 1988; Dean *et al*,1989; Gray, 1989; Hager, 1989).

(ii) the inductively coupled plasma

The ICP is a very efficient source of ions in a controlled, uncontaminated region of sufficiently high temperature to produce the required sample conditioning and excitation. Furthermore, it allows the rapid and complete introduction of the sample into that region (Gray, 1989). The sample is introduced via a laminar flow of argon gas to the point of atomization and excitation.

Figure 2.31: Detail of the ICP-torch showing plasma temperature variation and sample introduction point (Walsh & Howie, 1986; Gray, 1989).



The typical form of an ICP torch is shown in Figure 2.31. Three different gas flows meet at this point. The nebulizer gas containing the sample is introduced along the middle axis where it mixes with the auxiliary argon. The outer coolant gas forms the main part of the plasma and also cools the torch (Walsh and Howie, 1986). The plasma is generated by a fluctuating magnetic field induced by the RF coil (at 1 to 1.5 kW) which transfers energy to the plasma by accelerating free electrons which heat by collision. The plasma is started by a Tesla coil which introduces free electrons to overcome the dielectric resistance of the gas. The energy is transferred to the central gas stream via conduction. The distribution of temperatures induced and the plasma shape are also shown in Figure 2.31. Sample aerosol is desolvated and salt particles vaporized as they are introduced into the plasma. The molecular vapour is atomized and, as it passes out of the plasma, ionization occurs. The process takes a few milliseconds to occur (Houk, 1986) and the exact position in the torch at which it occurs is dictated by the gas flow and dielectric field pattern (Gray, 1989). On leaving the torch, the gas streams start to mix and the temperature falls to 6000 K at 10 to 12 mm from the load coil. Plasma sampling for ICP-MS and spectral observation for ICP-AES occurs here (Houk and Thompson, 1988).

The processes and temperature zones can be followed by aspirating a 1% solution of Y and studying the colours emitted (Meyer, 1987). The exact nature of the processes in operation in the plasma is still the subject of much research. The plasma is found to be in partial thermal and kinetic equilibrium over small volumes only (Bydder and Miller, 1989) and the coolant flow is found to significantly affects the asymmetry of the plasma, with potential implications for analytical performance (Bydder and Miller, 1988). It is also observed that the plasma potential and ion kinetic energy in the plasma vary with gas flow and that secondary processes, such as arcing and glow discharge are also influenced (Jakubowski *et al*, 1989). The conditions in the plasma are such that only 1% of the total mass is ionized and that the overall charge is neutral (Meyer, 1987; Houk and Thompson, 1988). The degree of ionization of the various species is described by the *Saha* equation (Houk, 1986; Houk and Thompson, 1988). The data to predict the degree of ionization are poor (Houk, 1986) but for most metals and metalloids the efficiency is estimated to be >90%.

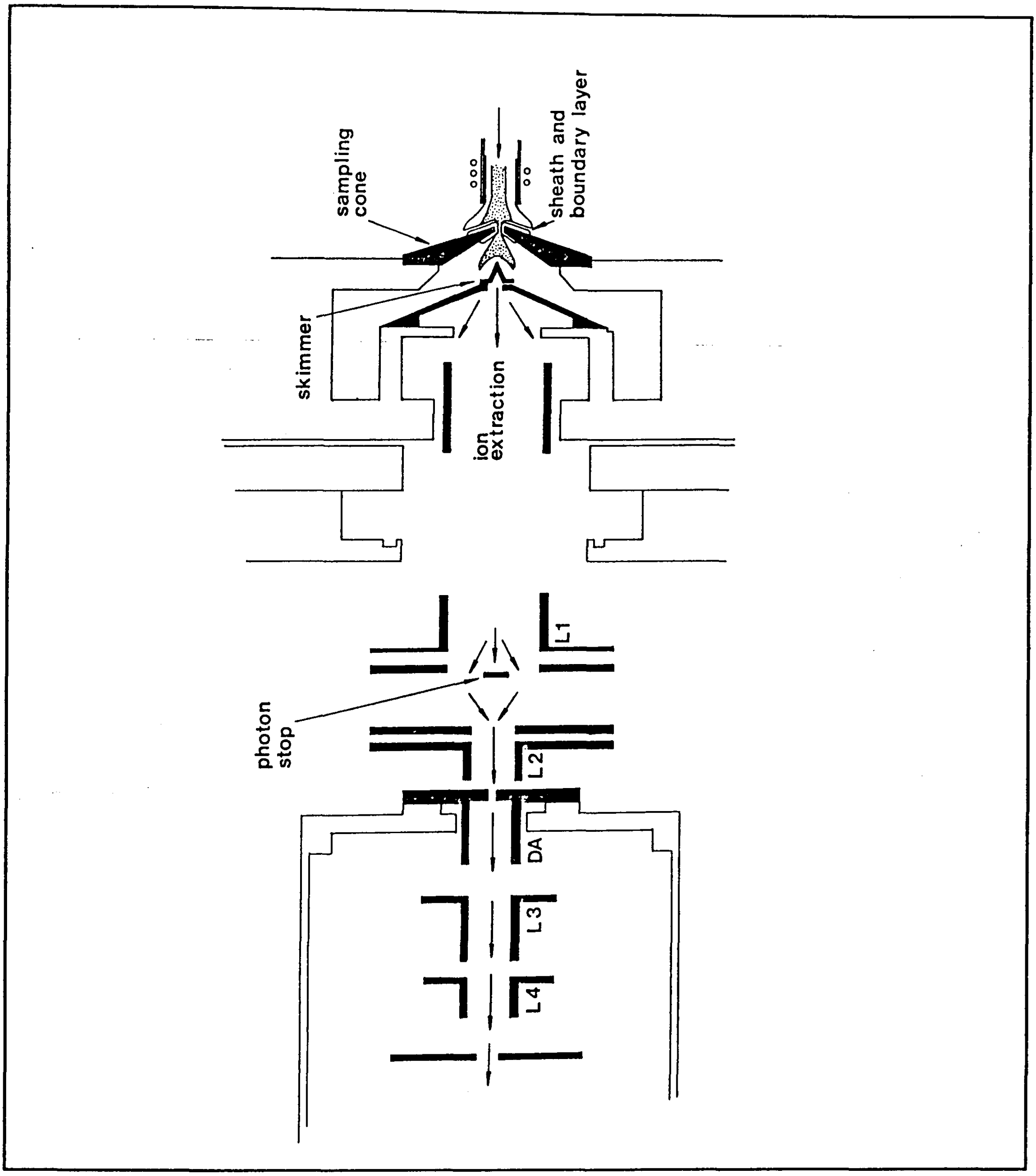
(iii) plasma sampling interface

The transport of a representative sample of the plasma ion population from atmospheric pressure into a high vacuum ($<10^{-5}$ torr) is the most crucial part of the ICP-MS system. A diagram of the VG PlasmaQuad sampling interface is shown in Figure 2.32. The sampler and skimmer cones are made of high quality nickel and contain apertures of 1.0 mm and 0.75 mm diameters respectively. The preservation of the size and condition of the surface is important to reduce sputtering of cone material, formation of polyatomic species and the build-up of and plugging of the aperture by solids (Houk and Thompson, 1988). The impinging plasma creates a boundary layer and a positively charged, sheath layer due to the cooling effect of the cone and the more rapid migration of electrons from the plasma (see Figure 2.32). This region contains high oxide levels (up to 100% for U). The main plasma passes through the layers. Behind the cone, a moderate vacuum (2 mBar) results in the supersonic expansion of the gas, cooling and freezing the ion population and thus preventing reactions between the ions (Gray, 1989). A number of "shock waves" are observed as the gas moves from the sampling cone. The skimmer cone is angled more sharply than the sampling cone to reduce further shock wave formation and is not water cooled. It is placed 6.5 mm behind the Mach disc shock wave which occurs 10 mm behind the sample cone (Gray, 1989). The efficiency of this stage is very low and only about 0.4% of the incoming ions pass on to ion focusing and mass analysis (Gray and Date, 1983).

(iv) ion focusing, mass analysis and detection

A stack of electrostatic lenses is used to focus the ions which pass on from the sampling interface, the configuration being shown in Figure 2.32. The different components of the lens system are held between -1000 and +30 V. The precise settings are variable and are part of

Figure 2.32: Detail of PQ1 plasma sampling and ion extraction (VG Isotopes, 1988; Gray, 1989).



the fine-tuning procedure for routine analysis. The extraction electrode is at a negative bias and extracts positively charged ions, whilst repelling negatively charged species and leaving uncharged molecular species to diffuse away. The currents to the lenses can be of the order of 1 mA (Houk and Thompson, 1988) and within the threshold for *space charge* effects which can change the spatial distribution of the beam. Although this has been used to explain some non-spectroscopic interferences, the mechanism is far from easy to elucidate (Gillson *et al*, 1988).

The mass analysis of the ions is performed by a quadrupole system similar to, but slightly larger than that used in organic analysis (Gray, 1989). The quadrupole system can tolerate fairly high pressures and significant spreads in ion velocities, can scan rapidly and transmit a large fraction of the injected ion beam (Houk and Thompson, 1988). However the resolution is not as high as for other types of mass-spectrometer and can be finely adjusted to give better resolution. The ion analysis system comprises three sets of radially arranged poles (two smaller units acting as filters). A sinusoidally varying voltage and a fixed DC potential on the central pole unit permit only ions of a certain mass : charge ratio to have a stable path through the fields. This also determines the resolution of the analyzer (VG Isotopes Ltd, 1988). The ions selected by the quadrupole are detected by a continuous dynode electron multiplier system, which can tolerate high count rates and operating pressures. The detector may be used at lower gain to give linear response for high ion densities. In the pulse counting mode, linear response over 5 decades in concentration is possible and can be improved to 8 decades using a mean current detection system (analogue mode) (Gray,1989). The dead time of the PlasmaQuad is 10 to 25 ns (VG Isotopes Ltd, 1988) and is accounted for in the software control.

The signal analysis is similar to that used for radiometric counting devices using a 4096 channel MCA. Scan time can be as short as 10 μs and, under the control of the central computer, skip scanning and total mass scans can be performed rapidly.

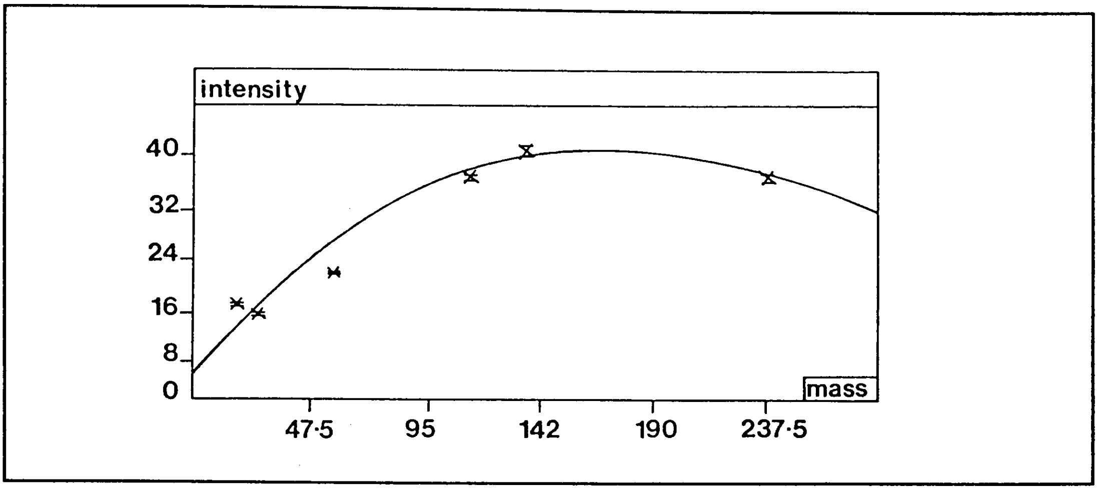
(c) operating characteristics of the ICP-MS

The practical applications of the multielement capability and very low detection limits of ICP-MS have been rapid and diverse. The excellent book by Date and Gray (1989) contains much of interest. Further applications in the earth sciences include: rare earth elements (Jarvis, 1988), trace elements in geochemical exploration (Date and Hutchinson, 1986), U and Th in tourmalines (Kantipulty *et al*, 1988) and Pt-group metals (Gregoire, 1988). Natural waters and marine biological samples have also been studied (Beauchemin *et al*, 1988a; 1988b; 1988c; Ridout *et al*, 1988; Garbarino *et al*, 1989). Clinical analysis of biological specimens for trace elements (Lyon *et al*, 1988) and studies of ultrapure materials (Paulsen *et al*, 1987a; 1987b; Luck, 1989) are further applications. During these studies there has been considerable improvement in practical detection limits, control of interferences and ion beam stability.

(i) plasma ion population and system response

The plasma equilibria are controlled by the properties of Ar and O and, to a lesser extent, H. The introduced matrix does not perturb those equilibria up to 1% concentration. The ion population is balanced by electronic charge and the system response for any element is the same for identical concentrations. However, this depends on the precise instrument settings which vary across the mass range and must be set at a compromise (Gray, 1989). When the mass range is scanned in the semi-quantitative mode, using single conditions, the response curve over the mass range shown in Figure 2.33 is obtained. This can be used to calibrate for approximate (± factor of 3) concentrations. More accurate determinations can be made using

Figure 2.33: Variation in PQ1 response with mass.



sets of specific standards.

(ii) backgrounds and peak interferences

The level of the background and the coincidence of peaks from the plasma or sample matrix with the analyte peak are important features to understand. The contribution of these interferences of non-analyte counts can be derived from: continuum background and background peaks, oxide and doubly charged ions, polyatomic ions, isobaric overlap, matrix suppression and physical or non-specific effects (Riddel *et al*, 1988).

(iii) continuum background and background peaks

When aqueous solutions are introduced, there are no background interferences above mass 80 except for Xe^+ and Kr^+ impurities in the argon gas (Gray, 1986; Houk and Thompson, 1988). The general background continuum is very low, of the order of a few counts (see Figure 2.34) and is derived mainly from stray photons which pass the photon stop (see Figure 2.32) and is particularly sensitive to vacuum UV photons from the plasma (Gray, 1986; Kawaguchi *et al*, 1988). There is also some contribution of charged species from contamination, memory effects and random electrical noise (Gray, 1975; Kawaguchi *et al*, 1988). The main peaks observed in the background spectrum are due to the isotopes of Ar, O and H as well as contributions from the acid solution used to introduce the sample and air entrained by the plasma (Tan and Horlick, 1986; VG Isotopes, 1988). Table 2.16 lists the interferences derived from water and plasma gas and from a number of mineral acids and the elements affected. The use of nitric acid is thus the recommended sample introduction medium due to the lowest abundance of interfering species. This is attributed to the higher ionization energy of N compared to Cl and S (Ridout *et al*, 1988). The first row transition metals are the most affected group of elements.

The abundance of these peaks varies with the PlasmaQuad operating conditions and the mechanisms operating in the plasma, much of which are uncertain (Long and Browner, 1988).

Table 2.16: Potential isobaric interferences derived from plasma gas, water, hydrochloric, perchloric, nitric, sulphuric and phosphoric acids (adapted from: VG Isotopes, 1986).

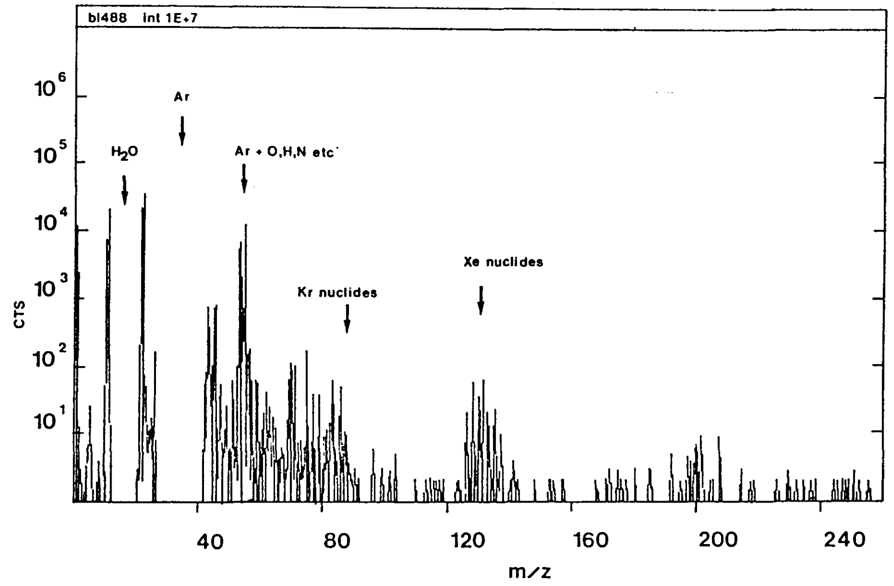
mass	species	interfered isotopes
19	OH_3^+	(^{19}F)
20	$^{40}Ar^{2+}$	(^{20}Ne)
28	N_2	^{28}Si
29	N_2H	^{29}Si
30	NO	^{30}Si
31	^{15}N, NOH	^{31}P
32	O_2	^{32}S
33	O_2H	^{33}S
34	$^{16}O^{18}O$	^{34}S
35	$^{16}O^{18}OH$, O_2H_3	^{35}Cl
36	^{36}Ar, $^{18}O_2$	^{36}S
37	$^{18}O_2H$, ^{36}ArH	^{37}Cl
39	^{38}ArH	^{39}K
40	^{40}Ar	^{40}Ca
41	^{40}ArH	^{41}K
47	PO	^{47}Ti
48	^{32}SO	^{48}Ti
49	^{32}SOH	^{49}Ti
50	^{34}SO	$^{50}Ti/^{50}V/^{50}Cr$
51	^{34}SOH, ^{35}ClO	^{51}V
52	$^{35}ClOH$	^{52}Cr
54	$^{37}ClOH$, ^{40}ArN	$^{54}Cr/^{54}Fe$
55	$^{40}ArNH$	^{55}Mn
56	^{40}ArO	^{56}Fe
63	PO_2	^{63}Cu
64	$^{32}S_2$, $^{32}SO_2$	$^{64}Zn/^{64}Ni$
66	$^{34}SO_2$	^{66}Zn
70	$^{35}Cl_2$	$^{70}Zn/^{70}Ge$
71	ArP	^{71}Ga
72	$^{35}Cl^{37}Cl$	^{72}Ge
74	$^{37}Cl_2$	$^{74}Ge/^{74}Se$
75	$^{40}Ar^{35}Cl$	^{75}As
76	$^{40}Ar^{36}Ar$	^{76}Se
77	$^{40}Ar^{37}Cl$	^{77}Se
78	$^{40}Ar^{38}Ar$	^{78}Se
80	$^{40}Ar_2$	^{80}Se

The presence of water in the plasma has already been shown to be important and can be reduced by cooling the spray chamber (Hutton and Eaton, 1988). If high stability of these peaks is found, simple background subtraction may be used to remove the interference.

(iv) oxide, hydroxide and doubly charged species

The formation of these species may cause isobaric interference with other masses if they are formed from the analyte, the population of the monocharged analyte ions is reduced and hence the instrument response suppressed. Under normal operating conditions, oxide levels are the most important and are expected to be of the order of 5% (Houk *et al*, 1980; Gray 1989). The precise level depends on operating conditions, elemental composition of the plasma, bond energies of the species and ionization energies of the element under consideration (VG Isotopes, 1987). The potential spectral interferences have been tabulated for a wide range of elements (Vaughan and Horlick, 1986). The instrumental parameters which have most effect on these levels have been studied in some detail and include the RF power and nebulizer flow (Gray and Date, 1983; Long and Brown, 1986; Lichte *et al*, 1987, Longerich *et al*, 1987; Ting and Janghorbani, 1988). In the case of nebulizer flow, the effect on ion levels appears to result from the change in the position of the plasma with respect to sampling cone, ie sampling depth (Vaughan and Horlick, 1986). Less significant effects arise from the solution uptake rate and the auxiliary and coolant gas flows (Ting and Janghorbani, 1988). Changes in plasma sampling geometry again being the proposed explanation. The behaviour of doubly charged and hydroxide species is very similar but their levels are much lower than those of the oxides and the positions in terms of instrument settings are slightly different. The "optimization" of instrumental parameters to give a maximum response for singly charged ions and minimum response for doubly charged species, oxides and hydroxides is complex and a compromise is

Figure 2.34: Background spectrum of entire mass range for 1% v/v HNO_3 showing plasma and solution-derived peaks. Main Ar and H_2O peaks are skip-scanned to preserve detector life.



usually required.

(v) polyatomic ion formation

It is possible for the analyte and matrix ions and atoms to undergo reactions with the plasma ions and form relatively complex polyatomic species. However, MAr^+ species are $<10^{-5}$ of M^+ and are the only significant species additional to those described above (Houk and Thompson, 1988).

(vi) isobaric overlap

The existence of several isotopes of an element (both natural and synthetic) means that, whilst isobaric interferences between neighbouring elements can be a serious problem (Lichte *et al*, 1987; Longerich *et al*, 1987; Gray, 1989), it is often possible to view a mass region for the analyte free from interference. A number of authors have produced algorithms for this process although instrument stability must still be accounted for using internal standards (Gabarino and Taylor, 1987; Lichte *et al*, 1987).

(vii) non-spectroscopic interferences

This category bulks together interferences encountered in the ICP-MS technique which cannot be accounted for by specific spectral observations. The presence of fairly high concentrations of matrix elements in the aspirated sample has generally been found to depress the analyte signal, although, in some situations, enhancement has been observed (Houk *et al*, 1980; Gregoire, 1988; Houk and Thompson, 1988; Gray, 1989). The more easily ionizable elements (Na, K, Cs, Ca etc) contribute most to matrix suppression (Houk *et al*, 1980; Gray and Date, 1983; Olivares and Houk, 1986; Garbarino and Taylor, 1987; Longerich *et al*, 1987). In severe cases, even the ionization of argon can be depressed (Olivares and Houk, 1986). At concentrations >0.1%, the easily ionizable, heavy elements cause more suppression than the lighter elements and suffer less from suppression effects as analytes (Houk and Thompson, 1988; Gray, 1989). The explanation of these observations is unclear. It has been attributed in part to blockage of the apertures in the skimmer and sampling cones (Houk *et al*, 1980; Olivares and Houk, 1986; Williams and Gray, 1988). More recently, a mechanism involving space charge effects and ion beam diffusion in the skimmer region has been modelled and found to fit experimental observations (Gillson *et al*, 1988). To minimise these effects, samples may be diluted to reduce salt loading of the plasma or the technique of isotope dilution can be used as the matrix effects will be the same for all isotopes of an element. Other non-spectroscopic interferences may result from memory effects from traces of solution remaining trapped in part of the system or as oxides deposited on sample and skimmer cones.

(d) the use and optimization of ICP-MS for ^{237}Np and other actinides

The discussion above has described a number of operational parameters which affect the relative proportion of analyte M^+ ions present in the plasma. The two most important settings affecting this distribution are RF power and nebulizer flow. For routine analysis, compromise settings are usually adopted. The levels of ^{237}Np in the environment were expected to be close to or below the detection limit of the ICP-MS and some form of preconcentration required. It was decided to study the effect of the nebulizer flow on the response of selected actinides (^{237}Np, ^{232}Th and natural U) and the generation of oxide and doubly charged species. ^{115}In was also included for comparison as it is routinely used as an internal standard to correct for response variation during sample runs and is used to tune the instrument daily. Solutions of standards of the metals were aspirated in 1% v/v HNO_3. The nebulizer flow was varied between 0.6 and 0.9 dm^3 min^{-1} and the mass regions of the singly charged nuclides, oxides and doubly charged species monitored. All other instrument parameters were kept constant (see Table 2.17).

Table 2.17: PQ1 instrument settings used during actinide optimisation study.

forward power (r.f.)		1357 W
reflected power		< 5 W
auxillary gas flow		0.41 l min^{-1}
coolant gas flow		14.2 l min^{-1}
sample solution uptake rate		0.7 ml min^{-1}
nebuliser type		v-groove (Kel-F)
spray chamber		double pass Scott, water cooled
load coil - sampling cone distance		10 mm
peak jump parameters:	points per peak	3
	dwell time	1 x10^5 μs
	peak jump sweeps	100
	DAC steps between points	10

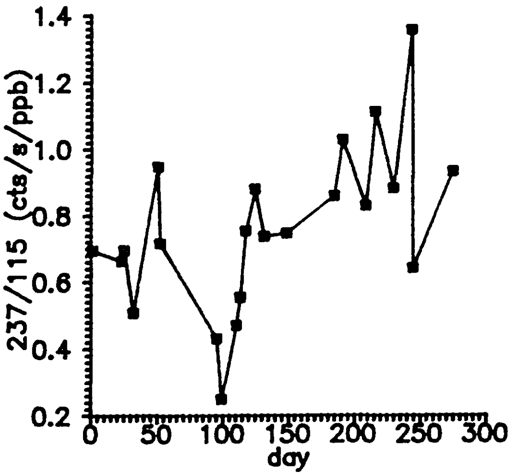
The response variation is shown in Figure 2.36 and a number of features are worth noting. Optimum flow rates for Th^+, U^+ and Np^+ production are equal at 0.725 dm^3 min^{-1}. This also corresponds to a minimum for the doubly charged and oxide levels. The oxide levels are all between 1 and 5% of the single, positively charged ion levels. The response variation at optimum flow (integrated area counts per second per ppb) is in the order ^{232}Th> ^{238}U> ^{237}Np which is in inverse correlation with the order of first ionization energy (Katz *et al*, 1986b). The doubly charged species levels tend to be higher than the oxide levels except in the case of Th which has significantly higher oxide abundances.

