CHAPTER THIRTY-SIX

ANALYTICAL CHEMISTRY OF PLUTONIUM*

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36.1 INTRODUCTION

In 1940, shortly after the discovery of fission, McMillan and Abelson studied the recoil range of fission products induced by neutrons incident on a thin uranium foil (McMillan, 1939; McMillan and Abelson, 1940). While fission products were mostly ejected from the foil, two activities were significantly retained, one with a half-life of 23 min and the other with a half-life of 2.3 days. The shorter activity was known (Meitner *et al.*, 1937) to belong to ^{239}U, produced by neutron capture in ^{238}U; the longer-lived activity was demonstrated to be the beta-decay daughter of ^{239}U, an isotope of the new element neptunium, which had an atomic number of 93.

$$^{238}\text{U} + \text{n} \rightarrow {}^{239}\text{U} \xrightarrow{\beta^-} {}^{239}\text{Np} \qquad (36.1)$$

By analogy, just as the beta decay of ^{239}U produces ^{239}Np, the subsequent beta decay of ^{239}Np must also produce an isotope of a new element with atomic number 94 (plutonium), which was not observable in earlier experiments because of a lack of sensitivity for the detection of radioactive species with long half-lives. The first isotope of plutonium to be discovered (Seaborg *et al.*, 1946)

was produced in 1940 during an intense bombardment of a uranium target with 16-MeV deuterons.

$$^{238}\text{U}(\text{d}, 2\text{n})\,^{238}\text{Np} \xrightarrow{\beta^-} \,^{238}\text{Pu} \qquad (36.2)$$
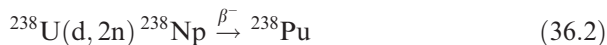
The most common and useful isotope of plutonium, ^{239}Pu, was discovered in 1941 (Kennedy *et al.*, 1941; Seaborg *et al.*, 1946), when approximately 0.5 µg was produced during a neutron irradiation of a large amount of uranium. In subsequent experiments performed on the sample, it was determined that ^{239}Pu underwent fission under the action of neutrons in a comparable way to ^{235}U (Seaborg and Wahl, 1948). More relevant to the subject of this chapter is that the first pure plutonium sample, free from carrier material, was isolated in the summer of 1942 (Cunningham and Werner, 1949a) as 2.77 µg $^{239}\text{PuO}_2$. Stoichiometric determination of plutonium, synthesized as the iodate by the same authors, provided the first direct evidence of an oxidation state of plutonium, Pu (IV) (Cunningham and Werner, 1949b).

The development of the chemistry of plutonium occupies a unique place in the history of chemistry and chemical engineering. In the summer of 1945, a plutonium-fueled nuclear explosive device was successfully tested at Alamogordo, New Mexico. The span of time from the first detection of the element on the tracer scale to production and chemical isolation on the kilogram scale was less than 5 years. What is particularly impressive in this effort was the fact that the periodic table provided very little guidance as to the chemical properties expected for the element; plutonium was initially placed as eka-osmium, but the observation of the stability of the trivalent states of plutonium, americium and curium led to the actinide hypothesis (Bohr, 1923; Seaborg, 1944; Seaborg and Loveland, 1990), the last major reorganization of the periodic table.

The study of plutonium chemistry has always been strongly influenced by the historical era in which the work was being performed. The analytical chemistry of plutonium in the 1940s–1960s was dominated by fuel cycle applications, including those having to do with recovering weapons-usable materials. In the 1970s–1990s, environmental concerns dominated; the emphasis of the science shifted from studies and measurements with highly radioactive samples to studies at ever lower limits of detectability. Now, with the resurgence of power applications (advanced fuel cycle), and a need to counter nuclear proliferation and the smuggling of nuclear materials, higher activity applications are again regaining the forefront of the science (see Section 36.6.2).

All isotopes of plutonium are radioactive. Known isotopes span mass numbers 228–247, with analytical chemistry applications being dominated by the isotopes from mass 236 through 244, whose properties are listed in Table 36.1. Most plutonium isotopes decay through emission of an alpha particle; the characteristic alpha-decay energies provide a means by which radiometric determinations can be performed.

The longest-lived isotope of plutonium, ^{244}Pu, has a half-life of 8.08×10^7 years, so long that it has a significant decay branch by spontaneous fission

Table 36.1 *Isotopes of plutonium of interest to the analytical chemist* (*Firestone and Shirley*, 1996). *The α-decay energies correspond to the transitions with the highest emission probabilities. Values given in parentheses represent the uncertainty in the last significant figure.*
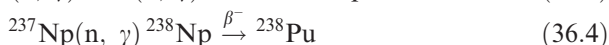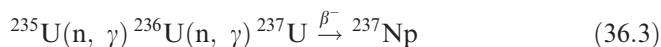
Mass number	Half-life	Decay mode	Method of production
236	2.858(8) years	α (5.7677 MeV) SF (1.37(7) $\times 10^{-7}$%)	^{235}U(d,n)^{236}Np $\xrightarrow{\beta^-}$ ^{236}Pu
237	45.2(1) days	EC (99.9958%) α (5.334 MeV)	
238	87.7(3) years	α (5.4990 MeV) SF (1.85(4) $\times 10^{-7}$%)	^{237}Np(n,γ)^{238}Np $\xrightarrow{\beta^-}$ ^{238}Pu ^{242}Cm→^{238}Pu + α
239	24110(30) years	α (5.1566 MeV) SF (3.0(8) $\times 10^{-10}$%)	^{238}U(n,γ)^{239}U $\xrightarrow{\beta^-}$ ^{239}Np $\xrightarrow{\beta^-}$ ^{239}Pu
240	6563(7) years	α (5.1682 MeV) SF (5.75(5) $\times 10^{-6}$%)	^{239}Pu(n,γ)^{240}Pu
241	14.35(10) years	β$^-$ (99.998%) α (4.896 MeV, 0.00245(2)%)	^{240}Pu(n,γ)^{241}Pu
242	3.733(12) $\times 10^5$ years	α (4.9005 MeV) SF (5.54(6) $\times 10^{-4}$%)	^{241}Pu(n,γ)^{242}Pu
243	4.956(3) h	β$^-$	^{242}Pu(n,γ)^{243}Pu
244	8.08(10) $\times 10^7$ years	α (4.589 MeV) SF (0.121(4)%)	^{242}Pu(n,γ)^{243}Pu(n,γ)^{244}Pu ^{243}Am(n,γ)^{244m}Am (EC) →^{244}Pu

(0.12%). It has been reported as being present at low levels in natural sources (Hoffman *et al.*, 1971); the spontaneous fission of ^{244}Pu in the early solar system is thought to have given rise to a significant fraction of the heavy xenon isotopes present in primordial materials. In nature, ^{239}Pu (half-life 2.41 $\times 10^4$ years) is produced in ultra-trace amounts in uranium ore bodies by neutron capture on ^{238}U followed by two successive β$^-$ decays. The neutrons necessary for this process arise from spontaneous fission of ^{238}U, neutron multiplication in the neutron induced fission of ^{235}U, and from (α,n) reactions caused by alpha particles emitted in the decay of the uranium isotopes and their daughter isotopes interacting with light elements in the ore bodies (Levine and Seaborg, 1951; Peppard *et al.*, 1951).

While plutonium can be argued to be naturally occurring, its only important source is synthetic. Simplistically, plutonium can be thought to arise in the competition between neutron capture in ^{238}U and neutron-induced fission of ^{235}U in reactor fuel or in a uranium blanket. In this way, the production of plutonium is inextricably entwined with the fission process, and many radio-analytical procedures begin with a mixture of uranium, plutonium and fission products.

The plutonium isotopes are produced mainly through neutron absorption by ^{238}U. The principal production pathway involves the subsequent beta decays of

^{239}U and ^{239}Np followed by sequential neutron captures to produce the heavier plutonium isotopes. Plutonium occupies a position on the chart of the nuclides on the brink of where spontaneous fission becomes a significant decay mode. The SF decay branch of ^{240}Pu limits the use of plutonium in nuclear explosive devices and impacts design requirements. Limitation of "weapons-grade" plutonium to material whose isotopic content is less than 8% mass 240 is a consequence of this. As a result, the operation of a reactor as an economical power source is often at odds with its use as a producer of weapons-usable plutonium. While irradiation of ^{238}U leads to the heavier isotopes of plutonium, competition of neutron capture with the neutron-induced fission of ^{235}U gives rise to ^{238}Pu.

$$^{235}\text{U(n, } \gamma) \,^{236}\text{U(n, } \gamma) \,^{237}\text{U} \xrightarrow{\beta^-} \,^{237}\text{Np} \qquad (36.3)$$

$$^{237}\text{Np(n, } \gamma) \,^{238}\text{Np} \xrightarrow{\beta^-} \,^{238}\text{Pu} \qquad (36.4)$$

This isotope has the undesirable spontaneous fission properties that occur in all of the even-mass plutonium isotopes, and it has an additional drawback of being intensely radioactive due to its short half-life and high alpha-particle energy. This has led to the use of ^{238}Pu as a heat source for thermoelectric generators (Lange and Mastal, 1994; Rinehart, 2001) and in batteries for cardiac pacemakers (Boucher and Quere, 1981; Freedberg *et al.*, 1992).

The different requirements of power and weapons applications lead to what can almost be thought of as two distinct fuel cycles, one involving short, high-flux irradiations of fuel with a minimal enrichment of ^{235}U intended to make weapons-usable plutonium, and one involving long-duration irradiations of ^{235}U-enriched uranium in which the fission products and undesirable plutonium isotopes build up. While of little use in weapons applications, plutonium recovered from power reactor fuel can be mixed with uranium isotopes and synthesized into fresh reactor fuel (Brandstetter *et al.*, 1984; Roepenack *et al.*, 1984). The use of mixed oxide fuel (MOX) is economical because the cost of recovering plutonium may replace the cost of enriching uranium and the cost of safe-guarding and storing excess plutonium (Hildenbrand, 1984).

36.2 PLUTONIUM PROPERTIES

36.2.1 Electronic configuration and oxidation states

A full discussion of this topic can be found in Chapter 7 of this work.

The valence electron configuration of monatomic plutonium in its ground state is 5f^{6}6s^{2}6p^{6}7s^2 (van der Berg and Klinkenberg, 1954; Griffin and McNally, 1955; McNally, 1955) exactly analogous to that of the lanthanide samarium; however, due to the electronic screening of the nuclear potential, the ionization potentials of the valence electrons are similar enough that plutonium has a much richer and varied chemistry than does its lanthanide homolog. In the

Table 36.2 *Ionic radii of plutonium ions in the indicated oxidation states* (*coordination number* 6) (*Shannon*, 1976).
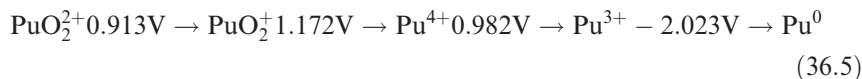
Cation	Ionic radius ($\mathring{A}$)
Pu^{3+}	1.00
Pu^{4+}	0.86
PuO_2^+	0.74
PuO_2^{2+}	0.71

metallic state in bulk, the electronic configuration is $5f^56s^26p^66d^17s^2$ (Soderlind, 1998; Moore *et al.*, 2003; Shim *et al.*, 2007).

The increase in 5f-character in the electronic structures of the actinides with increasing atomic number and the associated decrease in 6d-character leads to wildly variable alloying behavior from one element to the next, which is not observed in the lanthanides. The first ionization potential of plutonium is 6.0258(2) eV (Worden *et al.*, 1993; Erdmann *et al.*, 1998; Waldek *et al.*, 2001) leaving the singly-charged ion with an electronic configuration of $5f^66s^26p^67s^1$.

Plutonium is the first member of the actinide series with a tripositive ion that has enough stability in aqueous solution that it is of use in separations chemistry. The ability to selectively produce either Pu^{3+} or Pu^{4+} in solution and switch between the two at will is the basis of much of the analytical chemistry of the element. In non-complexing media such as perchloric acid, both Pu(III) and Pu(IV) exist as simple hydrated cations. Pu(VI) and Pu(V) are so highly charged that they form a bound dioxygen species, PuO_2^{2+} and PuO_2^+, respectively, similar in structure to the UO_2^{2+} (uranyl) cation, and called plutonyl by extension. Ionic radii for co-ordination number 6 are given in Table 36.2 (Shannon, 1976). As one might expect, redox reactions between Pu(III) and Pu(IV) proceed rapidly, as do reactions between Pu(V) and Pu(VI). Reactions which involve transformation between the simple cation and the dioxocation tend to proceed more slowly. Pu(IV) is a small, highly charged ion that tends to undergo extensive hydrolysis at low acidity, forming a variety of complex ions, and a long-chain polymer. One of the most important aspects of the aqueous chemistry of plutonium is the formation of complex ions caused by the displacement of water molecules in the hydration sphere by anionic ligands, much like hydrolysis can be thought of as the initial substitution of a hydroxyl ion into the hydration sphere.

The redox potentials in 1 M HClO$_4$ are (Lemire *et al.*, 2001):

$$PuO_2^{2+} 0.913V \rightarrow PuO_2^+ 1.172V \rightarrow Pu^{4+} 0.982V \rightarrow Pu^{3+} - 2.023V \rightarrow Pu^0$$

(36.5)

$$PuO_2^{2+} 1.043V \rightarrow Pu^{4+}$$

(36.6)

There will be small differences in the reduction potentials for HCl and HNO$_3$ media. The corresponding redox potentials in 1 M NaOH media are (Peretrukhin *et al.*, 1995):

$$PuO_2^{2+} 0.12V \rightarrow PuO_2^+ 0.67V \rightarrow Pu^{4+} - 0.96V \rightarrow Pu^{3+} \qquad (36.7)$$
$$PuO_2^{2+} 0.34V \rightarrow Pu^{4+} \qquad (36.8)$$

The relative tendency of plutonium ions to form complexes is

$$Pu(IV) > Pu(III) > Pu(VI) > Pu(V). \qquad (36.9)$$

The order of Pu-complex forming ability of some common anions (Comyus, 1960; Gel'man *et al.*, 1962) is:

$$Carbonate > Oxalate > Sulfate > Fluoride > Nitrate > Chloride > Perchlorate$$
$$(36.10)$$
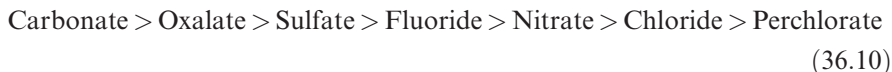
36.2.2   Methods of production

A detailed account of plutonium production methods can be found in Chapter 7 of this work. We reiterate the most relevant information from that chapter.

The first large-scale production and recovery process for plutonium from reactor targets and fuel assemblies involved coprecipitation of Pu(IV) with bismuth phosphate (Lawroski, 1955; Thompson and Seaborg, 1956). It is noteworthy that the industrial process was the result of scaling up microchemical separations by more than a millionfold without much work at an intermediate scale: Pu (VI) is not carried by $BiPO_4$, and a number of oxidation/reduction cycles between Pu(IV) and Pu(VI) through a series of precipitations resulted in a production method with high efficiency and a high decontamination factor from uranium and the fission products.

However, solvent extraction techniques are easier to apply in remote operations than a series of precipitations. In the REDOX process, Pu(IV) was oxidized to Pu(VI) with dichromate ion, followed by extraction into hexone (methylisobutyl ketone, or MIBK). The solvent extraction was carried out in a series of mixer-settlers. This was facilitated by salting the aqueous phase with $Al(NO_3)_3$, resulting in a high nitrate, low acid solution. The Butex process was similar to the REDOX process, but involved extraction into β,β'-dibutoxydiethyl ether instead of a monoketone (Palei and Milyukova, 1967). Both were replaced by the PUREX process in the mid-1950s.

Experience with several solvent-extraction methods has shown that tri(*n*-butyl)phosphate (TBP) is the "best" extractant, combining a great specificity for plutonium and uranium with inexpensive and radiation-resistant reagents and adaptability to remote handling (Morrison and Freiser, 1957; Marcus, 1963), see Section 36.3.7. The PUREX process, based upon mixed phases of aqueous nitric acid and TBP in an organic solvent (usually kerosene), was developed in the late 1940s and put into use at the Savannah River site in 1954 and at Hanford in 1956 (Coleman and Leuze, 1978; Swanson, 1990).

Variants of PUREX are used all over the world today in fuel recovery operations (Alcock *et al.*, 1958; McKay and Streeton, 1965; McKay *et al.*, 1990).

Radiolysis of TBP leads to dibutylphosphate, which forms such a stable complex with Pu(IV) that it is only slowly and incompletely reduced and stripped from the organic phase. As a result, it is customary to store spent fuel for about half a year or longer before processing. For applications where it is desirable for the organic phase to be the dense one, the TBP diluent can be CCl_4 (Pushlenkov *et al.*, 1970).

The production of plutonium metal is similar to the production of both uranium and thorium metals (Vol'skii and Sterlin, 1970; Coffinberry and Miner, 1961; Wick, 1967; McCreary, 1955), see also Chapter 7 of this work. The best reactants are PuF_4 and either Ca^0 or Mg^0 (Anselin *et al.*, 1956).

$$2Ca^0 + PuF_4 = Pu^0 + 2CaF_2 \tag{36.11}$$

PuF_3 can also be reduced by the alkaline earth metals:

$$3Ca^0 + 2PuF_3 = 3CaF_2 + 2Pu^0 \tag{36.12}$$
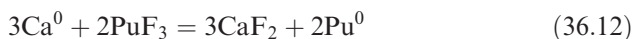
Optimal results are obtained with a 25% excess Ca^0 over the stoichiometric amount. In order to ignite the reacting materials about 10 g of I_2 per kilogram of plutonium is added as a booster. Reaction bombs are lined with magnesia and calcium fluoride, and filled with argon gas. Small amounts of O_2 are not a problem, but can lead to inclusions of Pu_2O_3 in the metal billet. The reaction is initiated in the booster by heating to about 325°C; during the reaction the pressure in the bomb rises to 35 atm and the temperature reaches 1,600°C.

Plutonium metal can also be produced in the reaction of Ca^0 or Mg^0 in 50% excess over the stoichiometric amount needed to reduce PuO_2:

$$2Ca^0 + PuO_2 = 2CaO + Pu^0 \tag{36.13}$$

This chemical system (''direct oxide reduction'', see also Chapter 7 of this work) offers the advantage of being fluoride-free, which reduces the neutron background in the laboratory caused by $^{19}F(\alpha,n)$ reactions. The reaction is usually carried out in CaO crucibles; the final product is small beads of Pu metal coated with CaO reaction product which prevents the formation of a billet. The beads are recovered by dissolving the slag with dilute acetic acid, then washing the product with nitric acid. Lithium metal has also been used to reduce PuO_2 to the metal (Usami *et al.*, 2002).

The initial plutonium metal product contains impurities of Ca^0 and colloidal inclusions of CaF_2, PuO_2, etc. It may also contain fission products from incomplete fuel reprocessing. There are several techniques for improving the purity of the product: (1) Vacuum refining, in which the billet is melted in a MgO or CaO crucible in a good vacuum. The temperature of the melt is increased until the partial pressure of plutonium metal vapor is between 10^{-5} and 10^{-3} torr, at

which point residual alkalis, alkaline earths, and their halide salts are purged from the melt. Pu metal only sparingly wets CaO or MgO, so the product can be delivered from the crucible after cooling. (2) Oxidation refining, in which a small amount of O_2 is introduced into the melt, which moves reactive refractory contaminants into the slag. (3) Electrolytic refining, in which the plutonium sample is immersed in a molten chloride salt under an inert atmosphere, where it acts as the anode in an electrolytic cell (Knighton and Steunenberg, 1965; Mullins *et al.*, 1968). At a high current density, liquid Pu metal is collected on the surface of a tungsten cathode, and drips off into a collector. Transition metal contaminants (and americium) tend to stay in the anodic sludge, rare earths and other actinides concentrate in the electrolyte, and the yield of purified Pu metal can be as high as 97%. (4) Zone melting, in which the plutonium billet is fabricated into a bar along which a high-temperature zone is passed (Blau, 1998; Spriet, 1965). Many impurities stabilize δ-phase plutonium (see below); as a melt zone is moved along the bar, impurities which form a eutectic with Pu concentrate in the melt, while impurities that raise the melting point effectively move in the other direction. After repeated passes, the ends of the bar contain most of the impurities, and are removed.

A freshly prepared plutonium metal surface is silvery white, but quickly oxidizes to a characteristic gray-brown color. It oxidizes more readily than does uranium, and its reactions in air are much like those of cerium metal, producing an adherent oxide layer. Plutonium is the most complex metallic element. Its *f*-electrons are on the verge of being localized; as a result, it undergoes a large number of phase transitions under minimal temperature and pressure variations.

Plutonium metal is very reactive. Its place on the electromotive table (ε° = 2.03 V) is near that of scandium. It is only slowly attacked by water, but is rapidly dissolved by halogen-based mineral acids. In nitric and sulfuric acids, dissolution is quite slow due to passivation of the surface; nitric acid reacts with plutonium oxide and is used to clean the surface of a metal sample with little involvement of the underlying material (Myasoedov, 1987).

Plutonium forms high-melting-point compounds with all A-subgroup metals and metalloids, but except for δ-phase and ε-phase mixtures, solid solubilities are limited. Most δ-phase solid solutions are stable at room temperature or can be retained by rapid cooling; the ε-phase is not retained at room temperature in any Pu mixture. Significant solid solutions in the other Pu phases are rare; Np and Pu are mutually soluble in the α-phase, and Th and U mix with Pu in both the β- and γ-phases. α-phase plutonium is highly reactive with oxygen, while δ-phase plutonium is less so. Alloys that stabilize the δ-phase are more corrosion resistant than the others and are more workable; this is similar to the situation with the bcc γ-phase of uranium.

Elements that are commonly alloyed with plutonium to stabilize the workable δ-phase include gallium and aluminum (Hecker and Timofeeva, 2000; Wick, 1967; Vol'skii and Sterlin, 1970) and, less often, americium (Timofeeva, 2003;

Ellinger *et al.*, 1968). Only addition of americium results in a stable δ-phase alloy at room temperature; the others produce metastable alloys. Plutonium also forms several intermetallic compounds (Bochvar *et al.*, 1958), the most important of which is Pu_6Fe, which tends to build up along grain boundaries in metal samples. Because iron is common in both the laboratory and in the industrial environment, it is dangerous to assign a significant iron concentration in a plutonium salt as an indicator of prior weaponization. Other common intermetallic compounds include Pu_6Co, $PuNi$, $PuMn_2$, and $PuBe_{13}$.

36.2.3 Safety

The penetrating radiations associated with the radioactive decays of the plutonium isotopes themselves are not very intense (see Table 36.3). For the major isotopes, most of the decay energy goes into the emission of alpha particles and low-energy electrons. For the 5.16-MeV alpha particle emitted in the decay of ^{239}Pu, for example, the range in air is less than 4 cm, and is only about 40 μm in soft biological tissues. For well-characterized samples of limited activity, gloves and a ventilated enclosure are adequate radiation protection.

However, all isotopes of plutonium are highly radiotoxic if they enter the body through the lungs, the digestive tract, or breaks in the dermis. Irradiation by alpha particles emitted in plutonium decay can produce significant irreversible changes in the bones, liver, kidneys and lungs; protocols must be observed to detect and control contamination on the benchtop, floors and protective clothing in the laboratory.

Control of the absorption of plutonium isotopes through the skin or digestive tract is largely a matter of good laboratory practice that applies in any radiochemistry laboratory, and can be obtained through the use of appropriate personal protective equipment. Practically speaking, inhalation is the most probable mode of entry of plutonium into the body, and the engineering solution to containment usually requires the maintenance of a negative pressure differential between the working point and the environment in which the analyst is located. The larger the radioactivity level being handled by the analyst, the more severe the engineering controls. Chemical form is also important, as is the isotopic mixture (and resulting specific heat) of the sample. As an example, an experienced analyst can probably handle up to a millicurie (~10 mg) of weapons-grade plutonium in solution in a fume hood; beyond that level, he/she should almost always plan on working in a negative-pressure gloved box. However, in applications involving plutonium metal or finely divided powders, the fume-hood limit should be reduced to 10 μCi because the possibility of the material becoming airborne in unmanageable concentrations becomes significant. A common path for unplanned release of airborne plutonium isotopes is in the production of high-level sources, where the plutonium is deposited from solution onto a solid substrate and heated to convert to the oxide (see Section 36.3.9).

Table 36.3 *Decay energies of the longer-lived plutonium isotopes and* [241]*Am. Emission probabilities in parentheses.* (*Firestone et al.*, 1996)

Nuclide	Alpha energies (MeV)	Gamma rays (keV)
[236]Pu	5.7677 (69.3%)	109.0 (0.012%)
	5.7210 (30.6%)	
	5.6138 (0.18%)	
[238]Pu	5.4990 (70.9%)	43.50 (0.039%)
	5.4563 (29.0%)	99.85 (0.0074%)
	5.3577 (0.105%)	152.7 (0.00094%)
[239]Pu	5.1566 (73.3%)	375.1 (0.00155%)
	5.1443 (15.1%)	413.7 (0.00147%)
	5.1055 (11.5%)	
[240]Pu	5.1682 (72.8%)	45.24 (0.045 %)
	5.1237 (27.1%)	104.2 (0.0071%)
	5.0212 (0.085%)	160.3 (0.00040%)
[241]Pu	5.042 (2.50×10^{-5}%)	59.54 (0.000845%)[a]
	4.972 (3.19×10^{-5}%)	103.7 (0.000102%)
	4.896 (2.04×10^{-3}%)	148.4 (0.000185%)
	4.853 (2.99×10^{-4}%)	208.0 (0.000518%)[a]
	4.798 (2.94×10^{-5}%)	
[241]Am	5.544 (0.34%)	59.54 (35.9%)
	5.4856 (85.2%)	335.4 (0.000496%)
	5.4429 (12.8%)	662.4 (0.000364%)
	5.388 (1.4%)	722.0 (0.000196%)
[242]Pu	4.9005 (77.5%)	44.92 (0.036%)
	4.8562 (22.4%)	103.5 (0.00781%)
	4.7546 (0.098%)	158.8 (0.000454%)
[244]Pu	4.589 (80.6%)	554.6 (20.9%)[a]
	4.546 (19.4%)	597.4 (11.7%)a

[a] Daughter in equilibrium.

Another common contamination pathway is through corrosion of a metal sample. Plutonium metal oxidizes slowly in dry air, with a rate determined by its surface properties, temperature, and alloying elements (if any). The oxidation rate is less for alloy-stabilized δ-phase plutonium than it is for pure α-phase Pu (Waber *et al.*, 1961). The rate of oxidation of plutonium by moist air is orders of magnitude more rapid than the rate of oxidation by dry air. Water acts catalytically, and the reaction intermediate involves the transient production of hydrogen and the metal/oxide interface (Stakebake *et al.*, 1993; Martz *et al.*, 1994). For more information on this topic, see Chapter 29 of this work.

There are special difficulties associated with the analysis of samples that are enriched in [238]Pu, or aged high-burnup materials in which significant ingrowth of americium has occurred. At high concentrations, the decay heat generated in these samples can be sufficient to boil their solutions. This can cause problems both in ion exchange (where the resin bed can turn over through convection)

and in solvent extractions (where phase separation becomes difficult). Even with small samples, any application in which the sample is handled in drops (e.g. effluent from a column separation) can result in severe contamination of the local environment through nuclear recoil and the resultant self-transfer of the parent isotope from the drop to the surrounding air.

Exposure to ionizing radiation from sources outside the body is not a significant problem if the analyst is handling small quantities of nearly pure plutonium. However, it may be significant in fuel cycle applications in which the analytical sample might contain fission products or in the case of plutonium oxide or fluoride compounds where neutrons can be formed via (α, n) reactions. An irradiated fuel element from a power reactor will generate a close-in radiation field of thousands of radians per hour, even after a substantial cooling time; an analytical sample taken from that fuel element will generate a dose roughly proportional to its relative mass. As with most radiochemical applications, dose remediation is through the control of time, distance and shielding. Remote operations from behind a shielding wall may be required.

It should be remembered that the fission products represent a significant fraction of the periodic table. In addition to the salts of plutonium, which constitute a tractable radiochemical analyte, a fuel element sample will liberate radionuclides during dissolution that are considered volatile under most conditions (e.g. [85]Kr, [129]I and [106]Ru); scrubbing of the gas-phase work-station effluent (e.g. caustic bubbling, electrostatic precipitation and activated carbon filtering) is a normal precaution when working with spent fuel samples. Generally, a manageable spent fuel sample has decayed to the point that dissipation of heat and the radiolytic evolution of hydrogen and oxygen are not important issues if the work station is adequately ventilated.

A criticality accident is an uncontrolled chain reaction that develops in fissile material. The amount of energy released is usually small by power standards, but local emission of neutrons and gamma rays can be quite intense. Fortunately, an analytical sample of plutonium is generally too small for criticality to be of concern during processing. However, sampling operations and storage and archiving protocols may require the analyst to consider criticality. This is particularly important in nuclear forensic applications where the sample may be a true unknown.

It is unlikely that the analyst will be working with substantial quantities of fissile plutonium isotopes without some interaction with a criticality safety engineer, either directly or indirectly. However, when setting up a new process, it is important to remember that the potential for a criticality accident depends on the mass and density of the fissile material present, to what extent neutrons emitted by the material are moderated, absorbed and reflected by the surroundings, and the geometrical distribution of the material. The use of hydrogenous materials should be minimized, but containers of small cross-sectional area and long linear dimension are helpful. Several kilograms of plutonium metal in a compact shape are required to produce a critical mass if reflectors are absent;

when suspended in water as a slurry of the oxide, the critical mass drops to as little as 500 g.

Special safety concerns exist when finely divided Pu must be handled. Plutonium metal powder can be made through the hydrogenation and dehydrogenation of plutonium metal. Plutonium reacts with hydrogen at room temperature, disintegrating the metal (via an enormous volume change) to a $PuH_{1.9-3.0}$ powder. Both the alpha and the alloy-stabilized delta phases are attacked by hydrogen. Heating this product in a vacuum furnace at 200°C results in the formation of plutonium hydride, PuH_2; however, unlike uranium, the hydriding/dehydriding process reduces plutonium to a much coarser powder, and the billet may have to be crushed (Handwerk *et al.*, 1965). Increasing the furnace temperature to 420°C recreates the metal in powder form, in the alpha phase. The apparatus in which this reaction takes place must be stringently free of oxygen. Similar techniques exist for powdering thorium and uranium through hydriding/dehydriding (Grainger, 1958; Ward *et al.*, 1979).

Plutonium is pyrophoric in air in bulk (see Fig. 7.64), burning with an intense white light, not unlike magnesium metal. Fine powders of the metal can spontaneously ignite unless protected from air. See Chapter 29 of this work.

36.3   SAMPLE PREPARATION AND SEPARATION METHODS

Plutonium analytical chemistry from both weapons (including non-proliferation) and power applications includes characterization of isotopic ratios, determination of plutonium contents, identification and quantification of contaminant species of nuclear materials. There are three types of sample that confront the analyst: (1) Samples whose matrix is mainly plutonium (nuclear forensics and heat sources); (2) samples where plutonium is a component in another matrix (fuel cycle, environmental applications), and (3) samples where plutonium is a minor or trace element. Many of the techniques required for the first two sample types are similar.