The variation between the actinide and ^{115}In response is more significant. Oxide levels are also a few %, despite a lower ionization potential. However, optimum ^{115}In response is obtained at a nebulizer flow of 0.710 dm^3 min^{-1}. Although there is only a 2% difference in flow rate, the response of the actinide nuclides is reduced by 25%. This important result suggests that the distribution of species in the plasma is very sensitive to sampling position and that, for analyses of groups of elements close to the lower limit of detection, it is advantageous to determine a series of optimal operating conditions and not to accept the compromise settings suitable for routine analysis.

(e) background, detection limits and instrument stability

The bulk of the analytical determinations were carried out periodically over a period of approximately a year between April 1988 and 1989. The data collected have enabled a unique insight into the long-term behaviour of an instrument which has been intensively used and has had a wide variety of analytical demands placed on it. Throughout the analytical programme, 50 ppb of ^{115}In were added to all samples and standards used to correct for instrument drift during analysis and the standards used for ^{237}Np calibration and the instrument operating parameters were kept constant. Figure 2.35 shows the variation with time in the ICP-MS response per ppb for the ratio of integrated counts per second of Np/ In. One would expect that this normalized ratio would remain constant over the entire timescale and that it would be close to unity as the ionization potentials of the two elements are close infact, there is no such pattern in the results highlighting the fact that In and Np behave very differently and very erratically in the instrument. The use of ^{115}In as an internal standard is not invalidated, as the different concentration standards used for ^{237}Np behave in a consistent manner and the calibration curves produced from them are highly linear (see section 2.3.4f). All plots show

Figure 2.35: The long-term stability of the PQ1 with time. Ratio of single ion response ppb^{-1} [day 1: 6/6/88, day 274: 11/3/89].



sharp changes in response which coincide in many cases with servicing of the instrument and there is generally an improvement in performance subsequent to these events. The short term instrument stability is shown in Figure 2.37. A plot of ^{115}In response with time through analysis for three long runs shows that the relative response levels are different, as would be expected from Figure 2.35, but that the instrument stability in the short term is not a problem.

Figure 2.36: Variation in actinide and In ion population with nebuliser flow rate (a) M^+, (b) MO^+/M^+ for Th, U and Np.

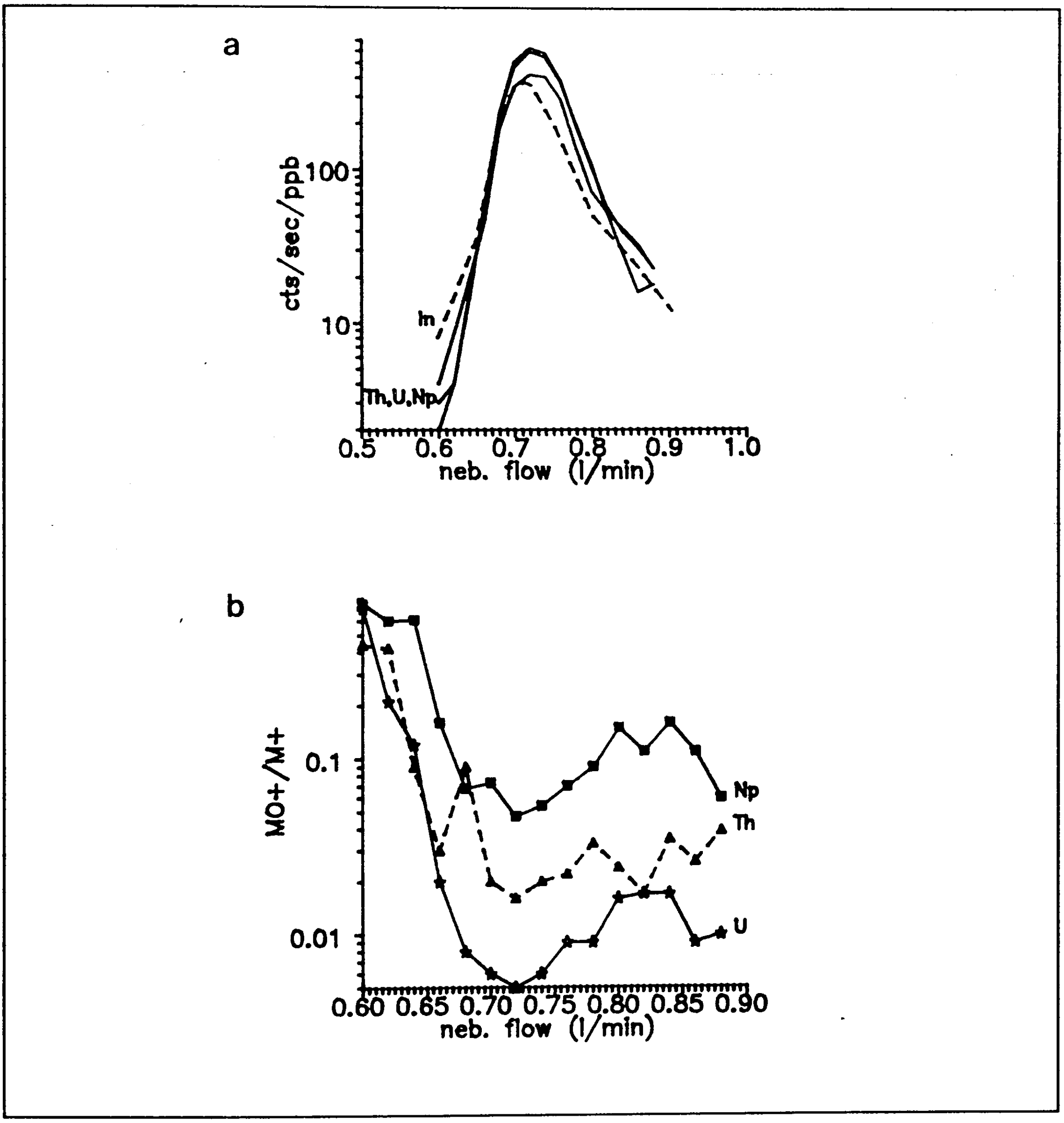
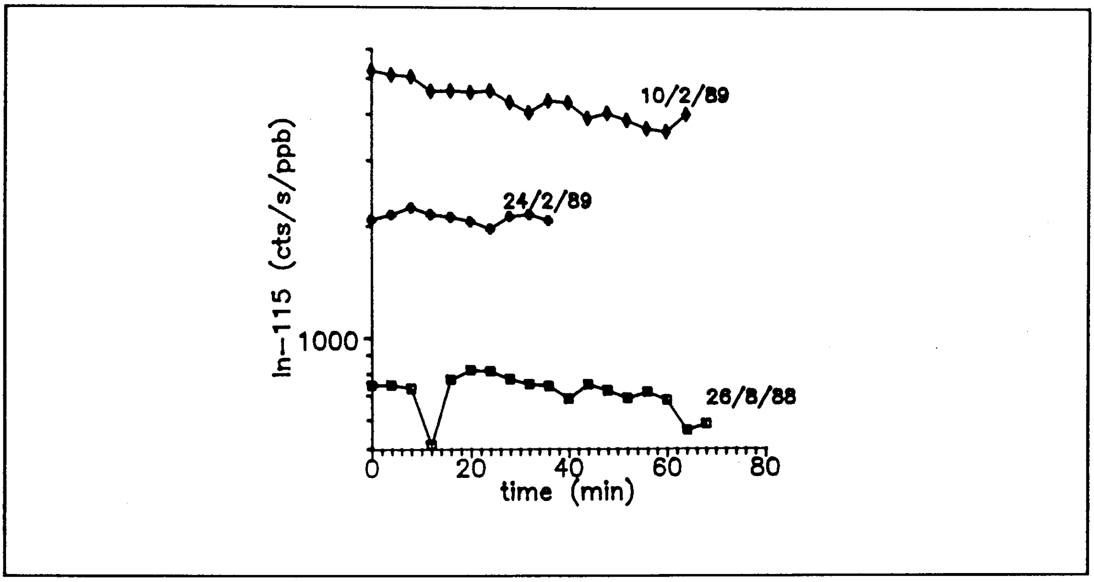


Figure 2.38a shows a background spectrum obtained from a short scan of the actinide mass region whilst aspirating 1% v/v HNO_3. The absence of any peaks from plasma components or the acid is obvious. The general continuum is low and stable and of the order of a few counts. The plot of background variation at 237 amu throughout the period of analyses (Figure 2.38b)

shows a variation of over an order of magnitude and the same erratic behaviour found in Figure 2.35. In general the level is <10 counts and frequently below 5. The detection limit of the system based on a 5 count background and the 3 x √background criterion is 1.5 x10^{-3} ppb. The factors which affect both the background and particularly the instrument response will determine the operational limit which, from the discussion above, is expected to vary daily. The translation of this detection limit to activity has been made in Table 2.18. For a number of nuclides with half-lives ≥ 10^6 years, the limits are close to if not an improvement on radiometric methods.

Figure 2.37: Short term stability of PQ1 using ^{115}In response (integrated count s^{-1} ppb^{-1}).



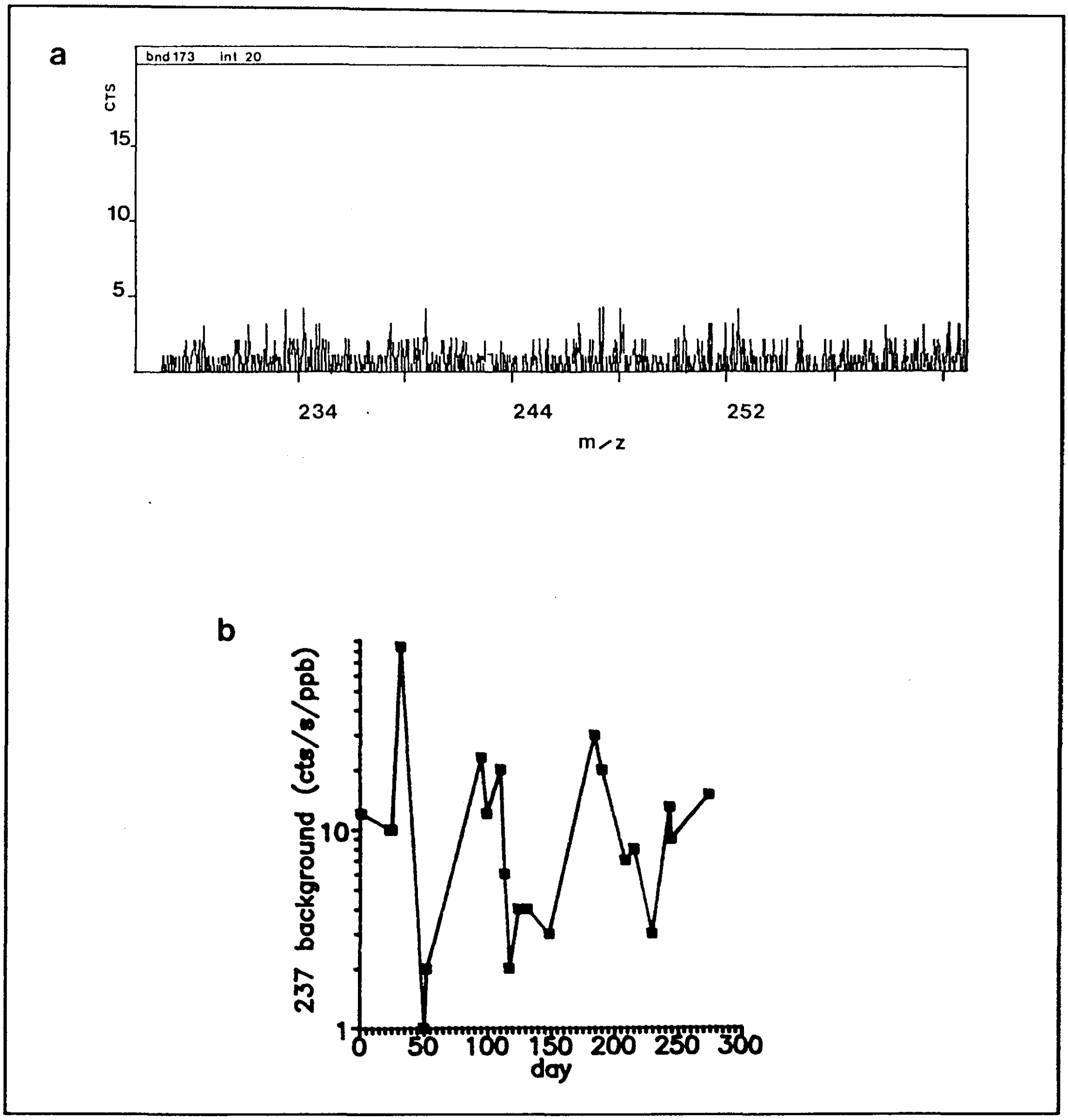
(f) calibration and quantification of ^{237}Np

All ^{237}Np analyses were performed using the multielement scan facility of the PlasmaQuad software (VG Isotopes, 1988) with ^{115}In as an internal standard to correct for instrument drift during runs. Standards of ^{237}Np were prepared by dilution of a stock solution of high purity ^{237}Np in 1M HNO_3 (CIS, UK) certified to ± 1%. Figure 2.39 is an example of a calibration curve produced using ^{115}In. The linearity is excellent over 2 or 3 orders of magnitude and the correlation coefficient 0.999.

(g) studies on the chemical processing of samples for ^{237}Np and actinide determination by ICP-MS

The application of ICP-MS to actinide determination in environmental samples, on the basis of detection limits, appears advantageous for a number of nuclides including ^{237}Np. The main interferences described above have little effect in the high mass region of the spectrum and any isobaric interference is likely to be derived from the actinides themselves. The mass region

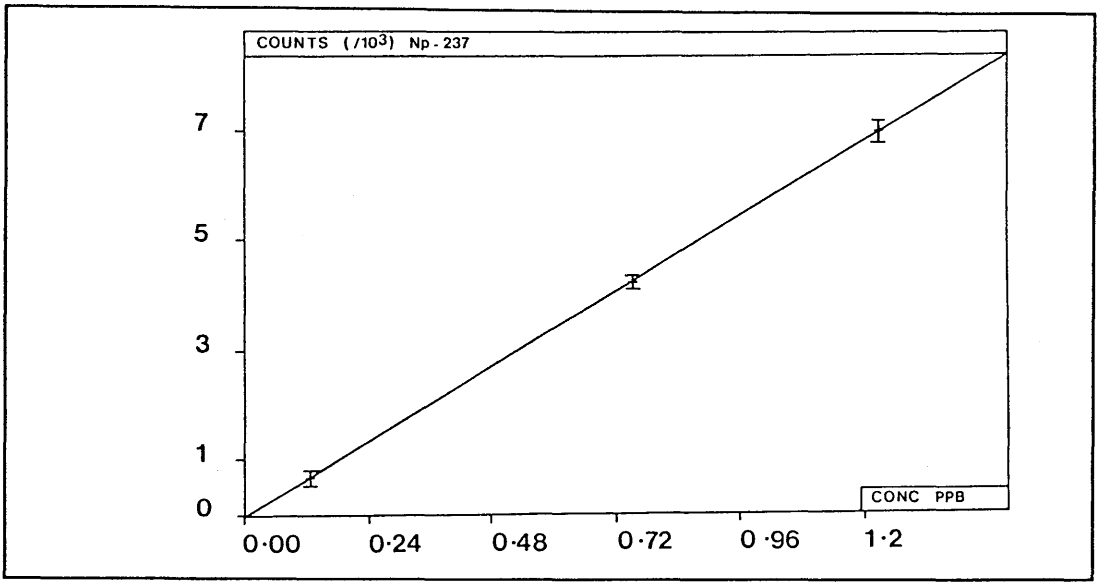
Figure 2.38: Actinide background (a) mass spectrum of actinide region (cts s^{-1} ppb^{-1}), (b) variation of background at mass 237 with time (cts s^{-1} ppb^{-1}).



between 232 and 241 amu covers a wide range of natural and anthropogenic nuclides of interest. There are two potential isobaric overlaps. At mass 238, the main uranium isotope overlaps with the relatively short-lived ^{238}Pu, routinely and more sensitively determined by α-spectrometry and at mass 241 there is the coincidence of short half-life Pu and Am nuclides. The use of ICP-MS would be inappropriate for the determination of most short-lived nuclides, considering the far superior sensitivity of conventional radiometric techniques, but may be of use for nuclides which emit radiations which are difficult to determine using conventional radiometric methods. The only situation where this interference would present a problem would be in the determination of low levels of ^{238}U in the presence of relatively high amounts of ^{238}Pu, an unlikely scenario the environmental context. Other likely interferences are of the non-spectroscopic type, but, these are of least importance at the high mass range (Houk and Thompson, 1988).

The levels of anthropogenic actinides in the environment are generally much lower than the lower limit of detection of this technique. Therefore direct analysis of dissolved samples only feasible for Th and U, which commonly occur at ppm levels in soils and sediments (Davies,

Figure 2.39: External calibration curve for the quantification ^{237}Np.



1980). Over 30 years of analytical development, numerous schemes for the preconcentration of actinide nuclides for assay have been developed primarily using radiometric methods, where chemical and radiochemical purity must be high. These techniques are ideally suited to the prime requirements of ICP-MS determination which are bulk matrix reduction and some preconcentration without a need for stringent purity. The analytical procedures studied in section 2.3.3 would appear to meet these requirements completely.

A number of studies were carried out for the determination of ^{237}Np, ^{239}Pu and ^{240}Pu in environmental samples. Figure 2.40a is an example of a sample of Ravenglass silt which has been partially purified using the analytical scheme from section 2.3.3f. The sample represents the 5M HCl "Np wash" from the anion exchange separation. The spectrum was collected in a few minutes of scan time and shows a wide range of natural and anthropogenic nuclides. $^{232}Th^+$, $^{234}U^+$, $^{235}U^+$ and $^{238}U^+$ are present at very high levels. The ratios of the uranium peaks, to the first approximation, show a natural mass ratio. There appears to be a small peak at mass 236, which is unlikely to represent $^{235}U^1H^+$, which would be at a fraction of a % of the ^{235}U peak. It may be attributed to the presence of ^{236}U ($t_{1/2}$ = 2.4 x10^7 years) which has been observed in plants and sediments from the Ravenglass area (Hamilton and Stevens, 1985). At mass 237 is $^{237}Np^+$, the nuclide under study, somewhat dwarfed by the $^{238}U^+$ peak next to it. The small shoulder on the high mass side of the Np peak is a *precursor peak* and is an artifact of the signal processing of the ^{238}U peak, due to non-ideal fields in the quadrupole at high

Table 2.18: Theoretical ICP-MS detection limits ($3x\sigma_b$) in Bq/ml for selected actinides, based on a 5 count/sec background (0.0015 ppb) from a 10 ml aspirated solution.

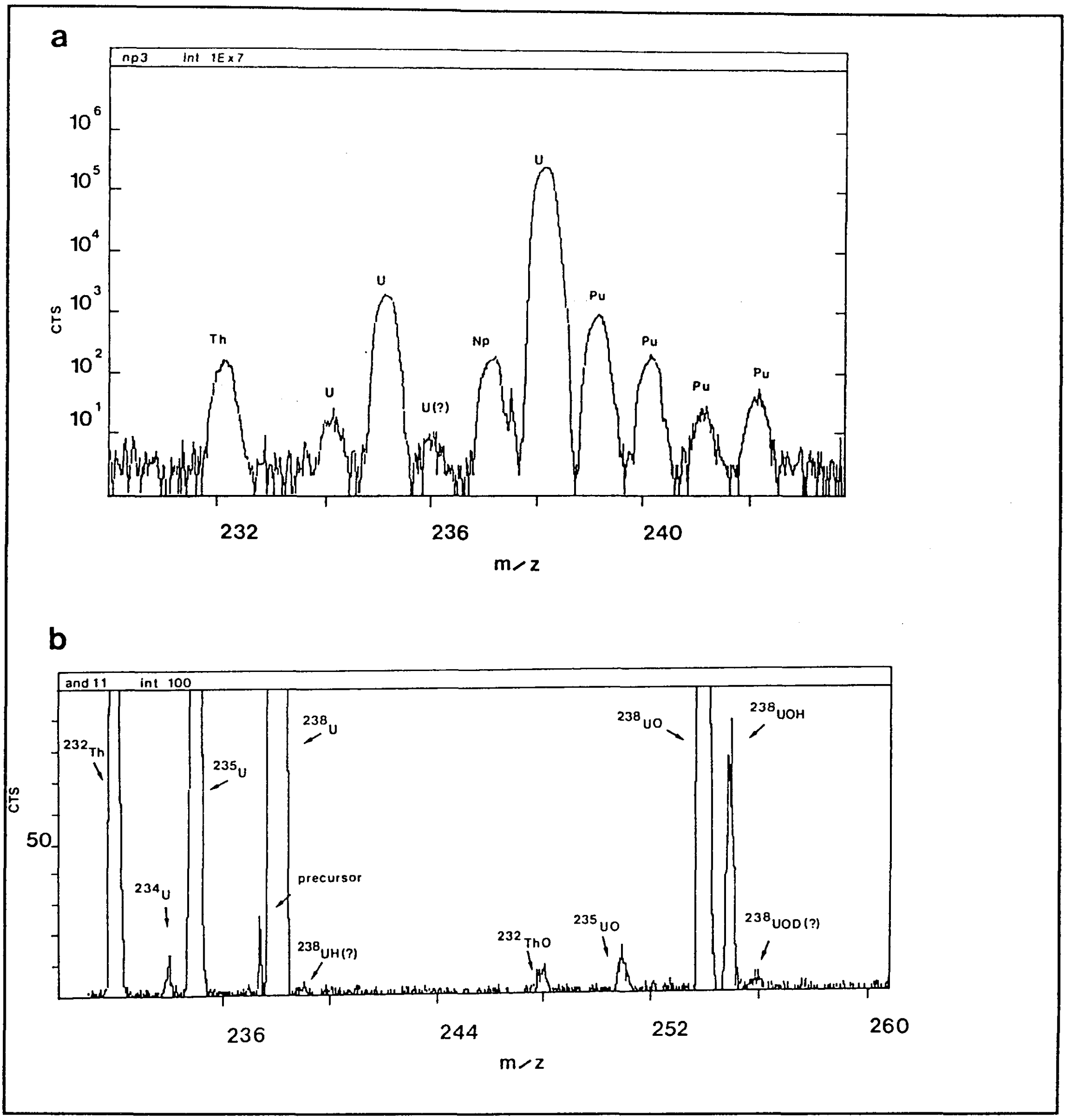
nuclide	half-life (years)	detection limit (Bq ml^{-1})
^{232}Th	1.14 x10^{10}	8 x10^{-9}
^{234}U	2.47 x10^{5}	3 x10^{-4}
^{235}U	7.10 x10^{8}	1 x10^{-7}
^{238}U	4.51 x10^{9}	2 x10^{-8}
^{237}Np	2.14 x10^{6}	4 x10^{-5}
^{238}Pu	86	0.97
^{239}Pu	2.4 x10^{4}	3 x10^{-3}
^{240}Pu	6.6 x10^{3}	1 x10^{-2}
^{241}Pu	13.2	6.2
^{241}Am	458	0.20

resolution which affects high mass numbers in particular (VG Isotopes, 1988). This has subsequently been remedied on the SURRC instrument by simple wiring adjustments on the quadrupole. Since the spectrum is from a sample that represents the degree of processing recommended by Byrne (1986) for pre-irradiation processing of samples for ^{237}Np assay by NAA, from the intensity of the peak at 238 amu it is not surprising that the problems of ^{239}Np generation by ^{238}U activation were encountered for that method.

Figure 2.40b is an example of the mass-spectrum from a sample of natural Th and U over the mass region 230 to 260 amu, ie the "natural background" with potential interference in the determination of anthropogenic actinides. The spectrum shows the presence of the singly charged ions and the precursor peak noted above, as well as the various oxide and hydroxide peaks at higher masses.

The peaks observed at masses 239, 240, 241, and 242 in Figure 2.40a can all be attributed to nuclides of plutonium. The ^{242}Pu ($t_{1/2}$ = 3.8 x10^{5} years) was added to the sample before processing. The mass ratio of 239 : 240 is 5.5 ±0.9 (2σ). The presence of plutonium in the 5M HCl wash indicates that the reduction step for Np was not sufficient to stabilize Pu^{III}, which is not retained on the column. The 5M HCl wash is at low enough concentration for the distribution coefficients of the sorbed actinides to become sufficiently small enough to be washed from the column in appreciable amounts (see section 2.2.4). The presence of the peak at mass 241 has been attributed to ^{241}Pu rather than ^{241}Am, for which ICP-MS is more sensitive, for a number of reasons. The presence of ^{241}Am is not expected due to its chemical behaviour during the analysis. Its trivalent oxidation state is preferred and, like Pu^{III} (Cleveland, 1970), does not form stable, negatively charged chloro complexes and hence passes through the anion

Figure 2.40: Mass spectra showing multiple actinide nuclides (a) partly purified Ravenglass silt (anion exch, Pu-242 internal std), (b) natural Th & U showing main single ions peaks and those attributed to polyatomic ions (int. cts s^{-1}).



exchange column. At least three acid washes follow the sample sorption step. Thus traces of the sample solution are unlikely to remain. The samples are γ-counted before aspiration, to determine the chemical yield from ^{239}Np. Since ^{241}Am emits a strong γ-ray at 60 keV, its detection should be easy on a Ge(Li) detector. This peak was not observed in any of the samples counted. The final piece of evidence against ^{241}Am is provided by the ratios of the peaks at 241, 240, and 239. Discharges of ^{241}Pu from Sellafield are 30 times the activity of those of ^{239,240}Pu. The ICP-MS spectrum gives values of 5.5 (239 : 240) and 35 (239 : 241) by mass for plutonium nuclide ratios. The 239 : 240 ratio on an activity basis is thus 1.5. Since

$$A_{241}/\,A_{239,240} = n\lambda_{241}/\,n\lambda_{239} + n\lambda_{240} = 30$$

then the expected number of counts from ^{241}Pu (n_{241}) is 29. The observed, background-corrected value is 28.

Figure 2.41: Mass spectrum of the neptunium fraction from a sample of Ravenglass silt purified by ion exchange and solvent extraction steps (int. cts s^{-1}).

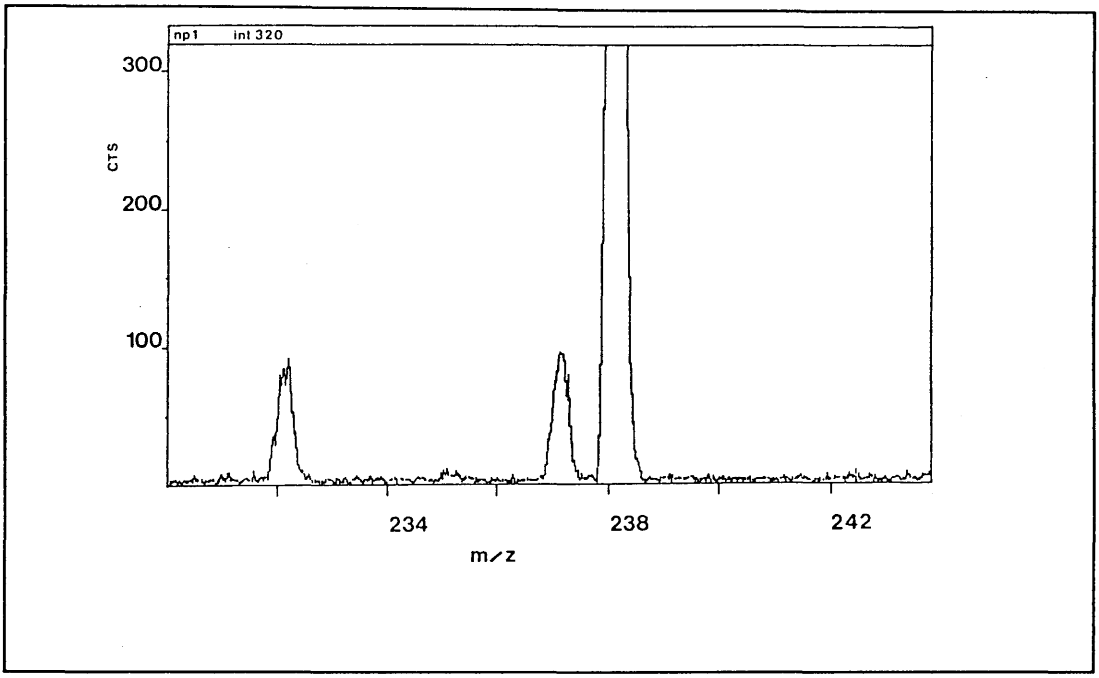


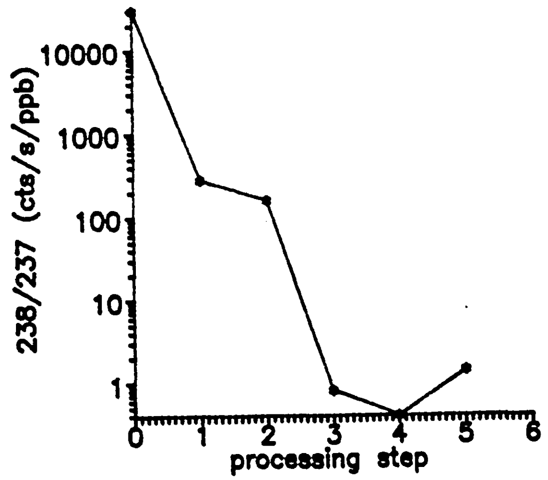
Figure 2.41 is an example of a sample of silt taken a step further in the analysis procedure, with one cycle of solvent extraction using TTA. The increase in chemical purity is obvious from the greatly reduced Th and U peaks and the absence of any nuclides of plutonium. The uranium precursor is also absent. The graph in Figure 2.42 illustrates the relative decontamination of ^{237}Np from ^{238}U with the degree of chemical separation using the method described in section 2.3.3 and assuming an initial starting concentration of 3 ppm for uranium (Davies, 1980; Hamilton and Stevens, 1985). It is evident that there is no real improvement in uranium "decontamination", after two additional cycles of TTA Np extraction, post ion exchange. The levels remaining were not found to interfere with the α-spectrometry method (section 2.3.5) and cause no further interference with the neutron activation analysis (section 2.3.3). This separation procedure also seemed well suited to the ICP-MS technique, since the level of uranium was greatly reduced by the inclusion of a single additional step, removing the potential of precursor interference and the potential of peak overlap from the down-mass tailing of a large 238 peak. The tailing of a peak into adjacent mass regions is instrument dependent. It can be described by the *abundance sensitivity* of the mass-spectrometer. In the ICP-MS scanning mode this can be simply defined as the ratio of the area of a mass window at a specific mass number (m) to the area of the same mass window at m±1 mass units (Russ, 1989). It is affected primarily by the size of the window used to monitor mass regions and can be increased (ie potential overlap

reduced) by reducing the mass window or increasing instrument resolution. This however, results in a reduction in instrument sensitivity. In some cases the application of a potential to the quadrupole rods, reducing ion energies, has been found to be helpful in increasing the abundance sensitivity (Russ, 1989). For the specific case of ^{237}Np determination in the presence of ^{238}U, it was decided that an analytical scheme comprising an anion exchange separation followed by a single cycle of TTA solvent extraction was the best approach. High instrument sensitivity could thus be maintained, essential for the determination of ^{237}Np at the concentrations expected in the environment and the threat of interference from mass 238 removed without compromising instrument performance.

Samples for analysis by ICP-MS were presented in 1% v/v HNO_3. Instrument blanks were run prior to each analysis using 1% v/v HNO_3. The ^{237}Np content of the samples was quantified using external calibration curves constructed from a series of standard solutions. ^{115}In was used to correct for instrumental drift in the standards and all samples. The chemical yield determinations were by γ-spectrometry of ^{239}Np in the same way as performed for NAA determinations. It was simplified somewhat by the absence of any geometry calculation as the samples were counted in the same scintillation vial 10 ml geometry before aspiration into the ICP-MS. The method was validated by a series of cross-comparisons and replicate analyses of a bulk sample of Ravenglass silt. The results are presented in Chapter 3.

Routine analyses of samples of soils and sediments were performed on aliquots from 2 to 120 g. The sizes of the anion exchange columns and reagent volumes were varied accordingly. Blank runs using 10 g of acid-washed sand were run periodically. All results were less than the

Figure 2.42: Relative decontamination of U from Np during chemical separation [(0) raw sample, (1) 5M HCl eluate from anion exchange, (2) anion exch. + 1x TTA solv extract, (3) anion exch. + 2x TTA, (4) anion exch. + 3x TTA, (5) anion exch. + 4x TTA].



lower limit of detection for the run conditions used.

In parallel to the main analytical programme, a number of supplementary studies were carried out. The initial studies (see Figure 2.40a) suggested that the simultaneous determination of Np and Pu nuclides, with minimal chemical processing, was perhaps the greatest attraction of this technique. This approach would also provide additional information in terms of nuclide mass ratios with reduced chemical processing and detection time.

A number of experiments using TTA solvent extraction cycles instead of anion exchange were performed on aliquots of Ravenglass silt. The results obtained were in good agreement with the replicates from routine analysis but the chemical recoveries were much lower than expected in nearly all cases and the subsequent ICP-MS assays produced data of poor precision. Plutonium was not extracted under these conditions. These effects may arise from the increased solubility of TTA in the aqueous phase which is known to occur at high salt loading (Poskanser and Foreman, 1965 and section 2.2.3). Semiquantitative analysis of the stable element contents of these samples revealed Na, Al, Mg and Zn at ppm levels. Runs using single anion exchange columns gave satisfactory agreement with much better chemical recoveries. However, the uranium decontamination was not as good and the need for larger sample aliquots as the ^{237}Np concentration decreased meant that the additional processing was prudent if not essential. The determination of the mass abundances of the ^{239}Pu and ^{240}Pu nuclides in a number of samples was performed using ^{242}Pu as an isotopic diluent. The procedure used and the information gained are described and discussed in section 3.8 of Chapter 3.

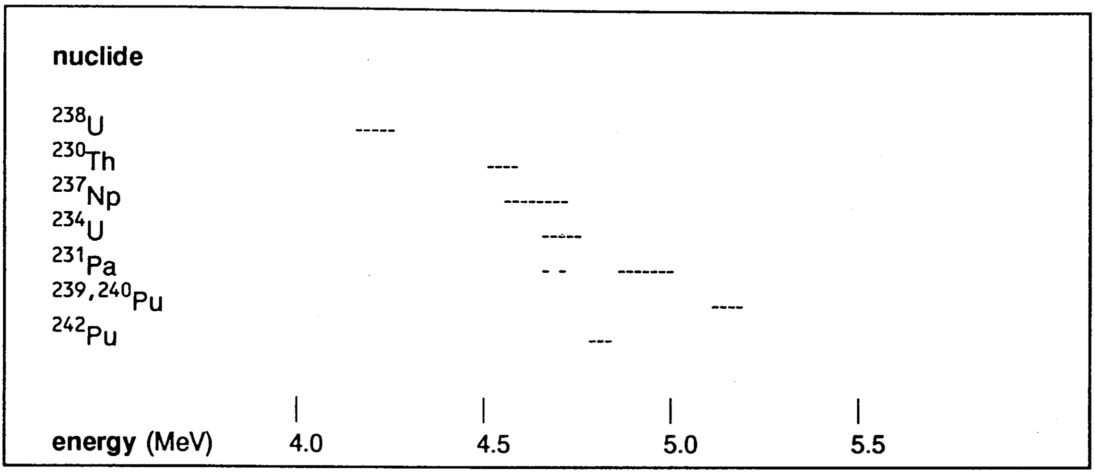
2.3.5 THE DETERMINATION OF ^{237}Np BY α-SPECTROMETRY

(a) introduction and previous work

This technique was used as a reference method for the development of studies on neutron activation analysis (NAA) and mass-spectrometry (MS). Alpha-spectrometry using surface barrier detectors has long been the mainstay of actinide analysis due to its high resolution, sensitivity, versatility and low cost (Cross and Hooper, 1987; Holm, 1988). The general principles and practical approach to α-spectrometry are summarized in section 2.4.1. Due to the need for α-spectrometry sources to be near weightless and because of the large number of α-emitting nuclides, rigorous chemical separation and source preparation procedures are needed.

A number of investigators have used α-spectrometry to analyze ^{237}Np in environmental materials. The main problem arises from its long half-life and consequently low specific activity and decay energies. ^{237}Np has a number of α-decay energies of moderate intensity: 4.765 MeV (17%), 4.777 MeV (19%), 4.787 MeV (51%). The resolution (FWHM) of the surface barrier detector is of the order of 30 keV at 6 MeV (Choppin and Rydberg, 1980; Ivanovich, 1982) and

Figure 2.43: Summary of the potential spectroscopic interferences with α-spectrometric determination of Np-237.



is such that the lower intensity emissions appear as a shoulder on the low energy side of the 51% emission. The major interfering nuclide is ^{234}U (see Figure 2.43) due to its 72% intensity 4.77 MeV decay. However, small traces of ^{234}U in the ^{237}Np source can be corrected for using spectral data. By mass, ^{234}U is 0.005% abundant in natural uranium. The ^{234}U contribution can be removed using a ^{238}U : ^{234}U ratio of activity of 1.12 (see Harvey and Thurston, 1988). Other potential interferences are from ^{231}Pa and ^{230}Th, although in this case the relatively high ^{237}Np activities and effective chemical separations eliminate them.

In poor quality sources, the ^{239,240}Pu peak may interfere due to peak-tailing. Pu nuclides are present at relatively high activities in the samples and ^{239}Pu is the β-decay product of ^{239}Np yield tracer (although the 400 Bq of ^{239}Np used will ultimately decay to 1 x10^{-4}Bq of ^{239}Pu). ^{242}Pu is not normally encountered in the environment. The routine technique of isotope dilution used for most other α-emitters cannot be used for ^{237}Np quantification since no suitable yield monitor exists (see section 2.3.2, Ballestra *et al*, 1978; Holm, 1984). This requires the use of a separate detection system to determine the chemical yield and absolute calibration of the α-spectrometry system used. Harvey and Thurston (1988) provide a detailed description of the α-spectrometric methods used for ^{237}Np determination in marine sediments and biota.

A number of authors have published methods for the determination of ^{237}Np by α-spectrometry in a wide variety of environmental matrices. These are summarized in some detail in Table 2.19. The methods vary in the degree of chemical processing but in general incorporate 3 or more major separation steps. ^{239}Np is the preferred yield tracer in most cases.

(b) the determination of ^{237}Np by α-spectrometry

Table 2.19: A summary of published methods for the determination of ^{237}Np in environmental samples by α-spectrometry.

Authors	sample	separations	comments
Sill (1980)	most environ. sample types	redox cycles and ppt^n steps	α-counting, thick source of $BaSO_4$
Holm & Nilsson (1980); Duniec *et al* (1984); Holm *et al* (1987)	marine sediments and waters	LaF_3/ mixed OH ppt^n, anion exchange, HTTA solv. extraction	^{239}Np tracer, ^{234}U interferes
Pentreath & Harvey (1981)	marine sediments, waters and biota	$Fe(OH)_3$/ NdF_3 ppt^n, anion exchange, HTTA solv.extrt.	^{239}Np tracer, ^{234}U interferes
Sakanoue (1987,1988) Sakanoue *et al* (1987)	soils and sediments	LaF_3 ppt^n, TOA solv. extrt. anion and cation exchange	^{239}Np tracer
Germain *et al* (1987)	marine sediments, waters and biota	anion exchange, $Fe(OH)_3$ ppt, anion exchange	^{235}Np tracer ^{233}Pa interferes
Morello *et al* (1986)	marine sediments and waters	$Fe(OH)_3$ ppt^n (vary pH), anion exchange	^{235}Np tracer
Stevens *et al* (1980); Rees (1980)	soils and waters	cation and anion exchange, HTTA solv. extraction	quantification std. addition
Golchert *et al* (1980)	soils, sediments and biota	single anion exchange	^{239}Np tracer
Rego (1980)	brine solutions	$La(OH)_3$ ppt^n, HTTA solv. extraction	^{239}Np tracer

Samples were ashed and leached (where appropriate) and ^{237}Np purified using anion exchange and two cycles of TTA solvent extraction before electroplating for α-spectrometry. The ^{237}Np activity in the samples is calculated from:

$$[(A_{OBS} \times 100)/ (Y \times 100/ D_E)]/ g = Bq/ g_{SAMP}$$

where A_{OBS} = observed activity of ^{237}Np, corrected for detector background. Interference from ^{234}U was removed by subtracting 1.12 x A_{OBS} (4.14-4.20 MeV), ie ^{238}U energy region. Y and D_E are the % chemical recovery and the % absolute detection efficiency of the counting geometries used.

D_E was determined for each of the counting chambers and detectors used in the study using a source of known ^{237}Np activity and the same counting geometry as the processed samples. All sources for high resolution α-spectrometry required to be very thin and both chemically and radiochemically pure to prevent α-particle attenuation and impaired spectral resolution (Glover, 1984; Lally and Glover, 1984; Holm, 1988). Many methods of source preparation have been proposed, including: evaporation (Kirby and Sheehan, 1984), vacuum sublimation and electrospraying (Lally and Glover, 1984), precipitation (Sill and Williams, 1981) and adsorption (Wyllie and Lowenthal, 1984). The most widely used method for the actindes is electrodeposition at the cathode of an electrolysis cell. At the SURRC, Cook *et al* (1984a; 1984b) use a method based on Talvitie (1971; 1972) adapted by Kressin (1977) and Hallstadius (1984) for the analysis of plutonium nuclides in environmental samples. The method involves deposition of the actinides from a 15% sodium sulphate and 10% sodium hydrogen sulphate buffer at pH 2. Hallstadius (1984) has shown that the deposition efficiencies are nearly quantitative for U (99%), Np (>90%), Pu (95%) and Am/ Cm (90%). The procedure for plating ^{237}Np used in this study is as follows;

To the 8M HNO_3 back-extract from the second TTA solvent extraction, 1 ml of 10% $NaHSO_4$ solution is added and the mixture taken to dryness. This eliminates any HNO_3 residue from the plating solution and the $NaHSO_4$ serves to prevent adsorption on the walls of the beaker. The residue is taken up in a few ml of demineralised water and transferred to a disposable plating cell (see Figure 2.44). 4 ml of 15% Na_2SO_4 solution is added and the Pt electrode inserted. The solution is electrolysed at 0.5A for 3 hours. 1 ml of c.NH_3(aq) is added 1 minute before switching off, to prevent re-dissolution of the plated sample. The solution is emptied out and the planchette washed with demineralised water and acetone.

(i) determination of D_E

An aliquot of standardized ^{237}Np was electroplated as described above. The plated source was counted close to the surface barrier detector in the same position used for samples. The residue and washings were plated twice as before using the same cell, to produce second and third planchettes. The two re-deposited planchettes were then counted. From the amount of ^{237}Np added and its distribution between three plates, the absolute activity of ^{237}Np on the first plate can be determined and hence the absolute detection efficiency of the detectors and counting geometries can be calculated. In duplicate experiments, this procedure gave a chemical recovery of 94.9% ±1.0 and 94.6% ±3.0 at 2σ confidence level. The detection efficiencies of the systems used were thus:

UNIT 2.2, (450 mm^2 area), +100 V bias = 26.1% ±1.1

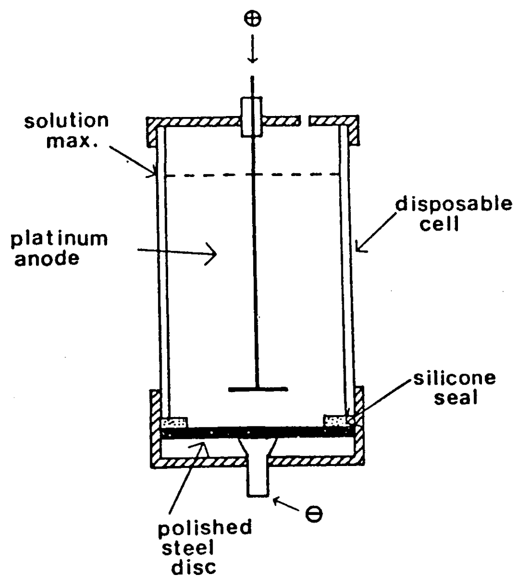
UNIT 2.4, (300 mm^2 area), +50 V bias = 27.7% ±0.5

(ii) determination of chemical yield Y

The calculation is the same as described for the pre-irradiation separation in section 2.3.3. A geometry correction factor is required to account for the difference in counting efficiency between the milked spike solution (10 ml in 20 ml scintillation vial) and the α-source planchette.

A known activity source of ^{239}Np was prepared using the sequential plating method above. An aliquot of ^{243}Am with ^{239}Np in secular equilibrium was plated as before. The proportion of ^{243}Am on the first plate was determined by α-spectrometry. The source was left for two weeks to ensure that any disruption of equilibrium by preferential electrodeposition of Am or Np is removed and secular equilibrium restored. Duplicate runs of the procedure gave 97.0% ±1.0 and 98.1% ±0.8 on of the ^{243}Am ($\pm 2\sigma$) on the first plate. The absolute detection efficiency of the Ge(Li) detector for this geometry was subsequently found to be 10.7% ±0.9 at 228 keV and 9.9% ±0.5 at 227 keV. The geometry correction factors were correspondingly 2.79 ±0.24 and 3.43 ±0.18. The calculation of the activity concentration of ^{237}Np in the samples processed must then include these two correction factors plus the decay-correction for the ^{239}Np. A number of samples of Ravenglass silt were analyzed by the procedure outlined in section 2.3.4 (g). 10 to 15 g aliquots of sample were processed and overall chemical yields were ≈50%. The yields of this method were surprisingly poor, perhaps because of the extra extraction steps involved. However, this did not appreciably affect precision or the exercise objectives as the low chemical recoveries could be compensated for by increased counting time. The results are tabulated and discussed in section 3.1 of Chapter 3.

Figure 2.44: The construction of the disposable electrodeposition system used in this study for the preparation of actinide sources for α-spectrometry.



2.4 METHODS USED TO COLLECT ANCILLARY INFORMATION

2.4.1 THE PRINCIPLES OF HIGH RESOLUTION α AND γ-SPECTROMETRY

A wide range of α-particle and γ-ray solid state, semiconductor detectors were used in this study in the mass-spectrometry and neutron activation methods and in the direct γ-spectrometry and α-spectrometry of the actinide nuclides. The principles of construction and operation are very similar for all types used but the exact nature of the construction and the properties of the radiations or particles to be determined dictate the type of detector used. The precise details of the processes in their construction and those which determine the operating characteristics have been described in great detail (see for example Kruger, 1971; Choppin and Rydberg, 1980; Faires and Boswell, 1981; Ivanovich, 1982).

The basis of both types of detection systems is the formation of a p-n junction transistor between two different solid phases. The solid phases comprise semiconductor materials (Ge or Si) with doped impurities. Group V elements (phosphorus) have the effect of adding an extra electron to the structure which can easily be promoted to the conduction band and an electron excess is created (n-type semi-conductor). Group III elements (indium or gallium) have the effect of depleting the semi-conductor electronic structure and providing energy levels slightly above the Si or Ge valence bands. Occupancy of these sites by the semi-conductor electrons leaves an electron hole which is of positive charge compared to the rest of the material (p-type semi-conductor). Combination of the two types of material allows electrons to move from the n to p regions forming a neutralized zone of charge. The application of a positive potential to the n-type material and a negative to the p-type material (*reverse bias*) increases the size of the neutralized or *depleted region* and increases the potential across it. Radiation entering this region creates a series of electron-hole pairs which are rapidly collected by the applied potential. The volume of the depleted region is determined by the capacitance of the junction and must be low to reduce signal : noise ratio. This conflicts with the collection time requirements which are proportional to the second order of the depleted region depth. Hence a compromise must be achieved.

(a) α-particle detectors

For the detection of α-particles, a *silicon surface barrier* detector (SSB) is commonly used Lally and Phillips, 1984), although more recent developments are the *passivated ion-implanted planar silicon* (PIPS) detectors with improved resolution (Amoudry and Burger, 1984; Canberra Industries Inc., 1986a; EG+G ORTEC, 1986). N-type silicon is oxidized in air to produce the p-type contact. A gold layer is evaporated on to one side to act as the positive contact and aluminium is deposited on the reverse side to act as the negative contact. PIPS detectors differ in having boron implantation as the p-type region. The detectors are operated at voltages up to 3 kV and depletion layers can be from 100 to 1000 μm and must be deep enough to stop the highest energy particle. The resolution of the detector is determined by: statistical fluctuation in the charge carriers produced, particle attenuation by the source and window thickness and operating vacuum. For commonly measured α-radiations (4 to 7 MeV), resolution is of the order of 10 to 20 keV (FWHM) with a uniform detection efficiency of 20% or so (Ivanovich, 1982; Canberra Industries Inc., 1986a).

A charge-sensitive preamplifier is used to respond to the detected pulse giving an output voltage proportional to the input charge. Pulse height analysis to give spectral information is performed using a multichannel analyzer (MCA). The shaped, input pulse is converted to a digital number proportional to the pulse voltage (proportional to the number of charge carriers from the particle and hence its energy) using an ADC. This corresponds to a memory location and a count is stored. The summation of the distribution of counts with pulse voltage constitutes the spectrum of energy. The MCA performs many other functions including timing and spectral manipulations. The spectral effects of charge collection time, electrical noise, amplification and pulse shaping are discussed by Kandiah (1984) with relevance to both α and γ-spectrometry.

(b) high resolution γ-spectrometry

The penetrating nature and low ionizing power of γ-radiation requires much larger detector volumes. This is accomplished by drifting Li atoms into Ge and Si lattices, with the application of a reverse bias generating the three regions of p-type, intrinsic and n-type semi-conductor as above. The use of Li also removes the effect of p-type impurities in the crystal. Ge, due to its higher atomic mass and greater stopping power for γ-rays, is more suitable than Si for γ-spectrometry. Si-based detectors are used for X-ray and low energy γ-ray analysis. Both types give excellent energy resolution (eg 1.7 keV (FWHM) at 1.33 MeV) compared to older, but more efficient, NaI(Tl) solid state scintillation detectors (approximately 10 keV at the same energy). The differences are due to thermal effects. The Ge(Li) detectors are cooled to 77K to reduce resolution effects and prevent drifting of Li from the crystal. High purity Ge crystals are now available which do not require drifting. Cryogenic cooling is still used to increase resolution and decrease electronic noise.