36.3.1   Obtaining the sample

Samples submitted for plutonium chemical analysis are as widely varied as are the uses of the element. Weapons applications are likely to produce plutonium metal samples, other structural materials that are contaminated through proximity, and salt cakes left over from casting processes. Reactor applications are more likely to produce ceramic samples, either before or after exposure to neutrons; because these materials are designed to stand up to extremes of temperature and a harsh chemical environment, they can be difficult to analyze. Nuclear forensic analysis of weapons-usable materials usually deals with storage forms, often powdered oxide samples. The byproducts of fuel reprocessing

can be solid, liquid or a mixture of solid and immiscible liquids as possible sample states. The material forms of samples arising in environmental monitoring can be literally anything, from floor sweepings or absorbent swipes from a nuclear facility, to water samples from deep underground, to loose soil or vegetation.

Activity levels can also span the gamut from curies to sub-picocuries. Sometimes the bulk of the activity is due to decays of the plutonium isotopes, and sometimes (as in fuel applications) the matrix is the major contributor to the radioactivity of the sample. Sometimes the majority of the mass of the sample is plutonium and criticality is a concern, and sometimes the plutonium concentration is so low that only a de minimis level can be estimated. Given the complexity of plutonium chemistry, the problem facing the analyst can be daunting.

36.3.2 Subsampling considerations

When subsampling is required, the analytical result as applied to the sample as a whole is no better than is the assumption of homogeneity of the medium of the material. From an analyst's perspective, in a perfect analysis the entire sample can be sacrificed, passed into solution (where homogeneity can be assumed), and quantitative aliquots taken (by volume or mass) that can be related back to the original solution. Unfortunately, this is rarely the case.

When an apparently homogeneous powder is to be analyzed, it should be thoroughly pulverized in a blending apparatus and heated at 90°C for an hour before being sampled. Either a given sample must comprise a single particle (homogeneity of the bulk medium does not apply) or a sufficient number of particles to satisfy the assumption that a representative sample has been taken. The materials from which the moving components of the blender are constructed should be compared with the analyte list – stainless steel is a preferred material, but a common analyte in a PuO_2 sample is iron. In this case, the analyst may want to use a classical ceramic mortar-and-pestle in the pulverization step. This also has the advantage of being inexpensive; to avoid cross-contamination it is a usual practice to discard the blending apparatus after a single use unless subsequent samples are related to one another or are part of the same process. The preferred material for the sample container used in drying operations is borosilicate glass. Weighing of the dried sample should take place as soon as possible after drying (consistent with weighing at room temperature), preferably in a dry box – low-fired plutonium oxide is somewhat hygroscopic.

Samples presented as a liquid must be stirred or agitated for at least half an hour before sampling, and during the sampling process. It is always more satisfactory to take an analytical aliquot shortly after the container is filled. In this way, even a fairly turbid near-solution can be treated as a homogeneous liquid during sampling operations; however, the procedure is not applicable if undissolved solids or heavy sediments are present. Agitation of large containers

like shipping drums containing high radionuclide contents requires some engineering. It should be remembered that plutonium (IV) polymer is invisible in suspension in small quantities; all liquid samples for plutonium analysis *must* be stirred during subsampling.

Sampling of plutonium metal, alloy, and hydride samples is complicated by pyrophoricity. When possible, the sample should be handled in nitrogen or an inert atmosphere. Foils that are less than 1-mm thick can be cut with scissors or shears; if the surface is not cleaned prior to cutting, the operation can be performed in air. Shearing and punching are used to sample heavier gauge material. Bulk metal such as rods or plates are sampled by milling or drilling in inert atmosphere and collecting the chips. Unless the surface is of interest, it should be removed prior to sampling. The depth of the cut and the speed of milling should be regulated so as to avoid excessive heating and consequent oxidation and phase destabilization. Small chips are preferred over large chips, but powder should be avoided. When cross contamination has been an issue, a hacksaw has been used if the planar extent of the material is not too great. For purposes of decontamination, it is generally sufficient to replace the blade between samples.

The properties of pure plutonium metal (cf. Section 36.2.2) make it difficult to handle. Most applications that employ large quantities of plutonium make use of a salt or the oxide. The major exception is in the construction of nuclear explosive devices, for which metal is required. Traces of common metallic contaminants in a sample of a chemical compound of plutonium could be an indication of prior use in weapons applications, of use to the nuclear forensic analyst.

### 36.3.3   Preparation of an analytical solution

The chemical methods used to separate radioactive substances from one another are the same as those used for stable substances with constraints introduced by half-life and the evolution of decay heat. Just as in classical separations, the merit of a radiochemical separation is judged in terms of both the yield and the purity of the separated material. The goals of high purity and high recovery are often inconsistent. We discussed subsampling concerns above (Section 36.3.2). If the concentrations of a variety of analytes are to be measured in a given analytical sample, it is often easiest to start from an analytical solution obtained by dissolving the material (either the sample or a subsample).

Plutonium metal is dissolved by most mineral acids that supply anions that overcome passivation. Hence, HCl, HBr, HI and $HClO_4$ are all effective, while HNO_3 and H_2SO_4 are not. The acid concentration of the entire solution should remain above 1 M and should be stirred and cooled during the entire dissolution process to avoid formation of plutonium(IV) polymer. It is normal to add a single drop of concentrated HF to the final solution to remediate polymer formation.

Most salts of plutonium, including carbides and oxides, will eventually dissolve in hot, concentrated nitric acid containing a small amount of HF or H_2SiF_6 (Tallent and Mailen, 1977). PuO_2 that has been ignited to very high temperatures ("high-fired oxide") can be particularly difficult to dissolve, and conventional dissolution can take a long time (Harvey *et al.*, 1947). PuO_2 prepared at temperatures below 800°C has small crystallites that may have defects. Crystal size is larger at temperatures in excess of 1,100°C. Samples calcined at this temperature and above are stoichiometric, but are most difficult to dissolve. Aged materials and neutron-irradiated samples tend to dissolve more readily, a function of radiation damage to the sample matrix (Gilman, 1965; Nikitina *et al.*, 1997).

Other methods have been proposed for dissolution of intractable PuO_2 samples involving exotic fluoride reagents (Malm *et al.*, 1984; Asprey *et al.*, 1986), fusing with molten salts prior to dissolution (Feldman, 1960; Partridge and Wheelwright, 1975), or prolonged treatment with hot H_2SO_4, H_3PO_4, or HBr. We do not recommend any of these procedures; they require reagents that are difficult to handle given the constraints of working with radioactive materials, can introduce contaminant analytes into the final sample, or do not perform reproducibly or predictably.

Yet another method, specifically for PuO_2, is electrolytic dissolution catalyzed by a transiently oxidized cation (Bray and Ryan, 1982; Bourges *et al.*, 1986; Wheelwright *et al.*, 1988). This technique, called CEPOD (catalyzed elecrochemical plutonium oxide dissolution), involves agitating PuO_2 grit in a solution that is 2–8 M in HNO_3, during which time a bias is applied to the dissolution cell, producing Ag^{2+} ions from a small amount of dissolved Ag^+:

$$Ag^+ = Ag^{2+} + e^- \ E^O = 1.98V \qquad (36.14)$$
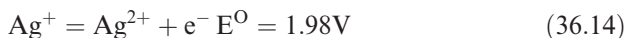
The reaction is truly catalytic, with Ag^{2+} being continually supplied by the bias across the solution. A standard electroplating cell with the bias applied backwards (bottom plate = anode) is a good apparatus for the dissolution. An applied potential results in a dark brown Ag^{2+} solution forming at the anode, in the vicinity of most of the PuO_2. Because Ag^{2+} reacts quickly with water, it is not distributed throughout the solution volume (Gordon and Wahl, 1958). The conversion of PuO_2 to PuO_2^{2+} takes place in two discrete interactions with Ag^{2+}, with the second oxidation step taking place more quickly than the first. Catalysts other than Ag^{2+} have also been used (e.g. Ce^{4+} or Tl^{3+}). Dissolution is rapid (particularly at elevated temperatures) and almost linear in rate until the oxide material is exhausted.

For samples involving minor amounts of plutonium in a complicated matrix, dissolution of the matrix is almost always the dominant problem. The final analytical solution should be prepared as either the nitrate or the chloride if at all possible; if fluoride was not involved in the production of the solution, a single drop of concentrated HF(aq) should be added to remediate colloidal

plutonium oxide and any polymer. The addition of HF is necessary, even though it can interfere with the chemical processing of some analytes, particularly those involved in the determination of the age of a sample, as described in Section 36.6.2 (c) (e.g. protactinium and neptunium) and group IV and group V fission products. Generally, after required tracers and carriers are added to an aliquot of the analytical solution and are equilibrated with the analytes, the resulting sample is evaporated to dryness several times following the addition of nitric acid (whose volatility is similar to that of HF) to eliminate excess fluoride.

Analytical solutions for plutonium analysis should be stored in glass because it provides a reasonably stable redox environment. Excess fluoride must be eliminated beforehand through repeated dry-downs with nitric acid. After an extensive radiochemical campaign, residual solution should be transferred to a fresh glass container, after which the nearly empty container should be counted for gamma rays emitted by any analytes that might have adhered to the glass. Addition of a single granule of CsCl to the original solution can help minimize adsorption to the glass, particularly if a noble-metal crucible was used in any step of the dissolution of the sample.

(a) Polymerization and hydrolysis

In aqueous solutions, all oxidation states of plutonium exist as positive ions of varying radius and charge. As a result, in the absence of complexing anions, there is a tendency for plutonium to undergo hydrolysis, with the effect being most severe with Pu(IV), decreasing for Pu(VI) and even more so for Pu(III). Pu(IV) does not hydrolyze as readily as Hf^{4+} or Zr^{4+}, being more similar to Ce^{4+} in this regard. Pu(VI), the plutonyl ion, hydrolyzes to a greater extent than would be expected based on the hydrolysis behavior of simple dipositive ions.

Hydrolysis of Pu(III) forms monomeric species only. Polymerization of Pu(VI) has been reported, but does not present a significant problem for the analyst. From the perspective of the radiochemist, the irreversible formation of Pu(IV) colloids, commonly referred to as "plutonium polymer", is one of the most important consequences of hydrolysis. In the early stages of polymerization, the polymer forms a colloidal species in pseudo solution that has chemical properties that are different from those of free Pu(IV), including different behavior during solvent extraction and ion-exchange separations (Tuck, 1958; Brunstad, 1959; Biggers and Costanzo, 1963). There is usually no visual clue to warn the chemist of the presence of polymer in solution. An added tracer will not exchange with the plutonium atoms in the polymer, which can lead to appalling failures in chemical yielding.

Polymer formation is enhanced in solutions of high Pu(IV) concentration, in solutions that have been maintained at elevated temperatures, and in solutions with low acidity. A good rule of thumb is to avoid acid concentrations below 0.5 M (Rainey, 1959), even if complexing anions are present. It is common

to store tracer and carrier solutions of plutonium in the form of Pu(III) to minimize the possibility of hydrolysis, and to perform an oxidation–reduction step after tracing the analytical aliquot and before performing any dilution steps; dilution with water can produce transient regions of high pH, which can promote the onset of hydrolysis even if the ultimate acid concentration exceeds 0.5 M.

Pu(IV) polymer is strongly adsorbed onto glass and silica from solutions of low acidity. On the macro scale it can be completely precipitated from solution in preference to unpolymerized plutonium through the addition of iodate or oxalate, provided that the anion is added in an amount considerably less than what would be required by stoichiometry. These facts indicate that the polymeric complex contains only a small positive charge and that cation exchange can be used to separate the colloid from the ''monomer'' (Ockenden and Welch, 1956).

36.3.4 Preparation of solutions containing individual oxidation states

While there are a large number of reagents that can be used to change the oxidation state of plutonium, in Table 36.4 we list those that we have used to greatest advantage.

In addition to reactions involving the reagents listed in Table 36.4, a pure Pu(III) solution arises when α-phase plutonium metal is dissolved in 6M HCl or 6M HClO$_4$, provided that products of corrosion with air are removed just prior to the dissolution. A Pu(III) solution can also be prepared electrolytically from a solution of plutonium in a higher oxidation state, by reduction with H$_2$ against a platinized electrode, provided no air is present, or by applying 0.75 V or less using a platinum cathode (Cohen, 1961). If anions that stabilize the tetravalent state (such as sulfate) are absent, the resulting Pu(III) solution is stable to reactions with oxygen in the air.

Pu(IV) solutions can also be prepared electrolytically (Nebel and Nebel, 1961) from Pu(III), with a potential of 1.2 V. While Pu(VI) is energetically accessible at this potential, its production rate is hindered due to the necessity of forming the dioxo-ion from the bare solvated cation (see below for more detail).

Table 36.4 *Oxidation and reduction reactions of plutonium ions in aqueous solution.*

Pu(III) → Pu(IV)	Pu(IV) → Pu(III)	Pu(IV) → Pu(VI)	Pu(VI) → Pu(IV)
Bromate in dilute acid	Iodide in HCl	Argentic oxide in HNO$_3$	Iodide in HNO$_3$
Ceric ion in HCl	Hydroxylamine in dilute acid	Sodium bismuthate in HNO$_3$	Ferrous ion in HCl
Dichromate in dilute acid	Zinc metal in dilute HCl	Nitric acid	Nitrite in HNO$_3$
Nitrite in HNO$_3$	Sulfur dioxide in dilute acid	Permanganate in HNO$_3$	Hydrazine in conc. HNO$_3$

Pu(IV) is best kept in HCl solutions more concentrated than 2 M as a long-term storage form; however, we have found that storage of Pu(IV) in nitric acid containing a "pinch" of ammonium nitrite is also an attractive option (Table 36.4).

Other methods for producing a Pu(IV) solution include: (1) reducing plutonium in nitric acid to Pu(III) with the addition of hydrazine followed by oxidation to Pu(IV) through addition of nitrite (Cunningham and Miles, 1956); (2) reducing plutonium to Pu(III) by an appropriate method, precipitating Pu(OH)$_3$, and dissolving the precipitate in hot, concentrated nitric acid; and (3) reducing the volume of a concentrated sulfuric acid solution of mixed Pu oxidation states by a factor of 2 by evaporation.

A standard method to produce a solution of Pu(VI) involves long-term boiling in perchloric acid. Pu polymer is only weakly attacked by boiling perchloric acid. Because the production of the dioxo cation is kinetically hindered, a substantial reflux period of several hours may be required. At ambient temperatures, perchlorate is a very weak oxidizer; its strength as an oxidizer and donor of oxygen increases dramatically with temperature, becoming important for plutonium at temperatures in excess of 140°C, where the oxidation potential passes 0.75 V (Smith, 1965). The perchloric acid concentration should exceed 50% or the conditions for oxidation to Pu(VI) are not met in a refluxing solution. On cooling and dilution, the Pu(VI) state is not retained indefinitely (Newton *et al.*, 1986).

There are several alternate methods of preparing Pu(VI), but most of them introduce unpalatable cationic species into the final solution (e.g. NaBiO$_3$, KMnO$_4$, K$_2$Cr$_2$O$_7$, etc.). Boiling in 0.5 M HNO$_3$ for extended periods of time can produce Pu(VI), but success depends on skirting the concentrations where Pu(IV) polymer production can compete. The use of Ag^{2+} is rapid and complete at room temperature, depending on the transient oxidation of Ag$^+$ with (NH$_4$)$_2$S$_2$O$_8$ in 1 M HNO$_3$.

An advantage of the electrolytic preparation of plutonium solutions in a given oxidation state is that foreign cations need not be added to the solution, which can interfere in subsequent determinations of concentration or separations. The potential applied to the system should be approximately 0.2 V more than the formal potential for plutonium reactions that do not break or form the Pu–O bonds in the plutonyl ion, or approximately 0.6 V more for those reactions involving those bonds. Performance is improved by increased surface area of the working electrode (cathode for reductions, anode for oxidations), decreased volume of the electrolyte, and stirring. Stirring is often accomplished through manipulation of an electrode (Ko, 1956), but agitating by bubbling a non-reactive gas through the cell is also used. A compartmented cell for electrolytic adjustment of oxidation states has been described (Helly and Gardner, 1958).

The radiolytic environment encountered in fuel reprocessing is quite severe; a consequence is that aqueous reprocessing operations must be significantly

delayed after the spent fuel is discharged from the reactor so that reagents are not decomposed by exposure to intense radiation fields. However, radiolysis is also encountered in chemically purified plutonium solutions, a consequence of the intense alpha radioactivity of the plutonium isotopes (Fomin *et al.*, 1957). Under high self-irradiation, maintaining pure oxidation states is difficult. The radiolysis products either oxidize or reduce the plutonium, depending on the medium and the oxidation state; however, in general, self-radiolysis in plutonium solutions results in a decrease in the oxidation state of the plutonium ions, a consequence of chemical reactions with the transient species formed by alpha-particle irradiation of water (H and OH radicals, and H_2O_2) (Nikol'skii *et al.*, 1960; Pages, 1962). This is magnified in solutions of plutonium in which ^{238}Pu is isotopically enriched, or in aged plutonium solutions containing ^{241}Pu into which ^{241}Am has grown (E_α = 5.50 MeV for ^{238}Pu, and 5.49 MeV for ^{241}Am, compared with 5.16 MeV for longer-lived ^{239}Pu and E_β = 0.017 MeV for ^{241}Pu). Application of external X-radiation to a plutonium nitrate solution results in oxidation (Popov *et al.*, 1958).

The redox potentials of the four principal oxidation states of plutonium lie so close together that all four states can coexist in solution in the right pH range. Plutonium is the only element for which this has been observed. Examination of the oxidation potentials leads one to conclude that both Pu(IV) and Pu(V) are unstable to disproportionation. Pu(V) is known to disproportionate at most conditions of pH and concentration. Tetravalent Pu is stabilized by low temperatures, high acid concentrations, and complexing agents such as sulfate or nitrate. In the absence of complexing agents, Pu(IV) is also stabilized at low acid concentrations due to irreversible hydrolytic formation of the polymer. Pu(V) is stable only in solutions that are very weakly acidic, with maximum stability observed near pH 3. Pu(V) rapidly disproportionates to Pu(IV) and Pu(VI) at pH < 2 and pH > 6 (Connick, 1949). A more comprehensive discussion of the disproportionation of plutonium ions in solution can be found in Chapter 7 of this work.

36.3.5 Preparation of tracer solutions

In traditional radiochemistry, where the tracer technique is based on radiation counting, most radionuclides used as tracers have half-lives between several hours and thousands of years. The identity and amount of the tracer that should be used in a particular application depends on several factors. If the chemical procedure used to isolate the tracer element and produce a counting source requires several days, it is clear that a very short-lived activity is an inappropriate tracer. The analyst must be careful to add enough tracer activity that it can be accurately measured in the final sample; this includes considerations of decay during the chemical procedure prior to counting, the efficiency of the radiation counter for detecting the characteristic emissions of the tracer nuclide, and the level of activity

of any radioactive sample analytes that might interfere with the observation of the tracer.

At low concentrations, the chemical behavior of trace elements can be unpredictable (Lavrukhina *et al.*, 1967; Guillaumont *et al.*, 1989). These phenomena are often ascribed to adsorption on container walls or on microparticles present in solution. To avoid these effects, "carriers" are added to the sample. In a way, the application of a carrier is similar to that of a tracer. If several milligrams of an element are placed in solution with a radionuclide that is one of its isotopes, and a stoichiometric compound exists such that the element concentration can be determined by weight, the gravimetric yield of the carrier can be applied to the radionuclide (Ruzicki, 1968).

Tracer and carrier solutions for plutonium analytical applications should be prepared from high-purity reagents to minimize the addition of unwanted analytes to samples with a complex matrix. The acid concentration of a tracer solution should be kept fairly high (≥ 2 M) to prevent losses to the walls of the vessel in which the tracer is kept. We have found that the most stable plutonium tracer and carrier solutions contain Pu(III) dissolved in hydrochloric acid; we store these solutions in glass. A "pinch" of KI is added to stabilize the oxidation state. Others (Bajo and Eikenberg, 2003) have produced stable Pu(IV) solutions in the presence of complexing anions such as bisulfate. For the lighter actinides, we store these solutions in Teflon; the uranium and thorium contents of glass can be high enough to interfere in a mass-spectrometric analysis, and protactinium is a "glass seeker" in the absence of fluoride.

For the purposes of analysis, the concentration of the carrier (plutonium or other analyte) in the final sample can be determined in several ways; for instance, the metal–ion concentration of a liquid fraction can often be characterized spectrophotometrically. Neutron activation analysis has been employed for this purpose (Girardi, 1969). The use of separated stable isotopes and mass spectrometry has become more common.

For applications in which it is necessary to characterize a mixture of plutonium isotopes by nuclear counting, an appropriate tracer is 2.86-year ^{236}Pu. It is produced in the irradiation of high-isotopic-purity ^{235}U with low-energy (ca. 11 MeV) deuterons. The (d,n) reaction produces both of the long-lived states of ^{236}Np, with little accompanying production of ^{235}Np (via the (d,2n) reaction) and ^{237}Np (via the (d,γ) reaction) (Lindner *et al.*, 1981). The authors performed these irradiations for weeks at a time to produce a 10-year supply of the tracer. The long-lived ground-state of ^{236}Np was retained as a mass-spectrometric tracer for ^{237}Np analysis. The 22-h isomeric state, produced in fivefold excess over the ground state, decays by beta decay approximately 48% of the time, resulting in ^{236}Pu (Firestone and Shirley, 1996).

Clean ^{236}Pu and ^{236}Np solutions were obtained by dissolving the target foil and preparing a nitrate solution, after which the elements were separated with successive TTA (thenoyltrifluoroacetone) extraction and anion-exchange procedures. For heavy-element analytical applications (including nuclear forensics)

an aged ^{236}Pu tracer also supplies ^{232}U, ^{228}Th and ^{224}Ra to trace, respectively, uranium, thorium and radium chemical fractions. The relative tracer concentrations can be calculated with Bateman's equations provided that the sample was completely purified of daughters at a known time. The ingrown daughter activities make it very difficult to calibrate a ^{236}Pu solution, because both the alpha and gamma radioactivities come to be dominated by the daughters. It is better to calibrate against a known ^{239}Pu standard, whose activity can be quite accurately related to a mass basis by dissolving an electrorefined piece of α-phase plutonium metal. A mixed sample of known amounts of a ^{236}Pu tracer and a ^{239}Pu standard is chemically purified to result in a Pu fraction, and a counting source is prepared. The relative alpha intensities at 5.768 and 5.16 MeV are equal to the related decay rates of ^{236}Pu and the sum of ^{239}Pu and ^{240}Pu in the sample. In this way, the ^{236}Pu concentration (and the ingrown daughter concentrations) can be known to an accuracy of better than 1%.

For mass spectrometric analysis, it is preferred to use a tracer of ^{242}Pu. Material with the highest possible isotopic purity should be used. Two samples of the analyte are processed, one traced and one untraced, and the plutonium concentration is determined by isotope dilution (see Section 36.5.3).

In the plutonium analytical laboratory, it is also convenient to have a calibrated solution of ^{243}Am. It serves the purpose of tracing both the americium and neptunium fractions. High-purity ^{243}Am is available commercially. It can be produced by the irradiation of high-isotopic-purity ^{242}Pu with low-energy neutrons. Decay of 5-h ^{243}Pu produces ^{243}Am, and if the separation is performed quickly enough after purification of the target material, the effect of the decay of 14-year ^{241}Pu (a common contaminant) is minimized and ^{243}Am can be obtained with very little ^{241}Am content. The only other avenue to this material is to perform a mass separation of mixed americium isotopes from high-burnup reactor targets.

The decay daughter of 7,380-year ^{243}Am is 2.36-day ^{239}Np, a β-emitter which is in secular equilibrium in an aged solution. Therefore, a calibrated solution of ^{243}Am contains a transient concentration of ^{239}Np that is of equal activity to that of the ^{243}Am content of the solution. If the tracer ^{239}Np can be equilibrated with the neptunium in an analytical aliquot, and a clean separation performed at a well-defined time before a significant fraction of the ^{239}Np half-life has elapsed, then the gamma-ray intensity of ^{239}Np in the analytical fraction, decay corrected to the time of separation, when compared to an aliquot of the tracer solution defines the chemical yield of the neptunium fraction. Because of the length of time required for equilibration, this method is considered inferior to tracing with ^{236}Np and performing mass spectrometry; however, in the absence of mass spectrometry, acceptable results are obtained. Depending on the application, the ^{239}Pu granddaughter, which also grows into the tracer, may have to be removed.

The ^{236}Np tracer is calibrated against a standard ^{237}Np solution whose concentration is determined by gamma-ray spectroscopy of an aged solution, or

by dissolving a weighed amount of neptunium metal. Aliquots of the two solutions are mixed, the nuclides are equilibrated, a neptunium fraction is chemically isolated (scrupulously clean of ^{236}U), and a mass spectrometric measurement is performed. The ^{237}Np solution, if appropriately aged, is a source of 27-day ^{233}Pa, which can be used to trace protactinium. Similar to the situation with ^{243}Am/^{239}Np, a complete chemical separation must be performed at a well-defined time for the method to be valid; with ^{237}Np/^{233}Pa, this can be challenging, and in practice is replaced by several separations performed over a short period of time.

In fuel applications or nuclear forensic analysis, it is often desirable to isolate a curium fraction from a sample that is largely plutonium. The concentration of ^{242}Cm in an aged sample is related to the concentration of ^{242m}Am, an important indicator of neutron spectrum. The concentration of ^{244}Cm is related to integral flux. This precludes the use of both of these nuclides as a tracer activity (unless the analyst is willing to perform an isotopic dilution measurement). Mass-separated ^{246}Cm has been used for this purpose.

Another class of radiochemical tracing involves the use of separated stable isotopes and isotope dilution measurements by mass spectrometry. This is particularly valuable in those applications where the analyte contains a large amount of ^{238}Pu, making the sample hard to handle on the analytical chemistry scale. Both ^{57}Fe and ^{71}Ga solutions have been used in this application, calibrated against solutions of optical standards of the normal element.

In the analytical chemistry of elements for which the chemical environment defines unambiguously the state of the ion in solution (e.g. the alkali metals) tracing can be accomplished by complete mixing, usually through agitation. With plutonium, while mixing is a necessary step to equilibration, the fact that plutonium can coexist in several oxidation states in the same solution, and that the extent of hydrolysis (particularly of Pu(IV)) in a tracer aliquot and an analytical solution may not be the same, requires that the analyst makes some effort to ensure that the tracer radionuclides are actually in the same chemical state as are the analyte isotopes of the same element, and that exchange has occurred.

It is preferred that tracer solutions be prepared with plutonium in the trivalent state; the chemical system should be simple enough that hydrolysis of the plutonium activity should be minimized. Hydrolysis of plutonium in the preparation of the analytical solution can be controlled using the methods described above; keeping the acid concentration above 0.5 M and adding a small amount of HF during the production of the analytical solution should be sufficient in most cases. Environmental samples from near-neutral pH sources may require extra treatment.

When the solute of both the tracer and the analyte solutions is hydrochloric acid, one method to reach equilibrium is to add a few granules of KI to the solution, warm it gently, and mix. SO_2 is then added to the solution by bubbling the gas through a transfer pipet. Complete reduction of the plutonium inventory

of the sample to Pu(III) is accomplished quickly; in practice, by the time any orange color imparted to the solution by iodine is destroyed by the SO_2, the reduction is complete. This method can cause the formation of elemental sulfur, which does not interfere with the equilibration.

When the solution medium is nitric acid, conversion of the plutonium inventory to Pu(IV) can be accomplished by warming and adding ammonium nitrite. Again, the conversion is fast and complete. The key to equilibrating the plutonium ions in a mixed acid medium is usually best accomplished by repeated evaporation and redissolution of the residue. Even though nitric acid is less volatile than HCl and tends to dominate the anionic content of the sample after a single evaporation, conversion of the sample to a chloride medium by repeated additions of HCl is preferred, particularly for metals and alloys analysis. For instance, if the sample contains a significant titanium component, evaporation in the absence of chloride ion can cause the formation of intractable rutile, which can form before the oxidation state of the accompanying plutonium ions have fully exchanged.

For very precise tracer work, reduction to Pu(III) in HCl is followed by an evaporation to dryness, after which the sample can be dissolved in nitric acid and adjusted to Pu(IV) with nitrite. The cycle can be repeated as required. Evaporation of the nitric acid solution provides for some minimization of any HF content of the original solution. Two redox cycles between HI/HCl and nitrite/HNO_3 and back is adequate to equilibrate all the actinides in a nuclear forensic chronometric analysis.

36.3.6 Separation by precipitation

Separation by precipitation is a common procedure that is familiar to most chemists, and is one of the most commonly used classical methods of analytical chemistry. All the same limitations that apply to the classical use of the technique (temperature, excess of precipitating agent, rate of formation, etc.) also apply when radioactive materials are involved.

Insoluble plutonium compounds that can be readily precipitated from solution include the peroxide, hydroxide, iodate and oxalate. Plutonium also makes precipitates with organic compounds such as 8-hydroxyquinoline and cupferron. Plutonium does not precipitate quantitatively from solution in the hexavalent state, and must therefore be reduced to Pu(IV) before precipitation. Precipitation must take place at low acid concentrations (Leary *et al.*, 1959; Mainland *et al.*, 1961). For instance, as the nitric acid concentration goes from 1.2 to 5.2 M, the solubility of Pu(IV) peroxide goes from less than 10 mg L^{-1} to more than 1 g L^{-1} (Ganivet, 1960). The collected, dried compounds share the property that they can all be fired in air to the dioxide at temperatures in excess of 850°C. Of course, this can only be performed if the mother solution contains no coprecipitating cations. Unfortunately, the final stoichiometry of the dioxide

is influenced by the starting composition of the precipitate (Hamaker and Koch, 1949; Hopkins, 1949; Koshland *et al.*, 1949; Drummond and Welch, 1957) unless the temperature is elevated in excess of 1,200°C. Stable plutonium oxides with oxygen contents higher than PuO_2 cannot be prepared by high-temperature calcining (Brewer, 1953).

In gravimetry, it is important that the preparation be dry, stable to radiolysis and the chemical environment, and that the compound be stoichiometric. Oxalates are unstable to radiolytic decomposition and contain a variable amount of water. Iodates almost always entrain an excess of the anion. The most satisfactory final material is the high-fired oxide, PuO_2; oxalates, peroxides, hydroxides and even fluorides and iodates will all be converted to PuO_2 if slowly heated to over 1,050°C in oxygen (calcination). It has been reported that PuF_3 and $Pu(SO_4)_2$ can be the basis for a gravimetric measurement, but the data are difficult to reproduce (Jones, 1953; Drummond and Welch, 1958; Waterbury *et al.*, 1961).

At the tracer level, the concentration is too low to permit precipitation by exceeding the solubility of even the most insoluble of compounds. It is necessary that a carrier be present that can be removed from solution by precipitation. The carrier is not simply a substance which can be precipitated; it must also carry the desired radioactive material with it.