The signal handling procedure is identical to that for α-spectrometry. The main differences are in the energy range studied (10's of keV to 2000 keV), much higher count rates with appreciable detector deadtime and the spectral background caused by the interaction of γ-radiation with the electronic structure of the detector material. Three interactions are responsible for the background continuum observed and its varying energy dependence. The *photoelectric effect*, in which a γ-photon with energy greater than the binding energy of an electron causes electron ejection with energy equivalent to (photon energy) - (binding energy). The effect decreases in probability with photon energy, but increases with atomic number of the absorber. Characteristic X-ray and Auger electron emission is observed as the hole is filled by an electron cascade from the outer shells. The *compton effect* is the partial transfer of photon energy to an electron. The interaction occurs with the less tightly bound electrons and the photon may go on to further interactions. This is the effect which is responsible for the majority of the raised background continuum at energies lower than an intense photopeak in a spectrum. It increases with target atomic number and decreases with photon energy. For photons with energies greater than 1.02 MeV, absorption may be through *pair production*. The photon ejects an electron/ positron pair of energy equivalent to the residual photon energy. The recombination of these particles is responsible for the 0.51 MeV annihilation peak characteristic of γ-spectra.

A wide range of γ-spectrometry detectors is available. The characteristics in terms of detection efficiency are variable and primarily dependent on crystal size and construction.

2.4.2 LOW-LEVEL ENVIRONMENTAL γ-SPECTROMETRY

(a) introduction

There is a wide range of natural β^- and γ-emitting nuclides present in the environment, arising primarily from the thorium and uranium decay series, together with ^{40}K which is a primordial nuclide constituting 0.0118% of the total potassium abundance. In addition, cosmogenic nuclide, produced by the interaction of cosmic particle fluxes with the earth's atmosphere produce ^{3}H, ^{10}Be and ^{14}C, as well as subatomic particles (Choppin and Rydberg, 1980). Weapons fallout and industrial releases have also introduced a range of γ-emitting nuclides which can be detected by suitable detection systems with minimal sample preparation. The basic properties of semiconductor radiation detectors have been described above (section 2.4.1). Quantitative analysis requires sample geometries calibrated against a known standard to determine the variation of absolute efficiency with energy. The systems are computer-controlled to deconvolute multiple peaks and subtract background spectra. Count rates are often very low and counting times of 24 hours or longer are required for peak analysis with low statistical uncertainty. Detector deadtime is seldom a problem compared to neutron activation analysis and samples are counted close to the detector.

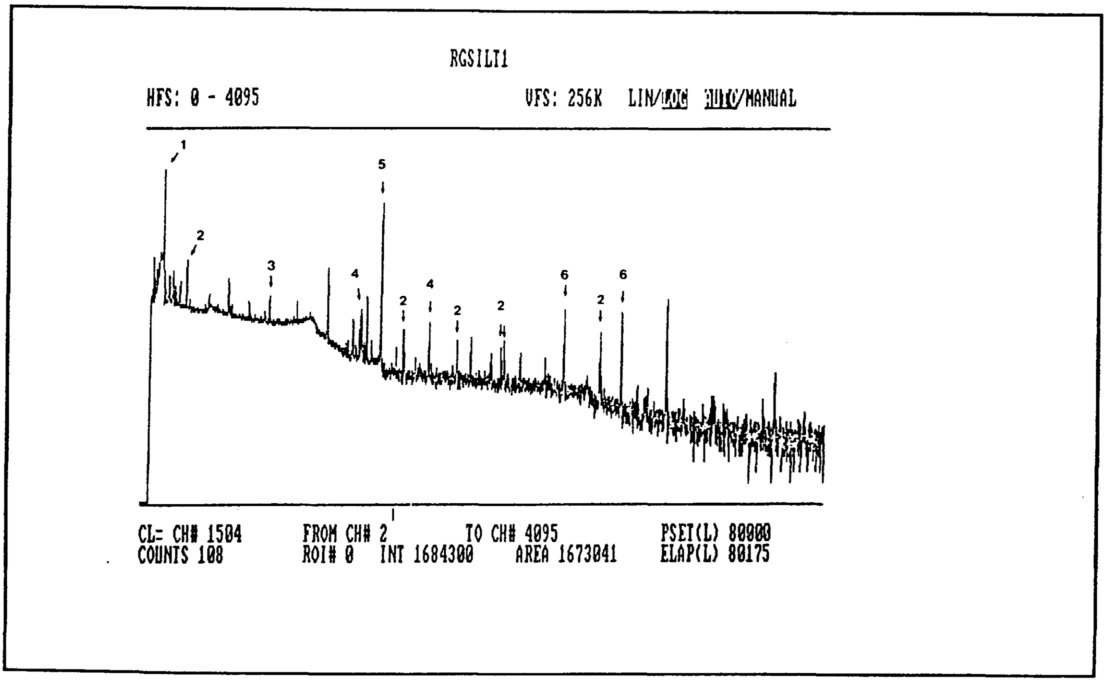
For this study samples of soils and sediments were counted on top of hyper-pure Ge and Ge(Li) detectors in defined counting geometries. All spectra were accumulated for 80 x10^3 seconds and stored on a Canberra Series 85 Multichannel Analyzer, which acquired data for up to four detectors. The spectra were transferred to an IBM-PC for subsequent analysis using Spectran-AT software (Canberra Industries, 1986b). To obtain a quantitative analysis report from the accumulated spectrum, a number of corrections must be made. The data are stored in a digital form in terms of counts per channel number (0 to 4096 in the case of a full spectrum). The algorithms used by the software are described in detail by East *et al* (1979) and Op de Beek *et al* (1976), Op de Beek (1979) and will only be summarized here.

Peaks are located by the smoothing of the data and the generation of a weighted first difference spectrum which is examined for zero crossings with negative slopes to indicate possible peaks. The option of multiplet analysis to resolve composite peaks is provided by an unsmoothed third difference spectrum and tests for statistical significance of the peaks found. The area of the peak is determined on the unsmoothed data and the background continuum removed by assuming a straight line between the peak sides. For multiplet peaks, a non-linear least squares fitting technique is used to determine the contribution of each component to the total peak. The uncertainty on the peak area is calculated using Poisson statistics. Energy calibration and nuclide identification are performed by the accurate determination of the channel location of peaks of γ-rays of known energy. A 29.6 kBq ^{152}Eu source was used in this study, this having a large number of strong γ-rays in the 122 to 1530 keV range. A least squares polynomial fit of peak channel versus peak energy is made and nuclide identification is then achieved by peak energy calibration and comparison with an analysis library of known peak energies and relative intensities. The decay of nuclides between collection and counting is performed using the familiar first order equation for radioactive decay. Any nuclide which has had more than 10 half-lives of decay is eliminated from the analysis. In addition, decay of short half-life nuclides during counting is corrected for using an algorithm of the same format to that described in section 2.3.3.

The background arising from the detector, shielding and sample containers may contain appreciable activities of natural and even anthropogenic nuclides and determines the lower limit of detection for the system. Whilst the continuum background is easily removed during peak integration, the contribution of these peaks to a sample can introduce appreciable uncertainties in the analysis. This effect may be overcome by the subtraction of a background spectrum from the sample spectrum if the background is stable. Thompson (1988) summarises the main factors of concern in low level γ-spectrometry in terms of the contribution of shielding construction materials to the background spectrum. Lead, used to shield the detector from ^{40}K in the laboratory construction materials, may contain appreciable quantities of U and Th series nuclides if it has not aged for at least 100 years. The interaction of γ-rays from the sample with the lead shielding can cause low energy lead x-rays which may be removed by lining with 1mm Cd and 0.6mm Cu metal.

The final step in quantitative analysis of a spectrum is the conversion of the stripped, decay- and background-corrected peak intensities to nuclide activities. The efficiency of the detectors varies with energy as described in section 2.4.1. A calibration of detector efficiency with energy is performed using standards of known activity and hence emissions of known intensity. For environmental determinations, a series of standard geometries was filled with ground and homogenized soil in which a known amount of mixed γ-emitting spike (QCY.44 and ^{241}Am, Amersham International Ltd.) had been evenly dispersed. The absolute efficiencies are then calculated from the γ-spectra generated by these sources and their known nuclide contents.

Figure 2.45: A γ-spectrum of a sample of Ravenglass silt showing the major anthropogenic nuclides 1- Am-241, 2- Eu-154, 3- Sb-125, 4- Cs-134, 5- Cs-137, 6- Co-60.



```
                         RGSILT1
HFS: 0 - 4095                  VFS: 256K   LIN/LOG  AUTO/MANUAL

CL= CH# 1504      FROM CH# 2        TO CH# 4095       PSET(L) 80000
COUNTS 108        ROI# 0   INT 1684300    AREA 1673041   ELAP(L) 80175
```

A polynomial calibration curve is calculated and stored. A peak at any energy in the spectrum can then be quantified. A complete report is generated for all samples analyzed including sample activity concentration and calculated uncertainty.

(b) practical

Sediment and soil samples were counted on top of the detector in 70 and 150 ml calibrated geometries. An example of a spectrum from a sample of Ravenglass silt is shown in Figure 2.45. Analytical accuracy was monitored by assay of a number of IAEA and NIST (formerly NBS) natural matrix SRM's. The results are presented in Table 2.20.

2.4.3 ROUTINE PLUTONIUM ANALYSIS BY α-SPECTROMETRY

The determination of plutonium nuclides in the samples collected was performed in the radiochemical laboratories at ITE(Merlewood). The analysis procedure used was developed from Livens (1985) (see also Livens and Quarmby, 1988) . In summary, a plutonium fraction is isolated from an ashed sample of soil or sediment by leaching with a mixture of hot, concentrated nitric and hydrochloric acids. ^{242}Pu is added as a yield tracer. Two cycles of solvent extraction with diisopropyl ether are used to remove Fe^{III}. Plutonium is separated from the bulk of the matrix and interfering actinide nuclides by anion exchange from 8M HCl. The sample containing Pu^{IV} is applied to the column in 8M HCl and Fe and U removed by washing with 8M HNO_3. The column is converted to the chloride form with concentrated HCl which also removes any traces of Th nuclides. Finally, the plutonium is removed by reduction to Pu^{III} with conc.HCl/ HI. The anion exchange process is repeated and the Pu eluate electroplated as described for ^{237}Np in section 2.3.5. The α-spectrum of the purified sample is collected with the source close to the face of a low background silicon surface barrier detector. Quantitative analysis of ^{239,240}Pu (5.2 MeV) and ^{238}Pu (5.5 MeV) is performed by comparison to the peak due to ^{242}Pu (4.9 MeV). All analyses here were performed in duplicate and the results are discussed in Chapter 3.

2.4.4 SAMPLE SITE LOCATION, COLLECTION AND CHARACTERIZATION

Six sample sites were chosen in an area close to the Sellafield plant in W. Cumbria. The sites were selected on the basis of attempts to cover a wide range of soil types and land use conditions of the area whilst remaining within zones previously defined as having significant levels of Sellafield-derived radionuclide contamination. The presence of high levels of major transuranic nuclides (Pu and Am) would be most likely to indicate sites containing high levels of ^{237}Np.

Table 2.20: Gamma-spectrometric analysis of intercomparison and standard reference materials.

sample description		**SURRC (±2σ)**		**reference value**	
IAEA SOIL-6*	^{137}Cs	52.2	±2.0	53.7 (51.4 - 57.9)	
IAEA AG-B-1*	^{137}Cs	15.2	±3.0	16.7 (15.3 - 20.0)	
	^{40}K	808	±48	798 (710 - 832)	
	^{60}Co	1364	±14	1360 (1327 - 1376)	
IAEA SOIL-6**	^{137}Cs	51.1	±3.2	53.7 (51.4 - 57.9)	
NBS 4353**	^{137}Cs	18.0	±2.0	17.6	±1.6
	^{40}K	695	±44	723	±139
	^{228}Ac	78.2	±3.9	69.8	±7.1
NBS 4350**	^{137}Cs	105	±3.8	100	±7.8
	^{40}K	550	±41	540	±45
	^{60}Co	151	±11	148	±15
	^{152}Eu	223	±8.0	240	±28
	^{154}Eu	52.1	±10.0	52.0	±8.0
	^{228}Ac	46.6	±3.6	34.0	±7.0

*IAEA intercomparison, January 1989; ** natural matrix standard reference materials, November 1989.

Livens (1985) identified areas of the Esk valley with high levels of artificial nuclides, derived primarily from direct marine incursion. Two of these sites were resampled (Beach Sand and Pasture gley) in order to relate the data obtained here to previous studies. Further sites close to the Sellafield perimeter (Coniferous and Deciduous Woodland) were selected to assess the combined effects of aerial discharges from the site and any of onland transfer which is known to influence nuclide inventories up to 15 km inland (Cambray and Eakins, 1982) besides the effect of differences in soil conditions. The final soil site was located on Ennerdale Moor and represented an upland rough pasture site known to be contaminated by Sellafield nuclides (Horrill, 1986; Cambray and Eakins, 1982) and from within the post Chernobyl restricted grazing zone. A sample of surface (0-5 cm) silt from the Esk Estuary at Ravenglass was collected by hand at low tide. In addition, two bulk surface (0 to 15 cm) sediment cores from the Irish Sea were also analyzed.

At each soil site an access pit 30 to 40 cm deep was cut to give a clean soil face, a full profile description being recorded and 20 by 20 cm samples of the profile taken in 5 cm increments to a depth of 30 cm. Each section was placed in a polythene bag and all samples were stored at $< 5\,^{\circ}C$ before wet weights were taken. They were then dried at $35\,^{\circ}C$ before sieving through a 2mm mesh sieve. The >2mm residue was weighed and retained. The soils and sediments were subject to a number of routine soil chemical analyses to provide basic information on their chemical status and to quantify factors or characteristics which were likely to influence radionuclide behaviour. The methods used are described below and the results obtained presented and discussed in Chapter 3.

(a) determination of soil and sediment pH

The hydrogen ion activity is one of the main factors influencing the chemical environment within the soil system (Brady, 1974). It dictates the availability and extent of equilibrium reactions for both toxic and essential elements and the chemical reactivity or speciation within the soil.

The pH of the samples collected was measured using standard procedures (MAFF, 1986). The measured pH of a soil suspension is only an approximation to the "real" pH observed by plants and organisms in the soil water films surrounding the solid soil components. The effect of adding demineralized water to a sample of soil is to dilute the relative hydrogen ion concentration within the liquid phase and a correspondingly high pH is observed. The determinations in this study were performed with 0.01 M $CaCl_2$ solution to reduce the dilution effect. Since the reactions controlling the hydrogen ion concentration are dynamic, a constant procedure must be used to allow at least relative comparison between samples. Such factors as soil: liquid ratio, mixture contact time, suspension settling time and probe depth are all known to affect the measurements (EPA, 1981; MAFF, 1986).

4 g of each sample were placed in glass vials and shaken with 10 ml of 0.01 M $CaCl_2$. The pH of the soil suspension was measured after 30 seconds settling time at a depth of 2 cm into the vial. A standard glass pH electrode was used, calibrated against pH 4 and pH 7 buffer solutions. The determinations were performed in duplicate and compared to determinations using demineralised water. The results were as expected, 1 pH unit higher.

(b) determination of organic matter

The method used is in routine analytical use for the analysis of agricultural materials (MAFF, 1986). A sample of ground soil (<0.5 mm) is weighed into a flask and suitable volume of 66.7 mM potassium dichromate solution (39.23 g $K_2Cr_2O_4$, 0.8 dm^3 H_2SO_4, 0.4 dm^3 H_3PO_4 all diluted to 2 dm^3) added. The dichromate solution and soil sample are heated close to boiling ($135\,^{\circ}C$)

for 2 hours in a flask with condenser attached. The excess dichromate solution remaining after the organic matter oxidation is then titrated against 0.4M ferrous sulphate, using barium diphenylamine sulphonate indicator. The determinations were performed in duplicate and blank solutions of dichromate analyzed to check for thermal degradation (must be <0.4 ml of 0.4M ferrous sulphate). The 0.4M ferrous sulphate solution (5 ml c.H_2SO_4, 320 g $(NH_4)_2Fe(SO_4)_2.6H_2O$ diluted to 2 dm^3) is standardized daily by titrating against the dichromate solution.

The percentage of organic matter is calculated from the half equations below:

$$Cr_2O_7^- + 8H^+ + 6e^- \rightleftharpoons 2Cr(OH)_3 + H_2O$$

$$Fe^{2+} + H_2O + OH^- \rightleftharpoons Fe(OH)_3 + e^-$$

Thus a 6 : 1 proportionality is used. Two assumptions are made: (i) 1 ml of dichromate oxidizes 1.2 mg of carbon and (ii) soil organic matter = carbon x 1.724. All reagents used were of analytical grade.

(c) the determination of the % of oxalic acid extractable Fe, Al and Mn

These analyses were performed in the laboratories of ITE(Merlewood) using standard laboratory procedures (Allen *et al*, 1974). The aims of the analyses were to determine the proportion of sesquioxide phases in the soil samples in a relative sense only. The approach suffers from the same problem as observed for sequential leaching and is discussed in more detail in section 2.4.6.

2 g samples of soil were contacted with 100 ml of 30% w/v oxalic acid in polythene containers and left to stand overnight. The samples were placed on an end-over-end shaker for one hour before filtration through Whatman 44 paper. The concentration of each element was determined by atomic absorption spectrometry on a PYE-UNICAM SP 1900 spectrometer using standards prepared from Spectrosol reagents. Fe and Mn were determined using an air/ acetylene flame and Al using nitrous oxide/ air flame. Total element concentration was determined by fusion with sodium carbonate/ sodium peroxide in platinum crucibles, dissolution in 20% v/v HCl and dilution were necessary. Blank analyses, duplicates and an in-house standard were run to assess accuracy and reproducibility of analysis. The results are given in Chapter 3.

(d) determination of carbonate in silt

The Ravenglass silt contained a component of carbonate material. This was determined by titration of the residue of an aliquot of 0.1 M HCl added to 10 g of sample with 0.2 M NaOH using methyl red indicator. The determinations were performed in triplicate and were in good agreement.

2.4.5 HOT PARTICLE ANALYSIS OF SOILS AND SEDIMENTS

Dielectric, solid α-particle sensitive film detectors have been used to estimate α-particle activity of soils and marine sediments by direct exposure of compressed samples (Hamilton, 1978; Hamilton, 1981; Hamilton, 1985, Baxter *et al*, 1989). Two types of film are available: CR-39, a polymer of oxydi-2,1-diethane-diyldipropenyl ester of carbonic acid and LR-115, a dyed cellulose nitrate deposited on a colourless backing (Qaqish and Bessant, 1976; Hamilton and Clifton, 1987).

Alpha-particles or other heavy particles such as fission fragments physically destroy the films with a characteristic track pattern emanating from a source region. The tracks are made visible by etching the films in alkali or strong acid. The damaged areas are etched at a faster rate than the fresh surfaces and can be viewed under an optical microscope. The technique is able to show the spatial distribution of α-emitting nuclides within a sample and activity can be calculated from a knowledge of track density and exposure time (Hamilton and Clifton, 1987). It has also been suggested that the α-energy may be determined from the angle and depth of the tracks (Qaqish and Bessant, 1976). Hamilton (1981; 1985) describes the distribution of hot particles <1 mm in diameter in samples from Ravenglass and Irish Sea sediment cores. Isolation and analysis of the particles revealed a high transuranic content. It was proposed that some of these particles represented original effluent from the processing of fuels.

In this study, a simple procedure was adopted to assess the relative content of hot particles in the samples collected. Samples were mounted on 13 x 6 cm strips of BENCHKOTE coated with a warm solution of gelatine (10 : 1) or double-sided tape mounted on clear acetate sheets. Excess material was scraped off and the samples contacted with KODAK LR-155 film in the dark for up to 110 days. After exposure, the detectors were carefully removed after the orientation relative to the sample was marked. The films were etched for 2.5 hours in 2.5 M NaOH at 40°C before washing with demineralised water/ ethanol solution and drying. The tracks were then counted under a transmitted light microscope. Samples were run in duplicate with two blanks. Photographs of hot spots are given in Chapter 3.

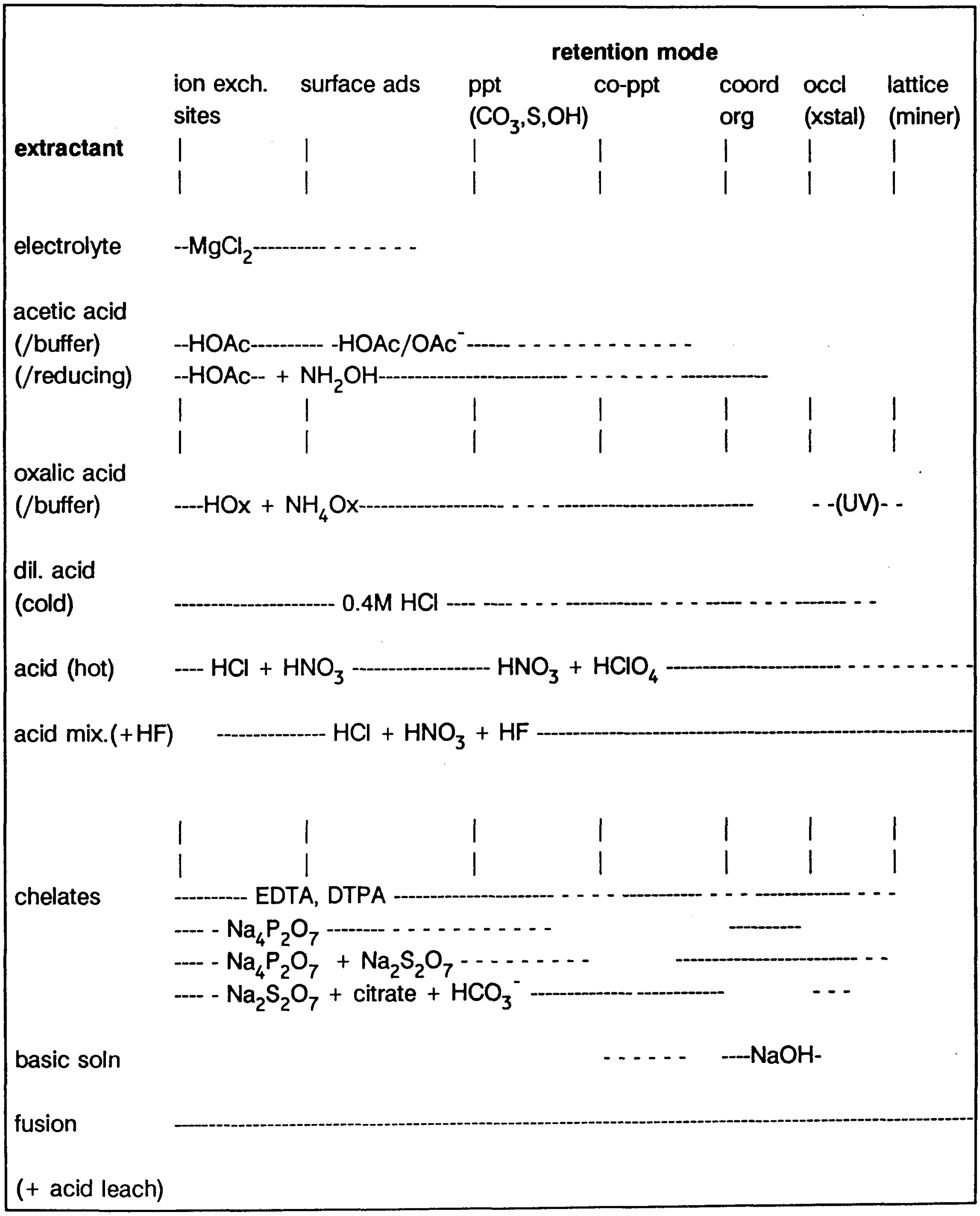
2.4.6 SEQUENTIAL LEACHING OF SOILS AND SEDIMENTS

The general behaviour of trace elements (IAEA, 1970; Salomons and Forstner, 1980; Forstner, 1981) and radionuclides (Aston and Stanners, 1981b; Chester and Aston, 1981, Mathew and Pillai, 1981; Wilkins and Green, 1988; Wilkins *et al*, 1984; 1986) has been studied for many years in order to understand more about the controlling processes and to attempt to predict their fate.

The speciation of neptunium in geochemical systems has already been discussed in earlier sections.

Wittman (1981) describes a particle size based classification of trace metal speciation in aquatic systems which illustrates the complexity of any study of elemental speciation. Metals are defined as existing as: (i) free ions, (ii) complex ionic species, (iii) inorganic ion pairs, (iv)

Figure 2.46: Common reagents used in sequential extraction schemes and their proposed phase selectivity (Salomons & Förstner, 1984).



organic complexes and chelates, (v) metals bound to high molecular weight organic matter, (vi) highly dispersed colloids, (vii) metals sorbed on to colloids, (viii) precipitates, mineral and organic particles, (ix) metals present in live or dead biota. It is obvious that, if reliable behavioural data are to be obtained, methods which accurately sample these species must be used. The methods used for the above classification include filtration, ultrafiltration and anodic stripping voltammetry (ASV) (Forstner, 1981; Morrison *et al*, 1989). Speciation in the solid phase has been studied using a wide range of chemical techniques (Salomons and Forstner, 1984). An operationally defined process, this approach depends on the ability of a specific chemical reagent or mixture of reagents to attack a specific solid phase of sample, releasing its elemental species into solution for analysis. Figure 2.46 is a schematic representation of the reagents commonly used in soil speciation studies and the discrete phases that are attacked. The combination of a series of these extraction steps, applied sequentially, constitutes the most intensive application of this approach. Many different sequential extraction schemes exist for both trace metal and radionuclide studies. Table 2.21 summarises a number of different schemes used.

As well as the more detailed leaching schemes shown in Table 2.21, a number of studies have been made using single step leaches. Nishita *et al* (1981a; 1981b) and Nishita and Hamilton (1981) studied nuclide extractability as a function of pH (see section 1.3) and used "weak" extractants (H_2O, $CaCl_2$, NH_4OAc) to assess bioavailability. Pennders *et al* (1986) used NaOH and HCl to study the leachability of transuranic nuclides from Irish Sea sediment.

More recently, the sequential leaching approach has received much criticism and discussion of the validity of the results obtained (Maher, 1984; Robinson, 1984; McKay and Baxter, 1985; Tipping *et al*, 1985; Nirel *et al*, 1986; Wilkins *et al*, 1986; Kheboian and Bauer, 1987; Bauer and Kheboian, 1988; Tessier and Campell, 1988; Sholkovitz, 1989). The main concerns are the selectivity of the reagents used and artifacts induced by the very act of performing the extraction. McKay and Baxter (1985) observed that drying at 100°C and grinding a marine sediment was sufficient to severely influence the partitioning of ^{137}Cs in the sequential extraction scheme. Tipping *et al* (1985) suggested that acidified hydroxylamine hydrochloride and oxalate leaches for Mn and Fe oxides released trace elements which redistributed on freshly exposed mineral surfaces. It is interesting to note that this was also suggested by Tessier *et al* (1979) in the discussion of the application of the scheme which has subsequently been the most used (and abused) leaching procedure published. Sholkovitz (1989) also identifies this problem for REE's even at low extractant pH. Maher (1984) suggests that the scheme proposed by Tessier *et al* (1979) is unable to resolve Fe/ Mn oxides in organic rich sediments due to complex physicochemical interactions of the phases. Robinson (1984) suggested that a number of procedures studied showed incomplete dissolution of the oxide phases and was strongly influenced by the substrate composition. A series of discussions by Kheboian and Bauer (1987), Tessier and Campbell (1988) and Bauer and Kheboian (1988) relate to problems with the use

Table 2.21: Published sequential extraction methods used to study trace metal and radionuclide speciation in the environment.

Author/sample	phase	reagent
Gibbs (1973, 1977) trace elements in river sediments	adsorbed	1M $MgCl_2$ (pH 7)
	oxide	Na dithionate/ citrate
	organic	Na hypochlorite
	residue	Li metaborate fusion
Chang *et al* (1984) heavy metals in soils	exchangeable	0.5M KNO_3
	adsorbed	deionized H_2O
	organic	0.5M NaOH
	carbonate	0.05M EDTA
	sulphide/ residue	4M HNO_3
Chester *et al* (1986) trace elements in marine aerosol	loosely bound	1M NH_4OAc (pH 7)
	carbonate	1M NaOAc (pH 5)
	oxide	25% CH_3COOH/ 0.25M $NH_2OH.HCl$
	organic	30% H_2O_2/ 1M CH_3COOH (pH 2)
	residue	HF/ HNO_3
Tessier *et al* (1979; 1980) trace elements in marine and river sediments	exchangeable	1M $MgCl_2$ (pH 7)
	carbonate	1M NaOAc (pH 2)
	oxide	0.3M Na bisulphite/0.175M Na citrate
	organic	0.02M HNO_3/ 30% H_2O_2/ 3.2M NH_4OAc
	residue	HF/ $HClO_4$
Cook *et al* (1984a,1984b) Livens & Baxter (1988b) Baxter *et al* (1989) radionuclides in solid phases	readily available	0.05M $CaCl_2$
	exchangeable	0.5M CH_3COOH
	organic	0.1M tetrasodium pyrophosphate
	oxide	0.1M oxalic acid/ 0.175M NH_4 oxalate
	residue	HF/ HNO_3

of the leaching scheme of Tessier *et al* (1979), primarily with regard to the reproducibility and accuracy of the approach. The arguments reach the same conclusion obtained from independent experiments (Martin *et al*, 1987). Phase heterogeneity between samples and readsorption affects, are important limitations even with attempts to buffer the solutions.

Thus it is obvious that sequential leaching techniques are restricted in the validity of absolute comparisons between samples. Diverse matrices and complexly related phase distributions mean that any data must be interpreted in terms of operationally defined procedures and not by the loosely classified mineralogical protocol. The approach does have some positive application (Martin *et al*, 1987) and at the present time is the only available technique which is suitable for this type of study. There has perhaps been too much emphasis on critical reviews of sequential leaching methods without adequate attempts to suggest or generate alternative positive approaches.

The leaching carried out in this study uses a method which has been applied to transuranic and fission product nuclide speciation in a wide range of sample types (Cook *et al*, 1984a; 1984b; Livens, 1985; Livens and Baxter, 1988b; Baxter *et al*, 1989). The method is summarized in Table 2.21 and identifies five phases. Aliquots of 2 g sample are placed in polythene bottles with the appropriate amount of leachate (see Table 2.21) and shaken on an end-over-end shaker for 18 hours. The suspension is filtered through fluted Whatman 44 paper and any filtered solids washed back into the bottle with demineralised water. The sample is rinsed and centrifuged with the rinsing returned to the leachate before the next leaching solution is added. The largest sample : solution ratio is for the organic (pyrophosphate) leach which dictates a maximum sample size of 2 g per bottle. In order to be able to leach enough ^{237}Np to resolve differences in phase distribution, 12 x 250 ml bottles were used here per sample and the leaches bulked acidified and spiked with ^{239}Np tracer after each extraction. The leachate is made up to a known volume and a 500 ml aliquot taken and counted over night on top of a Ge detector in a calibrated geometry to quantify any ^{241}Am present. The aliquot is returned to the bulk solution and the sample analyzed for ^{237}Np as described in section 2.3.4. The results are presented and discussed in Chapter 3.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 COMPARISON OF METHODS FOR THE ANALYSIS OF ^{237}Np IN ENVIRONMENTAL MATRICES

3.1.1 INTRODUCTION

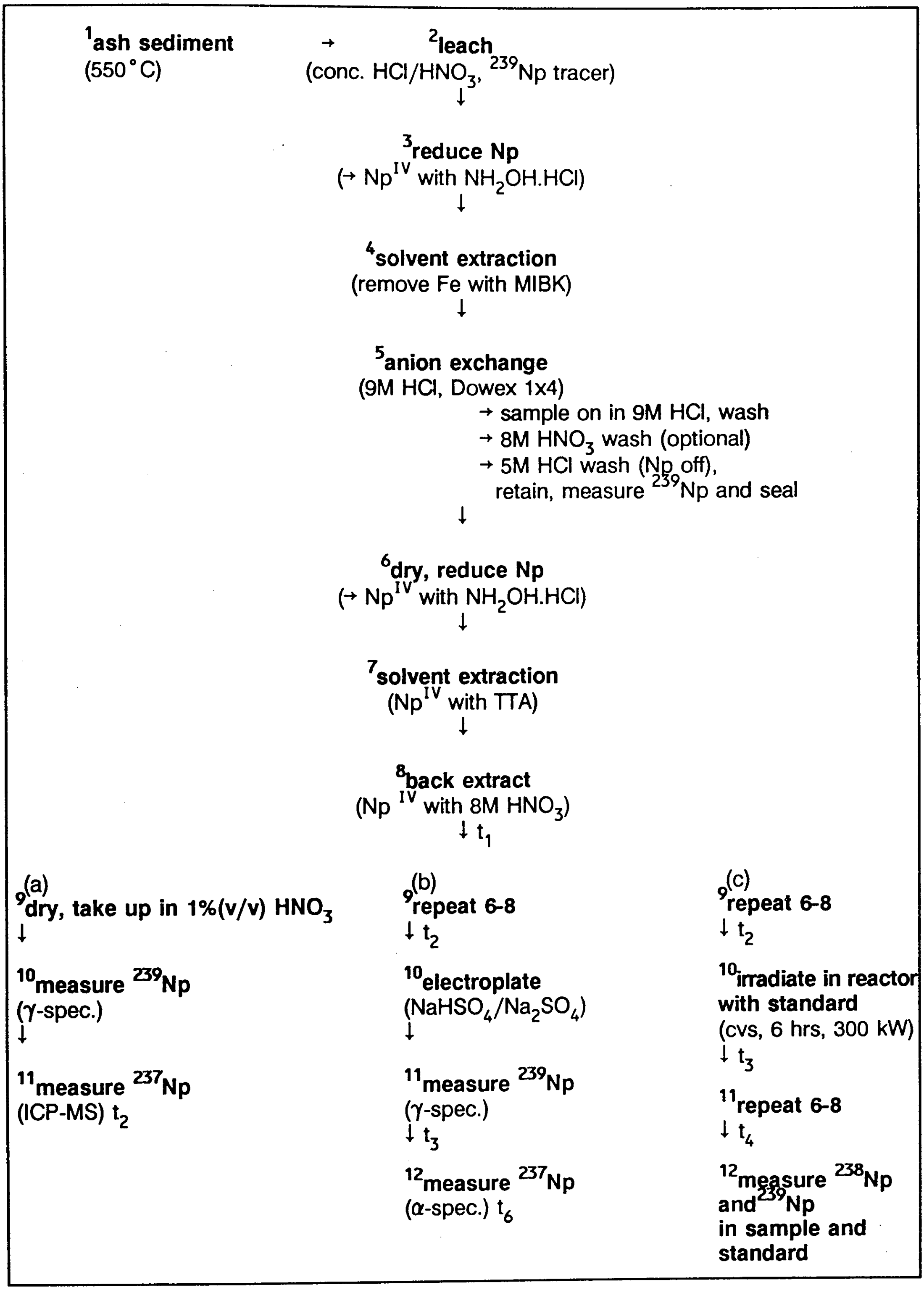
This section summarizes the experimental development of methods to determine ^{237}Np by NAA and ICP-MS. Much of the detailed information has already been presented (section 2.3).

The two techniques studied were compared to routine α-spectrometry. The choice of α-spectrometric measurement of ^{237}Np as a reference technique was further supported by the fact that NAA and ICP-MS assay required comparison to an external standard whilst α-spectrometry determination was based on ^{237}Np decay. Figure 3.1 is a schematic summary of the chemical processing steps required for sample treatment before assay by the different methods. It evolved from the study of the method of Byrne (1986) but includes additional processing to remove a number of interferences. One problem was common to all the analytical techniques although it interfered to a differing extent in each, namely, the high abundance of nuclides of naturally occurring uranium. For the mass-based analysis by ICP-MS, high 238 : 237 ratios could be tolerated without the risk of spectral overlap interfering with the determination of ^{237}Np and poor chemical separations were not problematic. However, it was considered prudent to reduce the 238 mass abundance to some extent and a scheme involving both anion exchange and solvent extraction was adopted.

For the methods involving radiometric assay, decontamination from uranium was more crucial. Despite the theoretically less rigorous source preparation requirements for γ-spectrometry, a high degree of chemical separation was found to be essential for ^{237}Np assay by NAA. The analytical separations used in the purification steps are based on equilibria (see section 2.2) and in practice are never 100% in any one direction. This, coupled with the high mass abundance of uranium compared to neptunium in the samples analyzed and some laboratory reagent contamination by uranium, proves to be a serious limitation of the technique. Even after the incorporation of additional processing steps into the approach used by Byrne (1986), the atom abundance of ^{238}U in the irradiated Np fraction was still sufficient to cause severe interference with the ^{239}Np yield tracer used in the post-irradiation chemical separations. The chemical recoveries of this second separation sequence, although high, were found to be variable and therefore the assumption of quantitative recovery (thus excluding the need for a tracer to quantify losses during the post-irradiation chemistry) could not be made.

The procedure of Byrne (1986) involved the addition of much higher levels of ^{239}Np tracer for the post-irradiation separation, which without doubt masked the effects of poor uranium decontamination. The interferences observed may also reflect, in part, the need to use much

Figure 3.1: Chemical separation scheme developed for the determination of ^{237}Np in environmental samples: t values, 1 to 6 = 3, 5, 6, 7, 8, 9 days processing time respectively.



larger quantities for analysis (ie 10 to 20 g) compared to the 2 g samples analyzed by Byrne (1986). The larger sample size was used in the development stage to compensate for the lower integrated neutron flux of the irradiations and the lower ^{237}Np content of the sample. By doing so, a greater amount of uranium was introduced into the analysis.

With the α-spectrometry analyses, the potential interference by ^{234}U was not found to be a problem using the scheme shown in Figure 3.1. However, the samples processed for α-spectrometry were smaller and contained a relatively high ^{237}Np activity compared to those routinely analyzed by ICP-MS. Therefore, the relative sensitivity of the method and its reliability in routine analysis cannot be fairly assessed here. It may suffer in the same way as the NAA technique when scaled up in that further chemical processing steps or spectral corrections may be necessary.

It is unlikely that any single chemical processing step will provide the preconcentration and purification required for all three methods of assay, in particular for those based on radioactive decay. The advantages of any new separation approach will almost certainly be in terms of speed of separation only. This is of particular importance for ICP-MS development as a routine assay technique for long-lived nuclides where radiochemical purity is not crucial and the tolerances of separations are less constrained than usual.

3.1.2 VALIDATION OF ANALYTICAL TECHNIQUES

The data presented in Table 3.1 show replicate analyses of ^{237}Np from a bulk sample of Ravenglass silt using the three techniques described in section 2.3. Replicate analyses of 10 g samples of silt are shown and were analyzed throughout the study mainly as checks on the performance of the ICP-MS method. The arithmetic and weighted means have been calculated for each set of analyses using standard procedures (Faires and Boswell, 1981; Bambynek, 1988). Although the number of analyses for each method differs considerably, a number of points are worth considering. The values for the weighted means for the α-spectrometry and ICP-MS are in good agreement, whilst those by NAA produce a mean which is 50 to 60% lower. The obvious explanation is that the problem of ^{239}Np generation from uranium activation has not been fully accounted for and the levels produced are significant with respect to the added spike. Despite the fact that all post-irradiation chemical recoveries are less than 100%, the improved chemical separation does not appear to produce the required degree of chemical purity. Closer examination of the data suggests that, in some cases, the observed yields may be interference-free. Unfortunately, the only way of assessing this possibly would be to count the samples without any post-irradiation processing and the practical difficulties involved in this would be severe. The sample secondary containment and traces of dust have been shown to contain a high abundance of uranium (see section 2.3). The decay of the short-lived activation products ^{24}Na and ^{27}Al would be required before sample handling and counting could begin.

Table 3.1: Replicate analyses of Ravenglass silt bulk sample and leachate.

(a) Bulk sample analyses (ng g^{-1} ± 1σ)

ICP-MS	α-spec	neutron activation anal
0.140 ±0.005	0.120 ±0.015	0.119 ±0.006
0.150 ±0.006	0.110 ±0.013	0.073 ±0.005
0.152 ±0.010	0.122 ±0.016	0.031 ±0.002
0.172 ±0.010	0.114 ±0.015	0.027 ±0.003
0.154 ±0.010		0.137 ±0.010
0.143 ±0.006		0.101 ±0.007
0.123 ±0.015		0.087 ±0.006
0.119 ±0.013		0.078 ±0.006
0.145 ±0.007		
0.159 ±0.018		
0.102 ±0.010		
0.110 ±0.007		
0.136 ±0.006		
0.169 ±0.009		
0.158 ±0.014		
0.116 ±0.009		
0.145 ±0.039		
0.107 ±0.014		
arithmetic mean (±1σ)		
= 0.139 ±0.021	= 0.116 ±0.005	= 0.081 ±0.036
weighted mean (± standard error)		
= 0.121 ±0.002	= 0.116 ±0.007	= 0.049 ±0.001

(b) Leachate replicate analyses (Bq dm^{-3} ±2σ)

ICP-MS	2.50 ±0.41	α-spec	3.62 ±0.45
	2.87 ±0.42		2.72 ±0.42

Since the irradiation fluxes available in the UTR-300 are low compared to those used by other authors, there would be a significant loss of analytical sensitivity if post-irradiation processing time was not minimised. The only alternative solutions to the problem would be to add a level of spike activity which would swamp that generated from uranium or to increase the number and type of purification steps prior to irradiation. These would detract much from the early promise of the neutron activation method as a rapid and sensitive alternative method for the assay of ^{237}Np in environmental samples. It is interesting and somewhat unfortunate to note, however, that this technique provides the most precisely determined data produced during this study.

The extensive number of ICP-MS analyses reflects the inclusion of aliquots of the silt in the routine analytical programme. The variable uncertainties reflect variable chemical recoveries and changing instrument performance (see section 2.3) over the year. There was some concern regarding the validity of using this material for analytical control since extensive homogenisation was not performed. For the 10 g sample sizes used here, γ-spectrometric analysis suggested that this would appear not to be a problem. However, a large sample of silt was leached with a mixture of concentrated acids and the leachate split for analysis by ICP-MS and α-spectrometry. The results in Table 3.1b are in good agreement.

In section 2.1.3 it was emphasized that there was an acute lack of natural matrix standard reference materials for the actinides and ^{237}Np. The closest material to meet these requirements was produced by an intercalibration exercise (Popplewell and Ham, 1987). No laboratory in the UK, even those which regularly publish ^{237}Np data, was able to provide any of this reference material or indeed any simple intercalibration samples. 2 g of the Popplewell and Ham material was kindly provided by the IAEA (Monaco laboratory) along with two α-spectrometry sources prepared from the same sample. The results obtained from the analysis of these samples by ICP-MS are shown in Table 3.2. They are in good agreement with the expected values and provide the best available validation of the methods used in the study.

Table 3.2: External validation for ^{237}Np determination by ICP-MS.

(a) NRPB Intercomparison Silt (Bq kg^{-1} $\pm 1\sigma$):

	SURRC result	=	6.40	±0.48
	published mean*	=	6.20	±0.10

* Popplewell and Ham (1987)

(b) α-spectrometric sources from IAEA (Monaco) (mBq $\pm 1\sigma$):

NP11	SURRC result	=	4.35	±0.23
	expected[a]	=	4.58	±0.15
NP12	SURRC result	=	5.01	±0.28
	expected[a]	=	4.91	±0.15

[a] calculated from: chemical recovery, weight of material used and NRPB mean.

3.1.3 PRACTICAL ADVANTAGES AND DISADVANTAGES OF METHODS OF ANALYSIS FOR ^{237}Np IN ENVIRONMENTAL SAMPLES

In summary, it is worthwhile to compare the advantages and disadvantages of the methods developed during this study. There are a number of basic features by which the methods can be assessed. These include: (i) sample throughput time, including the time required for chemical separation and detection or assay, (ii) interferences in both processing and assay, (iii) separation efficiencies and (iv) detection limits. The features are summarized in Table 3.3, the

Table 3.3: Practical performance characteristics of methods for ^{237}Np assay developed in this study.

	ICP-MS	α-SPEC.	N.A.A.
Typical processing time (batch^{-1})	5 DAYS	≥ 7 DAYS	≥ 7 DAYS
Signal analysis (sample^{-1})	2 - 5 MIN.	≥ 1 DAY	≈ 1 DAY
Interferences	sample < 1% salts	^{234}U, clean source required	^{238}U ±^{24}Na,^{82}Br
Typical chemical recoveries	50 - 95%	50 - 95%	30 - 80%
Lower limit of detection (x10^{-6} Bq g^{-1} 100 g sample^{-1})	3.7 - 19.1	1.8 - 2.6	3.1 - 12.5

values quoted being typical for the routine analysis of batches containing four samples of soil or silt. All chemical recoveries were determined by γ-spectrometry of ^{239}Np. On average, slightly lower recoveries were found for the NAA method, due to non-quantitative recovery in the post-irradiation chemical separations. This was determined from the processing of ^{237}Np standards irradiated with the samples, which were thus free from uranium contamination problems. The leaching of the dried, irradiated sample from the vials was not the source of this loss either.

In terms of time spent on analysis, assay by ICP-MS is the most advantageous in that the least time is required both for chemical separation and assay. The greatest sample preparation time is required for the radiometric techniques. Of these, NAA would appear to require still more time to be spent on separation procedures before it could be used as a routine technique. The ICP-MS method tolerates a relatively poor degree of chemical separation. It does not suffer from uranium interferences to the same extent as the other two methods. The single step separations appear to give adequate sample purity and anion exchange seems to be ideally suited to fairly rapid matrix removal from the types of samples analyzed with minimal losses. This further emphasises one of the potential advantages of ICP-MS, namely that any actinide nuclides of suitable half-life may easily be determined within the same solution so long as analyte/ matrix decontamination is sufficient to give < 1% total dissolved salts. The non-spectroscopic interferences and space charge effects are predicted to have the lowest effect on the heavier mass numbers (see section 2.3.4). If reagents and separation procedures are found which can effect the bulk isolation of actinide group metals, the possibilities of multi-actinide ICP-MS are great. Potentially suitable reagents may be the organophosphates DHDECMP and CMPO (see section 2.2.3) which allow fairly rapid isolation of actinides in a range of oxidation states from the same solution. However, these reagents are at developmental stages only and the judicious use of more established ion exchange procedures may still be able to provide the types of chemical separation required.

Detection limits presented in Table 3.3 are based on the 3 x $\sqrt{}$background criterion. All three techniques have broadly similar limits and on this basis there would appear to be no real advantage for any. The range observed is due to variations in detection background, the sources of which are different for each method. In the case of α-spectrometry, the ideal detector background is essentially zero, but detector contamination easily occurs during routine use. The limits quoted are for detectors with <100 counts in the ^{237}Np energy region after a count time of 9 x10^5 seconds. For neutron activation, there is a variation in detection limit over at least an order of magnitude. This is attributed to the variation in ^{24}Na and ^{82}Br content of the irradiated samples which caused variable background due to Compton scatter.

For the ICP-MS instrument, the detection limit varies by over an order of magnitude. The range quoted includes "best" and "poorest" values and the differences between mean and median values are significant, emphasising the somewhat erratic performance of the new instrument with time. In general, the detection limit was < 6.5 x10^{-4} Bq g^{-1} for a 1 g sample, which is a distinct improvement over the range observed for NAA. The variation is due to long-term changes in the sensitivity of the ICP-MS of the type described in section 2.3.4d. The reasons are uncertain and are likely to result from wear and tear of the sample and skimmer cones and build-up of material on the quadrupole rods and ion lens system. The poorest lower limits of detection and sensitivity were observed prior to routine servicing and major faults. Detection limits for samples run subsequent to these incidents showed great improvement. What is certain is that there is a great variation in the analytical performance of the VG PlasmaQuad ICP-MS over the long-term. Whilst this is not necessarily important for most trace and even ultratrace applications, its use for the analysis of samples close to absolute detection limits is severely limited by this behaviour. Careful monitoring of instrument behaviour over time is essential and the optimization of instrument response important to apply the capabilities of ICP-MS to the fullest for both stable and radioactive nuclides.

3.2 SAMPLE SITES AND SOIL CHARACTERIZATION.

The criteria used to identify potentially suitable site for studies of ^{237}Np behaviour have already been identified (see section 2.3.9). They were based on preliminary work by Livens (1985) on plutonium geochemistry in the area. The basic philosophy was that, since the available Sellafield discharge data indicated extremely low ^{237}Np annual releases compared to the other actinides, sample sites with the highest actinide activity concentrations were likely to contain the highest ^{237}Np concentrations. These would be the most suitable places to start to apply methods developed in Chapter 2.

3.2.1 SITE LOCATION AND SOIL DESCRIPTION

The soils sampled cover a wide range of types in terms of the parent material and soil-forming processes in operation. The locations of the sites with respect to W. Cumbria are shown in

Figure 3.2: Map showing location of sampling sites used in this study.