There are two types of carrier. The first is called an isotopic carrier, and is a salt of the element of which the radionuclide is an isotope. For instance, 12.8-day [140]Ba can be carried from solution by adding a soluble barium salt, mixing to give a uniform solution, and precipitating $BaSO_4$ with the addition of a soluble sulfate. For the heavy elements, nonisotopic carrying, or coprecipitation, is more important. Nonisotopic carriers are often used to separate "weightless" radioactive material when it is desirable to retain a high specific activity. For some elements, such as polonium or astatine, no isotopic carrier is available because there are no stable or long-lived isotopes of these elements.

In some instances (Hahn, 1936), ions of the nonisotopically carried element replace some of the carrier ions in isomorphous compounds, forming mixed crystals. The trace element is distributed through the carrier depending on the precipitation conditions, which can result in a considerable heterogeneity in each crystal. In other instances, carrying can be caused by adsorption of the tracer-level ions on the surface of the precipitate. There is also a mixed mechanism by which surface adsorption takes place and the precipitate crystals grow to cover and "trap" the tracer ions. An elevated temperature during precipitate formation results in larger particles and a precipitate that is easier to handle. At higher temperatures, coprecipitation tends to be more selective because distribution of the trace element in isomorphous compounds is favored while surface adsorption and trapping are reduced due to recrystallization of the outer layers of the particles. Overall yield is increased at lower temperatures, a

condition under which solubilities tend to be lower. The most effective copre-cipitation conditions begin with an initial digestion of the solution at high temperatures followed by cooling before separating the precipitate from the supernatant liquid. An increase in the electrolytic content of the mother solution favors the addition of otherwise colloidal particles to the precipitate.

For applications involving plutonium samples of negligible mass, isotopic carrying is considered disadvantageous because it interferes with subsequent mass-spectrometric and radiation-counting measurements. Nonisotopic carry-ing has many applications to the radiochemical analysis of the actinides (Bonner and Kahn, 1951; Hyde, 1954). Iron hydroxide, $Fe(OH)_3$, is very effective in carrying the actinides. Precipitation of mixed hydroxides is not very selective and tends to carry any multivalent ions out of solution (including all the common oxidation states of plutonium), but the process can be reasonably complete and is a valuable volume reduction step in certain applications, particularly those involving large quantities of amphoteric elements (e.g. Al^{3+}) or transition metals that make ammonia complexes (e.g. Ni^{2+} and Cu^{2+}). Following tracer equilibration, the first step in recovering plutonium from dissolved nuclear explosion debris involves precipitations of $Fe(OH)_3$ with both NaOH and NH_4OH.

Lanthanum fluoride, LaF_3, is often used to concentrate plutonium, americ-ium and curium from large solution volumes. Coprecipitation of plutonium with LaF_3 is a common concentration step in the analysis of biological material (Bowkowski, 1964; Schwendiman and Healy, 1958). Separation of plutonium by coprecipitation can take advantage of oxidation and reduction to enable purification. For instance, Pu(III) and Pu(IV) are carried on LaF_3, while Pu(VI) is not. This provides a means by which the analyst can deal with high calcium concentrations; CaF_2 can be difficult to redissolve once it forms, but if plutoni-um is oxidized to the hexavalent state before LaF_3 (carrying CaF_2) is precipi-tated, plutonium stays in solution, providing a separation from calcium (Scheidhauer and Messainguiral, 1961). An oxidation-reduction cycle can be devised incorporating a series of LaF_3 precipitations and the carrying of Pu(III) and Pu(IV) and the non-carrying of Pu(VI) until the desired purification is achieved. Of course, elements with redox behavior similar to that of plutonium can interfere (e.g. neptunium).

Like LaF_3, $BiPO_4$ carries both trivalent and tetravalent plutonium from nitric acid solution (Thompson and Seaborg, 1956). The coprecipitation of plutonium is most complete when strong complexing agents are absent and the precipitate is allowed to form slowly (Rydberg, 1955). $BiPO_4$ has been used to concentrate plutonium from large volumes of water and to scavenge Pu from urine (Holstein *et al.*, 1962). We include $BiPO_4$ in this section because of its historical impor-tance and its use in classical separation procedures; however, in practice we find that there are difficulties using $BiPO_4$ at the laboratory scale. Among these are a very irreproducible dependence of carrying on digestion conditions, and

the introduction of residual phosphates that can interfere with subsequent separation steps. We would encourage the use of LaF_3 over $BiPO_4$ in most circumstances.

Pu(III) and Pu(IV) can be carried on a wide variety of oxalates, which do not tend to carry Pu(VI). Bismuth and lanthanum are two common non-isotopic carriers for plutonium. Coprecipitation is reasonably complete from dilute mineral acid solutions. While oxalate coprecipitation is not as selective as are some other methods, the oxalate can be destroyed with warm aqua regia, leaving no interfering anions for subsequent separations.

Iodates are also used as coprecipitating anions in plutonium procedures. Their effectiveness in carrying Pu(III) and Pu(IV) is variable depending on the identity of the non-isotopic carrier. For example, lanthanum iodate carries both Pu(III) and Pu(IV) quite effectively from dilute HCl solutions, but zirconium, thorium and ceric iodates are more effective in carrying Pu(IV) than Pu(III), though the trivalent ion is carried fairly well. Like the oxalate, the iodate is destroyed by heating in concentrated acids; the resulting iodide can be distilled away. An attractive feature of the iodate precipitation is that it provides an effective step for removing residual uranium from the plutonium matrix (Thompson *et al.*, 1950)

Zirconium phosphate and zirconium phenylarsonate are specific carriers for Pu(IV), and have been used in procedures designed to determine what fraction of the plutonium in a sample is in that specific oxidation state (King, 1946; Starik *et al.*, 1959). Performance is improved if the acid concentration of the solution is kept below 1 molar, and addition of a small amount of hydroxylamine will "freeze" the distribution of Pu(III) and Pu(IV) for the duration of the precipitation procedure.

Thorium has been used as a non-isotopic carrier for plutonium. Thorium peroxide in particular is specific in carrying Pu(IV) (with Np(IV) being the main interference). Addition of H_2O_2 to an acid solution not only quantitatively precipitates thorium, but converts all the valency states of plutonium to the tetravalent state, which is quantitatively carried. Use of thorium has the drawback that, from a radiochemical perspective, it is a "dirty" material, and introduces its decay daughters (isotopes of Ac, Ra, etc.) into the sample. This can result in a step backward in radiochemical purity. One way around this is to use separated ^{230}Th when a thorium carrier is required.

Precipitation of plutonium on the macro scale (carrier free) is a common step in the production of the metal, and has been employed in the analytical chemistry of the element. The most common precipitation step on the path to producing either the oxide or the metal is the addition of either oxalic acid or an alkali metal oxalate to a weakly acid solution of Pu(III) or Pu(IV) (Gel'man *et al.*, 1957; Gel'man and Moskvin, 1958). The solubility of Pu(III) oxalate increases significantly with acid concentration while that of Pu(IV) oxalate decreases for acid concentrations up to 3 M; because coprecipitation of contaminant species is reduced at higher acid concentrations, oxalate precipitation of Pu(IV) is

preferred (Sokhina and Gel'man, 1960). Addition of ethanol to the solution further reduces the solubility of Pu(IV) oxalate. However, fluorides and sulfates interfere with the stoichiometry of the plutonium salt if a gravimetric measurement is to be performed.

Plutonium(IV) peroxide can be precipitated from both acid and basic solutions through the addition of a large excess of H_2O_2. An advantage of the method is that peroxide is not only the precipitant, but through both reduction and oxidation reactions it prepares the plutonium in solution in the tetravalent state. However, the initial valence of the plutonium has an effect on the completeness of the precipitation, probably due to the time delay in forming Pu(IV) (Leary *et al.*, 1959). If significant Pu(VI) is present it is advantageous to reduce it to the tetravalent state before adding H_2O_2. The acid concentration of the original solution (between 0.5 and 5 M) has little effect on the completeness of the precipitation (Mainland *et al.*, 1961), but the presence of small amounts of Fe, Cr, Mn and Ni can interfere – the peroxide reacts with these metal ions producing species that can oxidize plutonium to the hexavalent state. Uranium, neptunium and zirconium can coprecipitate with Pu, but Fe, Co and Mo are not carried. Performing the peroxide precipitation from concentrated carbonate solutions can hold uranium and neptunium in solution, resulting in a purified plutonium product (Kruger and Moser, 1966).

Both Pu(III) and Pu(IV) hydroxides are precipitated from mineral acid solutions through addition of sodium or ammonium hydroxide. When redissolving the precipitate, care must be taken to avoid production of polymer from Pu(IV) hydroxide. To ensure quantitative precipitation, fresh reagents should be used that have not had a chance to absorb CO_2 from the air, because the resulting carbonates produce soluble complexes with plutonium. Oxalates, fluorides, phosphates and other anionic species can interfere with the completeness of the precipitation.

PuF_3 and PuF_4 are precipitated from acid solution by addition of excess HF. Isolation of PuF_3 from solution is easier than is that of PuF_4 because of the crystalline morphology of the precipitate. Both fluoride compounds can be redissolved in mineral acid containing sufficient H_3BO_3 to complex the fluoride as BF_4^- ions; however, if the sample is stored for a long time or subjected to temperatures in excess of 400°C, borate-based dissolution is a slow process. In this case, a dry fusion with NaOH (or Na_2O_2 + NaOH) can produce a hydroxide that will dissolve in mineral acids. Polymer formation is rarely encountered in the dissolution of the fusion residue.

Tetravalent plutonium is precipitated from dilute acid solution by a variety of organic precipitants, including cupferron, 8-hydroxyquinoline, phenylarsonic acid and benzene sulfonate (Moiseev *et al.*, 1961). Most of these methods are not terribly specific for plutonium. As with other anionic species, it is normal to ignite the precipitate to the dioxide.

Typically, precipitates are separated from their associated supernatant liquids through centrifugation and decantation rather than by filtration, unless a

counting source is being prepared (Hunter and Chenley, 1959). Typical volumes on the laboratory scale involve milliliters of reagents, so mixing precipitants can take place in a capped centrifuge cone using a vortex mixer. Recovery fractions for plutonium are almost always increased by digestion in a hot-water bath followed by cooling to room temperature in cold water. In high activity applications, decanting post-centrifugation is actually effected by removing the supernatant liquid to waste with a transfer pipet. Mass purity is improved if the precipitate is thoroughly agitated with a dilute solution of the acid form of the precipitating anion (e.g. oxalic acid or HF) or an ammonium compound (e.g. ammonium oxalate or ammonium hydroxide) followed by digestion, centrifugation and decantation. For gravimetric determinations of plutonium, the analyst will sacrifice yield for mass purity.

36.3.7 Solvent extraction

Another class of separation methods of use to the plutonium analytical chemist involves solvent extraction. Unlike precipitation, solvent extraction does not require visible amounts of material for success. Generally, liquid-liquid extraction systems require intimate contact between immiscible liquid phases, which leads to a partitioning of inorganic or organic solutes between the two phases. When inorganic substances such as plutonium are being separated, one of the phases is usually aqueous.

For an inorganic substance to be distributed appropriately between two liquid phases, it must exist in a form that has a characterized affinity for both phases. Usually, this consists of a complex ion or compound. Extraction systems for plutonium can be based on the nature of the extractable species, either coordination complexes or ion-association complexes (Morrison and Freiser, 1957). Coordination complexes are formed through the interaction of an electron-acceptor cation and electron-donor ligand species. The tendency for complex formation correlates well with the strength of the ligand as a Lewis base, and is dependent on the electronic configuration of the cation. Chelating agents are also potential coordination ligands. Ion-association complexes are aqueous ionic species that are made to seek the organic phase through the formation of electrically neutral clusters that are stabilized through the incorporation of the organic solvent molecules into the cluster.

The extent to which a given solute A distributes itself between organic and aqueous phases is usually represented by a distribution coefficient, d:

$$d = [A]_{org}/[A]_{aq}, \tag{36.15}$$

where $[A]_{org}$ and $[A]_{aq}$ are the concentrations of the solute in the organic and aqueous phases, respectively. For an ideal system, in which the solute does not react with or alter the solvents, and where the immiscibility of the solvents is not affected by the results of the extraction, the distribution coefficient is independent of the amount of solute present. With macro amounts of solute, there are

very few extracting systems that approach the ideal (Grahame and Seaborg, 1938; Myers *et al.*, 1950). The distribution coefficient is a function of environmental variables. For example, d tends to decrease with an increase in temperature. The use of volumes of different size also affects d; this is particularly important in partition chromatography.

The value of d also changes if an inert diluent is used. For example, the extraction of uranium and plutonium into tri(n-butyl)phosphate (TBP) is the basis of the PUREX process; a non-polar diluent is usually added to the organic phase to decrease its viscosity and make the physical separation of the liquid phases easier. While the diluent does not participate in the reaction, it does affect d through the change in solubility of the solute species. The presence of an unextractable bulk impurity in the aqueous phase may cause an increase in d by changing the ionic strength of the aqueous phase, thereby altering the activity of the solute. As an example, the addition of a ''salting-out'' agent such as aluminum nitrate to the aqueous phase can increase the partition of plutonyl species into diethyl ether. Conversely, the presence of interfering substances that form an inextractable compound with the solute act to decrease d; the addition of small amounts of fluoride or phosphate to the previous example will interfere with the extraction of plutonyl species into most organic solvents.

Most extraction methods are based on the solubility of plutonium (IV) nitrates in various organic solvents. In aqueous nitric acid solutions, tetravalent plutonium forms a variety of nitrate complexes from $Pu(NO_3)^{3+}$ to $Pu(NO_3)_6^{2-}$. Neutral molecular compounds involving $Pu(NO_3)_4$, $Pu(NO_3)_5^-$ and $Pu(NO_3)_6^{2-}$ are extracted into ''oxygenated'' reagents such as alcohols, ethers, ketones and esters. The extraction of Pu(IV) and other ''high-valent'' actinides from nitrate media can be quite selective, because divalent and trivalent species are not extracted at all. The ease with which Pu(IV) can be reduced to Pu(III) is the basis for the recovery of plutonium from the organic phase in many of these procedures.

The classical laboratory method of performing a solvent extraction, in which both phases are placed in a separatory funnel and agitated by hand to mix the phases followed by a settling interval to effect the partition, is generally not used in analytical applications involving relatively large amounts of plutonium due to considerations of space. Typically sample sizes are small in physical extent and the resulting phase volumes need not be larger than a few milliliters. Usually, phases are mixed in a capped centrifuge cone using a vortex mixer; this is particularly convenient in a gloved box, where the loss of manual dexterity makes the manipulation of a separatory funnel and stopcock difficult. Any difficulties in phase separation are easily remedied through the use of a centrifuge. The classical separatory funnel is still used with larger volumes, but it is usually mounted in a fixed bracket and agitation is performed by insertion of a rotary cavitation mixer.

When dealing with complex matrices, the plutonium analyst finds several applications of the use of solvent extractions as mass-reduction steps prior to

performing chromatographic procedures. For example, if an iron hydroxide precipitation has been used to concentrate the actinides from a large volume, it is useful to dissolve the precipitate in a minimum volume of hydrochloric acid and extract iron into methylisobutylketone. Most of the iron can be removed in a single step, and the actinide analytes have little affinity for the organic phase in the chloride system. The final aqueous phase must be boiled to expel organic residues prior to any ion-exchange steps.

(a) Organophosphorus

In extractions involving organophosphorus compounds, the extractant interacts with plutonium through either of two mechanisms, one involving the extraction of a neutral complex into the organic phase by interaction with the phosphoryl oxygen (Healy and McKay, 1956), and the other involving acidic compounds which form an extractable chelate species by ion exchange.

The most important extraction of the neutral complex type is tri(n-butyl) phosphate (TBP), which is the basis of the industrial PUREX process. The order of extractability into TBP from nitric acid solutions is $M(IV) > M(VI) \gg M(III)$ (Best *et al.*, 1957). The extractability of the tetravalent actinides increases with atomic number: $Th(IV) < Np(IV) < Pu(IV)$. While other organophosphorus compounds have not been studied as much as has TBP, it has been established that in those applications where mass loading is a potential problem, extraction capacity decreases in the sequence $R_3PO > (RO)R_2PO > (RO)_2RPO > (RO)_3PO$ (Burger, 1958a; Petrov *et al.*, 1960), a function of the electronegativity of the oxygen atom in the phosphoryl group, as one would expect. Substituting electronegative groups such as phenyl into the alkyl chains reduces the effectiveness of the extraction (Burger, 1958a; Petrov *et al.*, 1960). Because the distribution coefficient for extraction of trivalent actinides approaches unity only for nitric acid concentrations greater than 10 M, a very effective separation can be accomplished through oxidizing Pu to the tetravalent state and extracting into the organic phase, followed by reduction to Pu(III) and back-extraction into nitric acid of moderate concentration, ca. 5 M. While pure TBP can be used in these extractions (Bernstrom and Rydberg, 1957), its density (0.97 g mL^{-1}) is nearly equal to that of water; combined with its high viscosity, this makes phase separations difficult. Typically, a TBP solution of 20–30 vol% in a non-polar aliphatic hydrocarbon diluent such as kerosene is used (Codding *et al.*, 1958; Rozen and Moisenko, 1959). While industrial-scale applications almost always involve extraction from nitric acid solutions, in the laboratory hydrochloric acid solutions can be used, and CCl_4 can be used as a nonpolar diluent (Shevchenko *et al.*, 1960b). Hydrochloric acid on the industrial scale is difficult to handle because of corrosivity.

TBP and other trialkyl phosphates tend to undergo both radiolytic (Bruce, 1956) and acid catalyzed dealkylation in the conditions under which fuel repro-

cessing occurs, leading to a dialkyl phosphoric acid. HDBP, the dialkyl compound arising in the decomposition of TBP reacts with dissolved chemical components to form insoluble compounds that can interfere with phase separation and soluble uranium salts that compromise the recovery of uranium from the PUREX process. At the laboratory scale, TBP should be washed with a mild alkaline solution to remove HDBP before use (Burger, 1958b).

In nitric acid systems, the maximum distribution coefficient for extraction of Pu(IV) into the organic phase is for nitric acid concentrations around 7 M. At higher concentrations, nitric acid reacts directly with TBP to form a neutral species $TBP.HNO_3$, which effectively reduces the amount of TBP available for complexing plutonium. Performance is improved by "salting out" the aqueous solution, replacing some of the nitric acid with ionic nitrates such as $NaNO_3$, NH_4NO_3 or $Al(NO_3)_3$. The increased nitrate concentration without increased reactions with TBP in the organic phase leads to higher distribution coefficients. Addition of uranyl ion to the aqueous phase causes a decrease in performance because of competition with Pu for available TBP molecules. This has important consequences to the industrial PUREX process (Moiseenko and Rozen, 1960).

At the laboratory scale, TBP extractions from hydrochloric acid solutions can give higher yields and better decontamination factors than similar extractions from nitric acid (Larsen and Seils, 1960). Extractions of other acid solutions have been studied, with success that depends upon the formation of a neutral coordination species between the acid and plutonium. For instance, TBP extractions from perchloric acid performs poorly (Solovkin *et al.*, 1959) due to the weak complexing behavior of the perchlorate ion. Residual sulfate and phosphate groups decrease the performance of a TBP extraction due to the formation of inextractable complex ions.

Other neutral organophosphorus compounds can be used to extract Pu(IV) and Pu(VI). Increasing the length of the alkyl chains in TBP from butyl to as long as octyl has little effect on the extraction (Siddall, 1960). There is also little effect in increasing the branching of the alkyl groups. Di(*n*-butylbutyl)phosphonate (Loehlin and Siddall, 1957), diamylamylphosphonate, di-2-amyl-2-butyl-phosphoric acid (Siddall, 1963), tri(*n*-octyl)phosphine oxide (TOPO) (Martin *et al.*, 1961; Mrochek and Banks, 1965) and tri(*n*-butyl)phosphine oxide (TBPO) (Umezawa, 1960) are also used for the lab-scale extraction of Pu(IV) and Pu (VI). TOPO in cyclohexane is particularly valuable as an extractant because the presence of small amounts of sulfate or phosphate in the aqueous phase are not as disruptive to the progress of the extraction as they are when TBP is being used.

The standard example of an acid alkyl phosphate extractant is di(2-ethylhexyl) phosphoric acid (HDEHP) (Weaver and Kappelmann, 1968). The extractability of plutonium from nitric acid into HDEHP in a kerosene diluent shows the same dependence on valence as does the extraction into TBP; namely Pu(IV) > Pu(VI) > Pu(III) > Pu(V) (Fardy and Chilton, 1969). Unlike TBP, the distribu-
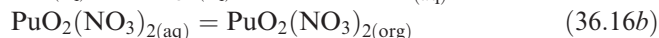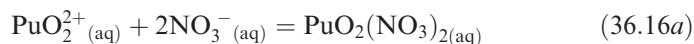
tion coefficients are larger at lower acid concentrations, with a maximum near 1 M nitric acid (Horner and Coleman, 1961). Back extraction of plutonium from HDEHP is difficult, and is usually accomplished by reducing the analyte to Pu(III) with HSO_3^- or $NH_2OH \cdot HNO_3$ and working only at very low HDEHP concentrations. Alkyl phosphates tend to form dimeric species in non-polar diluents and are monomeric in polar solvents (Peppard *et al.*, 1958).

While extractions involving organophosphorus compounds are widely used in industry, we have found little application for them in the plutonium analytical laboratory; residual phosphates interfere with most subsequent purification steps for higher-valent actinides.

(b) Ketones and ethers

Two types of ketones are effective extractants for plutonium, and they operate by different mechanisms. Monoketones, R–CO–R', solvate neutral complexes of plutonium; the 1,3-diketones, R–CO–CH$_2$–CO–R', react with plutonium to form chelates which are extractable. As one might expect, there can be a synergistic effect if an extraction is performed with a mixture of the two ketone types.

Methylisobutylketone (or hexone) is a monoketone that is widely used for the extraction of tetravalent and/or hexavalent plutonium from nitric acid solution. This is the basis of the REDOX process (Lawroski and Levenson, 1958), used in the mid 1940s to extract plutonium and uranium from spent nuclear fuels. Simple ketones tend to undergo radiolytic decomposition to form CO, H_2 and alkenes (Ausloos and Paulson, 1958). Distribution coefficients for the extraction of the hexavalent state are higher than those for the tetravalent state. The reactions can be written (Kuca, 1962; Laxminarayanan *et al.*, 1964):
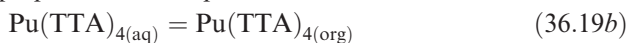
$$PuO_2^{2+}{}_{(aq)} + 2NO_3^-{}_{(aq)} = PuO_2(NO_3)_{2(aq)} \tag{36.16a}$$

$$PuO_2(NO_3)_{2(aq)} = PuO_2(NO_3)_{2(org)} \tag{36.16b}$$

and

$$Pu^{4+}{}_{(aq)} + 4NO_3^-{}_{(aq)} = Pu(NO_3)_{4(aq)} \tag{36.17}$$

$$Pu(NO_3)_{4(aq)} + 2HNO_{3(aq)} = H_2Pu(NO_3)_{6(org)}. \tag{36.18}$$
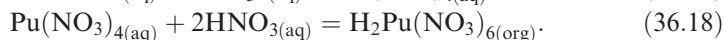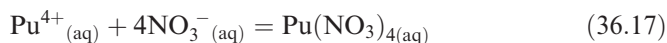
Nitrate systems have been studied the most. Both Pu(IV) and Pu(VI) are extractable at high nitrate concentrations while Pu(III) is much less so.

Thenoyltrifluoroacetone (TTA) can be used to complex Pu(IV) to a neutral chelate that can then be extracted into benzene, chloroform or toluene. TTA is the most widely used 1,3-diketone extractant. The reaction is written

$$Pu_{(aq)}^{4+} + 4\,TTA_{(aq)}^- = Pu(TTA)_{4(aq)} \tag{36.19a}$$

$$\text{Pu(TTA)}_{4(\text{aq})} = \text{Pu(TTA)}_{4(\text{org})} \qquad (36.19b)$$

Unfortunately, formation of the chelate suffers interference through competition with other complexing ligands (Palei and Milyukova, 1967). Even weak complexing agents such as Cl^- and NO_3^- interfere with the distribution of plutonium into the organic phase. Generally, keeping acid concentrations low and TTA concentrations high helps to drive the extraction, but strong complexing anions such as F^- can cause extraction failures. Extractions with TTA offer the advantages of high selectivity and the formation of very stable chelates (Moore and Hudgens, 1957).

We frequently find application for extractions involving the chelating agent TTA in an organic solvent, particularly involving the isolation of uranium, neptunium and plutonium from nitric acid solutions; some of the radiochemical milking experiments that are performed in determining the concentrations of small amounts of ^{236}Pu, ^{232}U, ^{233}U, or ^{243}Am in the presence of much larger amounts of other isotopes of the same elements start out with a TTA extraction. Unfortunately, most of the literature on the TTA/nitric acid system is based on benzene as the TTA diluent; there is a surprisingly large effect when the inert diluent is changed from carcinogenic benzene to the more environmentally friendly toluene (Heisig and Hicks, 1952). Because the volumes used in these procedures are small, we retain the use of benzene and deal with the issues of carcinogenic waste. Extractions involving ketones and ethers tend to not be as complete as those involving organophosphorus extractants, but are of greater utility in the analytical laboratory because organic residues can be destroyed in most cases before proceeding to the next analytical step.

(c) Amines and amides

As a rule, organonitrogen compounds have found little use in the extraction chemistry of plutonium, with the exception of amines and a handful of substituted amides (Keller, 1971; Swarup and Patil, 1976). If an appropriate amine can be found, amines offer certain advantages over other extractants including greater resistance to hydrolysis. Long-chain (8–12 carbons) tertiary amines, R_3N, have high distribution coefficients for transporting actinides into the organic phase and have proved to be quite valuable in the laboratory (Moore, 1952). On the industrial scale, a tertiary amine extraction is the final purification step for the plutonium fraction in the classical PUREX process. Quaternary ammonium salts (i.e. $[R_4N]Cl$) are also used in plutonium chemistry; symmetrical quaternary salts have higher extracting power than do unsymmetrical salts (Swarup and Patil, 1977).

Extraction of metal ions into an organic diluent such as benzene, chloroform, xylene or kerosene is accomplished by producing a quasi-neutral species that is more soluble in the diluent than in water. The tertiary amine molecule reacts

with a hydrogen ion and the anion that is characteristic of the mineral acid

$$nR_3N_{(org)} + nH^+ + A^{n-}_{(aq)} = \left[(R_3NH)_nA\right]_{(org)} \qquad (36.20)$$
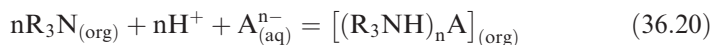
to form a quaternary ammonium salt that has a low solubility in water. In the equation, A^{n-} represents the anionic complex of the metal to be extracted. It is normal to precondition the organic phase by agitating it with a solution of the pure mineral acid prior to performing the actual plutonium extraction. The extracted salt may also have a limited solubility in the organic phase. This leads to the fairly common phenomenon of the formation of a second organic phase containing most of the analyte. If this happens, addition of a small amount of a long-chain aliphatic alcohol (e.g. dodecanol) causes the two organic phases to merge.

Amines extract plutonium as an anionic complex; in nitric acid systems the distribution coefficients decrease in the order Pu(IV) > Pu(VI) > Pu(III), while in hydrochloric acid systems the order is Pu(VI) > Pu(IV) > Pu(III) (Sheppard, 1957; Winchester, 1957; Keder, 1962). For tetravalent actinides, the order of decreasing affinity for the organic phase from both nitric and hydrochloric acid solutions is Pu(IV) > Np(IV) > U(IV) > Th(IV). From sulfuric acid solutions, Pu is better extracted with primary or secondary amines than with tertiary amines (Culler *et al.*, 1959), but this is an unusual situation that we will not pursue; however, one of the advantages of amines over organophosphorus extractants is their ability to extract tetravalent and hexavalent plutonium from solutions containing sulfuric acid (Shevchenko and Zhdanov, 1961; Vdovenko *et al.*, 1961).

The most important tertiary amines used in the extraction of Pu(IV) are tri-n-octylamine (Keder *et al.*, 1960; Shevchenko *et al.*, 1960a), triisooctylamine (Moore, 1960; Knoch, 1961) and trilaurylamine (Baroncelli *et al.*, 1962; Chesne *et al.*, 1963). They are usually prepared as a 10 vol% solution in a nonpolar solvent such as xylene. Maximum distribution coefficients usually occur for nitric acid concentrations between 4 and 6 M, for hydrochloric acid concentrations near 12 M, and for sulfuric acid concentrations near 0.1M.

While extractions involving organic amines are widely used in industry (Coleman, 1964), we have found little application for them in the plutonium analytical laboratory; residual amines interfere with most subsequent purification steps for higher-valent actinides.

(d)   Other extraction methods

There are other ways to perform a liquid-liquid extraction than those described above. One of these is extraction chromatography in which the organic extractant (including its solvent) is prepared as a thin coating on a solid support. In the radioanalytical laboratory, it is usually the organic phase that is attached to the support and the aqueous phase that flows (Bark *et al.*, 1967); however, the

reverse is a well-known technique in organic chemistry, where a piece of filter paper supports the aqueous phase and an organic solvent moves across the paper by capillary action, creating a lateral separation of organic compounds. The standard solvent extraction processes are carried out on a column (Gwozdz and Siekierski, 1960; Hulet, 1964; Hultgren, 1970). The organic phase is distributed on the surface of small, equally sized particles which are placed in a glass tube, called a chromatographic column; this provides the maximum surface area for chemical reactions and the means by which the mobile phase is prevented from taking selected paths through the column bed ("channeling"). The driving force that supplies the flow is either externally applied pressure or gravity.

There are several products available commercially that offer ion-specific organic materials on a solid support (Horwitz *et al.*, 1995; Maxwell, 1997). While the claimed selectivities of some of these materials are amazing, we have found that these products must be used with caution in non-routine applications in the plutonium analytical laboratory. Part of their limitation lies in their limited capacity, and part in the variety of interfering ions that can be found in unknown samples (Horwitz *et al.*, 1993). They are quite valuable in environmental applications. Trace amounts of the organic phase that elute from these columns can interfere with subsequent purification steps.
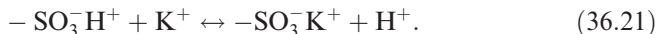
36.3.8 Ion-exchange

A class of separation methods of particular use to the plutonium analyst is that involving ion-exchange column chromatography. This term is usually applied to the selective partition of analytes between a flowing fluid and an insoluble solid, referred to as the support. Because of the limited chemical capacity of most supports, an increase in the size of the sample being processed often requires an increase in the size of the chromatographic apparatus. In the laboratory, we find that this effectively limits sample sizes input to chromatographic steps to less than a gram. However, the intrinsically high separation factors and high chemical yields attainable with column chromatography make this technique among the most powerful available to the radioanalyst (Girardi and Pietra, 1976). The phenomenon of ion exchange is of great utility in radiochemically isolating most of the species of interest to the plutonium analyst (Bauman *et al.*, 1952; Hyde, 1956; Katz and Seaborg, 1957; Rieman and Walton, 1970).