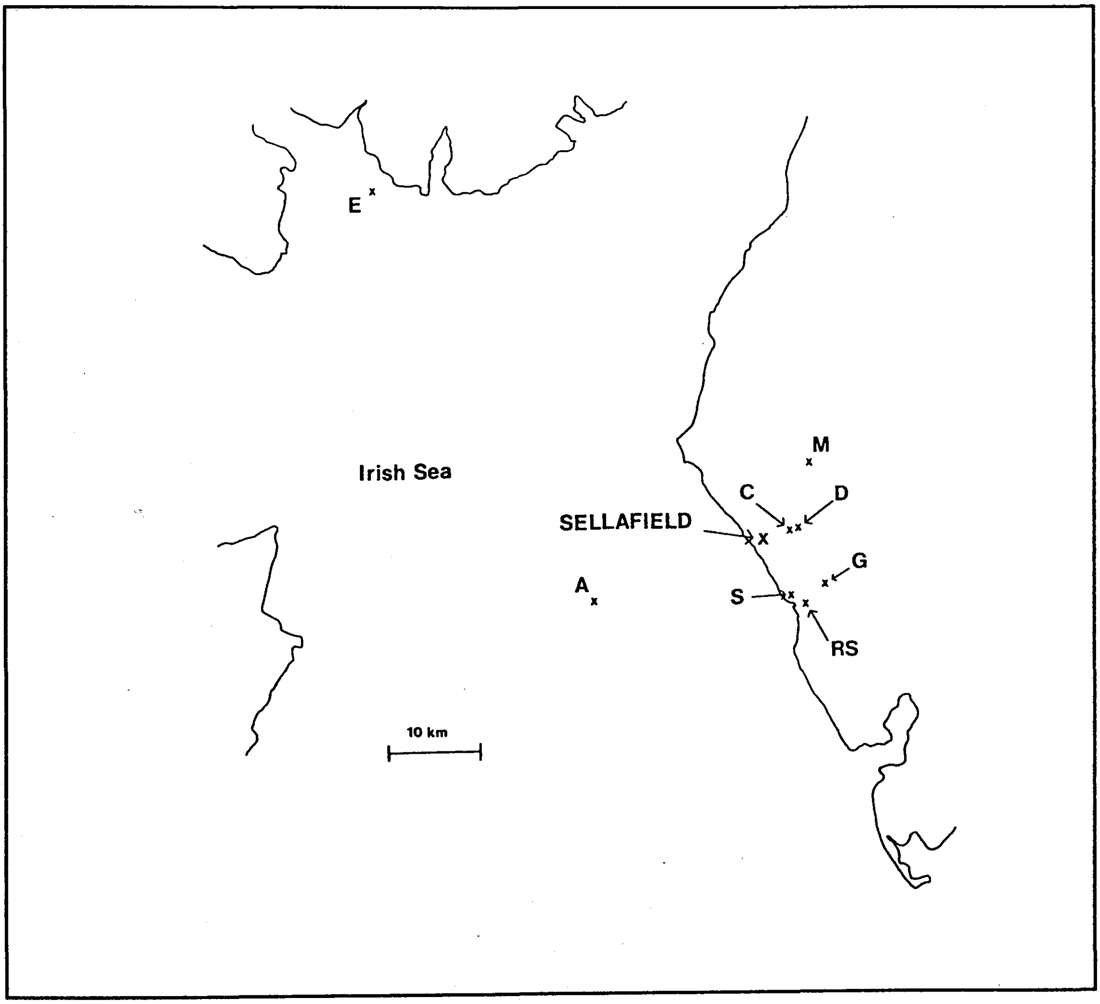


Figure 3.2. Each soil was sampled to a depth of 30 cm only. This did not constitute the whole profile but was likely to contain >99% of the anthropogenic nuclide input. Some profile development was observed at nearly all sites sampled. Formal soil descriptions (Avery, 1973) including soil colour (Munsell Colour Co. Inc., 1954) were made for each profile.

The beach sand [S] (SD 073 966) is a raw beach sand sampled 10 to 15 m from the high tide mark. There is some evidence of direct marine incursion. The parent material is wind-blown sand, populated by patchy areas of grass. Profile development is limited, with no evidence of large amounts of organic matter other than occasional patches of decaying grass and roots. Munsell colour description shows a slight variation with depth, from dark grey/ brown (10 YR 4/2) to dark yellow/ brown (10 YR 4/4). Slight reddening of the soil around the decaying organic matter is noted. At >30 cm depth, large rounded pebbles and boulders are observed. These comprise a mixture of acidic and basic volcanic and coarser grained plutonic rocks.

The conifer woodland [C] site (NY 037 048) is a brown earth of the WICK 1 soil association (Soil Survey of England and Wales, 1984). It is populated by mature spruce trees with no sign of disturbance since planting (30 years). Slope is a gentle 10 to 12° with a N. to N.E. aspect and the site is well drained. There is some profile development in the 0 to 30 cm depth sampled. A 2 to 3 cm H/O horizon comprising partially decaying pine needle litter (dark red/ brown, 5 YR 2/2) grades over 1 to 2 centimetres into a 6 to 7 cm deep humified A_h horizon (dark red/ brown, 5 YR 3/2). Occasional tree rootlets (approximately 0.5 mm to 0.5 cm diameter) are observed. This grades over a centimetre into a sandy, highly quartz-rich horizon (dark grey/ brown, 10 YR 3/2). Further gradation over the rest of the sample depth shows a slight gradation in reduction of identifiable organic matter and a slight lightening of the soil colour (dark brown/ brown, 7.5 YR 4/2 to dark brown, 7.5 YR 3/2) as blocks of rotting sandstone (10 cm diameter) increase in proportion. Soil structure is poorly defined.

The deciduous woodland [D] site (NY 039 047) is again a brown earth of the WICK 1 association. It is approximately 20 to 30 m down slope from the conifer site and shows completely different field characteristics. The woodland population comprises relatively thinly dispersed turkey oak with rhododendron and bramble bushes. Some profile development is observed but it is not as well developed as in the conifer site. At the surface, there is a 2 cm litter layer of moss and leaves in varying states of decay. This overlies a dark red/ brown (5 YR 2/2) weakly developed horizon, 5 cm deep, which grades over a few centimetres into a 15 cm deep horizon of a lighter reddish brown (5 YR 3/3) colour. A dark layer, 3 cm thick of similar colour (dark red/ brown, 5 YR 2/2) to the surface horizon, is noted at 20 cm depth. It overlies a coarser gritty sandy layer, dark red (2.5 YR 2/2) containing a few rounded pebbles of crystalline rock cm to dm in size.

The upland moor [M] profile (NY 064 130) is a typical brown podzol. The land use is for rough grazing and the site sampled was at the foot of a 40 to 50° slope. A surface root mat (0 to 5 cm) of partially decaying vegetation (black, 10 YR 2/1) grades over 1 cm into a 4 to 5 cm thick, very dark brown/ brown (7.5 YR, 4/4) H/A horizon containing well humified organic material. A sharp transition to a paler, brown A/E horizon (7.5 YR 5/6) suggests signs of iron eluviation. The mineral horizons are dominated by a clayey material containing cm size chips and angular fragments of a fine-grained rock which exhibits some cleavage. This increases in proportion with depth to the base of the profile where the clay is yellow/ brown (5 YR 4/6) in colour.

The waterlogged gley [G] site (SD 112 962) is an alluvial gley of the ROCKLIFFE association (Soil Survey of England and Wales, 1984). It is developed from a stoneless alluvium parent material (site on flood plain of river Esk, 5m from bank). The site is a flat pasture actively grazed by cattle with some evidence of puddling. There appeared to be little disturbance at the profile collection site. The area is periodically flooded by both river and estuarine waters and there is abundant grass and seaweed debris. Profile development is not striking and there is no obvious soil structure. The surface is very wet and the proportion of moisture decreases slightly with depth. Overall the profile is very moist and sticky throughout. Roots from surface grass are found to a depth of 15 cm. The profile is almost uniformly coloured very dark grey (5 YR 3/1) and has a silty clay texture. Some red mottling around the roots is apparent and is more noticeable at depth. This indicates that the soil is strongly reducing in nature.

The bulk sample of Ravenglass silt [RS] was collected from the top 5 cm of an area approximately 40 cm x 40 cm, 10 to 15 m from the highwater mark. The sediment samples were collected in August 1987 from mud patches in the Irish Sea, core A approximately 14 km from the discharge pipeline off the W. Cumbrian coast (54° 21.01N, 3° 43.70 W) and core E from Kirkudbright Bay, off the Solway coast, 63 km from the pipeline (54° 46.15 N, 4° 12.00 W).

3.2.2 CHEMICAL CHARACTERISTICS OF THE SOILS

Table 3.4 summarizes the soil chemical analyses described in section 2.4. The results show that, in terms of these basic chemical properties, a wide range of soil types was sampled. Organic matter contents vary from > 90% to < 0.5%. The range of pH is less variable. In all soils sampled, measured pH ($CaCl_2$) indicates strongly acid to slight acid conditions. This is a general characteristic of Cumbrian soils where rainfall is high and leaching of exchangeable cations promotes an increase in soil acidity (Bendelow, 1984; Soil Survey of England and Wales, 1984). The most acidic values were found for the sites in which there was a high concentration of organic matter in the surface horizons (conifer wood and upland moor) which may be an indication of the enhancement of acidity by the presence of organic compounds released into the soil water (Brady, 1974).

Table 3.4: Soil chemical analyses of the profiles sampled in this study.

Depth (cm)	% Organic Matter	pH ($CaCl_2$)	% Oxalic Acid Extracted		
			Fe	**Al**	**Mn**
Gley					
0-5	15.75	4.7	38	7.0	83
5-10	5.31	4.5	34	7.0	75
10-15	3.54	4.7	40	7.0	93
15-20	3.44	5.0	50	7.0	>99
20-25	2.78	5.1	57	7.3	>99
25-30	2.05	5.2	57	6.5	>99
Sand					
0-5	0.32	5.1	7.1	1.1	7.6
5-10	0.80	4.5	8.5	1.1	6.0
10-15	0.55	4.6	6.7	1.0	BDL
15-20	0.65	4.9	11	2.5	BDL
20-25	0.49	5.1	8.2	2.1	BDL
25-30	0.41	4.9	7.3	2.0	BDL
Deciduous					
0-5	8.81	3.0	52	8.5	12
5-10	4.30	3.3	46	13	10
10-15	3.52	3.5	46	13	26
15-20	3.21	3.6	48	29	14
20-25	3.49	3.7	45	14	29
25-30	2.08	3.8	52	14	36
Conifer					
0-5	66.52	2.0	7.8	13	BDL
5-10	18.22	2.2	2.0	32	BDL
10-15	3.11	2.5	BDL	1.9	BDL
15-20	1.63	2.7	BDL	0.9	BDL
20-25	0.98	2.7	BDL	1.3	BDL
25-30	1.22	2.7	BDL	2.1	BDL
Moor					
0-5	91.70	2.5	85	16	BDL
5-10	11.41	3.2	95	8.0	36
10-15	5.75	3.5	98	9.8	75
15-20	4.87	3.7	92	7.9	47
20-25	4.60	3.7	>99	13	51
25-30	3.69	3.9	>99	9.1	62
Silt	1.4	7.4	NA	NA	NA

The data concerning the % of extractable Al, Mn and Fe provide further details on the chemical status of these soils. The data show the non-primary mineral components of these elements in the soils and give an idea of the relative importance of the redox and pH sensitive sesquioxide components in the soils (Salomons and Forstner, 1984). Manganese shows the most variation in distribution. In the gley profile, nearly all the Mn is extracted by the oxalic acid but, in the conifer wood, it appeared to be insensitive to the reagent, possibly indicating a primary mineral host phase. Aluminium showed least variation, with $\leq$ 32% of the total content of any sample removed by the reagent. Iron extraction was greatest for the upland moor site. Increased extractability with depth in the profile is probably a reflection of the dynamic processes involved during podzolization and is hardly a surprising result in view of the soil description given above. This behaviour was not found for Al or Mn.

3.3 THE DISTRIBUTION OF ^{237}Np AND OTHER RADIONUCLIDES IN SOILS AND SEDIMENTS FROM W.CUMBRIA

The extensive development work required to obtain a reliable method for ^{237}Np assay means that only relatively few analyses of samples collected could be performed in the time available. Combined with the initial survey of samples by routine γ-spectrometry, the ^{237}Np data were further supplemented by a number of plutonium analyses for comparison to neptunium. Detailed consideration of nuclide ratios and relative distributions will be made in an attempt to describe and understand neptunium behaviour.

3.3.1 ^{237}Np DISTRIBUTION

Table 3.5: ^{237}Np analyses of samples of soils and sediments from W. Cumbria (mBq kg^{-1} ±2σ).

Depth (cm)	**Gley**		**Sand**		**Conifer**	
0-5	2,869	±680	73.0	±2.7	115	±2.6
5-10	441	±94	106	±40	22.0	±13.1
10-15	121	±16.5	60.8	±9.4	10.2	±5.2
15-20	48.0	±12.0	42.5	±8.6	9.6	±5.2
20-25	29.0	±8.1	36.0	±2.4	10.4	±5.8
25-30	30.0	±0.5	29.8	±4.8	13.0	±3.9

Ravenglass silt = 3,158 ±52
Core A = 248 ±100
Core E = 559 ±230

Complete depth profiles for the gley, conifer wood and beach sand sites were analyzed. Additional analyses of Ravenglass silt and two samples of surface sediment from the Irish Sea were also made. The results are tabulated in Table 3.5. The ^{237}Np data show a wide range in activity concentrations and, in the case of the gley and conifer wood sites, an exponential decrease with depth is observed. This latter trend is illustrated for the other radionuclides analyzed in these and other profiles and is consistent with the observations of Livens (1985) at similar sites. One would expect such a distribution for aerially deposited radionuclides, with little or no effect of biological mixing. Watters *et al* (1980) confirm the same exponential distribution for many sites in the US and invoke the idea of a non-diffusive migration mechanism. In the case of the beach sand profile, a sub-surface maximum is observed. Despite the large uncertainty associated with this feature, the effect is considered to be real as it correlates strongly with the distribution of the other radionuclides and with a subsurface maximum in organic matter content. The soil is a raw sand with variation in mineralogy down the profile. The slight variation in organic matter distribution, whilst low in absolute terms, appears to influence profoundly the behaviour of radionuclides and to an extent the oxalic acid extractable components of the total soil Al, Mn and Fe.

3.3.2 PLUTONIUM NUCLIDE DISTRIBUTION

The available data for a number of samples collected are presented in Table 3.6. Depth trends are similar to those seen for neptunium in the preceding section. Further information regarding the source terms for the plutonium can be obtained by considering the ^{238}Pu/ ^{239,240}Pu ratios. The two important sources for plutonium at these sites are from weapons fallout and Sellafield discharges.

Table 3.6: Plutonium nuclides in soils and sediment samples from W. Cumbria (a) ^{239,240}Pu activity concentrations (Bq/ kg), (b) 238/ 239,240 activity ratios. All data $\pm 2\sigma$.

(a) **Depth** (cm)	**Gley**		**Sand**		**Conifer**	
0-5	3,655	±460	28.8	±1.8	116	±10
5-10	297	±26	64.0	±4.0	7.2	±0.4
10-15	32.0	±3.0	30.5	±2.8	1.0	±0.1
15-20	15.9	±1.2	16.1	±1.5	0.34	±0.08
20-25	29.0	±8.1				
25-30	30.0	±0.5				

Ravenglass Silt = 960 ±72
Core A = 346 ±21
Core B = 242 ±21

(b) **Depth** (cm)	**Gley**		**Sand**		**Conifer**	
0-5	0.209	±0.06	0.205	±0.031	0.044	±0.008
5-10	0.093	±0.028	0.222	±0.034	0.040	±0.011
10-15	0.154	±0.039	0.226	±0.050	0.058	±0.021
15-20	0.170	±0.028	0.134	±0.034	<0.09	
20-25	0.207	±0.026				
25-30	0.187	±0.050				

Ravenglass Silt = 0.222 ±0.025
Core A = 0.215 ±0.019
Core B = 0.199 ±0.026

BNFL Sellafield discharge data provide enough detail to show that plutonium in the liquid discharges from the plant have a characteristic ^{238}Pu/ ^{239,240}Pu ratio (0.27 to 0.35), consistently an order of magnitude greater than the weapons fallout source term (0.02 to 0.04, Perkins and Thomas, 1980). The results presented here indicate that, for the silt, gley and sand profiles, Sellafield is indeed the most influential source term at these sites. The conifer wood soil shows a surprisingly low ^{238}Pu/ ^{239,240}Pu ratio, more characteristic of weapons fallout, which is nevertheless unable to account for all the observed deposition (see section 3.4). Its close proximity to Sellafield and location well within the observed field of influence of marine-derived airborne particulates (Cambray and Eakins, 1982; Pierson *et al*, 1982) must imply a significant Sellafield influence here. Both Pierson *et al* (1982) and Livens (1985) observed the same feature in terrestrial samples collected close to Sellafield. This was attributed to early aerial releases from the site but, although these are acknowledged and monitored by BNFL (BNFL, 1977-1988), the activities are not defined in enough detail to enable a characteristic nuclide ratio to be assigned. The 5 to 10 cm sample from the gley site also has a significantly lower ratio relative to normal Sellafield discharges in spite of samples above and below showing a strong Sellafield signature. The feature is consistent with observations by Livens (1985) in two cores from the same locality. The mechanism for the production of this feature is difficult to envisage. The biologically mediated mixing processes in operation in marine sediments which are responsible for the disruption of exponential trends in depth distributions in marine systems (Santschi and Honeyman, 1989) cannot be easily envisaged to be operating here. Whether this feature is an artifact of past Sellafield discharges is also uncertain. It is very unlikely that it simply represents the record from physical accumulation of soil material over the thirty or so years of discharges, even when the hydrological influences are as dynamic as they are at this site. Some physicochemical process or processes must be important, not only for plutonium but for the other nuclides too, in order to explain this ratio anomaly and the profile distribution.

3.3.3 Cs NUCLIDES AND ^{241}Am DISTRIBUTION

The same general pattern observed for the nuclides in the sections above is observed for these nuclides. Again a wide range of surface concentrations exists and analyses are presented in Table 3.7. All data have been decay-corrected to time of sample collection. The gley site contains the highest levels of Cs and Am nuclides. Data for ^{134}Cs and ^{137}Cs show a number of features worthy of comment. Three important sources of radiocaesium must be considered. Soils collected from Cumbria post April/ May 1986 will potentially contain components from (i) weapons fallout, (ii) Sellafield liquid and aerial releases and (iii) the releases and fallout from the accident at Chernobyl.

Liquid discharges from Sellafield have already been identified as the principal source for radionuclide activities in the gley and sand profiles, whilst aerial releases may be significant in the case of the conifer wood and, by virtue of its close proximity, the deciduous wood. The

Table 3.7: ^{134}Cs, ^{137}Cs and ^{241}Am activity concentrations (Bq kg^{-1} (dry) ±2σ) in soil and sediment samples from W. Cumbria (^{134}Cs/^{137}Cs ratios included where appropriate).

Depth (cm)	^{134}Cs	^{137}Cs	(134/137)	^{241}Am
Gley				
0-5	218 ±30	1.0 ±0.2 x10^4	(0.022 ±0.003)	9.0 ±0.1 x10^3
5-10	<11.4	670 ±15	-	436 ±16
10-15	<4.4	85.0 ±2.5	-	61.0 ±4.6
15-20	<4.4	23.0 ±2.1	-	23.0 ±2.1
20-25	<3.9	24.0 ±1.4	-	16.0 ±1.5
25-30	<3.8	23.0 ±1.7	-	13.0 ±1.9
Sand				
0-5	133 ±3.5	841 ±5.9	(0.158 ±0.004)	47.0 ±2.5
5-10	12.2 ±1.4	1.4 ±0.01 x10^3	(0.009 ±0.001)	94.6 ±4.0
10-15	5.2 ±1.0	593 ±4.7	(0.009 ±0.002)	62.6 ±3.1
15-20	<3.5	130 ±2.3	-	34.0 ±2.0
20-25	<3.3	158 ±2.5	-	27.5 ±2.1
25-30	<3.3	130 ±2.2	-	23.5 ±1.9
Conifer				
0-5	82.0 ±6.6	759 ±11.4	(0.108 ±0.009)	57.0 ±4.9
5-10	<4.7	200 ±3.8	-	<3.1
10-15	<3.5	50.0 ±1.8	-	<2.7
15-20	<3.1	14.0 ±1.1	-	<2.5
20-25	<3.1	6.0 ±1.0	-	<2.7
25-30	<3.3	3.0 ±1.0	-	<2.4
Deciduous				
0-5	28.0 ±2.0	325 ±11.0	(0.086 ±0.007)	10.4 ±1.9
5-10	<5.5	34.0 ±1.7	-	<2.8
10-15	<5.2	8.5 ±1.0	-	<2.7
15-20	<5.1	13.0 ±1.0	-	<2.6
20-25	<4.3	11.0 ±1.0	-	<2.6
25-30	<4.7	4.5 ±1.0	-	<2.4
Moor				
0-5	294 ±5.9	938 ±34.7	(0.314 ±0.013)	7.2 ±2.18
5-10	3.7 ±0.7	38.6 ±2.0	(0.095 ±0.005)	<2.6
10-15	<3.5	13.5 ±1.4	-	<2.5
15-20	<3.6	6.9 ±1.9	-	<2.7
20-25	<3.4	4.5 ±1.3	-	<2.7
25-30	<3.2	3.3 ±1.0	-	<2.5
Ravenglass	24.0 ±1.6	780 ±25.0	(0.031 ±0.002)	1.0 ±0.008 x10^3
Core A	13.0 ±0.9	1.2 ±0.008 x10^3	(0.008 ±0.001)	565 ±13.6
Core E	73.0 ±2.9	1.1 ±0.007 x10^3	(0.015 ±0.001)	580 ±5.2

upland moor site will be expected to have received a much lower marine and aerial-derived Sellafield input due to its distance from the sea and from Sellafield. However, from its height and geographical position, one would expect a significant input from weapons testing and Chernobyl. ^{134}Cs is recorded at depths greater than 5 cm in the moor and sand profiles. The

^{134}Cs/ ^{137}Cs ratios show a distinct variation between sites, indicating a variation in the significance of the source terms. The gley shows the lowest and the moor the highest values. From BNFL data, the cumulative discharge ratio from Sellafield (1969 to 1986) is calculated to be 0.0102 and the reported ratios for Chernobyl releases 0.6 to 0.5 (Imanaka and Kiode, 1986; Ballestra *et al*, 1987; Fulker, 1987). It is apparent that the greatest Sellafield influences on the Cs data are found in the gley, the silt and marine sediments. The gley and silt samples do show slightly elevated values implying the input of Chernobyl material. The mineral phase source term relationships between the gley and the silt are complex and it is uncertain whether it is an effect of terrestrial or estuarine-derived signals which is being seen here.

The ^{241}Am data show the normal exponential distribution in all sites. The interpretation of its distribution in the soil profiles is further complicated by the parent/ daughter relationship with ^{241}Pu, which is of sufficiently short half-life to contribute significant amounts from both weapons fallout and Sellafield sources, thus masking behavioural differences between Pu and Am.

A number of other γ-emitting nuclides were observed in the samples: ^{60}Co in gley 0 to 5 cm, conifer 0 to 5 cm and silt, $^{106+103}$Ru in gley 0 to 5 cm, sand 0 to 5 cm and the silt. The surface 5 cm of the gley and the silt sample also contained measurable quantities of: ^{144}Ce, $^{154+155}$Eu and ^{54}Mn.

3.4 RADIONUCLIDE INVENTORIES

Since there is such a large variation in soil type, detailed discussion of the quantities of the various nuclides within the soil profiles in terms of activity concentration (Bq kg^{-1}) is meaningless without compensation being made for the variation in sample density. More useful is a consideration of total deposited activity in terms of surface area and its integration over the total volume of sample collected. Thus activity deposition per m^2 can be calculated with a knowledge of activity concentration (Bq kg^{-1}), sample surface area (m^2), total sample weight (kg) and sample depth (cm). Table 3.8 lists the total nuclide inventories for all sites to a depth of 30 cm and the inventories for each individual depth section. The predicted contribution (Cambray and Eakins, 1982; Pierson *et al*, 1982; Efurd *et al*, 1984) of weapons fallout surface deposition for each of the sites is also included. Figure 3.3 shows the data from Table 3.8 in terms of the variation in the % of total profile inventory with depth. The trends illustrated by the activity concentration data are still evident and a general exponential decrease in activity with depth (except for the sand) is observed.

The calculated fallout contributions appear to have varying degrees of influence in the soil profiles. The theoretical deposition assumes the input activity will remain within the soil profile and cannot take into account losses by particle resuspension, leaching etc. Consequently further assessment of actual contributions within the sample sites, particularly for ^{237}Np, due to

Table 3.8: Nuclide inventories (Bq m^{-2}) with depth. Predicted fallout depositions included for comparison.