Inorganic ion exchangers such as zirconium pyrophosphate, MnO_2 and hydrated TiO_2 are generally more radiation resistant than are organic ion exchangers, but are often not reproducible in performance from batch to batch, have limited capacity, and are of limited use outside a relatively narrow range of pH (Pekarek and Marhol, 1991). They have been found to have little utility in the analytical chemistry of plutonium (Gal and Ruvarac, 1964;

Barsukova and Rodionova, 1968), particularly because the optimum acid concentrations do not preclude hydrolysis and the formation of Pu(IV) polymer.

Ion-exchange resins consist of an insoluble polymeric hydrocarbon to which ionizable functional groups are attached. The structural backbone is usually a cross-linked styrenedivinylbenzene polymer. These polymers are fabricated into small porous beads, almost perfectly spherical, over which an aqueous solvent is passed. Optimal separations are obtained when the beads are all about the same size, which helps prevent channeling of the solvent through a column packed with the beads. Resin beads are available in most mesh sizes from about 18 mesh (1-mm-diameter spheres) to colloidal size; most resins of use in the radioanalytical laboratory are between 100 and 200 mesh. Dry resin beads swell when immersed in an aqueous medium; the amount of swelling is controlled by the degree of crosslinking of the polymer strands, which is a function of the percentage of divinylbenzene used in fabricating the polymer. Most resins used in the radioanalytical laboratory are crosslinked between 4% and 12%. The higher crosslinked resins tend to be more selective, but the reaction kinetics are slower. Lower crosslinked resins react quickly, and are particularly useful in adsorbing large ions; a drawback is that the volume of the low-crosslinked beads can vary greatly when the ionic strength of the solvent is changed, resulting in a changed column length.

These resins are classified as either cation-exchangers or anion-exchangers, depending on the identity of the incorporated functional groups, which may consist of strong or weak acids or bases. A typical strong cation-exchange resin contains sulfonic acid groups; the $-SO_3H$ group is completely ionized in water and can exchange a coordinated hydrogen ion for another cation under the right conditions. For example:

$$- SO_3^- H^+ + K^+ \leftrightarrow -SO_3^- K^+ + H^+. \tag{36.21}$$

Similarly, a typical strong anion-exchange resin contains quaternary amine bases; the $=N-OH$ group can rapidly exchange hydroxyl ions with anions from the solvent, e.g.

$$= N^+ OH^- + Cl^- + H^+ \leftrightarrow = N^+ Cl^- + H_2O. \tag{36.22}$$
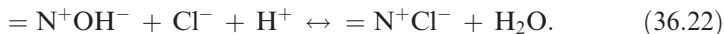
The capacity of the resin for adsorbing analyte ions depends on the structure of the polymer and the nature of the functional group. The strong anion- and cation-exchangers that are commonly used in radioanalytical chemistry have capacities that are effectively independent of environmental variables such as pH, and are usually expressed in terms of milliequivalents per milliliter of wet resin. For a standard strong anion-exchange resin such as DOWEX-1, a typical capacity is 1.2 meq mL^{-1}; for the DOWEX-50 strong cation-exchanger, a typical capacity is 2.0 meq mL^{-1}.

An ion-exchange column is a cylindrical tube, often made of glass, which supports a plug of glass wool or a porous frit that prevents the resin beads from flowing out of the column. For applications in which fluoride is part of the

column eluent, the glass-wool plug should be replaced with Teflon- or saran-wool. The resin should never be placed in the column dry, but rather always wet with water, to ensure that swelling is complete. After the column is packed, the resin bed should be thoroughly washed with water to reduce the level of manufacturing contaminants.

(a) Partition versus adsorption

There are two techniques for separating ions by means of an ion-exchange column, referred to as adsorption ("elution") and partition ("breakthrough"). In the elution technique (or classical ion-exchange chromatography), ions are adsorbed from a dilute solution that is passed through the column. Some ions have no affinity for the resin and pass through the column unhindered, while others interact strongly with the resin and are adsorbed in a narrow band at the top of the column. A "free-column volume" is defined as the volume of solution retained between the resin particles of the column; a truly unbound analyte will be mostly removed from the resin bed after the passage of a single free-column volume through the column. Of course, there is always straggling caused by the random motions of the solute molecules that makes it necessary to collect more volume to ensure a good separation. The elution technique can operate in two ways: (1) After undesirable species are washed from the resin, the eluting solution is changed such that the desired product is no longer bound to the resin, and elutes from the column; this is the usual case for the anion exchange of plutonium. (2) Undesirable species are retained by the resin and the unbound desired product elutes in a few free-column volumes.

In breakthrough (or differential) ion-exchange, as the solution of ionic species is passed through the column, the ions migrate down the column at a rate dependent on their affinities for the functional groups on the resin, given as a distribution coefficient similar to that defined for solvent extraction. The most weakly adsorbed ions are the ones that appear first in the effluent. Many cation-exchange procedures operate on the breakthrough principle; the analytical sample is loaded in a minimum volume of solution, and the product fractions are collected off the column in order of increasing affinity.

(b) Cation exchange

At low mineral acid concentrations, all three common analytical oxidation states of plutonium are adsorbed on cation-exchange resins. However, with the exception of non-complexing perchloric acid solutions (Nelson *et al.*, 1964a; Nelson and Michelson, 1966) plutonium desorbs with an increase in acid concentration, usually in the order of Pu(VI) before Pu(III) before Pu(IV) (Hardy, 1958). Cation-exchange processes have found only limited use in the separation and purification of plutonium because of the difficulty in achieving a high decontamination factor from ionic impurities without resorting to a many-

step procedure (Ryan and Wheelwright, 1958). Cation exchange of plutonium is often used in concentrating a large volume of a low acidity solution to a small volume of a solution of higher acidity; decontamination and final purification is preferably performed with anion exchange.

(c) Anion exchange

Anion exchange occupies a central position in the analytical chemistry of plutonium. Tetravalent and hexavalent plutonium are adsorbed on anion-exchange resins from many mineral acid solutions more concentrated than about 4 M (Campbell, 1956; Aikin, 1957; Chilton and Fardy, 1969), while trivalent plutonium is not retained by the exchanger at any acid concentrations (except for near-neutral solutions of certain brines (Kressin and Waterburg, 1962; Adar *et al.*, 1963). If plutonium is adsorbed from a hydrochloric acid solution, it can be eluted from the column with the same solution with the addition of an appropriate reducing agent (e.g. I^-, SO_2 or hydroxylamine).

While hexavalent plutonium is adsorbed from both nitric and hydrochloric acid solutions, tetravalent plutonium has a higher distribution coefficient, so most analytical procedures in the plutonium analytical laboratory focus on Pu(IV). The anion-exchange behavior of Pu(IV) in nitric acid solution is particularly important; because very few inorganic solutes form an extractable anionic complex with nitric acid (Overholt *et al.*, 1952; Ryan and Wheelwright, 1959; Ryan, 1960; James, 1963, 1966, 1967). From nitric acid solutions with acid concentrations near 8 molar, the distribution coefficient for $Pu(NO_3)_6^{2-}$ on anion-exchange resin can be greater than 10^3. Distribution coefficients are higher when the column separation is performed at low temperatures. Plutonium can be eluted from the column with dilute nitric acid; hydrolysis of Pu(IV) precludes the use of solutions with acid concentrations below 0.5 M. An alternative method involves adding hydroxylamine to the nitric acid eluting solution, warming, and reducing Pu(IV) to Pu(III). This method is not often used because of column performance issues having to do with the evolution of gas (Ryan and Wheelwright, 1959).

The sorption of Pu(IV) from hydrochloric acid is similar to that from nitric acid. The anion $PuCl_6^{2-}$ is strongly retained at acid concentrations over 6 M. As with the nitrate system, plutonium can be stripped from the column by lowering the acid concentration or by adding a reducing agent to form Pu(III), which is not adsorbed. In the chloride system, the usual choice of reducing agent is HI; performance is improved if the eluting solution is warm when loaded on the column. If the column contains a significant quantity of plutonium, I_2 and gas evolution can cause a degradation in flow performance. The eluting solution is usually 10–12 M HCl containing 0.1–0.5 M HI. HI can be introduced either from a gas source (lecture bottle), or from an aqueous acid; however, if the aqueous source is used, the analyst must be sure that the solution is not

stabilized with phosphate, which interferes with the column performance and subsequent separation steps.

The distribution coefficients of the tetravalent actinides from HCl onto anion-exchange resin are considerably reduced by the addition of small amounts of HF (Wish, 1959; Seyb and Herrmann, 1960; Nelson *et al.*, 1964b). If HF was used in the dissolution of the original sample or is present as more than a trace in the analytical solution, this can impact the performance of an anion-exchange separation. The use of HCl/HF solutions causes sharper and more rapid elutions from anion-exchange resin than does the use of HCl alone; volumes can be minimized in stripping steps through the addition of small amounts of HF.

A useful outline of an anion-exchange scheme for analytical separation of the heavy elements from a plutonium solution involves taking the traced sample, and preparing it as an 8M nitric acid solution. The solution is warmed, and nitrite is added to obtain tetravalent plutonium. This solution is passed through a DOWEX 1 × 8 column, which retains Pu(IV), Np(IV), U(VI), Pa(IV and V) and Th(IV), and passes the transplutonium actinides, radium and actinium with well defined separation times. The distribution coefficient for uranium in 8 M nitric acid is less than 10, so a large load volume will result in yield loss. The column is switched to concentrated HCl, which results in the elution of Th(IV). After most of the residual nitrate on the resin is replaced by chloride, a warm HCl solution containing HI is added to reduce Pu(IV) to Pu(III), which is no longer retained by the resin. The acid concentration must remain above 10 M or neptunium begins to elute with the plutonium. A solution of 4 M HCl containing 0.1 M HF causes neptunium and protactinium to elute together; uranium is then stripped from the column with 0.5 M HCl.

In a variation on this procedure, if the original sample is prepared in 10 M HCl (with a drop of nitric acid to stabilize tetravalent Pu), Th(IV) is not bound and ends up with the transplutonium elements; however, the elements that are indicators of prior weaponization, iron and gallium, are retained by the resin. Switching to 8 M nitric acid and washing the column with a generous amount causes iron and gallium to elute with a substantial fraction of the uranium activity.

As we have mentioned, the uranyl ion is only weakly sorbed from nitric acid solutions on strongly basic anion-exchange resins, with a maximum distribution coefficient smaller than 10 for acid concentrations near 8 M (Faris and Buchanan, 1964). This distinction from plutonium permits separations based on just nitric acid eluents. A copious wash of a DOWEX 1 × 8 column with 8 M nitric acid will eventually remove uranium (and neptunium), leaving plutonium (and thorium) adsorbed on the resin.

Plutonium (IV) polymer behaves differently on an ion-exchange column than does monomeric Pu(IV). If the polymer has formed in solution before that solution is loaded on the column, it tends to elute in a few free-column volumes,

independent of the molarity of the acid in the load solution. If the polymer forms on the resin after the column is loaded, it tends to be retained by the resin and can slow the flow rate of the column significantly. The easiest way to recover plutonium from polymer adherent on an anion-exchange column is to burn the resin in a muffle furnace and treat the residual material like a high-fired oxide.

36.3.9   Preparation of counting sources

Weightless sources are required by alpha spectrometry. The method of preparation and the substrate depend on the counting requirements. If an absolute alpha-particle disintegration rate is required, it is normal to prepare thin sources on platinum; the atomic number of the substrate affects the counter efficiency through alpha-particle scattering, and most calibration sources are prepared on platinum. This means that mixtures of HCl and HNO_3 should be avoided.

A common way of performing a radioassay is by ''stippling'' from a volumetric micropipette: the active solution is placed on the counting plate in a series of distributed small drops, which are taken to dryness under a lamp. The distance between the preparation and the lamp should be adjusted to prevent spattering. The micropipette (which is probably ''to contain'' rather than ''to deliver'') must be washed to the counting plate with clean solvent. Another way to prepare a radioassay is by weight. A single aliquot is delivered to the platinum substrate from a weighing buret, or after the platinum substrate is tared on a balance. Volumetric methods are falling out of favor; a skilled radiochemist can deliver a solution by volume to an accuracy of 0.1% or slightly better (with very good calibration of the glassware, temperature control, etc). If proper care is taken (buoyancy corrections, evaporation tracking, etc.) weight calibration can be an order of magnitude more accurate.

The plate is then heated in a Bunsen burner flame to an orange glow to fix the activity and volatilize away unwanted material. This is another reason to use a platinum substrate – other metals tarnish in the flame, or the plutonium migrates into the metal. Samples prepared in this way are generally not of good spectroscopic quality due to the inhomogeneity of the ''weightless'' radionuclide deposit, but 100% of the delivered activity is retained (Gol'din and Tret'yakov, 1956).

For samples with a large radionuclide content, it may not be possible to heat a sample in a flame outside of a gloved box or manipulator cell. In the past, an alcohol lamp has been used to fix the activity to the substrate of these sources; more modern safety practices preclude this procedure. It is not more common to use an induction heater (Curtis, 1950) mounted on insulators at a convenient height on the enclosure wall. When the generator is switched on, the sample is inserted into the coil and the resulting eddy currents in the metal substrate cause heating. The analyst is encouraged to become familiar with the

operation of the induction heater on the bench top before using one in a radioactive enclosure.

If the analyst does not care about a quantitative transfer of material to the counting plate, a source of better spectroscopic quality can be prepared through the addition of a spreading agent before the evaporation is performed. Tetra-ethylene glycol, lactic acid, collodion, and other reagents have been used for this purpose (Hurst and Hall, 1952; Sill and Williams, 1981; Sill, 1987).

Alpha sources to be used in the determination of isotope ratios must be thin and uniform. We produce these sources either by volatilization or by electrode-position. Volatilizing is a wasteful technique, in that approximately half of the final purified sample does not end up on the counting plate. An HCl solution containing the purified material is evaporated to dryness on a tungsten filament which is placed in an electrical fixture. The counting plate is suspended face-down over the filament and the resulting assembly is mounted in vacuum. When the pressure is less than 20 mtorr, a current is discharged through the filament, heating it white-hot, and transferring the adhering radionuclides onto the counting plate. The method is wasteful of sample but it is quick and produces spectroscopic-quality alpha sources, particularly if the filament-to-substrate distance is kept large (several centimeters).

An intermediate step, involving firing the filament at lower current before mounting the counting plate, can help reduce the amounts of alkali and alkaline earth salts in the final sample, which impacts the achievable resolution of the spectroscopic measurement. This can be performed without much loss of analyte. A variation of this technique is the sublimation method, in which prepared compounds of plutonium (usually halides) are heated more slowly and sublime in vacuum from a furnace to deposit on a cooled substrate (Parker *et al.*, 1960; Yaffe, 1962).

If the analyte signal is limited or the material is of particular value, alpha sources can be prepared by electrodeposition where the efficiency for depositing the radionuclide on the source substrate can approach 100%. The methods of electrodeposition are varied and are strongly dependent on the chemical nature of the analyte, but, in general, the acidity of the plutonium solution near an immersed cathode decreases, causing plutonium to deposit as a mixed hydrox-ide. A solution of significant acid content requires a higher current density to reduce the local acidity at the cathode (Moore and Smith, 1955; Samartseva, 1961; Sinitsyna *et al.*, 1959). For the actinide elements that are of the most interest to the nuclear forensic analyst, the analyte is dissolved in a minimum volume of dilute nitric acid and transferred to an electroplating cell with isopropanol. The counting plate comprises the bottom surface of the cell, and is connected electrically so as to be the cathode. A platinum wire anode is suspended in the liquid (Yakovlev *et al.*, 1956; Aumann and Mullen, 1974; Mullen and Aumann, 1975). The acidity of the isopropanol solution is low enough that, with plutonium, there are some unavoidable losses due to the formation of the Pu(IV) polymer; however, these are not as severe as one

might expect, which leads us to believe that the initially formed polymer is also deposited at the cathode. The low acidity of the isopropanol solution can require a bias of several hundred volts to increase the current density to a few milliamps per square centimeter; the yield becomes constant after about half an hour.

Electrodeposition of actinides has also been performed out of aqueous solutions of nitric acid, hydrochloric acid (Khlebnikov and Dergunov, 1958; Mitchell, 1960), and formic acid (Ko, 1957). Generally, as the acid concentration increases, the applied voltage decreases and the required current density increases. To electrodeposit plutonium from a pH 3 nitric acid solution requires approximately 100 mA cm^{-2}; if the acid concentration is increased to 0.1 M (nominal pH 1), the current density must be increased to 1,000 mA cm^{-2}. Dissipation of heat becomes important, and yield losses are often encountered due to the formation of the polymer.

Yet another method of electrodepositing the actinides involves a low-acid buffered plating solution (Yaffe, 1962; Kressin, 1977; Payne *et al.*, 2001). With most actinides, yield losses due to hydrolysis can become important if there is a significant time delay between the preparation of the solution and the onset of the plating process. After plating, the source plate is rinsed with isopropanol and flamed lightly to fix the activity. Sources prepared in this way are thin and uniform, and the resulting alpha spectra are of high quality. During the electrodeposition, alkali and alkaline earth cations tend to be retained by the solvent (Samartseva, 1961).

36.4 ANALYTICAL METHODS

36.4.1 Spectrophotometry

Aqueous and organic solutions of plutonium in all of its oxidation states display characteristic colors, many of them quite intense. (See electronic absorption spectra of plutonium aquo-ions in Chapter 7 of this work.) In many cases, quantification of transmission or absorption can be used to quantify the plutonium concentration of the solution by shining a beam of monochromatic light through a sample and applying the Beer's Law equation:

$$D(\lambda) = \varepsilon C \ell log(I_O/I) \qquad (36.23)$$

where $D(\lambda)$ is the optical density at a given wavelength (λ), I_O is the intensity of the incident photons and I is the intensity exiting the cell, ε is the molar extinction coefficient, specific to the wavelength of the incident light and analyte inventory of the solution, ℓ is the path length through the sample and C is the concentration of the analyte. Variations of the equation can be used for both transmission and absorption.

One class of these methods involves the reaction of plutonium ions with inorganic anions and with organic reagents that are, by themselves, colorless or weakly colored. The advantage of these methods lies in the fact that the optical properties of the solutions are stable for long periods of time provided that the plutonium oxidation state remains unchanged. One disadvantage of the method lies in its low sensitivity; it can only be used in accurate quantification of plutonium at concentrations exceeding millimolar. Each oxidation state of plutonium has its own characteristic absorption minima and maxima; this provides the means by which the speciation of a plutonium solution can be measured spectrophotometrically (Hindman, 1949; Seaborg and Katz, 1954; Shvetsov and Yorobyev, 1955). The identity and concentration of the complexing anions affect the absorption spectra in different ways, as does the temperature of the solution. As an example, Pu(IV) chloride is a red-orange color, while Pu(IV) nitrate is green. The emission and absorption spectra of Pu(III) do not vary much with the nature of the acid in the solution. The presence of interfering ions will influence the choice of which absorption lines to use for a particular sample determination. The analyte need not be in an aqueous solution; one of the industrial applications of spectrophotometry is in monitoring the plutonium content of the organic phase intermediate in the PUREX process.

An example of the measurement of a spectrophotometric endpoint is in the titration of plutonium with ceric sulfate (Caldwell *et al.*, 1962; Waterbury and Metz, 1964; Lerner, 1966), see Section 36.4.4. After the removal of interfering substances, plutonium in sulfuric acid solution is reduced to Pu(III) with zinc, and the solution is titrated against a standard Ce(IV) solution. Early attempts at performing this procedure relied on an added indicator of 1,10 o-phenanthrolin (ferroin); when the Pu(III) was exhausted, reaction of excess ceric ion on ferrous ion and the subsequent reaction of ferric ion with o-phenanthroline caused the solution to turn blue. However, if the sample contained a significant concentration of plutonium, the buildup of orange-brown Pu(IV) interfered with the observation of the endpoint. Incorporation of a spectrophotometer into the equipment removes the problem (Waterbury and Metz, 1959; Rost, 1961).

The spectrophotometric method requires that the acid concentration be known and the anion be present in excess. The ultimate accuracy of the technique depends on the preparation of suitable calibration standards; this is usually accomplished by dissolving a weighed sample of electrorefined α-phase Pu in a known volume of the appropriate acid. The accuracy of the plutonium concentrations of solutions prepared in this way can be better than 0.5% (Phillips, 1958).

A second class of spectrophotometric methods is based on the formation of intensely colored plutonium chelates (Milyukova *et al.*, 1967). Even if the chelating compound itself is strongly colored, redistribution of charge caused by interaction with the cation induces a significant shift in color. Methods based on these reactions can be quite sensitive and are useful for plutonium concentrations between the millimolar and the micromolar level.

An excess of the chelating reagent is added to a solution containing the plutonium analyte. Some of the organic reagent will remain unreacted, and some will react with the plutonium, resulting in a different absorption spectrum. The organic reagents most commonly used in carrying out these measurements (Metz, 1957) are the azo dyes, among them Thoron I, Thoron II, and the arsenazo compounds (Klygin and Pavlova, 1961; Ferguson *et al.*, 1964), which are fairly specific for Pu(IV). This specificity allows the analyst to ignore contaminants present at the percent level or lower. Analyses can be performed spectrophotometrically, as described above, or titrimetrically. The spectrophotometric determination depends not only on a series of standards, but on a plutonium-free solution of the dye. Titrimetrically, a solution of the dye is titrated with a standard plutonium solution until the spectrum (or critical frequencies therein) matches that of the experimental mixture, or the experimental mixture is titrated with a strong oxidizing or reducing agent to destroy the complex by changing the oxidation state of the tetravalent plutonium.

The dyes tend to be of limited solubility in aqueous solutions, limiting the concentration of the plutonium analyte. Most of the azo dyes are most effective in solutions that have acid concentrations approximately 0.1 M; procedures should be performed quickly and elevated temperatures should be avoided so that polymer formation is not important. The method, when employing Arsenazo III, is effective in solutions of nitric acid between 1 and 7 M.

A third class of spectrophotometric methods are based on solid phase color reactions between plutonium and a selected set of organic dyes (e.g. Rhodamine). Turbid suspensions of the compound formed are a different color than the original dye solution. The method tends to be poorly reproducible (Kuznetsov and Bol'shakova, 1960).

36.4.2 Arc or emission spectrometry

Arc or emission spectrometry detects the relative intensities of the optical lines emitted from a high-voltage spark source, with either graphite or copper electrodes (Wick, 1967), and is employed when it is desirable to analyze plutonium or its compounds simultaneously with impurities in the material. The sample is introduced into the spark by placing it in a cavity in the bottom electrode. Under these conditions, plutonium and its compounds display a large number of intense lines that can interfere with the detection of the characteristic frequencies of some contaminating elements; the intensity of the plutonium lines also limits the sample size that can be analyzed to roughly 50 μg. If only the relative contaminant concentrations are required, plutonium can be chemically separated from the contaminants to increase the effective sample size (Brody *et al.*, 1958). Direct sparking of PuO_2 results in an increased sensitivity for many contaminants and an increased sample size due to the refractory nature of the

matrix, which does not efficiently migrate into the hottest part of the spark under normal conditions (Wick, 1967). The sensitivity for the determination of Be, Mg, Al, Si, Cr, Fe, Ni, Cu, Zn, Sr, Ba, La and Pb is less than 500 ppm, with an uncertainty of approximately $\pm 10\%$ (Fred *et al.*, 1947).

A variation of the technique, providing an increased sample size (up to 500 µg Pu) involves drying a liquid nitrate sample in an indentation in a graphite electrode, along with a deposit of NaF, which enhances the impurity spectra relative to that of plutonium (Johnson and Vejvoda, 1959). Running the spark in an oxygen atmosphere suppresses the emission of carbon and cyanogen lines, also improving the signal strength. Impurity levels of as low as 25 ppm have been observed for many transition metals.

Calibration of the spectrophotometer used to detect the emissions from the spark is accomplished through running a series of standards for the set of impurity elements to be determined.

36.4.3 Methods based on volatility

Reactions between solid plutonium salts and HF in the gas phase produce the binary fluorides of Pu(III) and Pu(IV) (Dawson *et al.*, 1951). Reactions of these fluoride salts or PuO_2 with gaseous elemental fluorine between $300°C$ and $600°C$ will cause plutonium to be oxidized to the hexavalent state and produces PuF_6 (Florin *et al.*, 1956; Mandleberg *et al.*, 1956; Weinstock and Malm, 1956). Unlike UF_6, which sublimes, there is a narrow temperature interval at 1 atm pressure where PuF_6 is a liquid, between $51°C$ and $62°C$.

A lot of work has gone into the chemistry of the synthesis and storage of UF_6, a volatile compound that can be used as feed stock for isotopic enrichment of uranium. Preparation of PuF_6, also a volatile compound, stimulated studies on the potential use of distillation in the separation of uranium and plutonium from spent fuels (Jonke *et al.*, 1967; Barghausen *et al.*, 1970). At the laboratory scale, the difficulty of handling the reagents and the chemical reactivity of PuF_6 make it difficult to take advantage of its volatility.

Thermochromatographic techniques have been used in the separation of plutonium at the tracer scale (Zvara and Tarasov, 1962; Merinis *et al.*, 1970; Zvarova and Zvara, 1970). In thermochromatography, the sample to be studied is placed in the hot end of a column with a longitudinal temperature gradient. A gas flow is applied, usually containing a reagent to create volatile chemical species that are adsorbed from the gas stream at different temperatures according to the thermodynamics of their interaction with the substrate.

The sample can be introduced into the column as a dried deposit in a boat, or as implanted material in an accelerator catcher foil. Interfering chemical compounds (usually including oxygen) must be excluded from the gas stream. For the separation of volatile metals, the column is usually titanium and the inert carrier gas contains calcium metal vapor (Hickmann *et al.*, 1980; Herrmann and Trautmann, 1982; Fremont-Lamouranne *et al.*, 1985). The

study of compounds of the metals is usually accomplished in a glass or quartz column. The detection of the deposition position of alpha-emitting isotopes can be accomplished by inserting a central rod down the axis of the column; after the separation the system is cooled and the rod is withdrawn and surveyed for alpha radioactivity. The carrier gas facilitates heat transport, so the flow rate should be minimal to maintain the temperature gradient as applied from outside (Travnikov *et al.*, 1976).

In the thermochromatographic study of plutonium salts, the hot end of the column and the sample need to be heated to a temperature in excess of 800°C (depending somewhat on the chemical system being studied). In the fluoride system, the cold end of the column should be maintained below 0°C. Plutonium has been separated from americium under a $CCl_4 + Cl_2$ flow (Merinis *et al.*, 1970), and from lanthanides and heavier actinides (Travnikov *et al.*, 1976). Tetravalent plutonium chloride is more mobile at lower temperatures than is trivalent plutonium chloride and the other trivalent actinide salts, depositing at 360°C as opposed to $\geq$550°C. The bromides tend to deposit at lower temperatures compared to the equivalent chlorides.

There has been some interesting work using robust organic molecules to cause the volatilization of the actinides. One such molecule is hexafluoroacetylacetonate. See Chapter 14 of this work for more information on thermochromatography of the heaviest elements.

36.4.4   Titrimetry/volumetric methods

The importance of titrimetry in analytical determinations of plutonium concentrations has only recently competed with other determination methods, particularly when coupled with spectrophotometry or potentiometry to determine the endpoint. Because plutonium has three important oxidation states, Pu(III), Pu(IV) and Pu(VI), that can be stabilized over a wide range of conditions, two kinds of redox titrations are possible, those involving the Pu(III)/Pu(IV) half reaction, and those involving Pu(IV)/Pu(VI). The latter redox pair is involved in reactions that tend to be kinetically hindered, and may proceed at an acceptable rate only in special circumstances (such as elevated temperatures). The former redox pair proceeds via a simple electron exchange and is readily reversible, making it an appropriate choice as the basis for a redox titration. Titrations are often carried out in dilute sulfuric acid because sulfate ions stabilize Pu(IV).

Because plutonium in an analytical sample may be present in more than one oxidation state, a preliminary treatment of the sample to establish a single oxidation state is often required. The chemist must be careful to select a pretreatment method that does not interfere with the subsequent titrimetric method. For example, in the titration of Pu(III) with Ce(IV) in sulfuric acid solution, zinc metal can be used to reduce the entire plutonium inventory to the

trivalent state; any excess zinc is consumed by the acid in the solution and becomes Zn(II) which does not react with the titrant (Koch, 1949).

Titrimetry is a primary analytical method which plays an important role for high-accuracy analyses of nuclear material, e.g. for the purpose of nuclear material accountancy. It is used for quality control and for the calibration of radiometric methods. The uncertainties required from titration are therefore better than 0.15%, which can be achieved with automated titration procedures. Titration is essentially a cost effective, simple, and, most importantly a primary analysis method traceable to SI standards which serves as reference method for radiometric and other secondary methods.

In titrimetric analysis, the quantity of a substance, the analyte, is determined by the addition of measured increments of a standardized solution, the titrant (Ewing, 1975). At the equivalence point or theoretical endpoint the exact chemical equivalence of titrant has been added to the analyte. The detection of the endpoint and knowledge of the reaction mechanism allows for the calculation of the amount of analyte. As no calibration curves are needed the method is absolute and is considered a primary reference method. Titrimetry is used since a number of years for absolute measurements of plutonium samples (Drummond and Grant, 1965; Macdonald and Savage, 1978), along with other techniques such as gravimetry and isotope-dilution mass spectrometry.

Several types of reactions between the analyte and titrant, such as acid/base, complexometric, precipitation, and redox reactions may occur (Ewing, 1975). During a redox reaction, the potential difference between an indicator electrode and a reference electrode changes with the addition of the titrant. The change is largest at the equivalence point with the equivalence point corresponding to the inflection point of the S-shaped titration curve. For this so-called potentiometric titration various titrants are used, including oxidizing agents such as potassium dichromate and cerium(IV) salts or reducing agents such as ammonium iron(II) sulphate. Standard titrimetric substances are very stable and pure and are directly traceable to an international standard.

Depending on the solution composition of a potentiometric titration, an appropriate indicator electrode (which provides a potential depending on the composition of the solution) and a reference electrode (which supplies a potential independent of the solution composition) are chosen. For redox measurements, indicator electrodes with a platinum wire or plate are mainly used. The reference electrode is an Ag/AgCl or calomel electrode. The typical concentration range for a plutonium titration is in the order of 0.001–0.1 mol L^{-1}.

When dilute solutions are to be titrated, the potential jump in the potentiometrically obtained titration curve is not sufficiently steep. Indication of the equivalence point with polarized electrodes is the better option. A high constant potential is maintained between the electrodes that causes a diffusion current measured with either one (amperometry) or two (biamperometry) polarizable electrodes. Amperometric titrations are very sensitive and allow for the determination of very low concentrations (down to 10^{-6} mol L^{-1}) (Ewing, 1975).

(a) Plutonium assay by titration

Given the multiplicity of the valence states of plutonium, several redox pairs can in principle be used for titration. Various titration methods for plutonium have been proposed in the past (Drummond and Grant, 1965; Macdonald and Savage, 1978), two of them have been turned into norms.
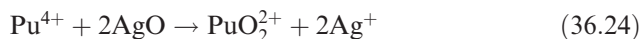
The potentiometric determination of plutonium by argentic oxidation, ferrous reduction, and dichromate titration developed by Drummond and Grant (1965) of the UKAEA reactor group at Dounreay (UK) in 1965 forms the basis for the ASTM standard test method C 1206 (ASTM, 2002) and the German norm DIN 25704 (DIN, 1993). This method is routinely used as primary method for plutonium determination, see e.g. Cromboom *et al.* (1991).

The ISO norm 8298 (ISO, 2000) is the modified and scaled down Macdonald and Savage titrimetric procedure which was published in 1978. Its application is, e.g., described in Kuvik *et al.* (1992). AFNOR, regulating the French national norms, has adopted the ISO norm.
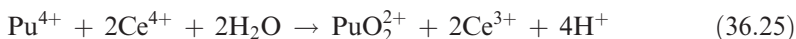
Both methods are based on the addition of a well defined excess of iron(II) sulphate solution which is back-titrated with a potassium dichromate solution. The titer of the iron(II) solution is determined with the same potassium dichromate solution for each titration run.

The two methods differ in the oxidant used: silver(II) oxide for the Drummond and Grant method and cerium(IV) nitrate for the Macdonald and Savage method. The redox processes of the two methods are shown in the following scheme:
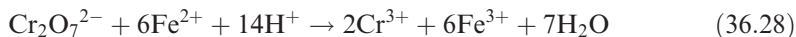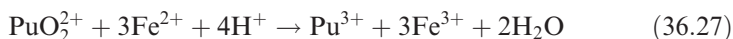
Oxidation by AgO:

$$Pu^{4+} + 2AgO \rightarrow PuO_2^{2+} + 2Ag^+ \tag{36.24}$$

Oxidation by Ce (IV):

$$Pu^{4+} + 2Ce^{4+} + 2H_2O \rightarrow PuO_2^{2+} + 2Ce^{3+} + 4H^+ \tag{36.25}$$

$$Pu^{3+} + 3Ce^{4+} + 2H_2O \rightarrow PuO_2^{2+} + 3Ce^{3+} + 4H^+ \tag{36.26}$$

Reduction by Fe(II):

$$PuO_2^{2+} + 3Fe^{2+} + 4H^+ \rightarrow Pu^{3+} + 3Fe^{3+} + 2H_2O \tag{36.27}$$

$$Cr_2O_7{}^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \tag{36.28}$$
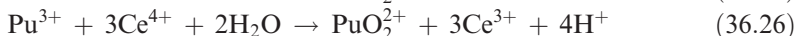
With the last two equations the concentration of Pu can be calculated from the amount of $Cr_2O_7{}^{2-}$ used for back-titration of Fe^{2+}.

The ASTM norm and the original Macdonald and Savage method use amperometry for end point detection. The modified methods and the other norms have adopted potentiometric detection.

Both standard methods are highly precise and accurate. They fulfill the requirements for safeguards applications, in particular for the accountancy of nuclear material, as recommended in the European Safeguards Research and Develop-

ment Association (ESARDA) target values (Aigner *et al.*, 2002). These are 0.15% for the uncertainties arising from random and systematic effects in the case of pure plutonium solutions and 0.20% in the case of uranium/plutonium mixtures. Note, that the methods allow for selective plutonium analysis also in mixed uranium/plutonium solutions with ratios up to 20. Typical analyses based on the Drummond and Grant method (Cromboom *et al.*, 1991) are carried out for mg quantities of plutonium. Drummond and Grant tested the method between 2–280 mg of plutonium with optimal conditions for 20–80 mg of plutonium. The ASTM norm gives 7–15 mg while the German norm indicates 6–50 mg.

An example for an amperometric determination of plutonium with ferrous ammonium sulfate as the titrant to reduce a solution of Pu(VI) is given in (Seils *et al.*, 1963; Bergstresser and Waterbury, 1964; Drummond and Grant, 1965). The plutonium sample is prepared as a 0.2 M sulfuric acid solution, and is oxidized to the hexavalent state with argentic oxide (AgO) in excess; the excess oxidant is destroyed by heating. The sulfuric acid concentration of the solution is increased to 9 M, after which it is titrated with a standard ferrous ammonium sulfate solution. The endpoint is detected amperometrically by measuring the excess current generated by the titrant after the reduction to tetravalent plutonium is complete (Helbig, 1961). The current is detected with a platinum electrode versus a saturated mercury sulfate electrode. Most elements do not interfere with the determination. Cerium, manganese, vanadium and chromium, which are oxidized by AgO and reduced by Fe(II), are exceptions.

Coulometry, i.e. electrolysis at controlled potential, is a method in which an electrical current is applied to a solution and the integrated charge is interpreted as the induced number of gram-equivalents of reactant. One of the limitations of the method involves selectivity, which depends on the different redox potentials of the ions present in solution. This can be improved through the addition of appropriate complexing agents. The advantages of the method include its high analytical accuracy, the wide range of concentrations of plutonium that can be analyzed (tens of micrograms to grams), the inherent accuracy with which the integrated charge can be measured, and the ease with which it can be introduced into remote-controlled systems (Holland *et al.*, 1978). Measurements have been made to an accuracy better than 0.1%; the limitation on the accuracy are related to side reactions occurring near the electrode due to asymmetric potentials.

Direct titration using an iron(II) solution suffers from unfavorable kinetics. In sulfuric acid solution the reaction is very slow and in the presence of nitric acid fails to complete. Back titration after addition of excess iron(II) using a standard titrimetric substance such as potassium dichromate is preferable. A sufficiently large excess in the order of 50% needs to be added. Iron(II) is not only oxidized by plutonium but also by nitric acid. This autocatalytic reaction can be suppressed by, e.g., sulfamic acid. It is advisable to start the titration with potassium dichromate immediately after stirring the solution, because the excess iron has a limited stability in nitric acid solution of at most 10 min.

The accuracy of the plutonium analysis is limited by the accuracy of the concentration of the iron(II) solution. Its titer is not stable and it is essential that the iron solution is titrated on the same day as the plutonium titration. The measurement precision of the iron factor should be better than 0.05%. The potassium dichromate solution is either prepared from a standard titrimetric substance such as NIST SRM 136, or its titer is directly checked against such a solution, or indirectly verified by the titration of certified plutonium reference material.

Drummond and Grant extensively investigated the different methods proposed for plutonium element assay (1965). In the presence of uranium, use of the Pu(III)/(IV) redox reaction is not possible, because uranium interferes significantly in the reduction step. Reduction of Pu(VI) to Pu(IV) is a more generally applicable titration reaction.

Ions that are oxidized or reduced in the various steps of the plutonium titration can interfere and produce a bias (Kuvik *et al.*, 1992). Significant positive biases can be caused by vanadium, chromium, and manganese, which can be corrected for at impurity concentrations below 200 g (g Pu)$^{-1}$. Thallium, selenium, calcium, and barium give negative biases. Also a fluoride solution above 0.05 mol L^{-1} disturbs the plutonium determination due to complexation. The influence of the fluoride ions can be suppressed by an excess of Al(III). Americium only interferes in fractions larger than 10% to plutonium. In the nuclear materials analyzed for plutonium the interfering elements are usually not present in quantities causing significant interference.

Neptunium is a particular case in that it behaves electrochemically similar to plutonium. It can be present in plutonium bearing samples at a concentration up to 1% relative to plutonium, and about half of it was found to be titrated with Pu (Kuvik *et al.*, 1992). An appropriate separation method or independent analyses must be used for correction.

36.4.5 Scanning and transmission electron microscopy

Electron microscopes are powerful and versatile tools for the microstructure characterization but also for elemental analyses of solid samples. Scanning Electron Microscopy (SEM) coupled to Energy Dispersive X-ray Spectrometry (EDS) or Wavelength Dispersive X-ray Spectrometry (WDS) analysis provides invaluable information on morphologies, surface structure and elemental composition and distribution up to a resolution of a few nanometers.

Transmission Electron Microscopy (TEM), developed by Max Knoll and Ernst Ruska in the early 1930s was the first technique of electron microscopy that has been developed (Ruska and Knoll, 1931). In TEM, electrons from the primary beam are deflected by electrostatic interactions with the positive atomic nuclei and negative electron clouds. A crystalline material interacts with the electron beam mostly by diffraction rather than absorption, although the intensity of the transmitted beam is still affected by the volume and density of

the material through which it passes. The intensity of the diffraction depends on the orientation of the planes of atoms in a crystal relative to the electron beam (Williams and Carter, 2009). Tilting the specimen to specific angles allows obtaining specific diffraction conditions, and apertures placed below the specimen allow the selection of electrons diffracted in a particular direction. A high-contrast image can therefore be formed by blocking electrons scattered away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons to pass through which produces a variation in the electron intensity that reveals information on the crystal structure. This technique known as *Bright Field* (BF) is particularly sensitive to extended crystal lattice defects in an otherwise ordered crystal, such as dislocations, defect clusters, precipitates. As the local distortion of the crystal around the defect changes the angle of the crystal plane, the intensity of the scattering will vary around the defect. It is also possible to produce an image from electrons deflected by a particular crystal plane. By either moving the aperture to the position of the deflected electrons, or tilting the electron beam so that the deflected electrons pass through the centered aperture, an image can be formed of only deflected electrons, known as a *Dark Field* (DF) image. The spatial resolution of a TEM is ~0.1 nm in both BF and DF. Many spectroscopy tools can be implemented in a TEM making use of the electron–matter interactions. This is the case for spectroscopy tools such as Electron Energy Loss Spectroscopy (EELS).

In the Scanning Electron Microscope (SEM) conceived by Ardenne (1938) and mainly developed in the early 1960s, a sample surface is scanned with a high-energy beam of electrons (typically 30 keV). The electrons interact with the atoms that make up the sample producing signals that contain information about the surface topography and composition of the sample. The types of signals obtained by SEM include secondary electrons, backscattered electrons, and characteristic X-rays. These signals result from the beam of electrons striking the surface of the specimen and interacting with the sample at or near its surface. In its primary detection mode, secondary electron imaging, the SEM can produce very high-resolution images of a sample surface, revealing details down to about 1–5 nm in size. SEM images have a very large depth of focus yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. Characteristic X-rays are the second most common imaging mode for SEM. X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher shell electron to fill the hole. These characteristic X-rays are used to identify the elemental composition of the sample. Back-scattered electrons (BSE) that come from the sample may also be used to form an image. BSE images are often used in analytical SEM along with the spectra made from the characteristic X-rays as clues to the elemental composition of the sample.

The scanning and transmission electron microscopy data that are shown in this paragraph have been obtained with a Philips XL40 SEM and a Hitachi H700 ST TEM respectively. Both instruments have been adapted for the exami-

nation of nuclear materials (Amelinckx *et al.*, 1997). The SEM (high voltage unit, column, chamber and turbomolecular pump) is mounted inside a gloved box and the primary vacuum system, water cooling circuit and acquisition electronics are placed outside. In the TEM the goniometer has been tightened and the transfer of the sample holder is made via a double deck system connected to a gloved box.

Typical fields of analytical application for electron microscopy on plutonium are

- – Nuclear forensic studies: particles detection and characterisation, microstructure characterisation of seized materials to determine a materials fingerprint (e.g., Ray *et al.*, 2002; Wallenius *et al.*, 2006), see Section 36.6.2 (d)
- – Studies of the aging of nuclear materials by alpha-damage: microstructural characterisation of samples doped with ^{238}Pu (e.g., Noé and Fuger, 1974; Fuger and Matzke, 1991; Wiss *et al.*, 2007a)
- – Basic studies of plutonium-compounds (intermetallic alloys, ceramic oxide or nitrides or carbides) (e.g., Zocco and Schwartz, 2003; Jutier *et al.*, 2007)

(a) Sample preparation

There are a number of drawbacks to the TEM technique. Many materials require extensive sample preparation to produce a sample thin enough to be transparent to electrons, which makes TEM analyses a relatively time consuming process with a low throughput of samples. The structure of the sample may also be changed during the preparation process. Also, the field of view is relatively small. Therefore, the region analyzed may not be characteristic of the whole sample. There is a risk that the sample may be damaged by the electron beam, particularly in the case of biological materials. Standard techniques devoted to the thinning of plutonium containing samples have been adapted in gloved boxes as shown for example in Fig. 36.1 where an electrochemical thinning setup has been mounted on a Peltier cooling system to maintain the temperature of the electrolyte at around –10°C. The method of electropolishing is particularly suited for the preparation of plutonium metal TEM disks given the strong reactivity of plutonium with air (see for example Schwartz *et al.*, 2005).

(b) Internal conversion for strong alpha-emitters

Artifacts due to the handling of radioactive materials have to be taken into account in, e.g., Energy dispersive X-ray analyses (EDX). The use of X-ray elemental analysis tools such as EDX has been recently described in the context of the investigation of nuclear materials (Wiss *et al.*, 2007b). These materials contain radioactive elements, particularly alpha-decaying actinides which affect the quantitative EDX measurement by producing interferences in the X-ray spectra. These interferences originate from X-ray emission after internal con-
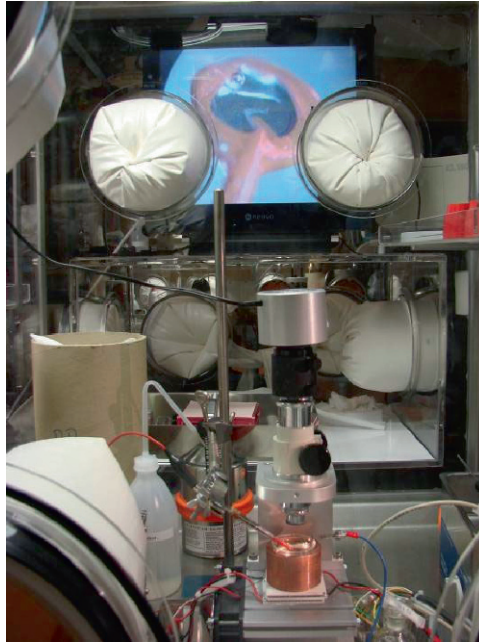
Fig. 36.1 *TEM sample preparation for radioactive materials. The etching of the sample – cooled down by a Peltier system – is followed by a camera (and viewing screen as seen at the back of the image) placed on top of an ocular above the sample clamped in tweezers (copyright European Communities).*

version by the daughter atoms of the alpha-decaying actinides. The strong interferences affect primarily the L-X-ray lines from the actinides (in the typical energy range used for EDX analyses) and would require the use of the M-lines for anlysis. However, it is typically at the energy of the actinides M-lines that there is peak overlap for neighbouring elements. Plutonium emits uranium X-rays by virtue of the internal conversion process that occurs after alpha decay. It also emits its own X-rays by virtue of alpha-particle-induced X-ray fluorescence.

The X-ray elemental analyses of actinide containing materials should therefore be performed with care regarding the potential interferences that can be produced from internal conversion of the alpha-decaying radioisotopes. For the shortest-lived actinides the X-ray lines could be determined where special attention should be paid especially for quantification but also for qualitative analyses. In surface analyses the contribution of X-rays that are emitted in the bulk (through internal conversion) can be a source of error. On the other hand the presence of some short-lived actinides can be detected (from internal conversion) even if not significantly present at the surface (first micrometer) of specimens. Figure 36.2 shows a SEM secondary electron image of a 38-year old
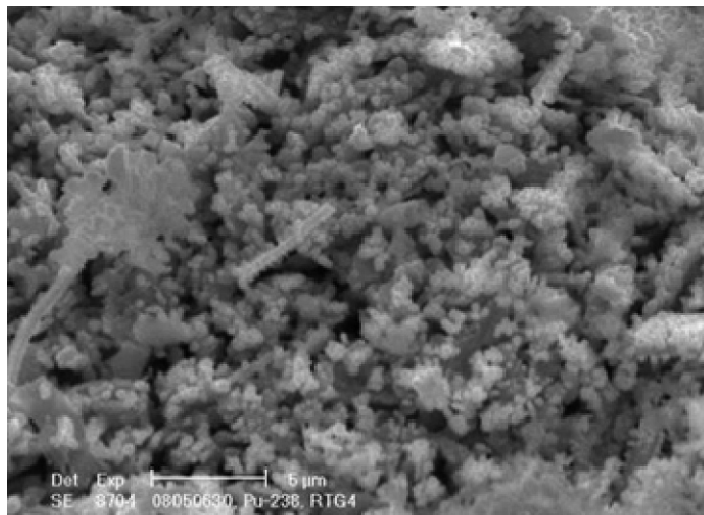
Fig. 36.2 *Secondary electron micrograph showing a $^{238}PuO_2$ sample from a radioisotopic thermal generator after 38 years storage in inert atmosphere. The dendrites growing on the original grains are attributed to the strong sputtering effects from alpha-decay (copyright European Communities).*

$^{238}PuO_2$ sample. Dendrites growing on the original grains can be observed. The EDX spectra taken respectively with and without electron beam are shown in Fig. 36.3 illustrating the above described internal conversion effect.

36.4.6   Energy-dispersive X-ray techniques

Energy-dispersive X-ray techniques represent a category of analysis methods, which are being advantageously applied for quantitative plutonium element concentration analysis in liquid samples. The X-ray techniques are utilized in two different ways:

1. Spectrometry of the energy-differential transmission of an X-ray continuum at the element-specific absorption edge energies of plutonium. The respective methods are colloquially referred to as *L-edge densitometry* (*LED*) when the absorption measurements are performed at the L_{III} absorption edge, or as *K-edge densitometry* (*KED*) when the measurements are made at the K-absorption edge.
2. Spectrometry of fluoresced characteristic X-rays as widely applied in the various modes of the traditional X-ray fluorescence (XRF) analysis technique. For the time being, quantitative concentration measurements are mostly made through the analysis of fluoresced K X-rays.
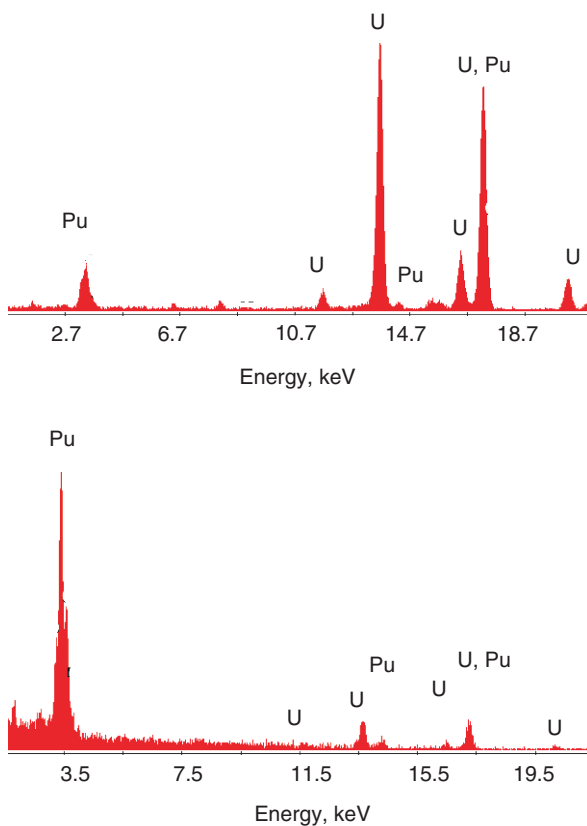
Fig. 36.3 *EDX spectra of a $^{238}PuO_2$ sample from a Radioisotope Thermal Generator (RTG) fabricated at ITU in 1970. The upper spectrum was recorded without impinging electron beam showing the production of typical L-X-ray lines from the daughter product of the alpha-decay of ^{238}Pu namely ^{234}U. The lower spectrum recorded in standard conditions (with electron beam) shows the expected peaks (both plutonium and uranium from decay) with the expected relative intensities (copyright European Communities).*

Although not reaching the ultimate accuracy level of about 0.1% as obtained with primary analytical methods such as gravimetry, coulometry/titrimetry (cf. Section 36.4.4) or isotope-dilution mass spectrometry (IDMS), the X-ray techniques nonetheless provide, at a somewhat inferior accuracy level, an interesting option because of a number of practical advantages such as speed of analysis, reduced handling of the radioactive samples, reduction of analytical wastes etc. It is mainly this practical aspect which has made them an attractive alternative and complement to the classical analytical techniques in the field of nuclear material analysis.
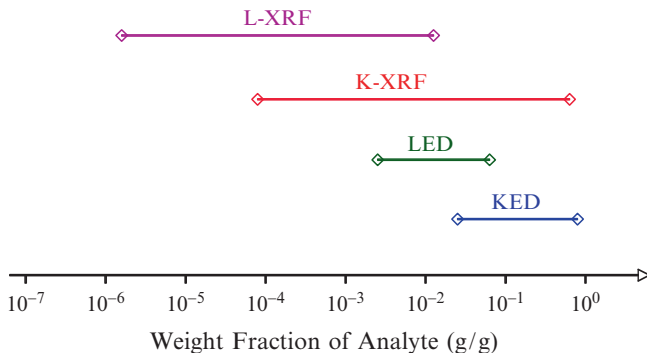
Analytical chemistry of plutonium

Fig. 36.4 *Typical useful concentration ranges for KED and LED, and for K- and L-XRF (copyright European Communities).*

The useful range of applicability of the X-ray techniques is more or less restricted to fairly high concentration levels. This is particularly true for the absorption edge measurement techniques KED and LED, which have a relatively limited dynamic range as indicated in Fig. 36.4. A somewhat larger dynamic range is offered by the XRF techniques, which in the case of K-XRF extends the useful range of measurements down to concentration levels of about 10^{-4} g/g, and in the case of L-XRF down to about 10^{-6} g/g in favorable measurement situations.

For practical reasons most of the X-ray techniques in actual use employ the 'K-mode' of analysis (KED and K-XRF) because of the better penetrability of the radiations involved (around 100 keV), which facilitates the adaptation of the instrumentation to installations such as gloved boxes and/or hot cell facilities required for safe sample handling. The respective instruments often combine KED and K-XRF for enhanced measurement versatility (Ottmar *et al.*, 1987; Ottmar and Eberle, 1991). This can be easily realized because both techniques utilize the same basic equipment.

LED for plutonium analysis is rarely used in practice up to now, while L-XRF for actinide elements is occasionally employed in wavelength-dispersive spectrometers ('Bragg spectrometer'), but rarely in XRF analyzers based on the energy-dispersive mode of analysis.

For the practical analytical work it should be recalled that the measurement principles of the X-ray techniques are based on interactions in the innermost atomic electron shells (K- and L-shell). This feature makes them insensitive to the valence and/or chemical compound state of the plutonium to be analyzed. The plutonium-bearing liquid samples therefore can be analyzed directly without prior addition of any reagents.

(a) Absorption edge spectrometry

The application of absorption edge spectrometry as an analytical tool for the determination of element concentrations, mainly for heavy elements, was first reported more than 80 years ago by Glocker and Frohnmayer (1925). In the following 5 decades, however, the technique has not gained any relevance in analytical measurements, probably because of its restriction to heavy element analysis at fairly high concentration levels. Only in the late seventies, in the course of the development of nondestructive assay techniques for nuclear material accountancy and control for international safeguards, the technique has been rediscovered as a useful tool for uranium and plutonium assay in solutions. It has been established during the last 20 years as a valuable analysis technique mainly in the area of nuclear fuel reprocessing, where naturally most of the relevant samples exist in the liquid form (Ottmar *et al.*, 1986, 1997).

Absorption edge spectrometry makes use of the abrupt change of the total photon mass attenuation coefficient for photon energies encompassing the binding energy of an electron in its atomic shell. This physical effect leads to a discontinuity in the transmission of an external photon beam of continuous energy distribution at the respective electron binding energy. Corresponding measurement examples of photon transmission measurements made with an X-ray continuum from an X-ray tube around the L- and K-shell electron binding energies of plutonium are shown in Figs. 36.5 and 36.6. Note that the [109]Cd gamma and X-ray lines in the K-edge spectrum in Fig. 36.5, and the Ti
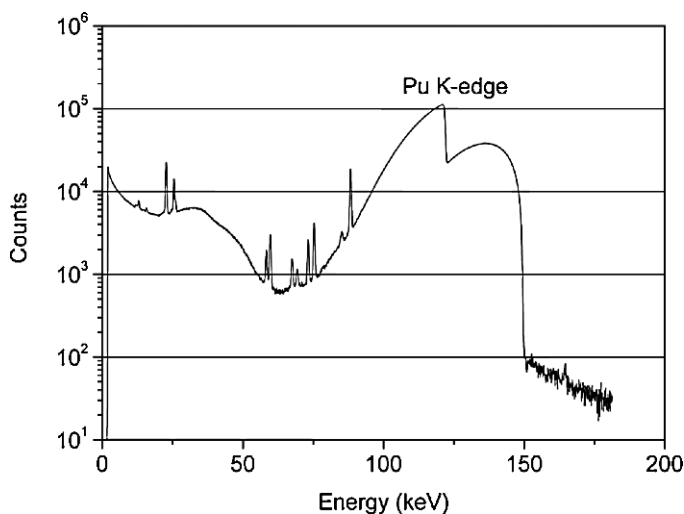

Fig. 36.5 *Photon transmission for a plutonium nitrate solution with 263 g Pu L^{-1} in the vicinity of the K-shell absorption edge (copyright European Communities).*
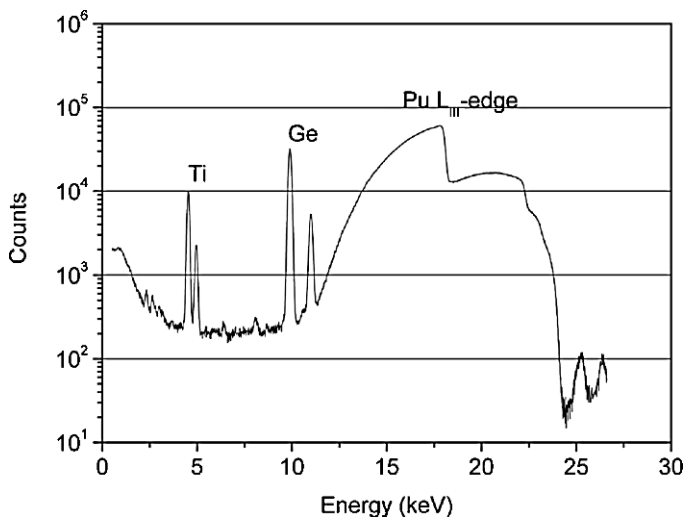
Fig. 36.6 *Photon transmission for a plutonium nitrate solution with* 30 *g Pu* L^{-1} *in the vicinity of the L-shell absorption edges* (*copyright European Communities*).

and Ge X-ray peaks in the L-edge spectrum in Fig. 36.6 were deliberately added for the purpose of energy calibration).

The K-absorption edge of plutonium occurs at an energy of 121.80 keV. The required X-ray continuum for the K-edge densitometry measurements is provided by standard 160 kV X-ray generators, which are typically operated at a voltage setting of 150 kV. The obtained X-ray continuum is strongly filtered by about 20 mm of iron to form a broad continuous distribution around the K-absorption energy. For L-edge densitometry at the L_{III}-absorption edge of plutonium (18.06 keV), which offers the largest differential change for the photon transmission among the three L-sub shells, a 30 kV X-ray generator operated at a voltage setting of about 25 kV provides a convenient X-ray continuum for the absorption edge measurements. Additional beam filtering is not required in this case because the walls of the (quartz) measurement cell and the analyzed plutonium solution itself effectively filter out the useless low-energy X-rays.

Both the L-edge and K-edge densitometry measurements are performed with highly collimated X-ray beams. Beam collimators with a diameter of 1 mm or less are commonly used to reduce the high X-ray intensity obtained from the X-ray generators to levels that can be reasonably processed by the respective spectroscopy systems. The K-edge spectra are recorded with high-resolution HPGe detectors (FWHM $\approx$ 500 eV @ 100 keV), while for the L-edge measurements Peltier-cooled Si drift detectors (FWHM $\approx$ 140 eV @ 5.9 keV) represent an advantageous detector choice.

When analyzing plutonium-bearing solutions contained in a measurement cell of well-defined path length d (cm), the plutonium concentration C_{Pu} (in g cm^{-3}) is simply obtained from the measured ratio R of the photon transmission across the respective absorption edge of plutonium through the densitometry equation:

$$C_{Pu} = \frac{\ln R}{\Delta\mu_{Pu} \cdot d} \tag{36.29}$$

where the quantity $\Delta\mu_{Pu}$ (in cm^2 g^{-1}) represents the difference of the total photon mass attenuation coefficient of plutonium directly above and below the absorption edge energy. The respective $\Delta\mu$-values at the L$_{III}$- and K-absorption edge are $\Delta\mu_{LIII} = 56.00$ cm^2 g^{-1} (theoretical value from Storm and Israel, 1970), and $\Delta\mu_K = 3.272$ cm^2 g^{-1} (experimental value from Ottmar *et al.*, 1987). The effective $\Delta\mu$-value, which can slightly vary from densitometer to densitometer depending on the aperture of the beam collimation, represents a calibration factor that has to be determined from measurements on known plutonium reference solutions.

The value of $\Delta\mu$, the path length of the measurement cell and the plutonium concentration itself represent the ruling factors, which determine the magnitude of the observed change in photon transmission across the absorption edge, and hence also the range of concentrations that can be measured with good precision. Obviously, the concentration levels measurable by L-edge densitometry are about 10–20 times lower than for K-edge densitometry because of the larger value of $\Delta\mu$ at the L$_{III}$ edge ($\Delta\mu_{LIII} = 17 \cdot \Delta\mu_K$). The curves in Fig 36.7 show the
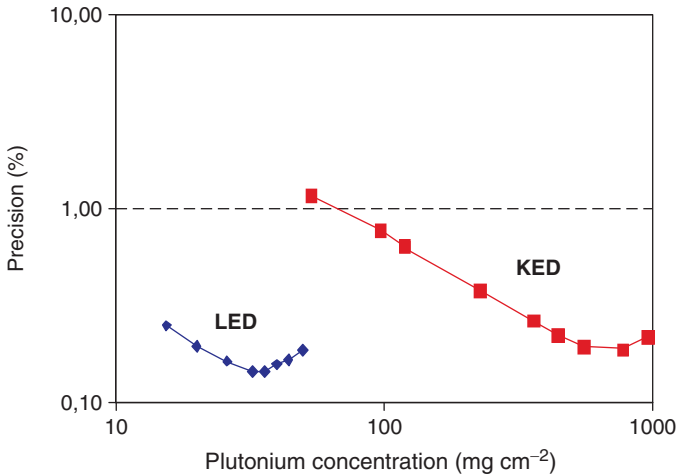

Fig. 36.7 *Measurement precision for the plutonium concentration from L-edge and K-edge densitometry as a function of the areal density (counting time = 1,000 s) (copyright European Communities).*

typical measurement precision of L- and K-edge densitometry as a function of the areal plutonium density for single plutonium solutions (assumed counting time = 1,000 s). For L-edge densitometry optimum measurement precision is obtained for an areal density of plutonium of about 20–50 mg cm^{-2}, corresponding to a plutonium concentration of 20–50 g L^{-1} with the use of a reasonable cell length of 1 cm. For K-edge densitometry the highest measurement precision is obtained for areal density values of plutonium above $\sim$400 mg cm^{-2}. The higher photon energies with their higher penetrability encountered in K-edge densitometry offer a larger flexibility as to the choice of the cell length, which in principle can be chosen as long as 10 cm. Depending on the cell length, the optimum concentration range for precise K-edge densitometry measurements therefore covers plutonium concentrations from about 50–500 g L^{-1}. Plutonium concentration measurements on the plutonium product solutions from a reprocessing plant, with typical plutonium concentrations up to 300 g L^{-1}, represent a practical example for the application of K-edge densitometry. The measurement example shown in Fig. 36.5 refers to this type of sample.