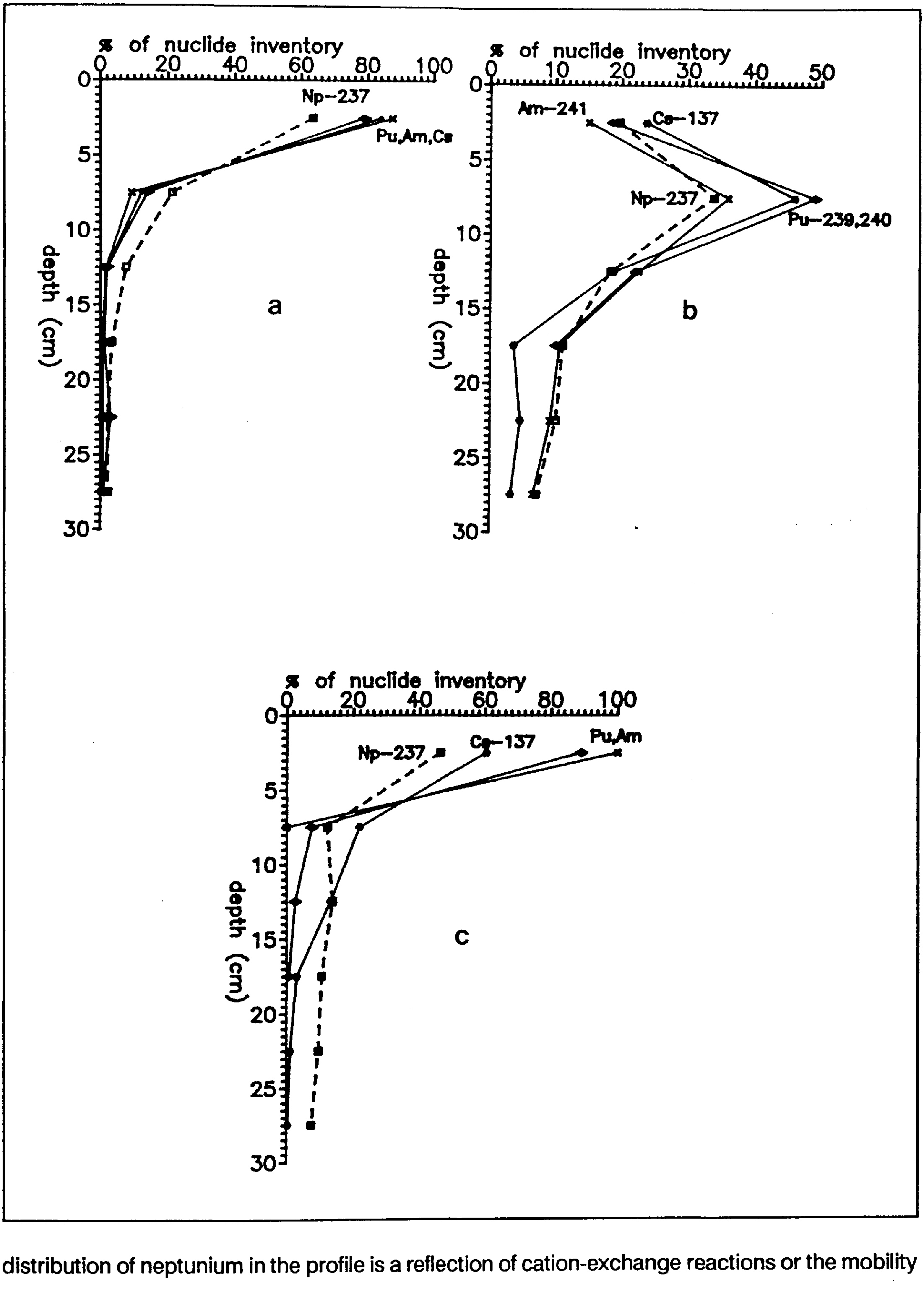
Depth (cm)	^{237}Np	^{239,240}Pu	^{137}Cs	^{241}Am
Gley				
0-5	77.5	9.8 x10^{4}	2.7 x10^{5}	2.4 x10^{5}
5-10	25.9	1.7 x10^{4}	3.9 x10^{4}	2.6 x10^{4}
10-15	9.3	2.4 x10^{3}	6.5 x10^{3}	4.7 x10^{3}
15-20	4.2	1.4 x10^{3}	2.0 x10^{3}	2.0 x10^{3}
20-25	2.6	3.8 x10^{3}	2.2 x10^{3}	1.5 x10^{3}
25-30	2.7	1.2 x10^{3}	2.1 x10^{3}	1.2 x10^{3}
Total	*122*	*1.3 x10^{5}*	*3.2 x10^{5}*	*2.8 x10^{5}*
(Fallout)	(2.9)	(3.0 x10^{3})	(1.6 x10^{5})	(68)
Sand				
0-5	5.2	2.1 x10^{3}	6.0 x10^{4}	3.4 x10^{3}
5-10	9.0	5.5 x10^{3}	1.2 x10^{5}	8.0 x10^{3}
10-15	4.9	2.5 x10^{3}	4.8 x10^{4}	5.1 x10^{3}
15-20	3.0	1.1 x10^{3}	9.1 x10^{3}	2.4 x10^{3}
20-25	2.7	-	1.2 x10^{4}	2.1 x10^{3}
25-30	1.9	-	8.2 x10^{3}	1.5 x10^{3}
Total	*26.8*	*1.1 x10^{4}*	*2.5 x10^{5}*	*2.3 x10^{4}*
(Fallout)	(2.5)	(2.6 x10^{3})	(1.4 x10^{5})	(58)
Conifer				
0-5	2.6	2.6 x10^{3}	1.7 x10^{4}	1.3 x10^{3}
5-10	0.7	2.2 x10^{2}	6.2 x10^{3}	-
10-15	0.8	77.3	3.8 x10^{3}	-
15-20	0.6	21.0	8.7 x10^{2}	-
20-25	0.5	-	3.2 x10^{2}	-
25-30	0.4	-	96.8	-
Total	*5.6*	*2.9 x10^{3}*	*2.8 x10^{4}*	*1.3 x10^{3}*
(Fallout)	(2.5)	(2.6 x10^{3}	(1.4 x10^{5})	(58)
Deciduous				
0-5	-	-	1.9 x10^{4}	6.2 x10^{2}
5-10	-	-	2.5 x10^{3}	-
10-15	-	-	5.6 x10^{2}	-
15-20	-	-	7.5 x10^{2}	-
20-25	-	-	4.9 x10^{2}	-
25-30	-	-	2.5 x10^{2}	-
Total	-	-	*2.3 x10^{4}*	-
(Fallout)	(2.5)	(2.6 x10^{3})	(1.4 x10^{5})	(58)
Moor				
0-5	-	-	1.2 x10^{4}	88.2
5-10	-	-	6.1 x10^{2}	-
10-15	-	-	3.8 x10^{2}	-
15-20	-	-	2.3 x10^{2}	-
20-25	-	-	96.8	-
25-30	-	-	92.4	-
Total	-	-	*1.3 x10^{4}*	-
(Fallout)	(3.3)	(3.4 x10^{3})	(1.8 x10^{5})	(76)

its potential mobility, and ^{241}Am, due to ingrowth from ^{241}Pu, is fraught with uncertainty. Further discussion will be restricted to the gley, conifer wood and beach sand sites.

Comparison of the inventory distribution of ^{237}Np within these profiles reveals interesting behaviour of neptunium relative to the other nuclides. The gley contains $\geq$80% of the ^{137}Cs, ^{241}Am and ^{239,240}Pu total inventories within the surface 0 to 5 cm. For ^{237}Np, however, only 63% of the total nuclide inventory is in the top 5 cm. The remaining fraction of the total inventory is more evenly dispersed down the profile with > 2% of the total in the 25 to 30 cm section compared to < 1% for the other nuclides listed. In the conifer woodland, despite the limited data set for ^{239,240}Pu, the effect is much more pronounced than in the gley. 46% of the total ^{237}Np is found in the top 0 to 5 cm, compared to 60% for ^{137}Cs and 100% of the detectable ^{241}Am. If the inventories to 20 cm are considered, 56% of the ^{237}Np is in the surface 5 cm compared to 89% for ^{239,240}Pu and 61% for ^{137}Cs. It appears that, in spite of the potentially variable source terms for nuclide contamination in the soil profiles, to a first approximation, neptunium is behaving in a very different way to Cs and the other transuranics. The gley site is strongly reducing (Livens, 1985) with moderately high organic matter content and acid pH. A large proportion of the Fe, Al and Mn is present in oxalic acid extractable phases which are suggested to represent exchangeable and amorphous oxyhydroxides (see section 2.3.11). The soil also contains a significant proportion of the clay-sized particle fraction (Livens and Baxter, 1988a). From the previous discussions (section 1.3 and 3.3) it is unlikely that this distribution is an artefact of past Sellafield discharges. The accumulation rates at the gley site are such that ^{134}Cs is not able to penetrate to any appreciable depth before it decays. This suggests that the nuclide input is integrated in the surface horizons of the soil and movement to depth is slow. The physicochemical status of the gley is such that the transuranic and Cs nuclides are immobilized in the top few centimetres of the profile by ion exchange and complexation reactions with soil components. In the case of neptunium, however, immobilization is not so favoured. The data of Harvey and Kershaw (1984) (see section 1.3) indicate that there is only partial reduction of more mobile Np^{V} to Np^{IV} observed in Irish Sea sediment pore waters. It may be the case for the gley site that, whilst conditions are known to be sufficiently reducing to convert plutonium oxidation states to Pu^{IV} (Livens, 1985), the conditions of E_h and pH are not suitable for the complete reduction and immobilization of neptunium and that the apparent "smearing" of its distribution in the profile is a reflection of the dispersal of a mobile component.

For the conifer woodland site, the mobility of ^{237}Np with respect to the other radionuclides is even greater. The soil is the most acidic of the profiles studied and physically appears to be well aerated. From these observations one would expect that the neptunium would be in the least complexing and more mobile pentavalent oxidation state. The highly organic surface horizons are expected to have the most influence on the soil acidity (Brady, 1974) and on the subsequent speciations of the nuclides released into the soil solution. Whether the observed

Figure 3.3: Variation in the % of nuclide inventory with depth in (a) gley, (b) sand and (c) conifer.



distribution of neptunium in the profile is a reflection of cation-exchange reactions or the mobility of Np-organic complex species is uncertain.

In the sand profile, the distribution is very different again. There is no striking difference between the relative distributions of the nuclides with depth. It has already been suggested (see section

3.2) that the most important features of the profile are the low pH and sesquioxide phases and the subsurface organic matter maximum. The correlation of highest % of total inventory with organic matter further emphasises this relationship.

To attempt to compare the processes operating in the conifer woodland profile with those in the gley and the sand would be unwise since both the source terms for the radionuclides and the chemical reactions appear to be very different. It may be that the natures of the mobile phases of neptunium are similar and that the differences in distribution are a reflection of the differing redox status between sites. However, the soil textures at each site and the proportions of sesquioxides are very different, suggesting that such a model is too simplistic. Without doubt, on the basis of the distribution of nuclides with depth, the most important observation is that the neptunium distribution is very different from all the other nuclides determined within the same profiles. The very different behaviour of neptunium between soil profiles is quite unlike that of the other transuranics measured.

3.5 THE RELATIVE BEHAVIOUR OF NEPTUNIUM IN THE MARINE AND TERRESTRIAL ENVIRONMENTS OF W. CUMBRIA

Whilst absolute activity concentrations and nuclide inventory distributions have revealed behaviourial differences between neptunium and other Sellafield-derived nuclides, further information is available from a detailed consideration of nuclide ratios. The ratio of one nuclide to another of the same element has been shown to be an important fingerprint of the source of the activity. In the case of nuclides of different chemical elements, the ratio of activities not only reflects the nuclide source term but also the significance of chemical processes which have operated between source and sampling point. Table 3.9 presents radionuclide ratio data for ^{237}Np with respect to ^{239,240}Pu, ^{137}Cs and ^{241}Am. The ranges of Sellafield discharge values and weapons fallout are included. It is assumed that from the plutonium and caesium nuclide ratios and the total observed inventories, the dominant source of contamination for the gley site are Sellafield discharges. The mechanism for contamination of this site can be envisaged to be dominated by the solid phase and to involve:

(i) transfer of contamination from the pipeline to Irish Sea sediments and waters,
(ii) transfer from the sediments and waters to Ravenglass silt
(iii) transfer from Ravenglass to the gley site.

This model, although simplistic, includes the logical pathways and major physicochemical changes between sites. The presence of mm diameter hot particles in both the silt and gley sites would also emphasise the relationship. The ratio data in Table 3.9 are calculated from data for which ^{237}Np values are only available back to 1978. The much higher discharges during the mid 1970's observed for other transuranics may well have indicated similar trends for ^{237}Np and

Table 3.9: Nuclide activity ratios for ^{237}Np relative to ^{239,240}Pu, ^{241}Am and ^{137}Cs.

		^{239,240}Pu/^{237}Np	^{241}Am/^{237}Np	^{137}Cs/^{237}Np
BNFL Sellafield discharges		100-20	20-3	7000-1500
Irish Sea	**Core A**	1395	2280	4700
Sediment (Aug-87)	**Core E**	433	1040	2010
Ravenglass Silt		264	284	215
Gley				
0-5cm		1270	3124	3500
5-10cm		637	990	1520
10-15cm		271	500	700
15-20cm		331	480	480
20-25cm		1400	550	830
25-30cm		430	433	760
Sand				
0-5cm		394	643	11500
5-10cm		603	890	13000
10-15cm		500	1030	10000
15-20cm		380	800	3000
20-25cm		NA	763	4400
25-30cm		NA	790	4300
Conifer				
0-5cm		1000	495	6600
5-10cm		330	NA	9000
10-15cm		100	NA	5000
15-20cm		35	NA	1500
20-25cm		NA	NA	600
25-30cm		NA	NA	200
Weapons Fallout		1020	23	53600

integrated discharge ratios influenced accordingly. However, whilst it is possible to calculate the likely ^{241}Am discharge and ingrowth inventories (Day and Cross, 1981 and section 1.3) and the data for ^{239,240}Pu and ^{137}Cs are more comprehensive, the ^{237}Np totals cannot be realistically assessed by back-calculation. This limitation in the range of discharge ratios used in the following discussion must not be overlooked but, despite it, the behaviour implied from such a mechanism provides an interesting insight into the geochemistry of neptunium.

On discharge, the ratios for Np to Pu and Am all increase by an order of magnitude in the solid phase, whilst those to Cs are preserved. Fairly similar behaviour is implied for both cores which are approximately 40 km apart, although it would appear that Np is lost preferentially relative to Pu as a fuction of distance from Sellafield. It appears that with respect to Pu and Am, Np is fairly mobile and behaves more coherently with Cs than with the other transuranics. This is not so surprising in view of the K_d values (see section 1.3) of the species expected to be stable in the discharges and the Irish Sea. Neptunium shows a significantly lower particle affinity than the other transuranic nuclides (Holm, 1981; Pentreath and Harvey, 1981; Harvey and Kershaw, 1984; Byrne, 1986). Assuming that the Irish Sea sediment is the dominant nuclide source for the Ravenglass silt, then the change in nuclide ratios from sediment to silt implies a relative enrichment process for Np relative to Pu, Am and Cs. A possible explanation of this anomaly may be related to the observed remobilisation of Pu from the solid phase in the Esk estuary as salinity decreases. However, the exact mechanistic details are unclear for Pu and cannot be elucidated for Np using the information here. Livens and Baxter (1988a) performed particle size analysis of samples of silt and gley. The highest ^{239,240}Pu activities in both the gley and the silt were in the fine (< 2 μm) size fractions, although the coarser, organic-rich (250 to 2000 μm) fraction showed some enrichment. Moving from the silt to the gley, there is a slight change in the particle size distribution with a loss of approximately 10% from the 8 to 125 μm fraction to the finer fractions. This change in distribution may be responsible for the enrichment of activities in the gley relative to the silt. The silt is the obvious source of activity for the gley, the amount of silt-derived material in the gley is uncertain. Further observations from sequential leaching studies will be presented in section 3.6 but they have identified an association of Np with a carbonate component of the silt (approximately 2.5% by weight $CaCO_3$; the gley is carbonate-free). Dissolution of this phase during transfer to the gley could provide a relatively mobile Np fraction capable of moving within the soil. This, however, can only be a partial explanation since this carbonate-associated Np "pool" is smaller than the losses observed.

At the sand site, the situation is somewhat different. The site is sufficiently close to the sea to be heavily influenced by sea-to-land transfer of nuclides from the Irish Sea and to be inundated by estuarine waters at hightide. The Pu, Am : Np nuclide ratios are significantly lower than in the marine sediments and are slightly higher than in the Ravenglass silt. The dominant feature is still the subsurface maximum of organic matter. ^{137}Cs data are undoubtably influenced by Chernobyl deposition and are not really of use here. However, there is a slight difference between Pu and Am with respect to Np. The ^{241}Am/ ^{237}Np maximum ratio occurs 5 cm lower than the ^{239,240}Pu/ ^{237}Np ratio maximum. Whether this reflects preferential Am movement relative Pu is uncertain as the difference is within propagated uncertainties (2σ). The general decrease of ratios with depth in the gley and sand reflects the greater mobility of Np in the profiles.

The conifer woodland site is not influenced by direct marine incursion. Nuclide source terms have already been discussed and include weapons fallout, aerial releases from Sellafield and onland transfer. Of these only the fallout ratio Pu, Am : Np is known and, from Table 3.8, weapons fallout is expected to have a significant contribution, although it cannot account for all the observed activity. Thus for ^{239,240}Pu/ ^{237}Np in the 0 to 5 cm section is similar to Irish Sea sediment values, whilst the ^{241}Am/ ^{237}Np ratio is midway between the Irish Sea and fallout signatures. Any potential mechanism affecting ^{237}Np deposition and mobility based on nuclide ratios is complex to interpret especially when the source-term signatures are unknown and, from the anomalous ^{238}Pu/ ^{239,240}Pu ratio, aerial discharges may be important.

3.6 SEQUENTIAL LEACHING OF SOILS AND SEDIMENTS

The results for the sequential leaching of a sample of Ravenglass silt and a sample of the surface 0 to 5 cm of the gley soil are presented in Table 3.10. The sum of the leached activities of both ^{237}Np and ^{241}Am agree well with the theoretical sum of activities.

The limitations of the sequential leaching approach to nuclide speciation have already been discussed in section 2.3.11. In spite of these, the comparative use of such an approach, preserving sample to leaching reagent ratios and sample manipulations, provides the most appropriate approach to the problem and the most reliable observations. The results presented in Table 3.10 and Figure 3.4 show that, with respect to Am, Np displays a significantly different geochemical association in both of the samples studied. For the Ravenglass silt, the order of association is:

Table 3.10: The distributions of ^{237}Np and ^{241}Am in fractions from sequential leaching of gley and silt samples (% of total activity $\pm 2\sigma$).

Fraction	^{237}Np		^{241}Am	
Gley (0 to 5 cm)				
Exchangeable	11.3	±3.5	<0.3	
Adsorbed	7.9	±1.1	1.6	±0.2
Organic	54.9	±10.1	44.9	±2.4
Hydroxide	10.8	±1.9	9.0	±1.4
Residual	15.4	±2.5	44.2	±6.6
Ravenglass silt				
Exchangeable	5.7	±1.5	<3.9	
Adsorbed	35.4	±8.1	22.2	±2.5
Organic	28.8	±5.5	48.9	±7.0
Hydroxide	26.7	±3.1	17.2	±3.4
Residual	3.5	±1.1	7.8	±1.9

Np: adsorbed> hydroxide≈ organic> exchangeable> residual

Am: organic> adsorbed> hydroxide> residual> exchangeable

and for the gley:

Np: organic> residual> hydroxide≈ exchangeable> adsorbed

Am: residual≈ organic> > hydroxide> adsorbed> exchangeable

The organic phase is important for both nuclides in each of the samples analyzed. These results agree well with Am data presented for the same sites by Livens (1985) and Livens and Baxter (1988b), using an identical leaching scheme. In these studies, Pu was found to be predominantly associated with the organic phase, with oxide and residual phases following in importance. What is striking about the distribution of neptunium is the relatively high proportion contained in the more readily available exchangeable and adsorbed phases in both samples. The specifically adsorbed phase (acetic acid) also includes carbonate mineral material, which has been shown to be important for Am (Wilkins *et al*, 1984; Livens and Baxter 1988b) in estuarine sediment samples from the area. It has been suggested that the proportion of the nuclides associated with this mineral phase is lost to the organic and oxide phases during the transition from predominantly marine influence to the surface of the gley soil (Wilkins *et al*, 1984). The Am data in this study appear to follow the same trend, although the residual phase does increase in importance in the gley soil. To an extent, the same effect is seen for Np. It has already been suggested (Billon, 1981; see section 1.3 also) that soluble Np^V carbonate complexes are important in the marine speciation of Np. From the leaching results and the discussion in section 3.5 above, the carbonate phase in the silt may be an important influence on Np speciation. Transfer from the marine to the terrestrial environment shows an increase in the importance of the organic and residual phases but to a lesser extent than for Am. Dissolution of carbonate-associated Np, probably as Np^V, as the E_h and pH conditions change, may release a significant proportion of the Np which is then not readily immobilized in the surface horizons of the gley in the manner of Pu, Am or Cs. This could then form a more mobile component which is partly responsible for both the deeper penetration of Np down the gley profile and also the apparent dilution or loss of ^{237}Np activity during the transition from the silt to the gley.

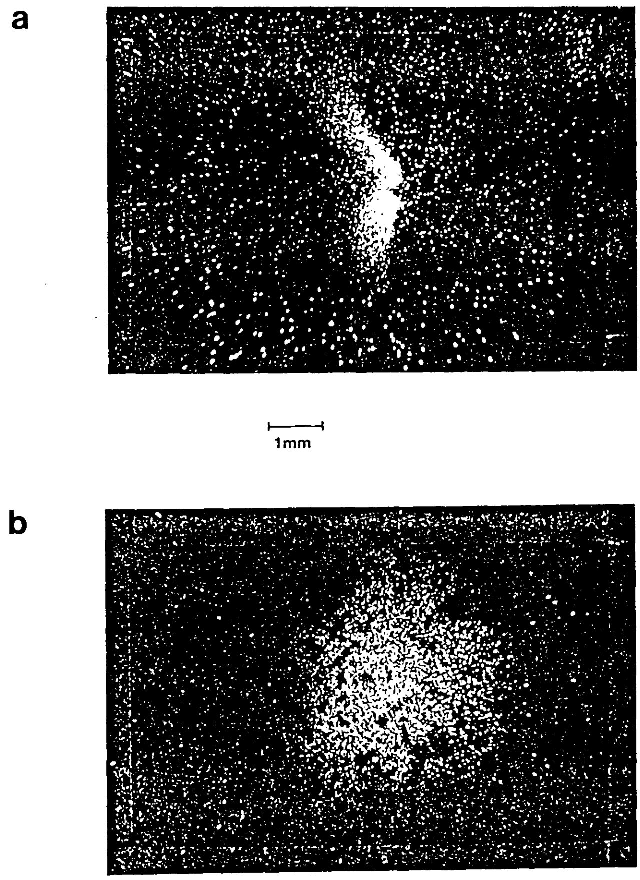
Certainly the data provide circumstantial evidence only for this type of mechanism. Further follow-up work is essential to gain a better understanding. Unfortunately, there was in sufficient time available to carry out such work during the postgraduate study programme. However, combined with the nuclide ratio data and nuclide inventory distributions (sections 3.3 and 3.4), relative to the other transuranics and important fission product nuclides, the results suggest that neptunium has a greater environmental mobility than closely related nuclides.

3.7 "HOT PARTICLES" IN SOILS AND SEDIMENTS FROM W.CUMBRIA

This section presents qualitative results from the series of preliminary experiments described in section 2.3.10. In short, hot particles have been observed in surface horizons from a number of the soils sampled and also in the Ravenglass silt. Attempts to isolate and analyze the particles were unsuccessful. However, a number of observations are worth discussing here.

The "hot spots", as expressed on the plastic detectors, varied in intensity from very sharply defined regions, in which the centre of the detector had been "burnt out" on etching to much lower activity, "warm spots" where individual overlap of the tracks was less pronounced but a definite accumulation above the general background was apparent. Table 3.11 summarizes the relative abundances of hot spots and warm spots observed in the samples analyzed. The spots were all of the order of 0.5 to 1.0 mm in diameter as defined by tracks at 90° incidence to the detector. The variation in the shapes is considerable and is concluded, in the comprehensive study by Hamilton and Clifton (1987), to be due to geometric factors between the location of the hot particle source, the surrounding sediment particles and the detector surface. Hot particle sizes were identified from the distribution of tracks caused by α-particles impinging normally to

Figure 3.4: Examples of hot spots from particles observed in surface samples of soils and sediments from W. Cumbria (a) gley (0 to 5 cm), (b) conifer (0 to 5 cm).



the film (ie circular holes were generated). The particles detected in this study are similar in size to those observed in Solway coastal samples (Baxter *et al*, 1989) and considerably larger than the average sizes observed previously in the Esk (Hamilton, 1981). Figure 3.4 illustrates the range of hot spots observed in this study. The problems of the subjective definition of hot spots are obvious pitfalls in this approach (Hamilton, 1985). Further limitations in extending the qualitative results to some form of quantitative abundance are in the sample preparation and presentation to the detector. A wide range of soil and sediment types was studied and, for each sample exposed, approximately 1.3 to 1.4 g of material was used. Some selectivity of the fixing media was observed for the silty and sandy samples in particular and consequently a bias in the grain size presented may have occurred during source preparation.

Further consideration must also be given to the presence of natural hot particles from minerals containing relatively high concentrations of uranium and thorium series nuclides. These will include zircons, apatites and some biotites (Wedepohl, 1978; Deer *et al*, 1980). However, the absence of any hot spots from samples from >5 cm depth would appear to exclude this possibility. Hamilton (1981; 1985) suggests that the sharply defined hot spots are derived from

Table 3.11: Relative hot particle abundance in samples of soil and sediments from W. Cumbria.

Sample	Hot Particles (Y/N)	Relative Abundance /Comments
Gley		
0-5 cm	Y	>10, very intense
5-10 cm	Y	8, moderate intensity
10-15 cm	N	
15-20 cm	N	
20-25 cm	N	
25-30 cm	N	
Sand		
0-5 cm	Y	4, moderate intensity
5-10 cm	N	
Conifer		
0-5 cm	Y	3, moderate intensity
5-10 cm	N	
Deciduous		
0-5 cm	Y	2, diffuse
5-10 cm	N	
Upland Moor		
0-5 cm	N	
Ravenglass Silt	Y	3, intense

fresh Sellafield particulate material associated with the liquid effluents and that the more diffuse spots may represent nuclides associated with mineral coatings or some inert component of the phase. Certainly, where there is direct contact with marine-derived material (ie gley and beach sand), the hot spots observed are more sharply defined and are of higher activity. More diffuse material may represent aged deposits or a different source term. The presence of more diffuse hot spots in the surface horizons of the conifer and deciduous wood profiles, which have already been shown to exhibit a possible signature from aerial releases, is a significant observation regarding the nature of this material.