The densitometry equation given above applies, when the ratio of photon transmission across the absorption edge is determined directly at the absorption edge energy. In this case the analysis virtually becomes insensitive to matrix effects. Because the actually measured photon transmission shows some dispersion across the edge due to the finite energy resolution of the Si and Ge detectors, extrapolation techniques need to be applied for determining the transmission ratio exactly at the edge energy (Ottmar and Eberle, 1991).

All measurements in absorption edge spectrometry are made on a relative basis. The photon transmission as a function of energy is measured relative to a reference spectrum from a blank sample, and the concentration of the analyte derives from the transmission ratio at the absorption edge. This unique feature has made absorption edge spectrometry (LED and KED) to one of the most accurate radiometric analysis techniques. A measurement accuracy of 0.2% or even better for the determination of the plutonium concentration can be safely assured if strict procedures for measurement control are applied.

(b) X-ray fluorescence analysis

The XRF technique favorably applies if the plutonium concentration to be measured is falling below the useful range for absorption edge spectrometry or if plutonium is present as a minor constituent besides another major actinide element. There are a number of applications of this kind in nuclear fuel analysis, e.g. plutonium in mixed uranium–plutonium fuels or in spent uranium fuels. The larger dynamic range of the XRF technique, and its ability for simultaneous element analysis at larger element ratios up to 100 or somewhat above, offers useful analysis capabilities in such cases.

The production and analysis of fluoresced characteristic X-rays as a means for qualitative and quantitative element analysis offers a variety of choices of

how to use the XRF technique for a particular application. The majority of the XRF measurements made for quantitative plutonium analysis, or in general for actinide element analysis, are based on photon-induced fluorescence of K-shell X-rays. K-series X-rays from actinide elements have energies in the range between about 90 and 130 keV. Among the K-series X-rays the most abundant Kα_1 and Kα_2 X-rays are usually used for analysis. For plutonium the respective X-rays have energies of 103.73 and 99.53 keV.

In order to stimulate the emission of the characteristic K X-rays, the primary photon radiation must have an energy larger than the electron binding energy in the K-shell of the respective element, i.e. for plutonium larger than 121.80 keV. To efficiently excite fluoresced K X-rays from actinide elements, the X-ray tube used as primary photon source should be operated with a high voltage of at least 140–150 kV. This corresponds to the same operating condition as required for K-edge densitometry. KED and K-XRF analysis are therefore often combined in a single instrument as realized, for example, in the so-called Hybrid K-Edge Densitometer (Ottmar and Eberle, 1991). A typical measurement configuration with two separate measurement cells for KED (a 2-cm glass cell) and K-XRF (a cylindrical polyethylene vial with an inner diameter of 9 mm) is shown in Fig. 36.8. Instruments using a single measurement cell for the parallel KED and XRF measurements are also in use.
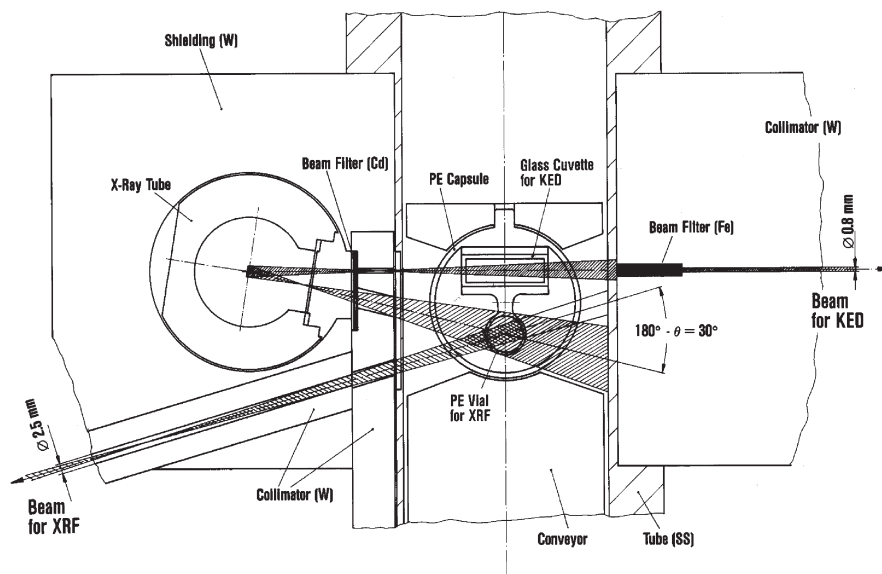

Fig. 36.8 *Measurement configuration designed for simultaneous X-ray tube excited K-XRF and KED measurements* (*Ottmar and Eberle*, 1991) (*copyright Forschungszentrum Karlsruhe, reproduced by permission*).

A common problem to all energy-dispersive XRF measurements arises from the fact that most of the primary photon beam intensity used for the production of characteristic X-rays is scattered from the sample and recorded in the detector together with the X-rays to be analyzed. This situation has real detrimental effects for the XRF measurements (in contrast to K-edge absorptiometry where scattering processes do play a minor role) for two reasons:

1. The detector and the data acquisition chain are overloaded with a large rate of useless signals.
2. The scattered radiation leads to an increased background which limits the detection sensitivity and the precision of the XRF analysis.

A partial solution to the first difficulty could be only achieved by applying special techniques for sample preparation such as evaporation of liquid samples onto thin backing foils. The second difficulty can be partly overcome through the choice of an optimized measurement geometry, taking into account the facts that for liquid samples (i) the dominating scattering process is due to inelastic scattering (often also called 'Compton scattering') on the low-atomic number elements in the matrix (H, C, N, O), and (ii) that the energy of Compton-scattered photons decreases with increasing scattering angle. If the fluoresced K X-rays are observed at an angle of 150° relative to the direction of the exciting beam from the X-ray tube as shown in Fig. 36.8 one is able to achieve the favorable situation where the Compton-scattered primary X-rays are removed from the energy region of the characteristic plutonium K X-rays. This is illustrated in Fig. 36.9. In the given example, where the X-ray tube was operated at 150 kV and the XRF detector was positioned at an angle of 150° relative
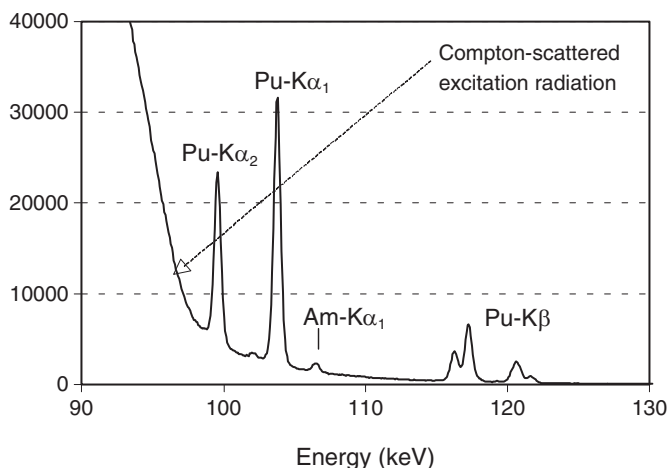

Fig. 36.9 *K-XRF spectrum from a sample of plutonium nitrate solution with 5.34 g Pu L^{-1} and 0.21 g Am L^{-1} (Ottmar and Eberle, 1991) (copyright Forschungszentrum Karlsruhe, reproduced by permission).*

to the direction of the primary photon beam, the onset of inelastically scattered primary photons occurs at an energy of about 97 keV. In this manner a favorable signal-to-background ratio is achieved for the characteristic K X-rays from plutonium.

With an optimized counting configuration as shown in Fig. 36.8 the technique of energy-dispersive K-XRF is able to reach a detection limit of about 50 ppm for actinide elements. The detection sensitivity is about the same for liquid and solid samples. However, the practical range of applicability for accurate quantitative analysis usually starts only at concentration levels of a few hundred ppm, where relatively precise measurements become feasible. The measurement example in Fig. 36.9 also illustrates that the energy-dispersive K-XRF analysis can easily discriminate the characteristic X-rays of neighboring elements (in the given example Pu and Am). The energy difference of K X-rays from neighboring elements is about 2.5 keV, which is five times larger than the typical detector resolution of about 0.5 keV for the respective X-ray energies.

XRF measurements generally require a more elaborate calibration compared to KED for accurate quantitative analysis. This is mainly because the measured fluorescence intensity (i) is more sensitive to variations of the sample matrix, and (ii) does not show a linear dependence on the analyte concentration. For the energetic K X-rays both effects are fortunately less pronounced than for the softer and less penetrating L X-rays, but dedicated calibrations for given types of samples are nonetheless needed for an accurate analysis. For solution samples with a thickness of less than 10 mm the linearity of the instrument response versus concentration is normally assured for concentrations up to about 5 g L^{-1}. For higher concentrations the response is starting to deviate from linearity due to increasing attenuation of the radiation incoming to and outgoing from the sample. This feature has to be accounted for by a corresponding calibration curve.

In practice it is difficult or nearly impossible to reach with the XRF technique a similar level of accuracy (0.1–0.2%) as obtained with K- or L-edge absorptiometry. This holds at least for absolute concentration measurements made by XRF. However, XRF can provide very accurate results when it is used just for element ratio measurements. For the analysis of uranium and plutonium-bearing samples there are a number of sample types containing both elements at varying ratios. For the analysis of those samples the combination of KED and K-XRF offers a useful scheme for analysis, where XRF with its larger dynamic range helps to provide an assay result for the minor element(s) not measurable by KED. An important practical example for this useful combination of KED and K-XRF applies, for example, to the uranium and plutonium determination in reprocessing input solutions, where KED provides an accurate result for the main element uranium (with a typical concentration of 200 g L^{-1}), and K-XRF for the U/Pu element ratio. The combination of both measurements then also delivers an accurate result for the minor element plutonium (with a typical concentration of 1–2 g L^{-1}).

36.4.7   Mass spectrometry

Mass spectrometry involves the measurement of isotope ratios through the electromagnetic separation of a beam of (singly-charged) ions extracted from an ion source according to their rigidities (a combination of mass-to-charge ratios and the extraction voltage). The instrument consists of an ion source, a method of extracting, accelerating and focusing a beam of analyte ions into a vacuum, a stage in which the trajectories of the ions are sorted out from one another by mass, and one or more detectors that measure the intensity of the beam at a given charge-to-mass ratio. Samples submitted for mass spectrometry typically require no special handling beyond the requirements of cleanliness; samples are submitted in small volumes of liquid or as a dry deposit, preferably in a Teflon container.

For the analytical chemist, preparation of the sample for mass spectrometry involves considerations that mostly revolve around the ion source and the physical and chemical form of the analyte. However, the construction of the instrument controls several important issues, including mass bias: because ions of different mass take different trajectories through the machine, the efficiencies of their detection are not necessarily constant, and must be corrected in an isotope ratio measurement. In a well-designed instrument, the mass-bias correction is small because of the employment of compound ion lenses or other compensation apparatus (Denoyer *et al.*, 1995). Mass bias is determined through the measurement of multi-isotopic standards, either alone or (preferably) incorporated into a replicate of the analytical sample being processed (Hamelin *et al.*, 1985; Russell, 1971).

Another issue of which the analyst must be aware is abundance sensitivity (or dynamic range), which is also a function of the design of the instrument as a whole. Stated simply, the abundance sensitivity is defined as the contribution of a signal due to mass m to the signal due to neighboring mass (m $\pm$ 1). An abundance sensitivity of 10^6 means that the signal at a given mass is too high by 1 ppm of the signal at adjacent masses. In a modern instrument in which the mass analysis is performed with a quadrupole rather than with a dipole, the abundance sensitivity can exceed ten orders of magnitude.

Mass spectrometric methods are essential in the determination of small amounts of plutonium in other matrices. In part, this is due to the sensitivity of the method; counting techniques are more sensitive than mass spectrometry only for nuclides with relatively short half-lives. The ''cross-over'' half-life is a function of the decay properties of the nuclides and the behavior of the element comprising the nuclide in the mass spectrometer, but can be thought of as being approximately 100 years for the alpha-emitting actinides. However, the interference of isobaric nuclides (and polyatomic ions) in a mass spectrometric measurement may make radiation counting more appropriate in certain circumstances; for example, the mass spectrometric measurement of ^{238}Pu in a sample derived from a mixed matrix may suffer from a background of residual

^{238}U, which will not interfere with an alpha-spectrometric measurement. Another advantage of mass spectrometry is that the decays of ^{239}Pu and ^{240}Pu (the major constituents of most plutonium samples) result in alpha particles with very similar energies. Resolving these nuclides by alpha spectrometry has only recently become possible with superconducting calorimetric sensors which offer an energy resolution of about 1 keV for 5.3-MeV alpha particles (Horansky *et al.*, 2008). Conventional gamma-ray spectrometry is only useful in this measurement for samples containing tens of milligrams of plutonium or more.

(a) Thermal ionization mass spectrometry

For many years, the workhorse technology for the mass spectrometric analysis of small amounts of plutonium was Thermal Ionization Mass Spectrometry (TIMS). Processing a sample for a TIMS analysis was labor intensive because the sample has to be chemically purified and evaporated to dryness on one or more filaments (Keck and Loeb, 1933; Inghram and Chupka, 1953). For plutonium, a good sample size is 100 ng. The filaments are inserted into the ion source of the instrument, where they are heated so that the semi-volatile compound of the analyte is evolved as a gas. This vapor collides with another hot electrode and becomes ionized; the first ionization potential of plutonium is 6.03 eV, making it an optimal analyte for this application.

An indirect method of preparing plutonium for insertion into the TIMS ion source involves loading it from solution onto an anion-exchange resin bead (Walker *et al.*, 1974). Plutonium is adsorbed from 8 M nitric acid onto a single resin bead, low cross-linkage, less than 300 µm in diameter; thorium, uranium and neptunium are also significantly adsorbed. The bead is dried under a lamp, and loaded on a V-shaped filament that is resistively heated on the bench top to ash the organic compounds before being incorporated into the ion source. Several improvements have been added to this scheme (Smith and Carter, 1981) such that an effective TIMS measurement has been claimed for samples as small as 5 fg Pu (Smith *et al.*, 1994). Clearly, the elimination of laboratory contamination is a driving concern at these levels.

It has been suggested that plutonium can be electrodeposited directly on a TIMS ion-source filament (Bergey *et al.*, 1980; Perrin *et al.*, 1985). The idea seems promising and should be pursued.

(b) Inductively-coupled plasma mass spectrometry

Inductively-coupled plasma mass spectrometry (ICP-MS) has become an important method for the determination of trace amounts of plutonium in a variety of samples including process solutions, nuclear fuels and weapon materials, and environmental and biological materials (Houk *et al.*, 1980). Samples, typically in solution, are introduced into a nebulizer and converted into an

aerosol (Montaser *et al.*, 1998). The incorporation of an autosampler can greatly increase the sample throughput of an instrument, especially for a series of similar samples where cross-contamination is not an issue. Analyte levels in a liquid sample are low, typically nanograms per liter, and the sample solution is introduced at a rate of hundreds of microliters per minute. The fine droplets are swept with a carrier gas (usually argon) into a plasma torch which decomposes the sample particles into individual atoms. Analyte atoms are ionized in the plasma and are extracted into a vacuum; a series of differentially pumped chambers pass the ion beam into the high-vacuum stages where mass analysis and detection occur.

The sensitivity of an ICP-MS instrument tends to be greater for high-mass elements. It is desirable that the instrument have a collision/reactive cell to fragment or neutralize polyatomic ions coming out of the ion source; in particular, hydrides of residual uranium in the sample can interfere with the measurement of ^{239}Pu.

Neither mass spectrometer discussed above is appropriate for the introduction of solid-phase samples, an application that is becoming more important in the field of nuclear forensics. Again, the introduction of the sample is the most important issue for the analyst.

(c) Ultra-sensitive mass spectrometry techniques

There is a longer discussion of ultra-sensitive methods for actinide analysis (including plutonium) in geological and environmental matrices in Chapter 30 of this work.

Accelerator mass spectrometry (AMS) is an ultra-sensitive analytical tool for the measurement of radioactive isotopes. As other mass spectrometric techniques, AMS is more efficient and more sensitive than traditional radiometric techniques for long-lived (i.e. $t_{1/2} > 100$ years) radionuclides, or isotopes that have weak or ambiguous modes of decay. AMS is similar to other mass spectrometric methods in that samples are introduced into an ion source and the resulting ions are filtered by a combination of magnetic and electrostatic elements based on their mass to charge ratio to isolate the isotope of interest. The feature that separates AMS from other mass spectrometric methods is the use of a tandem accelerator which offers two distinct advantages. First, because all molecular bonds are effectively destroyed during the stripping process that occurs at the terminal of the accelerator, AMS is insensitive to molecular isobaric interferences (e.g., ^{14}C vs ^{13}CH or ^{12}CH$_2$). Second, the high energy of the accelerated ions (>MeV) enables the use of classic nuclear physics detection schemes, such as differential energy loss in a gas ionization chamber, that can be exploited to discriminate atomic isobaric interferences (e.g., ^{36}Cl vs. ^{36}S). These two features permit AMS to precisely quantify trace levels of rare radioisotopes in the presence of an overwhelming stable isotope. Consequently, isotope ratios

as low as 10^{-15} are routinely measured by AMS in samples containing as few as 10^5 atoms of an isotope of interest.

Over the past 15 years, several AMS laboratories throughout the world have measured isotopes of the actinide elements, including ^{239}Pu, ^{240}Pu, and ^{244}Pu (e.g., Fifield *et al.*, 1996; Wallner *et al.*, 2000; McAninch *et al.*, 2000; Vockenhuber *et al.*, 2003; Fifield, 2008). Plutonium has several attributes that require special consideration in terms of the AMS measurement setup. First, because there is no stable isotope of plutonium, a known quantity of a reference isotope, typically ^{242}Pu, must be added for normalization. Because it is not feasible to add sufficient quantities (i.e., mg) of ^{242}Pu to produce macroscopic beam currents as with other AMS isotopes, normalization must be performed on the basis of counts of the isotope of interest against counts of ^{242}Pu. Second, plutonium isotopes are much heavier than most other species routinely measured by AMS and therefore the post-accelerator analyzing magnets of most systems are not capable of transporting plutonium at high energies. This has required AMS laboratories to either compromise transmission efficiency by operating their accelerators at lower voltages, or build dedicated beamlines for the measurement of plutonium and other heavy isotopes. Examples of AMS measurements of plutonium isotopes from a wide range of scientific endeavors including human health, environmental monitoring, earth science, nuclear safeguards, and astrophysics can be found in the above references.

Another ultra-sensitive technique that has been used for plutonium determinations in safeguards and nuclear materials relevant applications as well for the analysis of ultratrace amounts in environmental samples is Resonance Ionization Mass Spectrometry (Donohue *et al.*, 1984; Peuser *et al.*, 1985; Trautmann *et al.*, 2004; Erdmann *et al.*, 2008). In this technique, neutral species are introduced into the ion source from a heated sample or from sputtering with a primary ion beam. The gas phase atoms of the selected element are ionized in a selective multi-step process with laser light tuned to the respective atomic transitions, followed by mass spectrometric ion detection. The technique combines highest elemental selectivity with lowest detection limits in the range of 10^6 atoms per sample. Isotopic selectivities of up to 10^{13} have been achieved (Wendt and Trautmann, 2005). The technique has been applied for the determination of isotope ratios and lowest abundances of long-lived radioisotopes such as $^{238-244}$Pu, ^{90}Sr, ^{41}Ca and ^{236}U.

(d) Other mass spectrometry techniques

Spark source mass spectrometry has long been used for determining impurities in plutonium metal samples. It takes advantage of the fact that the erosion of material by an arc and its introduction into the plasma are roughly independent of the identity of the element (Craig *et al.*, 1959). The efficiency of extracting the ions from the ion source into the mass spectrometer is limited, requiring larger sample sizes

(tens of milligrams), but the sensitivity of the method has been quoted as being better than 1 ppm for most common analytes (Brown *et al.*, 1963). Estimates can be made of the concentrations of light elements such as H, C, N, and O, but the result should be treated as upper limits because of their presence in the residual gas (air and hydrocarbons) in the source region, and their tendency to return to the source region rather than adhering to surfaces in the mass spectrometer as do the refractory elements. The sample is incorporated into the source as part or all of one or both electrodes. Other materials exposed to the spark should be compatible with the desired analytes. Freshly cut plutonium metal source parts should be protected from air to avoid surface oxidation.

In Secondary Ion Mass Spectrometry (SIMS), an ion beam (the so-called primary beam, usually Ar^+, Cs^+ or O_2^+) is used to sputter secondary ions from a surface, which are introduced into the ion source of the mass spectrometer. When combined with imaging of the sample stage, a spot on the sample surface can be selected for analysis, defined by the lateral extent of the primary ion beam. Sample preparation usually involves nothing more than producing a clean, smooth surface on the sample. The ultimate accuracy of the technique for the determination of isotope ratios depends on the availability of isotopic standards of the analyte in the appropriate matrix (Deloule *et al.*, 1992). SIMS is used, e.g., for particle analysis in safeguards and for spent fuel examinations. A study on the use of high-resolution SIMS for the detection of uranium isotopes was conducted by Ranebo *et al.* (2009). The aim of the study was to improve uranium detection sensitivities for the monitoring of undeclared nuclear activities. Similar work on plutonium particles is on-going. The use of SIMS for investigations of irradiated nuclear fuel and cladding was reported by Portier *et al.* (2007).

36.4.8 Nuclear counting

Isolating a chemical fraction from a sample of nuclear material is only the first part of a radiochemical analysis. The relative concentrations of the analytes must be determined, a chemical yield applied, and the absolute concentrations of the analytes in the original sample must then be derived. For radiation counting, the geometric extent of the radionuclide sample, whether liquid or solid, affects the efficiency of the detector and the accuracy with which the concentrations of the radionuclides can be determined. On the other hand, there are also types of nuclear counting measurements that are practically insensitive to the geometric extent of the samples, and further do not require any radiochemical separation prior to the analysis. For example, the quantitative plutonium assay by calorimetry and by neutron coincidence counting, and the determination of plutonium isotope abundances by gamma spectrometry, belong to this category of measurements.

Liquid sources can be counted for gamma rays. As long as the radionuclide analytes are in a true solution, germanium photon detectors can be calibrated to

accurately determine their concentrations in well-defined geometries. One standard counting sample configuration consists of 10 mL of source solution confined in a cylindrical plastic vial that has a cross sectional area of exactly $10\,cm^2$. For those cases where the chemical yield is obtained from the mass of an added carrier, this method is consistent with the requirements of spectrophotometry or other optical techniques.

Solid sources can be either "thick" or "weightless". Unlike alpha-particle counting, gamma-ray and some beta-particle counting can be fairly forgiving of the mass of the sample. The same is true for calorimetry and neutron counting. Corrections for self attenuation, where needed, can be calculated or measured with standards. When the chemical yield of an element is determined gravimetrically through the weight of a stoichiometric compound, sources are often prepared by filtration; the precipitating agent is added to the liquid sample and, after digestion, the liquid is drawn by vacuum through a flat filter paper mounted on a frit. With care, this method can result in a uniform deposit of well-defined extent, necessary for accurate counting.

Beta counting and some alpha counting are performed with proportional counters, which give no energy information on the detected nuclides. The emission of beta particles results in a continuum of electron energies between zero and the Q-value energy, and the detector efficiency is always a function of the decay energy and the shape of the beta continuum. Unless a small number of components comprise the mixture of beta emitters, it is difficult to quantify the beta decay rate of the sample. The situation is even more complicated for low-energy beta emitters such as ^{241}Pu, where the preparation of the source affects the counter efficiency, and conversion and Auger electrons can also interact with the detector (See scintillation counting, Section 36.4.8(d)). On the other hand, the efficiency of detection of alpha particles by proportional counters can be reasonably independent of energy, and if counting sources are prepared on the same substrates as are calibration standards, the efficiency can be known to $\pm 2\%$. The analyst must be careful to adjust a lower-level discriminator so as to reject beta events while not losing a significant number of alpha events; a discriminator setting that is the equivalent of a detected energy of 2.0 MeV is in use at many laboratories.

(a) Alpha, beta and gamma spectrometry

Alpha-particle and gamma-ray spectrometry share many features having to do with the way data are taken (Siegbahn, 1964; Knoll, 2000). The energies of incident alpha particles, which stop in a limited thickness of matter, can be detected using either a gridded gas-filled counter operated at proportional voltages (e.g. a Frisch-grid detector) (Knoll, 2000) or, more commonly, with a solid-state junction-diode room temperature semiconductor counter (e.g. silicon surface-barrier detector) (Tait, 1980; Knoll, 2000). Gamma rays and high-energy X-rays require considerably more material to deposit their energy, and

interact more effectively with materials of high atomic number; consequently, photon spectroscopy is usually performed with germanium semiconductor detectors (Knoll, 2000), cooled to liquid-nitrogen temperatures to reduce noise and improve resolution. Detectors made of other materials, based on the detection of induced light (scintillators) or ionization have been developed, but their performance in spectrometric measurements and utility in the analytical laboratory is, in general, inferior to the detectors mentioned above (James *et al.*, 1993; Knoll, 2000).

The detectors operate in pulse mode, and the output of the detector element (whether gaseous or solid) is converted from a low amplitude current or voltage pulse to a higher amplitude linear voltage pulse whose amplitude is proportional to the energy of the deposited radiation. Preamplification of small current or voltage signals must take place at the detector to minimize the magnitude of signal-to-noise caused by cable capacitance. For proportional counters, where scalers are used to record the number of pulses as a function of time, the demands of signal processing are minimal. When energy information is required, an amplifier converts the preamplifier output pulse to a logic-pulse voltage signal whose amplitude is proportional to energy. It is at the amplification step that issues of peak shape/rise time, pileup rejection, continuum reduction, and timing are dealt with. The amplitude of the amplifier output pulse is measured and converted to a digital number with an ADC (analog-to-digital converter), which is stored as an event in a multichannel analyzer (MCA). The counts in each channel of the MCA represent the spectrum of radiation reported by the detector element.

The energy-dependent response of α- or γ-spectrometers can be measured with standards. For α-spectrometry, a multi-line standard whose isotopic composition has been characterized by mass spectrometry can be used to measure the relative efficiency of the detector as a function of energy; absolute efficiency is determined against a single-nuclide calibration source using a proportional counter. Multi-line γ-spectrometry standards are available commercially. 13.2-year [152]Eu, a popular calibration nuclide, has more than 100 known gamma-ray lines in its decay scheme, with high-intensity lines spanning the energy interval between 120 and 1,408 keV; the strong 344.1-keV line is emitted with a probability of 27.2% (Firestone and Shirley, 1996). If the analyst prepares samples of significantly different geometrical extent, amount or dilution, he/she should calibrate the detector as a function of detector-to-source distance using a point source, and correct for other factors geometrically (Gunnink *et al*., 1968; Gunnink and Niday, 1972; Routti and Prussin, 1969). The use of attenuators can be an important tool; the low-energy γ-ray emissions of [241]Am can dominate the detected spectrum from a plutonium sample, and unless a significant thickness of cadmium and/or lead is incorporated into the counting configuration, it may prove impossible to move the source close enough to the detector to see weaker high-energy lines. The calibration must be able to correct for external attenuation.

(*i*)   α-*counting*

Figure 36.10 shows a section of a representative alpha-particle spectrum, taken with a silicon surface-barrier detector. The sample is freshly purified weapons-grade plutonium, volatilized onto a stainless-steel substrate. The sample was essentially weightless, and the energy resolution of the peaks and their shapes are defined by the response of the detector. Any residual mass in the sample results in a broadening of the peaks and an increase in the amount of the "tailing" of high-energy peaks into low-energy peaks. The shapes of the tops of the peaks are caused by fine-structure in the decay; in the case of even-mass plutonium isotopes there is some probability of alpha decay to the first excited state of the daughter, giving rise to a low-energy satellite peak. The conversion of MCA channel number to energy was accomplished through a calibration function, obtained by counting standard sources. The efficiency of the detector is not precisely known, but is effectively independent of energy, so ratios of activities can be measured. Pileup events caused by more than one alpha particle entering the detector during the resolving time may preclude the observation of a decay, e.g. of ^{236}Pu at 5.77 MeV. The detector also responds to rare fission events due to the spontaneous-fission decay of ^{240}Pu; these events have pulse
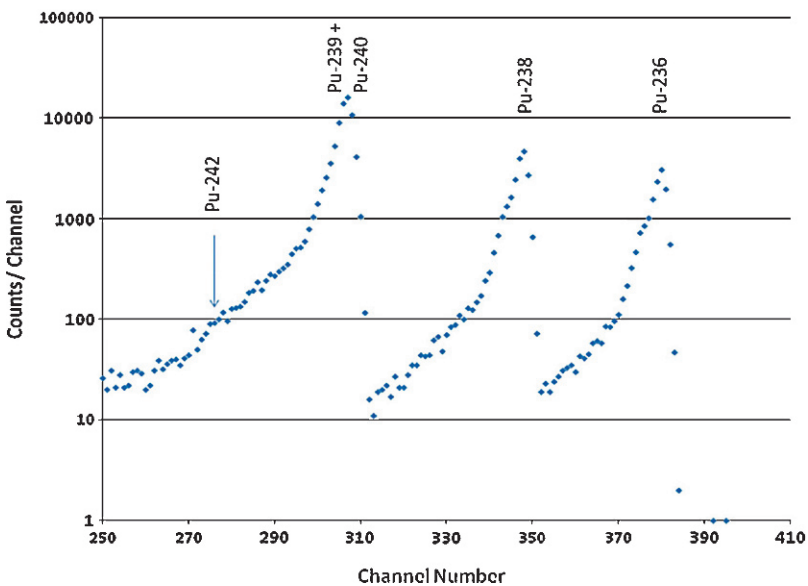

Fig. 36.10   *Spectrum of alpha particles emitted by a traced (^{236}Pu) sample of plutonium, chemically isolated from nuclear explosive debris and volatilized onto platinum. Alpha particles emitted by ^{236}Pu, ^{238}Pu and the combination of ^{239}Pu and ^{240}Pu are clearly visible; ^{242}Pu is not. The resolution of the detector was such that satellite peaks in ^{236}Pu and ^{238}Pu should have been visible in the absence of broadening due to sample thickness (copyright European Communities).*

heights that far exceed the range of the multichannel analyzer, and are tracked separately with a scaler.