3.8 PLUTONIUM ANALYSIS BY ICP-MS

3.8.1 VALIDATION AND APPROACH

A limited number of samples were analyzed for plutonium nuclides by ICP-MS under the same operating conditions as used for ^{237}Np assay (see section 2.3.4). Based on normal spectrum background, the lower limits of detection for plutonium nuclides by ICP-MS are not as low as those for routine radiometric methods (see section 2.3.4). However, the ratio of $^{240}Pu/^{239}Pu$ is not readily determined by conventional radiometric techniques, although complex, low energy, γ-photon counting systems have been used in some situations (Himsamatsu and Sakanoue, 1984; Komura *et al*, 1984; Sakanoue *et al*, 1987). A mass-based system provides the most suitable technique for this determination. Thermal ionization mass spectrometry (TIMS) has been used by a number of authors as an alternative to radiometric assay for plutonium in environmental samples (Noshkin, 1980; Buesseler and Halverson, 1987; Buesseler and Sholkovitz 1987b). As is the case for ^{237}Np (section 2.3.4), sample preparation for plutonium analysis by TIMS is more rigorous than is needed for routine analysis by ICP-MS. Nevertheless, TIMS offers ultimately superior detection limits to the ICP-MS configuration used in the present study. However, the use of electrothermal vaporisation for sample introduction in ICP-MS has been reported to increase instrument sensitivity by 1 or 2 orders and will no doubt increase the versatility of ICP-MS analysis for nuclides of plutonium in environmental samples.

Samples of soil and sediment were treated as described for routine α-spectrometry, except that at the stage prior to electrodeposition, the final column eluate was taken to dryness and redissolved in 1% v/v nitric acid before direct aspiration into the ICP-MS. ^{242}Pu ($t_{1/2} = 3.87 \times 10^5$ years) was used to account for losses during chemical separation and to quantify the ^{239}Pu and ^{240}Pu by isotope dilution. An example of the type of spectra obtained is shown in Figure 3.5. Very low abundances of ^{232}Th and ^{238}U are found in the fractions analyzed. The presence of a small peak at mass 241 is probably due to ^{241}Pu (section 2.3.4).

To test the validity of the analysis, the combined $^{239}Pu + ^{240}Pu$ activity was calculated from the measured mass abundances and compared to the $^{239,240}Pu$ activity found in the solution

Table 3.12: A comparison of ICP-MS and α-spectrometric analysis for nuclides of plutonium (a) Bq kg^{-1} ±2σ, (b) 240/239 mass and activity ratios ±2σ.

(a) **Sample**		ICP-MS	α-spectrometry	
			SURRC	(ITE)
Ravenglass Silt	^{239,240}Pu	1.038 ±0.036	0.874 ±0.222	(1.060 ±0.080)
	^{238}Pu	NA	0.200 ±0.060	(0.200 ±0.032)
Gley 5-10 cm	^{239,240}Pu	0.289 ±0.012	0.311 ±0.006	(0.299 ±0.026)
	^{238}Pu	NA	0.030 ±0.008	(0.029 ±0.008)
10-15 cm	^{239,240}Pu	0.042 ±0.004	0.038 ±0.006	(0.034 ±0.003)
	^{238}Pu	NA	0.006 ±0.001	(0.005 ±0.001)

(b) **Sample**	(mass)	(activity)
Ravenglass Silt	0.217 ±0.089	0.769 ±0.059
Gley 0-5 cm	0.182 ±0.023	0.667 ±0.089
	0.208 ±0.004	0.769 ±0.024
5-10 cm	0.080 ±0.026	0.294 ±0.095
	0.092 ±0.008	0.333 ±0.033
10-15 cm	0.167 ±0.036	0.588 ±0.138

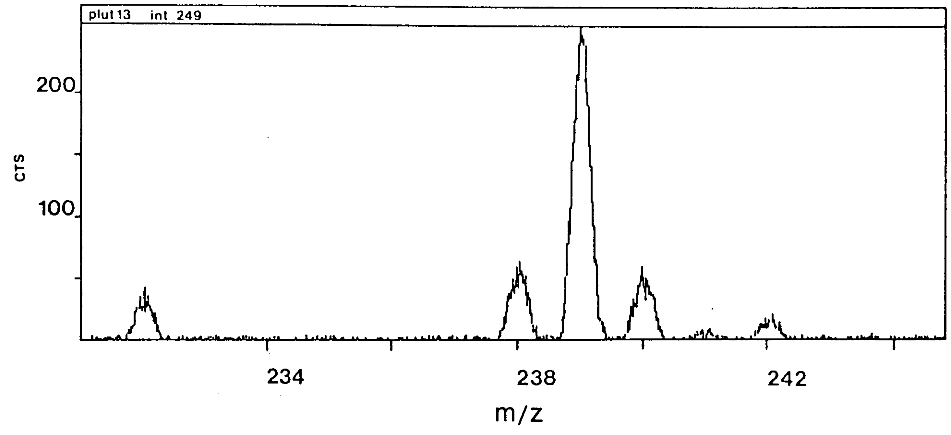
residue by α-spectrometry. The results were also compared to the routine plutonium analyses carried out at ITE (Merlewood) and discussed in earlier sections (see 3.3.2). The data are compared in Table 3.12a and are in good agreement within ±2σ criteria.

3.8.2 ^{240}Pu/ ^{239}Pu NUCLIDE RATIOS IN SAMPLES FROM W. CUMBRIA

The results obtained for the determination of ^{240}Pu/ ^{239}Pu in a limited number of soil and sediment samples are summarized in Table 3.12b. The mass ratio of ^{240}Pu/ ^{239}Pu is close to 0.2 for all samples except the 5 to 10 cm section of the gley which is considerably lower (≈ 0.09). The resolution of the sectioning may have had some effect on the 10 to 15 cm sample and resulted in some tailing of this feature to a lower depth. Table 3.12b also shows that the feature in the 5 to 10 cm section is seen in the value of ^{238}Pu/ ^{239,240}Pu which was noted from earlier analyses (section 3.3.2).

The ^{240}Pu/ ^{239}Pu ratio is a sensitive indicator of the source of plutonium and is highly dependent on the operational neutron flux. In studies of fallout plutonium, a number of

Figure 3.5: Mass spectrum showing ^{240}Pu and ^{239}Pu (integrated counts s^{-1}) from a sample of W. Cumbrian soil after partial radiochemical purification and preconcentration. ^{242}Pu added as an internal standard.



determinations of this ratio have been made. These are shown in Table 3.13. The mean world-wide fallout ratio is 0.179 ±0.014 (Perkins and Thomas, 1980) and is generally constant, except in the region 30°N to 30°S, where it is slightly lower. This feature has been attributed to smaller tests carried out on the US mainland, these involving lower total neutron fluxes and fallout material being deposited closer to the test sites. Larger tests with higher total neutron fluxes generated a higher proportion of ^{240}Pu, which penetrated the stratosphere and was circulated over wider latitudes. Koide *et al* (1985) are able to resolve two components of weapons fallout on the basis of the ^{240}Pu/ ^{239}Pu ratios in ice cores from Greenland. These are early, pre-moratorium (1963) tests, with higher neutron fluxes and a higher ratio close to the MIKE test and the post-moratorium tests of smaller devices with generally lower ratios. Recently, McCarthy and Nicholls (1990) have shown that ^{240}Pu/ ^{239}Pu ratios in samples of soil and sediments from W. Cumbria are, in some sites, much lower than values expected for fallout or high burn-up material. It is suggested that this is due to the release to the atmosphere of low burn-up plutonium from, for example, irradiated uranium oxide during the period 1952-1955.

The W. Cumbrian samples have a significantly different ^{238}Pu/ ^{239,240}Pu ratio compared to weapons fallout and consequently mark the plutonium inventories as being dominated by Sellafield. The measured ^{240}Pu/ ^{239}Pu ratios show similar values to fallout and indicate that the Sellafield releases were of plutonium derived from Magnox fuel with a high "burn-up" to give a modest inventory of ^{240}Pu. Figure 3.6 shows the variation in nuclide composition for ^{239}Pu and ^{240}Pu in a number of different fuel types as a function of fuel burn-up. In the case of Magnox fuel, the 0.182 mass ratio is reached after 2 to 3 GWD/Te of operation and for the other fuel types after 8 to 10 GWD/ Te. It can been seen that the measurement of this nuclide ratio is potentially a very sensitive indicator of fuel burn up. This may well become increasingly

Table 3.13: Published $^{240}Pu/^{239}Pu$ ratios for samples contaminated by weapons test fallout material.

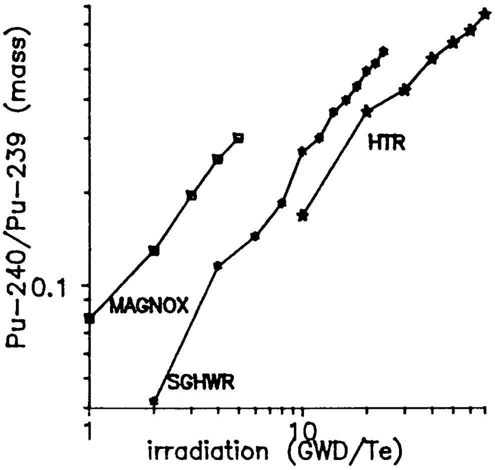
mass ratio	source/ comments
0.179 ± 0.014	world wide fallout average, (Perkins & Thomas, 1980)
0.364	MIKE test debris at T_0 (Perkins & Thomas, 1980)
0.116 0.092	water samples, Enewetak Lagoon, 1972 (Noshkin, 1980)
0.309 ± 0.067	fish bone, Glenn Island, Enewetak
0.341 ± 0.023	viscera, Glenn Island, Enewetak (Noshkin, 1980)
0.207 ± 0.017	live coral, Bikini, 1976
0.309	soil/ vegetation mean, Bikini, 1976 (Noshkin, 1980)
0.220 - 0.090	post-moratorium (Koide *et al*, 1985)
0.340 - 0.210	pre-moratorium (Koide *et al*, 1985)
0.193 - 0.105	sediment cores, Atlantic Ocean, (Beusseler & Sholkovitz, 1987b)
0.163 - 0.052	pore waters, Atlantic Ocean, (Beusseler & Sholkovitz, 1987b)

important in following the future discharges from Sellafield when the nature of the fuel processed changes (see section 1.3). The high ratio observed at depth in the gley would indicate that it may represent lower burn-up Magnox fuel. It is uncertain whether the feature represents the expression of the events responsible for the aerial releases in the liquid discharges from the site. It is unlikely that such a marine-dominated site, so far from Sellafield, would contain significant input from atmospheric debris. Since quantifiable ^{134}Cs does not occur at depth, it is not expected that the gley site would have a sufficiently high net accumulation rate to preserve such historical events which may have been expressed in the liquid discharges at the time. What is clear is that, despite the consistent fuel type processed, from these few analyses it can be shown that there has been some variation in plutonium source in the discharges and that a combined mass-spectrometric/ α-spectrometric analytical programme can provide important and more detailed information on the source of plutonium nuclides than would be available from routine analyses.

3.9 SUMMARY AND CONCLUSIONS

The three methods studied (α-spectrometry, ICP-MS and NAA) are all very different in their approach to ^{237}Np assay. In principle, they are all equivalent in terms of detection limit and all require some form of chemical separation and preconcentration before analysis.

Figure 3.6: The variation in ^{240}Pu/ ^{239}Pu (mass) with burn-up for different types of nuclear fuel (data from Tyror, 1971).



The neutron activation method is a highly sensitive approach, which, due to the characteristics of the UTR-300 and the operating procedures used, cannot be utilized to its full potential at the SURRC. Interference from the nuclides of naturally occurring uranium is a problem with ^{237}Np analysis in general but is severe in the case of neutron activation analysis. This study has shown that these interferences can be reduced or even removed by additional chemical separation steps. This does, however, increase the time required for analysis. The commonly used alternative of adding a much higher activity of yield tracer for the post-irradiation chemical separation is not considered advantageous. These observations prompt the question of whether the problems with this method prevent its use as a routine method of assay for a diverse range of sample types and sizes. Further disadvantages are the need to work with activated samples which require more skilled operational control than for conventional low-level environmental radiochemical assay. The half-lives of the nuclides involved mean that the post-irradiation manipulations need to be conducted in controlled radiation areas close to the activation source. The size of the neutron source is the fundamental factor in determining the analytical sensitivity. The phrase "the bigger the better" is an apt description of the flux requirements which not only places further emphasis on radiological protection but also on irradiation source accessibility and availability.

Alpha-spectrometry, as a reference technique, is still a versatile and sensitive method and will no doubt continue to be the most used detection system for the analysis of the α-emitting nuclides. For ^{237}Np, the main problems are the radiochemical purity and source preparation requirements. The specific activity of ^{237}Np and the low levels encountered in the environment necessitate very long counting times and this an important factor to be considered with respect to sample throughput.

ICP-MS appears to be one of the most important recent developments in radioanalytical technology. For the long-lived radionuclides and actinides in particular, it has comparable if not improved, sensitivity to routine radiometric methods. The most striking feature is the very rapid sample throughput which is a small fraction than for conventional radiometric methods. In the case of ^{237}Np, there are no real interferences and the background in the actinide mass region is low and stable. With the advent of electrothermal vaporization sample introduction, detection limits are reported to be improved by 1 or 2 orders of magnitude, with smaller sample size requirements. Should this promise be translated to routine analysis, the scope of the technique in general and more specifically in application to the actinides, will be enormous. Sample preparation requirements are far less rigorous than for conventional radiometry. Although there is still a need for preconcentration and chemical separation, minimal processing of samples has shown that the simultaneous determination of Np and Pu nuclides in the same sample concentrate is possible. Further development of more efficient mass-spectrometry systems will also increase the power of this technique.

Of the anthropogenic elements, analysis of the nuclides of Np and Pu will benefit greatly from the new breed of chemical reagents which allow bulk group extractions. There are a number of potential candidates including the organophosphorus compounds DHCEMP and CMPO. These reagents selectively extract tri, tetra and hexavalent actinides and are currently being developed and assessed in the treatment of high level liquid wastes from the reprocessing industry.

A few problems still exist for the ICP-MS technique, although none seriously detracts from its potential. Because of the wide mass range capabilities, the operational parameters of ICP-MS instruments are often run at a set of compromise positions for the whole mass range. When analysis of nuclides (stable or unstable) is required for levels close to the instrument detection limits, a series of optimal operating conditions should be determined. These can increase the sensitivity of the instrument by up to 25%. Further observations over a year or more of routine analyses suggest that instrument stability in the long-term is an important variable. There can be a large variation in detection limit and response factors and, at the levels of ^{237}Np analyzed here, these have been important factors in determining the success of the sample analyses. It may not be so surprising that this type of variation does occur when such very different techniques are coupled, the rate of wear and tear on components is high and regular servicing essential. It is certainly not the "all singing, all dancing" panacea for the analyst. Although it requires dedicated operating personnel to monitor long-term behaviour, it is still a very significant addition to the field of analysis.

The quantification of ^{237}Np was made by external calibration and the chemical yields monitored by short-lived tracer. Whilst this provides excellent results in general, it is apparent that, for the full potential of ICP-MS for ^{237}Np assay to be realized, a long-lived Np nuclide must be used to allow quantification by isotope dilution. For Pu assay, ^{242}Pu is of suitable half-life and Pu analysis is relatively straightforward, with the added advantage of reduced matrix interference. Unfortunately there are few nuclides of Np of suitable half-life and the radiochemical purity of the available standards is relatively poor. The need for natural matrix standard reference materials for ^{237}Np analysis cannot be emphasised too strongly. Until such a material or series of materials are provided for the analytical community, the quality of the data on ^{237}Np in the environment must be regarded with some caution.

The literature on neptunium behaviour in the environment is very sparse and is restricted mainly to laboratory and field studies of varied sophistication and relevance. A limited number of reports on the behaviour of Np in the marine environment appears to indicate that it is relatively mobile compared to the other transuranics and does show some redox sensitivity. Terrestrial data are absent except for one study which would appear to indicate mobility within soil horizons.

The analyses here from a limited number of sediments and soil samples indicate that predominantly Sellafield-derived ^{237}Np has a significantly higher mobility in the soils when compared to the other transuranics. The mechanisms involved in the transfer of the observed nuclide inventories from the Irish Sea and this accumulation in the terrestrial environment indicate that Np is associated with the environmentally sensitive components in the solid phase and that a significant portion of the inventory is "lost" during the transition. Np generally appears to exhibit its hybrid U/Pu chemical nature in the environment. What has been shown so far is that Np exhibits unique environmental behavioural characteristics which warrant much further study and that the analytical technology for such studies is now available.

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Appendix A

The derivation of the equation to correct for the decay of short-lived nuclides during counting

The derivation can be found in a number of publications (Hoffman and Van Camerik, 1965; Junod, 1974; Heydorn, 1980). The variables are defined as:

N_0 = no. of radioactive atoms at the start of the count
N_T = no. of radioactive atoms at the end of count time T
$t_{1/2}$ = half-life of radionuclide
λ = decay constant of radionuclide
Δt = time correction

The time correction (Δt) is the time from the start of counting at which the observed activity (total counts/ count time) is the true activity of the sample. This is added to any decay correction required for pre-count decay (eg Appendix B.).

From the standard decay equations:

$$-dN/dt = N\lambda \qquad \text{and} \qquad N = N_0e^{-\lambda t}$$

in time T:

$$N_T = N_0e^{-\lambda t} \qquad \text{and} \qquad \begin{aligned}\Delta N &= (N_0 - N_T)\\ &= (N_0 - N_0e^{-\lambda t})\\ &= N_0(1 - e^{-\lambda t})\end{aligned}$$

The observed disintegration rate (DR) for counting interval T is:

$$DR = \Delta N/T \quad = N_0(1 - e^{-\lambda t})/T$$

which occurred at some time (Δt) after the start of the count and as:

$$DR = -dN/dT \quad = N\lambda = \lambda N_0e^{-\lambda\Delta t}$$

the DR's can be equated:

$$N_0(1 - e^{-\lambda t})/ T = \lambda N_0 e^{-\lambda\Delta t}$$

$$\therefore \qquad e^{-\lambda\Delta t} = [(1 - e^{-\lambda t})/ \lambda T] = [-\lambda\Delta t] = [\ln ((1 - e^{-\lambda t})/ \lambda T)]$$

since $\lambda = \ln 2/ t_{1/2}$
then:

$$-(\Delta t \ln 2/ t_{1/2}) = \ln [t_{1/2}(1-e^{-T\ln 2/t1/2})/ T \ln 2]$$

$$\therefore \qquad \Delta t = (-t_{1/2}\ln [t_{1/2}(1-e^{-T\ln 2/t1/2})/ T \ln 2])/ \ln 2$$

if R = number of half-lives counted (ie $T/ t_{1/2}$), then:

$$\Delta t = (-t_{1/2}\ln [\quad (1-e^{-R\ \ln 2})/ R \ln 2])/ \ln 2$$

this simple relationship is applied to all decay corrections used for ^{239}Np and ^{238}Np calculations in the main text.

Appendix B

The calculation of ^{237}Np concentration in samples assayed by neutron activation analysis

The ^{237}Np activity in the samples analyzed in this study is determined by a lengthy series of calculations, which are outlined below. A number of observations were made, which constitute the input raw data for the calculation. Each measurement has an associated uncertainty which must be propagated through the calculation. The combination of the uncertainties for this study was made using standard equations from Faires and Boswell (1981) and described in great detail by Bambynek (1988).

Since two suitable γ-rays were available for both ^{238}Np and ^{239}Np, mean values were determined from the individual treatment of the spectrum peaks.

Measurements taken:

weight of sample (grams) = g
amount of ^{237}Np standard used = C_{sd}
time samples removed from the reactor = T_0

γ-spectrum of purified samples and standards, post-irradiation:

count start = T_{AMI}(sam/sd)
count duration (s) = t_{AMI}(sam/sd)
activity of ^{238}Np at 984 or 1030 keV (counts sec^{-1}) = A_{MI}(sam/sd)
activity of ^{239}Np at 227 or 277 keV (counts sec^{-1}) = B_{MI}(sam/sd)

γ-spectrum of ^{239}Np tracer, post-irradiation:

count start = T_{SBMI}
count duration (s) = t_{SBMI}
activity of ^{239}Np at 227 or 277 keV (counts sec^{-1}) = B_{MI}(sp)
weight of tracer solution (g) = W_{TI}
weight of aliquot of tracer added (g) = W_{SI}

γ-spectrum of iron wire flux monitors:

count start = T_{FS}
count duration (s) = t_F
activity of ^{59}Fe at 1099 or 1291 keV (counts sec^{-1}) = A_{MF}
weight of flux monitor (g) = W_{FLUX}

γ-spectrum of purified samples and standards, pre-irradiation:

count start = T_{BMP}
count duration (s) = t_{BMP}
activity of ^{239}Np at 227 or 277 keV (counts sec^{-1}) = B_{MP}(sam)

γ-spectrum of ^{239}Np tracer, pre-irradiation:

count start = T_{SBMP}
count duration (s) = t_{SBMP}
activity of ^{239}Np at 227 or 277 keV (counts sec^{-1}) = B_{MP}(sp)
weight of tracer solution (g) = W_{TP}
weight of aliquot of tracer added (g) = W_{SP}
geometry correction factor 10 ml vial to 3 ml pot = CF_{GEOM}

The overall calculation for ^{237}Np activity concentration in the samples analyzed (Bq g^{-1}) is given by:

$$X\ (\mathrm{Bq\ g}^{-1}) = (C_{SAM}/\ g) \times (100/\ Y_{PRE} + Y_{POST})$$

where C_{SAM} is the total activity of ^{237}Np found in g grams of material and is obtained from the simple activity : concentration relation:

$$C_{SAM}/\ C_{SD} = Z_{SAM}/\ Z_{SD}$$

where Z_{SAM} and Z_{SD} are the induced activities and Y_{PRE} and Y_{POST} are the % chemical recoveries of the pre- and post-irradiation separations respectively. However, the Z and Y values must include some correction for the decay of the short-lived nuclides involved, variations in the neutron flux irradiating the samples and standards. Consequently:

$$Z_{SAM} = A_{MI}(\mathrm{sam}) \times CF_{FLUX} \times CF_{COUNT} \times CF_{DECAY}$$
$$Z_{SD} = A_{MI}(\mathrm{sd}) \times CF_{FLUX} \times CF_{COUNT} \times CF_{DECAY}$$

A_{MI}(sam/ sd) are the ^{238}Np activities measured above and the CF values are ^{238}Np correction factors for the flux variation, decay during counting and decay after removal from the reactor at T_0.

(i) CF_{FLUX} is the flux variation monitored by iron wire monitors attached to the base of the sample and standard vials during irradiation. The specific activity of the wires at T_0 is given by: $(A_{MF}/\ e^{-\lambda(TFS-TO)})/\ W_{FLUX}$ and are all normalized to $CF_{FLUX}(sd) = 1$. For a sample with a higher integrated neutron flux $CF_{FLUX}(sam) > CF_{FLUX}(sd)$ and a lower integrated neutron flux $CF_{FLUX}(sam) < CF_{FLUX}(sd)$.

(ii) CF_{COUNT} is the decay correction for decay during the accumulation of the γ-spectrum using the equation derived in Appendix A and where $R = t_{AMI}(sam/ sd)/ t_{1/2}$ to give appropriate values of Δt.

(iii) CF_{DECAY} is the correction for decay of ^{238}Np from T_0 to the start of the count. This involves a simple decay term $e^{-\lambda[(TAMI-T0)+\Delta t]}$

The calculation of the pre- and post-irradiation chemical recoveries for purified samples and standards involves a similar series of corrections to obtain Y_{PRE} and Y_{POST}:

(i) Y_{PRE} is the chemical recovery of the samples only for the pre-irradiation separation and is defined by:

$$[\text{observed activity } (X_{obs})/ \text{ expected activity } (X_{exp})] \times 100.$$

X_{obs} is given by:

$$B_{MP}(sam)/ e^{-\lambda[(TBMP-TSPBMP)+\Delta t]}$$

and for X_{exp} the term

$$B_{MP}(sp)/ e^{-\lambda\Delta t} \times (W_{SP}/W_{TP}) \times CF_{GEOM}$$

(ii) Y_{POST} is the % chemical recovery of the samples and standards for the post-irradiation separation and is defined by:

$$[\text{observed activity } (V_{obs})/ \text{ expected activity } (V_{exp})] \times 100.$$

V_{obs} is given by:

$$B_{MI}(sam/sd)/ e^{-\lambda[(TAMI-TSBMI)+\Delta t]}$$

and for V_{exp} the term

$$B_{MI}(sp) / e^{-\lambda\Delta t} \times (W_{SI}/W_{TI}) + (X_{OBS} / e^{-\lambda(TSBMI - TSBMP)} \times 1/ CF_{GEOM}).$$

The last term takes into account any undecayed ^{239}Np from the pre-irradiation separation. It is simply the X_{OBS} value decayed from T_{SBMP} to T_{SBMI}. The interaction of neutrons with nuclei of ^{239}Np is not accounted for. The nucleus has a low reported fission cross-section ($\sigma_f < 1$) and a moderate neutron capture cross-section to give ^{240}Np and ^{240m}Np (25 and 23 barns respectively). The time involved between the end of the pre-irradiation separation and irradiation was generally such that the ^{239}Np present had decayed to insignificant levels and this factor could be ignored.