The characteristic peak shape in each alpha spectrum is somewhat different, being a complicated function of the detector response and the thickness and extent of the deposited radionuclides that comprise the counting source. Alpha peaks are often treated as histograms, summed between low and high limits defined by a fraction of peak height (usually 1–2%, depending on the separation of peaks). The intensity underlying lower-energy peaks due to tailing from high-energy peaks is subtracted from the histogram graphically. This correction can be relatively small, as in the tail intensity under the ^{239,240}Pu peak, and can be large, as in the tail correction to ^{242}Pu. More elaborate techniques for the analysis of alpha spectra employ methods of least-squares-fitting of the spectral data to appropriate response functions as practiced in the analysis of high-resolution gamma spectra (Blaauw *et al.*, 1999).

For plutonium isotopes, alpha spectrometry is a competitive technique with mass spectrometry when sensitivity is being considered. For ^{238}Pu, the background due to isotopes of uranium precludes it being measured by mass spectrometry except in unusual circumstances (Alamelu *et al.*, 2005). The ^{238}Pu activity in an alpha spectrum is often reported as an ''alpha ratio'' or S value (Aggarwal *et al.*, 1980), which is the ratio of the α-peak area of ^{238}Pu to that of ^{239}Pu + ^{240}Pu (isotopes with similar α-decay energies); therefore, in order to report atoms of ^{238}Pu in a sample based on α-spectrometry, a mass-spectrometric determination of ^{240}Pu/^{239}Pu is also required (Farwell *et al.*, 1954; Chamberlain *et al.*, 1954). Because ^{241}Pu is a low-energy beta emitter (difficult to quantify by radiation counting) and ^{242}Pu is a long-lived nuclide often used as an isotope-dilution chemical yield tracer, mass spectrometry is an unavoidable collateral technique to alpha spectrometry for the light plutonium isotopes. Because the α-decay energies of ^{241}Am and ^{238}Pu are similar, an accurate measurement of the α-ratio requires that the time and completeness of separation of americium from plutonium are known, and for significant ingrowth times, the ^{241}Pu content of the mixed plutonium isotopes.

As discussed above, ^{236}Pu is often used as a chemical-yield tracer for α-spectrometric measurements of plutonium isotopes. Because the decay daughters of ^{236}Pu form a complicated inter-related chain of radionuclides many of which decay by α-particle emission, the tracer is of most utility in the α-spectrometry of recently purified samples. Yielded samples should not be overtraced, both because of the buildup of daughters and because the ^{236}Pu tracer has the highest decay energy in the source, making a tailing correction necessary.

The measurement of ^{236}Pu intrinsic to a sample is a valuable fingerprint of the processes resulting in the plutonium material. Usually, the ^{236}Pu activity level in a plutonium sample is too small to be observed directly over the presence of the other plutonium isotopes. In this case, α-spectrometry is combined with a radiochemical milking technique; the plutonium sample is scrupulously purified

of uranium decay daughters at a well-defined time. At a later time, ingrown uranium is removed from the plutonium sample, purified, and a counting source is produced. The value of $^{232}U/^{234}U$ in this sample is related to $^{236}Pu/^{238}Pu$ in the original sample by the Bateman decay laws. A large amount of sample (hundreds of milligrams of plutonium) is required for this measurement.

Other analytes in a plutonium sample are also measured through tracing, chemical separation and α-spectrometry. For the thorium, uranium, and neptunium isotopes, a mass-spectrometric analysis of the material is valuable collateral information, but $^{232}U/^{234}U$ and $^{228}Th/^{230}Th$ are best determined by alpha counting.

(ii) γ-counting

Figure 36.11 shows a section of a representative gamma-ray spectrum, taken with a coaxial germanium semiconductor detector. Data were collected for photons with energies between 60 keV and 2 MeV, stored in 4096 MCA channels, but only the data between 250 and 750 keV are displayed in the figure. The figure shows many of the features common to gamma-ray spectra.

The shapes of the gamma-ray peaks in a germanium detector spectrum do not show the same dependence on the source properties as do the α-peaks. The gamma-ray peaks change shape with energy in a regular and calculable way,
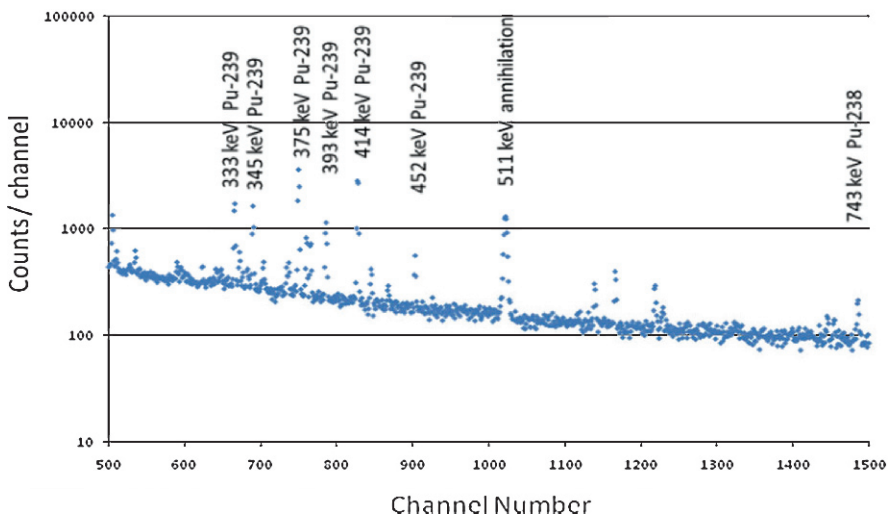

Fig. 36.11 *Spectrum of photons emitted by a plutonium sample, in the energy interval of 250–750 keV. Gamma-rays emitted by ^{239}Pu and ^{238}Pu are clearly visible. The photon intensity from decays of ^{241}Pu is at lower energies. The sample was purified of americium shortly before the count was taken. Note that for the analysis of plutonium samples the energy region around 100 keV with several high-intensity gamma-rays is mainly used (copyright European Communities).*

which paves the way for the automated analysis of gamma-ray spectra. An exception to this is in the detection of X-ray photons; the actinide K X-rays are characterized by different shapes when observed with detectors with good energy resolution. The quantification of the intensities of the photopeaks observed in a gamma-ray spectrum is a mature field of study (Routti and Prussin, 1969; Gunnink *et al.*, 1968; Gunnink and Niday, 1972). Computer software exists that can take as input efficiency functions, energy calibrations, and background information, and integrate the areas of peaks in the spectra taken from experimental counting samples, subtract a component for the intensity of the continuum under the peak (the quantification of which is a matter of some dispute), and generate a table of photon energies and associated intensities in absolute photons per minute. Energy and efficiency calibrations are benchmarked against counting standards but are largely theoretical constructs that can be modified for attenuation (both from the source and from intervening foils) and finite source extent. A functional fit to the peak shape, whose width is a function of energy, is used in the resolution of multiplets in complex spectra.

Gamma spectrometry is irreplaceable in the detection of short-lived activities that are used as chemical yield tracers, either as added species or as daughters of nuclides originally in the sample. As an example of the latter, a well-defined separation time allows the analyst to use the concentrations of ^{231}Th and ^{234}Th (observed with γ-spectrometry) to tie the chemical yield of the thorium fraction to that of the uranium fraction. In the section on tracing, above, we already discussed the use of ^{239}Np (in secular equilibrium with ^{243}Am) and ^{233}Pa (in secular equilibrium with ^{237}Np) to trace the neptunium and protactinium fractions, respectively; this is accomplished through gamma-ray spectrometry.

The fission products, which are common analytes in power and weapons applications, are best observed through their gamma-ray emissions.

High-resolution gamma spectrometry (HRGS) is finding a very important application in the international safeguarding of nuclear materials, where it is advantageously employed for the determination of the plutonium isotopic composition (ASTM, 2000a). The pertinent measurements are usually made either for a verification of the nature of the plutonium (weapons or reactor-grade material), or in support of other nuclear counting techniques (for example, neutron coincidence counting) requiring the knowledge of the plutonium isotopic composition for a quantitative plutonium assay. The measurement technique is truly non-destructive and applicable to any arbitrary plutonium-bearing sample, liquid or solid, irrespective of its physical nature and chemical composition, and it can be executed even with portable gamma-spectrometric equipment. The method also does not require any calibration, because it bases on the so-called 'intrinsic calibration approach' (Gunnink, 1980; MGA, 1990). As a by-product, the plutonium isotopic measurement also provides an accurate result for the weight fraction of ^{241}Am in the plutonium.

The method is based on the spectrometry of isotope-specific gamma rays emitted by the plutonium isotopes and by ^{241}Am. The directly measured quantities are

isotope ratios, which for two isotopes (1) and (2) are obtained according to the relation:

$$\frac{N_1}{N_2} = \frac{P_1 \cdot (t_{1/2})_1 \cdot B_2 \cdot ORE_2}{P_2 \cdot (t_{1/2})_2 \cdot B_1 \cdot ORE_1} \qquad (36.30)$$

with

N = isotope atom abundance

P = measured net peak area of the specific isotopic gamma ray

$t_{1/2}$ = isotope half-life

B = branching intensity (photons per second and per gram of isotope) of the specific gamma ray

ORE = overall relative detection efficiency of the specific gamma-ray energy as determined by the gamma attenuation in the sample, in any absorber material between sample and detector, and by the intrinsic detector efficiency.

The right-hand term in the above relation contains two quantities to be determined from the measured gamma spectrum (the peak area P and the overall relative detection efficiency ORE), and two quantities representing known physical constants (half-life $t_{1/2}$ and branching intensity B). Practically all plutonium isotope abundance measurements are based on the so-called intrinsic calibration approach, where the quantity ORE is determined from the gamma spectrum itself (Gunnink, 1980). This allows to perform the isotope ratio measurements, without any external calibration, on any arbitrary sample, independent of sample mass, physical shape and chemical composition.

The measured isotope ratios are usually determined relative to the main isotope ^{239}Pu. HRGS can directly measure the ratios ^{238}Pu/^{239}Pu, ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{241}Am/^{239}Pu. The ratio ^{242}Pu/^{239}Pu cannot be measured because ^{242}Pu does not emit a detectable gamma-ray signature. This failure causes some problems for the evaluation of the complete isotopic composition for those plutonium materials, in which ^{242}Pu is present at significant abundance. As a sort of makeshift, isotope correlations are normally applied for an approximate estimate of the abundance of this missing isotope (Bignan *et al.*, 1998).

In order to minimize the impact of uncertainties related to the overall relative detection efficiency, most of the plutonium isotope abundance measurements made by HRGS try to evaluate the measurable isotope ratios from gamma rays with closely spaced energies. To this end the energy region around 100 keV represents an important region for analysis, because it offers in a narrow energy range from 94 to 104 keV the most abundant isotopic gamma and X-ray signatures normally accessible in a gamma spectrum from plutonium (the even more abundant isotopic gamma rays in the energy region between 40 and 50 keV are usually masked by the ^{241}Am activity). However, a serious obstacle to the analysis of the 100 keV region stems from the fact that even the best resolving HPGe detectors (FWHM $\cong$ 500 eV @ 100 keV) are not able to fully resolve the closely spaced gamma and X-rays. Elaborate fitting procedures with proper response functions are therefore needed for the unfolding of the

measured gamma spectrum. Two different analysis codes known under the acronyms MGA (Gunnink, 1980; MGA, 1990) and FRAM (Sampson *et al.*, 1989; Vo and Li, 2001), which are in practical use internationally, are capable to provide this kind of analysis. A fitting example obtained with the MGA analysis code is shown in Fig. 36.12. The spectral fitting has to account for two different line shapes: the basically Gaussian-shaped gamma-ray peaks and the Lorentzian-broadened X-ray lines resulting from the decay (uranium and neptunium X-rays) or from induced fluorescence (plutonium X-rays).

A significant improvement in the gamma-spectrometric plutonium isotopic analysis might be realized in the near future once the new Transition Edge Sensors (TES) currently under development (Doriese *et al.*, 2007) will have matured to a practical and efficient tool for gamma detection. This new type of photon detection sensors operating at the transition between superconductivity and normal conductivity offer a 10–20 times higher energy resolution (FWHM $\cong$ 25 to 50 eV @ 100 keV) compared to the traditional germanium detectors of today.

The performance of the plutonium isotopic composition measurement by gamma spectrometry depends to some extent on the isotopic grade of the plutonium. Favorable measurement conditions exist for low-burnup material
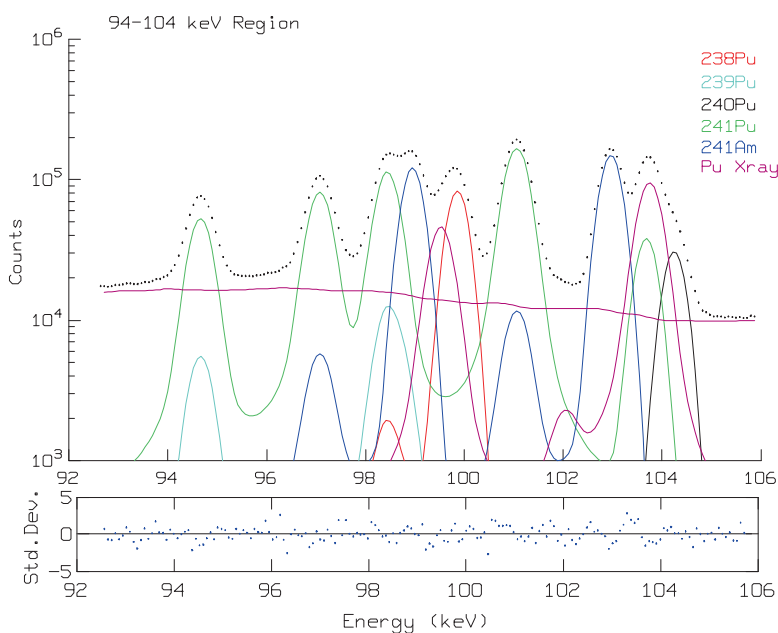

Fig. 36.12   *The spectral response of plutonium and americium isotopic components in the 94–104 keV region (Gunnink, 1980). The residuals (standard deviation) between experimental and fitted data are shown at the bottom (copyright European Communities).*

with a relatively high content of ^{239}Pu (>80 wt%). For this type of plutonium the major isotopic gamma rays in the 94–104 keV region are reasonably balanced in intensity, which helps for the fitting and unfolding of the complex gamma spectrum. The isotope ratios ^{238,240,241}Pu/^{239}Pu and ^{241}Am/^{239}Pu can be determined in this case with a relative precision and accuracy of about 0.5–1%, and sometimes even better depending on the quality of the measured gamma spectrum.

With decreasing ^{239}Pu abundance also the performance of the isotopic measurements starts to deteriorate to some extent because of the less favorable spectral situation. The diminishing gamma-ray signatures from ^{239}Pu, and the dominating gamma-ray intensities of the shortest-lived plutonium isotope ^{241}Pu represent some of the limiting factors. Realistic values for the accuracy of the measured isotope ratios are therefore rather settled in the range from about 1% to 3% for higher-burnup plutonium.

(b) Neutron detection

Weapons-grade plutonium, with nominally about 6% ^{240}Pu, undergoes spontaneous fission at a rate of approximately 30 s^{-1} g^{-1} (Firestone and Shirley, 1996); the rate in reactor-grade plutonium is substantially higher. The average number of neutrons emitted per fission is 2.16 (Diven *et al.*, 1956; Boldeman, 1968), emitted in a Maxwellian spectrum (Watt, 1952) associated with a characteristic energy parameter of 1.19 MeV (Bonner, 1961). The penetrating nature of these neutrons provides a means of determining the approximate amount of plutonium in an unknown without opening the shipping container, important for safety in the analytical laboratory.

Survey-type instruments are usually based on ionization chambers filled with gaseous BF$_3$, embedded in a polyethylene ball. The neutrons lose energy in the polyethylene without being significantly attenuated, and the resulting low-energy neutrons are captured by boron to produce alpha particles, which fire the ionization counter. Another method involves scintillation counting where the scintillator is loaded with cadmium, gadolinium or some other material with a large capture cross section, with associated capture gamma-rays (Allen, 1960). Calibration of these laboratory-scale counters is usually performed with a ^{252}Cf standard.

For plutonium compounds (e.g. oxides or fluorides) total neutron counting does not represent a viable method for determining the amount of plutonium because of the emission of additional neutrons from concurrent (α,n) reactions taking place, for example, on ^{17}O and ^{18}O in plutonium oxides, or on ^{19}F in plutonium fluorides. In this case the method of Neutron Coincidence Counting (NCC) has to be applied for a quantitative plutonium assay (Reilly *et al.*, 1991). The coincidence method allows to discriminate the 'multiplicity' neutrons originating from the spontaneous fission of the plutonium isotopes against the 'single' neutrons produced in the (α,n) reactions.

The fission rate for even-even plutonium isotopes is typically 10^3 higher than for the odd-even isotopes (Table 36.1). Of practical importance for the assay of common plutonium materials by means of neutron coincidence counting are therefore the even-even isotopes 238, 240 and 242, while the odd-even isotopes 239 and 241, except for multiplicity neutrons generated by the secondary effect of induced fission, remain largely invisible to neutron coincidence counting. The isotope ^{240}Pu being typically the most abundant one among the spontaneously fissionable even-even isotopes provides the largest contribution to the observed rate of fission neutrons. The specific emission rate of ^{240}Pu amounts to 1,020 fission neutrons $g^{-1}\,s^{-1}$. The minor isotopes ^{238}Pu and ^{242}Pu, although having a somewhat higher specific neutron emission rate compared to ^{240}Pu, contribute to a lesser extent because of their lower isotope abundances. For weapons-grade plutonium their relative contribution amounts to only about 2%. For higher-burnup plutonium, however, the relative contribution of 238 and 242 can increase up to 40–50%.

In order to practically deal with the dependence of the measured rate of coincident fission neutrons on the plutonium isotopic composition, one has adopted in NCC measurements the concept of measuring an effective mass of ^{240}Pu, expressed as a weighted sum of the masses of the even plutonium isotopes:

$$m_{240eff} = \gamma_{238} \cdot m_{238} + m_{240} + \gamma_{242} \cdot m_{242} \qquad (36.31)$$

where the coefficients γ_{238} and γ_{242} proportion the contributions of the isotopes 238 and 242 per unit mass to the neutron coincidence response of the neutron coincidence counter relative to ^{240}Pu. The respective coefficients have been experimentally determined to $\gamma_{238} = 2.714$ and $\gamma_{242} = 1.667$ for a specific neutron coincidence counter operated with a coincidence gate width of 128 μs (Ottmar *et al.*, 1999). The actual numerical values for the coefficients can marginally vary from counter to counter, depending on specific characteristics of the neutron counter such as the variation of the counter detection efficiency with neutron energy and the hardware and/or software methods applied for the registration of coincident neutrons.

The conversion of the experimentally measured value of m_{240eff} into the total mass of plutonium, m_{Pu}, via the relation

$$m_{Pu} = \frac{m_{240eff}}{\gamma_{238} \cdot w_{238} + w_{240} + \gamma_{242} \cdot w_{242}} \qquad (36.32)$$

requires the exact knowledge of the isotopic mass fractions w_{238}, w_{240} and w_{242} of ^{238}Pu, ^{240}Pu and ^{242}Pu in the plutonium material under assay. This information can be obtained, within certain limits, from a nondestructive gamma measurement. The largest drawback in this gamma-spectrometric isotopic measurement is the lack of a directly measurable gamma signature from the isotope ^{242}Pu. Best accuracy for the quantitative plutonium measurement by

means of NCC is therefore obtained with mass spectrometry data for the plutonium isotope abundances, if available.

Basic components of a neutron coincidence counter comprise the neutron detector block and the coincidence analyzer. The detector block commonly consists of a block of polyethylene acting as neutron moderator for the fast fission neutrons, which has embedded a number of ^{3}He tubes as neutron detectors. Optimized small sample neutron coincidence counters equipped with a moderate number of 18 ^{3}He detection tubes reach a detection efficiency for fission neutrons of about 40%. An example of such a counter interfaced to a gloved box is shown in Fig. 36.13. A unique feature of this so-called Neutron-Gamma Counter is the combination of NCC and High-Resolution Gamma Spectrometry (HRGS) for simultaneous neutron coincidence measurements and isotopic analysis by HRGS (Davidson *et al.*, 1993). The counter is built around a measurement well of stainless steel fixed to the bottom of the gloved box, into which the samples are loaded from the interior of the gloved box.

The detection of the time-correlated fission neutrons has been made for a long time with a so-called shift register circuitry, which allows to identify time-correlated neutrons within pre-defined time intervals (gate width) of typically 64 or 128 μs duration (Reilly *et al.*, 1991). The output of a shift register circuitry delivers the rate of real dual plus accidental coincidence events, and separately the accidental coincidence rate. More recently multiplicity analyzers providing
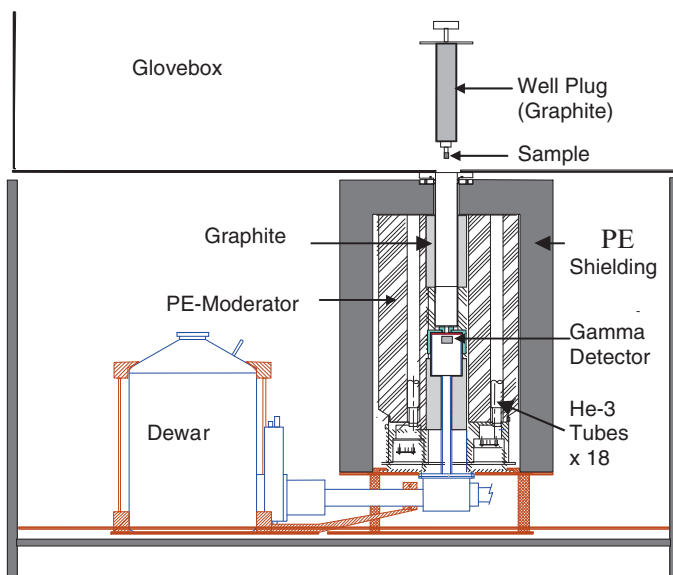

Fig. 36.13 *Typical configuration of a combined neutron-gamma counter for plutonium element assay (copyright European Communities).*

Analytical chemistry of plutonium

Table 36.5 *Typical coincidence rates and measurement times for a 0.2% counting precision for various plutonium containing samples.*

Material type	Type and total weight of sample	Coincidence rate (cps)	Counting time (h) for 0.2% precision
LWR-PuO$_2$	Powder, 1 g	20–30	4–6
	Powder, 2 g	40–60	3–4.5
LWR-MOX (3–6% Pu)	1 Pellet (~7 g)	5–15	8–20
	2 Pellets (~14 g)	10–30	6–14
	Powder, 5 g	4–10	10–30
FBR-MOX (15–25% Pu)	1 Pellet (~5 g)	20–45	3–6
	2 Pellets (~10 g)	40–90	2–4.5
	Powder, 5 g	20–45	3–6

both dual and triple coincidence rates are also in use, mostly for the assay of bulk quantities of plutonium providing statistically significant rates of higher multiplicity events.

In the analytical field the technique of NCC is preferably applied to the analysis of gram-sized solid plutonium-bearing materials such as PuO$_2$ powders or mixed uranium-plutonium materials in the form of oxide powders or pellets. With such counters plutonium quantities from a few 100 mg upwards can be measured with good precision and accuracy within reasonable counting times. Table 36.5 indicates for different types of samples the approximate measured neutron coincidence rate (dual coincidences) and the resulting counting times needed for a counting precision of 0.2%.

In carefully controlled and evaluated small sample measurements it is in principle possible to determine the plutonium content with a total measurement uncertainty of about 0.2%, provided accurate isotopic data are available and careful corrections are applied for all relevant effects influencing the measured coincidence response of the neutron coincidence counter. For example, an important source of uncertainty encountered in practically all NCC measurements is related to the effect of neutron multiplication, a cumbersome effect that cannot be ignored even in small sample measurements. A detailed analysis of the measurement uncertainty of NCC, covering also the aspect of instrument calibration, is found in van Belle and Ottmar (2001).

(c) Fission track counting

The interactions of neutrons with fissile isotopes such as [235]U and [239]Pu produce fission fragments, which are heavy ions moving at high velocities. The interaction of fast-moving fission fragments with matter is characterized by a very high charge density produced along the path of the ion, and, consequently, damage

to the structure of the material. This was first observed in transmission micrographs of exposed samples of mica (Silk and Barnes, 1959). It was soon realized that chemical etching could attack the damaged sites in appropriately chosen track detectors at a greater rate than the bulk detector material, leaving ''pits'' that could be observed with conventional optical microscopy, one pit per incident fission fragment (Fleischer and Price, 1964). In quantitative applications, considerable effort is spent to determine the efficiency of the detector to fissions; fissions resulting in emitted fragments near-parallel to the detector surface are not observed.

A wide variety of solid materials record the passage of charged particles in such a way that the tracks can be developed chemically (Fleischer *et al.*, 1968, 1975). These have seen wide application in geology, cosmology, radiation dosimetry and nuclear physics. For the plutonium analyst, the main value of the method is in sample selection or concentration, mainly from environmental media: A sample is crushed and distributed over an area, a track detector is used to cover it, and the assembly is irradiated with neutrons. The track detectors are then removed and etched to result in the equivalent of a mirror-image map of the areas in which fissile materials are concentrated. By comparison of the etched detector with the sample, the analyst can select those areas that are either enriched or depleted in ^{235}U and/or ^{239}Pu, depending on the application, and process them separately from the bulk material.

For support of the plutonium analytical laboratory, a source of thermal neutrons is required, typically an external irradiation in a nuclear reactor. Track detectors should be selected so as to be relatively insensitive to damage by both neutrons and ionizing particles that produce lower charge densities along their interaction paths (e.g. alpha particles), and should be fabricated from materials that incorporate little or no uranium. Historically, annealed mica, plastics such as Lexan and CR39 (Gautier *et al.*, 2008), and phosphate glass (Wang *et al.*, 1988; Price *et al.*, 1991) have been used for fission-track analysis.

(d) Liquid scintillation

Liquid scintillation counting is particularly useful for measuring very low-level beta activities (for ^{241}Pu, e.g.), or beta activities with low-energy endpoints (Cook *et al.*, 2003). Liquid scintillation offers very high sensitivity and efficiency, even for large samples, but these fractions must be meticulously purified of all traces of the residual heavy-element sample matrix or the signal from the analyte of interest will be lost in background events. The analyst must prepare either a solid or liquid sample that is soluble in the scintillating liquid, or a finely-divided solid that can be suspended in the scintillator. The analyst should be familiar with acceptable solubilizing agents; for example, aqueous samples can be introduced into toluene-based scintillator liquids through solubilization with ethanol.

(e) Calorimetry

The calorimetric assay of plutonium is the process of measuring with a calorimeter the rate of heat released by the radioactive decay of the different plutonium isotopes. Depending on the knowledge of the plutonium isotopic composition, calorimetry can represent the most accurate nondestructive assay technique for the determination of the plutonium content in plutonium-bearing solid materials, being comparable in precision and accuracy to a chemical assay. The main advantages of calorimetry are the independence of sample geometry, matrix material composition and distribution, and the distribution of plutonium in the sample.

Most of the plutonium decay energy is released as alpha or beta particles (see Table 36.1) and the consequent recoil energy of the residual nucleus, and converted to heat energy through absorption in the sample. A small portion of the decay energy is carried away by neutrons and gamma rays, but this portion is generally less than 0.01% of the total decay energy. The plutonium isotope exhibiting the largest specific thermal power by far is the shortest-lived alpha emitting isotope ^{238}Pu with a thermal power (P) of 567.57 mW g^{-1} of isotope (see Table 36.6). The specific thermal power values for the different plutonium isotopes are generally known to better than 0.1% (except for ^{242}Pu).

The calorimetric assay rests on the assumption that the complete radioactive decay energy is converted into measurable heat, and that concurrent endothermic reactions consuming a significant fraction of the decay energy do not take place, nor exothermic reactions producing extra sources of heat. This condition is normally met for all common solid plutonium material such as oxides. However, the condition is not met for liquid samples where a notable portion of the decay energy is consumed for the dissociation of molecules of the solvent. For example, the thermal power of reactor-grade plutonium in the form of a nitrate solution was measured to be 13% lower than for the same material in oxide form (Ottmar *et al.*, 2003). Calorimetry is therefore not the best choice for high-accuracy measurements of the plutonium content in liquid samples.

Table 36.6 *Specific thermal power values for plutonium isotopes and ^{241}Am (ASTM, 2000b).*

Isotope	Disintegration energy (MeV)	Principal decay mode	Specific thermal power $(P) \pm 1\sigma$ (mW g^{-1})
Pu-238	5.592	Alpha	567.57 ± 0.26
Pu-239	5.243	Alpha	1.9288 ± 0.0003
Pu-240	5.255	Alpha	7.0824 ± 0.0020
Pu-241	0.0055	Beta	3.412 ± 0.002
Pu-242	4.985	Alpha	0.1159 ± 0.0003
Am-241	5.640	Alpha	114.57 ± 0.18

The calorimetric assay of relatively small (gram-size) plutonium samples is usually performed by heat flow calorimeters (Bracken and Hypes, 2000). The rate of heat transfer from the sample cavity holding the sample and the (iso-thermal) heat sink consisting of a highly temperature regulated water bath or metal block is proportional to the temperature difference between the sample chamber and the heat sink. Advanced small sample calorimeters are normally equipped with so-called 'thermopiles' as heat flow sensors, a serially inter-connected array of a large number of thermocouple junctions with a sensitivity of up to 100–200 $\mu V\ mW^{-1}$ thermal sample power. This high sensitivity allows high-precision thermal power measurements even at the level of milliwatts. The only drawback of calorimetry is the relatively long measurement time needed to reach thermal equilibrium after sample loading into the calorimeter. A typical calorimeter response function for a 1-g sample of reactor-grade plutonium is shown in Fig. 36.14. In this example thermal equilibrium at the 0.1% level had been reached after 6–7 h of measurement time.

The measured thermal power of a plutonium sample is the sum of the power of each plutonium isotope and of ^{241}Am, which as the decay product of ^{241}Pu is inevitably present in practically all plutonium samples. The conversion of the measured thermal power of the sample, P, into the amount of plutonium, m_{Pu}, is made through the relation:

$$m_{Pu} = \frac{P}{\sum\limits_{i=1}^{n} w_i \cdot P_i} \tag{36.33}$$

where the sum n of the products of the isotope weight fraction w_i times the specific thermal power P_i is taken over the plutonium isotopes and ^{241}Am. For weapons-grade plutonium with a ^{239}Pu isotope abundance of 90% or higher the isotopes ^{239}Pu and ^{240}Pu contribute 95% or more to the observed thermal
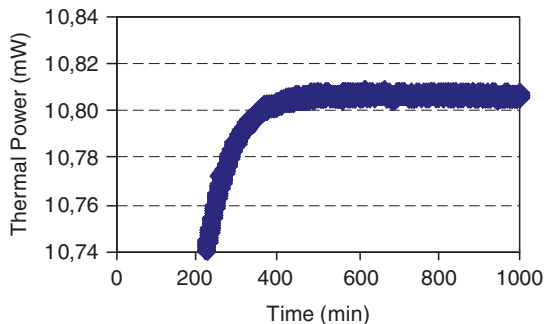

Fig. 36.14 *Typical response of a heat flow calorimeter. The thermal power is given as a function of time (copyright European Communities).*

power of the sample. The required isotope abundances of the two isotopes are normally available with high accuracy from mass spectrometry or even from high-resolution gamma spectrometry.

A completely different situation, however, exists for the calorimetric assay of higher burnup reactor-grade plutonium with ^{238}Pu isotope abundances of up to 2% or more. In this case, where the two minor isotopes ^{238}Pu and ^{241}Am are typically responsible for 70–90% of the measured thermal power, the accuracy of the calorimetric plutonium assay solely depends on the accurate knowledge of the responsible isotope abundances. Alpha spectrometry as the preferred technique for ^{238}Pu abundance measurements – because of the risk of isobaric interferences in mass spectrometry for this isotope – can realistically determine the ^{238}Pu abundance to an accuracy of not much better than 0.5%. This would then practically represent the accuracy limit of the calorimetric plutonium assay for this type of plutonium material. Improved accuracy can be achieved with mass-spectrometric ^{238}Pu isotope abundance measurements performed after an efficient U-Pu separation by means of extraction chromatography with separation factors exceeding 10^6 (Ottmar *et al.*, 2003).

36.5 DATA HANDLING AND ERROR ANALYSIS

36.5.1   Spectral analysis

In Section 36.4.8 (a) we described the acquisition of counting data, and the processing of spectral information through various means to net peak areas. In the analytical laboratory it is normal to process radiation spectrometry data as spectra, even if these spectra must be constructed from data taken in list mode (time-tagged event information). Scalar radiation counting data are handled similarly to mass spectrometry data in that, barring small corrections (e.g. a background subtraction for counting data, or a mass-bias correction to isotope ratio data) the uncertainty of a given number of counts is essentially the square root of that number.

(a)   Decay curve analysis and averaging

Establishing a common time to which all radionuclide concentrations are referenced is required by the radioactive nature of the chronometric species. This means that measurements of emitted radioactivity must be made at known times; this is less important in mass spectrometry applications because the half-lives of the analytes tend to be longer. The time associated with the data attributed to a particular count is the midpoint of the counting interval. As long as the length of the counting interval is short relative to the half-life of the analyte species being measured, the midpoint time can be used in

decay-curve analysis and in simple extrapolations back to the reference time. However, radioactive decay is exponential rather than linear, so for long counting intervals a "finite-counting-time" correction must be made. For a single-component simple radioactive decay the count time associated with a counting interval of duration Δt is calculated to be a time δ after the start of the interval (Palágyi, 1991):

$$\delta = (1/\lambda)ln\{\lambda\Delta t/[1 - exp(-\lambda\Delta t)]\} \tag{36.34}$$

In the limit of long half-lives or short counting intervals, $\delta \rightarrow \Delta t/2$, as expected.

For nuclides that undergo a simple exponential decay (rather than those that grow in through a more complicated mother-daughter relationship), the observed activity can be corrected for decay to a reference time (usually a chemical separation time) by multiplying the measurement by $exp[\lambda(t_1+\delta-t_0)]$, where δ is given above in equation (36.34), t_1 is the start time of the measurement interval, t_0 is the reference time, and λ is the decay constant. Multiple measurements of the activity at different times, when corrected to the same time, can be averaged to obtain a best value at that time. A weighted average of two or more values is appropriate if the uncertainties associated with each corrected measurement are significantly different:

$$y = [\Sigma y_i/\sigma_i^2]/[\Sigma 1/\sigma_i^2], \tag{36.35}$$

and

$$\sigma = [\Sigma 1/\sigma_i^2]^{-1/2} \tag{36.36}$$

where σ_i is the uncertainty associated with the experimental value of the count rate, y_i. For applications where there are three or more data points, whose uncertainties are always about the same size, it is usually considered more appropriate to take a straight average and calculate a standard deviation.

Because photons of several different energies can arise in the decay of certain nuclides, if the efficiency of the detector has been modeled correctly, they should all give rise to the same number of parent atoms when corrected for the appropriate decay branches. The best value for the number of atoms is obtained by taking a weighted average over the values determined from all the photons emitted by the radionuclide; however, some fraction of the uncertainty in both the nuclear intensity data and the efficiency response of the detector is systematic rather than random in origin, and should be applied to the results of the averaging procedure rather than in the construction of the average.

For more complicated decay formulae, particularly those involving an unobserved parent activity, decay-curve analysis is required. The reader is referred to (Bevington and Robinson, 2003; Sydenham, 1982) for least-squares fitting to an arbitrary function. For data best described by ingrowth or by the decay of more than one nuclide, the equation for δ is no longer valid, and $\Delta t/2$ should be used in its place. The best fit of a function f to a set of data points (x_i, y_i), each

point characterized by an uncertainty in y_i of $\pm \sigma_i$, is determined by picking parameters for the function which give a minimum χ^2:

$$\chi^2 = \Sigma(1/\sigma_i^2)[y_i - f(a_1, a_2, a_3, ...a_n, x_i)]^2 \tag{36.37}$$

where i is the data point index, and a_1, a_2, a_3,. . .a_n are the parameters of the function to be determined. Minimization of χ^2 with respect to each parameter leads to a system of n equations in n unknowns. For a set of non-linear equations, this can be solved iteratively with a computer code. When the parameter set converges, the diagonal elements of the inverse of the transformation matrix are good approximations of the uncertainties associated with each of the parameters (Bevington and Robinson, 2003).

36.5.2 Background subtraction

For gross α or gross β counting, it is normal to take a long background count in the detector and subtract the resulting background rates from the value of each count. A background sample should be a clean plate of the same material in which the source is prepared, mounted in the same fashion and position. Because "virgin" platinum (platinum that contains no component recovered from previous applications involving radionuclides) is no longer easy to find, the best background is obtained by counting source substrate plates before the source is prepared. It is preferable to collect background data just before counting the experimental samples; decay of radionuclides in counting sources can lead to decay products recoiling into the detector volume and to self-transfer of the parent material, both of which will increase the detector background. There is the issue that the efficiency of detecting the decays of these contaminating species is not the same as the efficiency for detecting decays originating in the source itself. Most of the time, the fraction of the source radionuclides that contaminate the detector is small and the effect can be ignored; however, there are exceptions to this.

When counting volatilized sources (see Section 36.3.9) of radionuclides that include a short-lived radon daughter (e.g. ^{220}Rn) in their decay chains, a significant fraction of the decays of the radon isotope and its daughters can occur outside the source deposit, a consequence of the gaseous nature of radon. If a windowless gas proportional counter is used, the efficiency for detecting radon in the gas volume is roughly twice that for detecting radon residual in the source. The efficiency drops for detection of longer-lived radons (e.g. ^{222}Rn) in the gas phase because they tend to be swept from the counter before they decay. For gross count-rate measurements of radon-emitting samples, a windowed counter with an unventilated sample stage should be used; even so, the unquantified uncertainty associated with counting these samples can be substantial.

If the number of detected counts in an analytical sample is A, the 1-σ uncertainty is, roughly $\pm A^{1/2}$. If the count interval is Δt_A, the gross count rate

of the sample is $(A/\Delta t_A \pm A^{1/2}/\Delta t_A)$. Similarly, if the background of the detector is B counts in Δt_B time interval, the gross background rate of the detector associated with the sample counts is $(B/\Delta t_B \pm B^{1/2}/\Delta t_B)$. The background-corrected decay rate of the sample is, therefore, $\{(A/\Delta t_A - B/\Delta t_B) \pm (A/\Delta t_A^2 + B/\Delta t_B^2)^{1/2}\}$ (Bevington and Robinson, 2003). Clearly, the best way to minimize the impact of the subtraction of background on the uncertainty of the corrected data is to take long background counts.

For spectral data, the method of background subtraction depends on the width of the peaks in the spectra (in units of numbers of channels) with respect to the stability of the energy calibration over long periods of time, and on the relative activity of the sample with respect to the magnitude of the background to be subtracted.

For gamma spectra, where photo-peaks are typically only a few channels wide, the instability of the energy calibration of the detector/MCA combination over long times can amount to shifts of significant fractions of a channel energy width. In this case, it is normal to process both the gamma spectra acquired from the sample and the background spectrum acquired from the detector separately. The areas of the peaks in the background spectrum are tabulated with their associated energies. When the sample spectra are processed, the energy of each peak is compared with the background table associated with the detector, and if there is a match the background peak area, scaled by $\Delta t_A/\Delta t_B$, is subtracted from the peak in the sample spectrum. This calculation is performed before correction for the detector's efficiency response; a lot of thought goes into the energy comparison algorithm, which must allow for a less-than-perfect energy match (Gunnink *et al.*, 1968; Routti and Prussin, 1969), but an accurate energy calibration is crucial.

For alpha spectra of limited activity, data should be handled in the same way, with background correction following peak-area processing of both spectra. In the limit of alpha spectra taken from samples with significantly higher activity than the detector background, the analyst can take advantage of the fact that the peak width of a sample spectrum is usually broader than the change in detector response over a limited time. In this case, the background spectrum can be subtracted from the sample spectrum on a channel-by-channel basis, with the background spectrum channel values weighted by the different count lengths, $\Delta t_A/\Delta t_B$. In the limit that the background correction is small, the spectrum can be processed as if it had no associated background with only a minor additional unquantified uncertainty.

36.5.3 Isotope dilution

In isotope dilution (Webster, 1960; Heumann, 1988) a known amount of a spike isotope, preferably a long-lived radonuclide or a separated stable isotope with a minor natural abundance, is added to the sample. The sample must be completely dissolved or vaporized to thoroughly mix the tracer aliquot

("spike") with the analyte. After this dilution step, the element is chemically isolated and the isotope ratios are determined either mass spectrometrically or by radiation counting.

Isotope dilution is a fairly standard method of establishing the chemical yield of plutonium, with the usual tracer being ^{242}Pu, containing as little as possible of the other plutonium isotopes. Following preparation of the analytical solution, two aliquots are taken: one, which need not be quantitative, is not traced (unspiked); the other, whose content must be related to the sample as a whole either volumetrically or gravimetrically, is traced (spiked) with a known amount of ^{242}Pu. Enough ^{242}Pu must be added to significantly change ^{242}Pu / Σ Pu in the spiked aliquot so that the *change* can be determined to the required precision, yet not to the extent that measuring ^{242}Pu interferes with the measurement of the other isotopes of plutonium. It should be noted that this method of yielding plutonium is comparable in accuracy with tracing with ^{236}Pu or ^{238}Pu and alpha counting the chemical fraction (see Section 36.4.8 (a)). Like the mass spectrometry technique, use of ^{238}Pu as an alpha-active tracer requires a "spiked/ unspiked" analysis due to the intrinsic ^{238}Pu content of most mixed plutonium samples.

Isotope dilution is also used in the determination of contaminant species in a plutonium sample. The mathematics of processing the "spiked/unspiked" isotope ratios to an elemental concentration of a contaminant is the same as that used in determining the plutonium concentration.

As an example, we have used isotope dilution to measure the gallium content of a plutonium alloy. The technique is particularly applicable to gallium because there are no isobaric interferences; however, there is a non-zero yield from the fission process at the gallium masses, so an unspiked sample should be processed if the sample was heavily irradiated with neutrons. To do this, we employed a separated isotope of ^{71}Ga, which contained only a small contaminant of ^{69}Ga; normally gallium consists of 60 at.% mass 69 and 40 at.% mass 71. After the sample was dissolved in a standard volume, an aliquot was taken for gallium analysis. To minimize uncertainty, the separated isotope was added to the sample such that the ^{71}Ga/^{69}Ga isotope ratio was adjusted to roughly 1. If it can be assumed that the gallium in the sample is of natural isotopic abundance, then only a spiked sample need be processed; otherwise (as in the case of plutonium isotopes), an unspiked aliquot must also be taken and processed.

A quantitative plutonium aliquot was spiked with a known amount of ^{71}Ga. The solution was mixed thoroughly, evaporated to dryness, and the deposit dissolved in 9M HCl + one drop nitric acid. Purification chemistry was based on anion exchange. Plutonium (IV) and gallium are adsorbed on DOWEX 1 × 8 resin from hydrochloric acid, and gallium is eluted with nitric acid. The resulting solution was evaporated to dryness, the deposit was dissolved in 9 M HCl, and the anion-exchange procedure was repeated. The final eluent was evaporated to dryness and the deposit dissolved in 1 M nitric acid. ICP-MS

was performed on the solution, and a value of $^{71}Ga/^{69}Ga$ was returned. To first order, we treat the spike as if it has no ^{69}Ga in it:

$$\left(^{71}Ga/^{69}Ga\right)_{spiked} - \left(^{71}Ga/^{69}Ga\right)_{unspiked}$$
$$= \left[atoms\,^{71}Ga\ in\ spike\right]/\left[atoms\,^{69}Ga\ in\ sample\ aliquot\right] \tag{36.38}$$

From the known amount of ^{71}Ga in the spike, we can solve for ^{69}Ga, which can be converted to the total number of atoms in the analytical solution as follows:

$$\left[atoms\ Ga\ in\ sample\ aliquot\right] = \left[atoms\,^{69}Ga\ in\ sample\ aliquot\right]$$
$$\times\left[1 + \left(^{71}Ga/^{69}Ga\right)_{unspiked}\right] \tag{36.39}$$

Of course, in reality any separated ^{71}Ga sample will have some ^{69}Ga in it. In this case,

$$\left(^{71}Ga/^{69}Ga\right)_{spiked} = \left[^{71}Ga_{unspiked} + ^{71}Ga_{in\ spike}\right]/\left[^{69}Ga_{unspiked} + ^{69}Ga_{in\ spike}\right] \tag{36.40}$$

If we perform a Taylor expansion around $^{69}Ga_{unspiked}$, and truncate to two terms, we get the following relationship:

$$\left[atoms\,^{69}Ga\ in\ aliquot\right] = \left\{^{71}Ga_{in\ spike} - \left(^{71}Ga/^{69}Ga\right)_{unspiked} \times ^{69}Ga_{in\ spike}\right.$$
$$- \left[^{71}Ga_{in\ spike} \times ^{69}Ga_{in\ spike}\right]/\left[atoms\,^{69}Ga\ in\ aliquot\right]\Big\}/\left[\left(^{71}Ga/^{69}Ga\right)_{spiked}\right.$$
$$- \left(^{71}Ga/^{69}Ga\right)_{unspiked}\Bigg] \tag{36.41}$$

where the term "[atoms ^{69}Ga in aliquot]" embedded in the right-hand side of the equation is derived from the mass-69-free equation (36.38). The number of atoms of gallium in the sample aliquot is obtained by inserting equation (36.41) into equation (36.39).

We have also performed an iron analysis by isotope dilution, using a spike of separated ^{57}Fe. The purification and recovery of iron from plutonium is similar to that of gallium. While there are no isobaric interferences at masses 56 or 57, the nuclides ^{54}Cr and ^{58}Ni can interfere with mass spectrometry on the minor iron isotopes. The best isotope dilution measurement should use ^{56}Fe as the reference nuclide.

Separated isotope spikes of the stable elements are calibrated against natural elemental standards, which are inexpensive and available from commercial vendors. The same mathematics are used to manipulate the isotope ratio as

described above, but the concentration of the separated isotope is the unknown. The ^{242}Pu mass spike is calibrated against the mass of a ^{239}Pu electrorefined metal standard, through multiple quantitative dilution and subsequent isotope dilution. The admixture of minor isotopes in both the ^{239}Pu and ^{242}Pu solutions must be determined prior to mixing; care must be taken to perform an oxidation/reduction cycle to ensure that the two sources of plutonium are chemically identical.

36.5.4   Data obtained from standards

Implementation of standards is the basis by which measurements made by different laboratories can be compared. Stable-element and/or radionuclide standards are used in the calibration of instruments such as calorimeters, spectrophotometers, mass spectrometers and radiation detectors. They are also used in chemical yielding and calibration of chemical techniques (e.g. titration).

The limit of data quality is usually defined through the use of calibration sources/standards. Gamma-ray standards are available from various organizations (e.g. Marshall, 1998), but the absolute uncertainties of the photon intensities are rarely significantly better than ±2%. This can lead to a ±2% systematic bias to radionuclide concentrations determined with detectors calibrated with these sources. This extra uncertainty does not propagate with the random uncertainties associated with making a measurement, but should be reported separately during intercalibration experiments (Sydenham, 1982).

The best radionuclide standards are those whose accuracies derive directly from the energy emitted by the source, measured with a calorimeter, or derive from the mass of a pure stoichiometrically characterized material, measured with a balance. However, even if a standard is characterized to a given precision, its effect on measurement uncertainty is defined through its use. For example, in the efficiency calibration of a gas-filled beta counter a set of standards is used, each with a different beta endpoint, usually including a ^{147}Pm source. Depending on the similarity of preparation and positioning, the uncertainty associated with the ^{147}Pm source is the limit of the uncertainty with which we can know the efficiency of the counter for the detection of ^{147}Pm. If the set of sources is being used to calibrate the detector for nuclides that are not represented in the source set, the uncertainty associated with the efficiency calibration becomes dominated by issues of nuclear structure, and application of the uncertainties associated with the members of the calibration set is misleading.

Simple standards can be fabricated in-house from first principles or can be purchased; purchased standards should have a pedigree that makes it possible to assure the competence with which the standard was prepared. ''Traceability'' back to a calibrating service (Maxwell, 1997) does not absolve the experimenter from checking and understanding the systematic uncertainties arising from the use of a source or other calibration sample.

Analytical chemistry methods are key for evaluating the content and behavior of plutonium in the environment, which is the result of fallout from nuclear testing, reentry of nuclear powered satellites, releases from nuclear reactors (both controlled and accidental, and activities related to the production of nuclear weapons (Silva and Nitsche, 1995).

In 2005, the inventory of plutonium world-wide was approximately 2,000 metric tons, the sum of used fuel, weapons, inventories and waste (Albright and Kramer, 2004). This amount grows 70–75 metric tons per year as a byproduct of nuclear power production.

36.6.1   Environmental presence of plutonium

As Chapter 32 is devoted to the presence and the behavior of the actinides in the geosphere, we shall limit our considerations to aspects of the plutonium behavior more relevant to the concerns of the analyst. Approximately 10^{15} Bq of plutonium has been deposited into the oceans from atmospheric nuclear testing (Choppin, 2006, 2007). In marine environments, plutonium may exist simultaneously in four oxidation states (III–VI) (Keeney-Kennicutt and Morse, 1985; Morse and Choppin, 1986; Choppin, 2006, 2007) and exhibits strong redox behavior as a function of E_h, pH, and the presence of complexing species. Hydrolysis, disproportionation, and dissolved organic material also factor into the speciation of dissolved and adsorbed plutonium (Morse and Choppin, 1986; Choppin *et al.*, 1997; Choppin, 2006, 2007). Humic and fulvic acids play a role both in complexation and redox reactions (Morse and Choppin, 1986). $Pu(V)O_2^+$ is the dominant soluble species of plutonium found in natural, oxic waters (Keeney-Kennicutt and Morse, 1985; Morse and Choppin, 1986; Baxter *et al.*, 1995; Choppin *et al.*, 1997; Choppin, 2006, 2007). Most of the plutonium activity released into the oceans, however, is not present as soluble species but rather exists as insoluble species that have been incorporated into sediments resulting in a seawater surface activity of about 10^{-5} Bq kg^{-1} of water (Baxter *et al.*, 1995; Choppin, 2006). The majority of plutonium activity has been removed from ocean waters through adsorption onto particle surfaces (Morse and Choppin, 1986). Surface mediated redox reactions with inorganic minerals and compounds (carbonates, bicarbonates, chlorides, oxides, oxyhydroxides, etc.) as well as dissolved and colloidal humic and fulvic acids play an important role in removing dissolved plutonium from natural waters through the strong tendency for plutonium to undergo precipitation and adsorption (Morse and Choppin, 1986; Baxter *et al.*, 1995; Choppin *et al.*, 1997). The plutonium associated with sediments and dissolved organic matter is predominantly in the reduced Pu(IV) state (Keeney-Kennicutt and Morse, 1985). Hydrolyzed Pu(IV) in the form $PuO_2 \cdot xH_2O$ is extremely insoluble and determines the limiting solubility of plutonium in any oxidation state in marine systems.

The most likely adsorbed species is $Pu(OH)_4$ (Morse and Choppin, 1986; Baxter *et al.*, 1995; Choppin *et al.*, 1997; Choppin, 2006). Plutonium is continuously removed from solution by the reduction of plutonium to Pu(IV), formation of the hydrolyzed species $Pu(OH)_4$, followed by sorption to humic and fulvic acids, colloids, and mineral surfaces (Choppin *et al.*, 1997; Choppin, 2006). Most of the deposited plutonium has been incorporated into bottom sediments (Choppin, 2007).

The behavior of plutonium in mixed-phase environments is largely dependent on the sorptive properties of plutonium ions and their ability to exist simultaneously in multiple oxidation states. The sorption of plutonium onto environmentally occurring species is influenced by the concentration of both the plutonium and the sorbing species, ionic strength and pH of any water in the system, presence of organic substances, and the sorptive capacity and total available surface area of the surrounding rock (Torstenfelt *et al.*, 1988). In soil matrices, plutonium tends to sorb to various components such as clay minerals, hydrous oxides, and organic substances (Lee *et al.*, 2004). Surface phenomena such as complexation and precipitation dominate plutonium–soil interactions (Lee *et al.*, 2004). Studies on the sorption of plutonium on marine sediments and iron and manganese oxides suggest that the surface complexation involves inner-sphere or specific adsorption processes rather than ion exchange or outer-sphere processes (Duff *et al.*, 1999).

Studies with dissolved plutonium show that it sorbs strongly to smectites, manganese, and iron oxyhydroxide minerals, which can mediate redox transformations between the dissolved plutonium and plutonium sorbed to the solid surfaces (Duff *et al.*, 1999). The sorption of soluble Pu(V) to redox-active surfaces has been shown to both oxidize the plutonium to Pu(VI) and reduce it to Pu(IV). This complex behavior ultimately determines the potential transport of plutonium in the vadose zone and in naturally occurring ground-waters, which is particularly important for the long-term storage of radioactive wastes.

The chemistry of plutonium in solution is the most complex and varied among the known elements. Five oxidation states have been prepared; many of these can coexist in a given solution unless care is taken to stabilize a single state, a consequence of the redox potentials and reaction kinetics of the five chemical species. Pu(VII) is stable only in strongly alkaline solutions and in the presence of strong oxidizing agents (Krot and Gel'man, 1967). Pu(V) is important in near neutral solutions such as those encountered in environmental and biological media; it is prone to disproportionation into Pu(IV) and Pu(VI) (Nigon *et al.*, 1954; Kraus and Dam, 1949). Neither Pu(V) nor Pu(VII) has found much application in separations chemistry, though the chemistry of Pu (V) has significant importance to the transport of plutonium through the environment.

There is a longer discussion of the trace analysis of actinides (including plutonium) in geological and environmental matrices in Chapter 30 of this work.

36.6.2 Nuclear forensics investigations on plutonium

Illicit trafficking of nuclear material is a phenomenon that arose in the first half of the 1990s. The record year according to the IAEA illicit trafficking database was 1994 when 45 confirmed cases of illicit trafficking of nuclear material were recorded. The number has decreased since then and stabilized to around ten cases per year (see ''Illicit Trafficking Database'' at www.iaea. org for more detailed information). Besides the number of incidents, the relative danger of the illicit material has decreased over the years. The majority of the 18 illicit trafficking cases of weapons-grade material (highly-enriched uranium or plutonium) took place in the 1990s while presently the typical nuclear seizure consists of either natural or depleted uranium. However, poorly guarded nuclear material still presents a radiological hazard arising from inappropriate handling, transport or storage. Even more serious concerns arise if the material is considered in the context of terrorist organizations. Nuclear material could either be used in a radiological dispersal device, a so-called ''dirty bomb'' or – if available in sufficient quantity and quality – in improvised nuclear explosive devices.

Nuclear forensic investigations have to be considered as part of a comprehensive set of measures for detection, interception, categorization and characterization of illicitly trafficked nuclear material (IAEA, 2006; Smith *et al.*, 2008). The aim of the analysis is to answer questions such as: what was its intended use; where is its origin and who was its last legal owner? For each seized sample a specific analytical strategy needs to be developed, taking into account the particular conditions of the seizure, the nature of the material and its packaging and other evidence. The analytical strategy follows a step-by-step approach, where the next step is defined and performed based on actual findings.

Nuclear forensic analysis may result in important conclusions about the origin of the material and thus provide the most essential contribution to the prevention of future diversions from the same source. The methodology developed in nuclear forensics may also be applied for source attribution of nuclear material in environmental samples, e.g. illegal dumping of nuclear waste, contaminated scrap metal or accidental release, as well as in nuclear safeguards when more investigative methodologies are applied.

(a) Methodology

Analytical methods adapted from nuclear safeguards serve as the basis for nuclear forensic analysis. However, it was soon noticed that these methods were not sufficient to provide answers to all the questions. Therefore, a dedicated nuclear forensic methodology has been developed. This approach combines methods used in the nuclear fuel cycle, materials research and environmental studies, including radiometric and mass spectrometric techniques as well as electron microscopy.

Nuclear forensic investigations draw upon the information inherent to the material. Nuclear material is generally of anthropogenic origin, i.e. the result of a production process. The nature of this process is reflected in the elemental and isotopic composition of the material as well as in its microscopic and macroscopic characteristics. The conclusions from such investigations need to be supported by reference data whenever possible. This can be in the form of open source information, databases or reference samples. However, due to the sensitive nature of nuclear material production data (both military and commercial), it is often difficult to obtain such information. Therefore, it has been proposed to establish a ''database of databases'', which would include information about various databases owned by different organizations and states (Lützenkirchen and Mayer, 2007).

(b)   Reactor type determination

A key parameter of seized plutonium material is the reactor type where it was produced, which may allow one to trace back its origin. To this end, an isotope correlation has been established, which depends upon the reactor type (Wallenius and Koch, 2000). The correlation is based on the calculated ratios (Bell, 1973; Croft, 1980) of isotopes ^{238,240,242}Pu (Fig. 36.15). The initial ^{235}U enrichment of the fuel determines the ^{238}Pu abundance, whereas the hardness of the neutron spectrum influences the production of the heavier plutonium
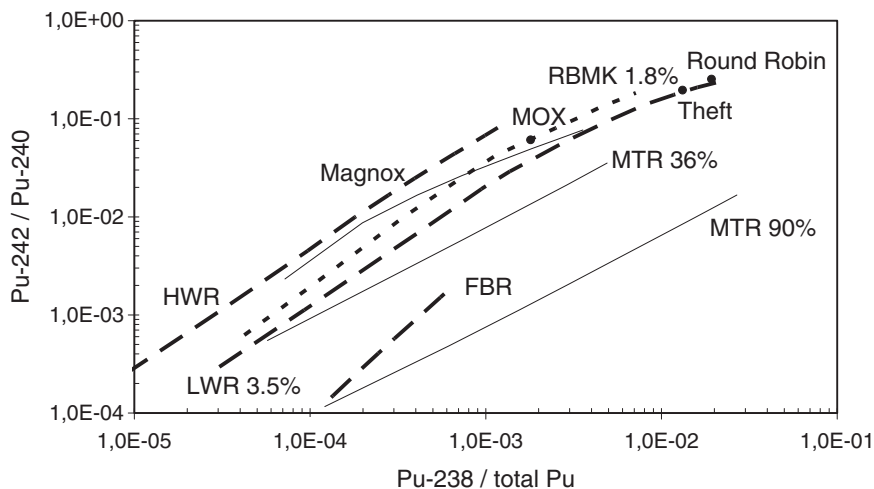

Fig. 36.15   *Use of plutonium isotope correlations for reactor type determination. The figure shows the isotope ratio* ^{242}*Pu/*^{240}*Pu as a function of the ratio* ^{238}*Pu/total Pu for various reactor types. The percentage values in the figure refer to the* ^{235}*U enrichment (adapted from Wallenius et al., 2007).*
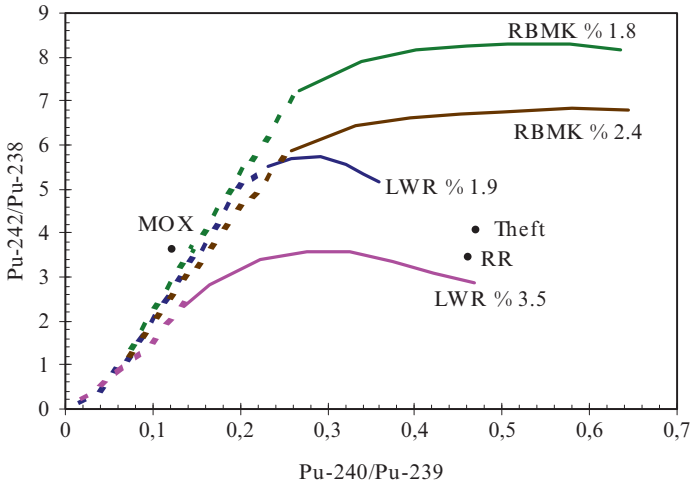
Fig. 36.16 *Isotopic correlation to distinguish between LWR and RBMK reactor types* (*copyright European Communities*).

isotopes. With a softer spectrum, relatively more heavy plutonium isotopes are produced. In Fig. 36.15 isotopic correlations are shown for the most common reactor types, i.e., heavy-water reactors (HWR), gas-cooled reactors (Magnox), graphite-moderated reactors (RBMK), light-water reactors (LWR), fast-breeder reactors (FBR) and material-testing reactors (MTR). In addition, the correlations identified for the case studies described in Section 36.6.2 (e) are plotted in the figure where they are designated by MOX, Theft, Round Robin.

Another correlation can be used to distinguish between RBMKs and LWRs (Fig. 36.16). In Fig. 36.15 the curves of these two reactor types may overlap as their [235]U enrichments are very similar. However, due to the softer neutron spectrum in the RBMK, relatively more, heavier Pu isotopes are produced compared to the LWR.

One should notice that when the isotopic correlations are based on computer code calculations, they give the average plutonium composition in the reactor core. Therefore, depending on the location where a fuel assembly was exposed to neutrons, the calculated plutonium compositions and the actual sample compositions may be different. In addition, if the plutonium sample is a mixture of different spent fuels, any correlation may give misleading results.

(c) Age determination

The age of a sample of nuclear material refers to the time span since the last chemical separation. The age is a very important parameter for the determination of origin, because it may serve to exclude certain production or reprocessing plants, which were not operating at the given time or were not processing

the type of material in question. Plutonium has four parent/daughter relations that can be used for its age determination, namely ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U and ^{241}Pu/^{241}Am. The advantage of using several parent/daughter ratios is that systematic errors can be minimized and that residual uranium or americium from reprocessing can be detected through inconsistent results.

The age of nuclear material can be determined very precisely by several techniques. The fastest method which does not require chemical separation is gamma-spectrometry of the ^{241}Pu/^{241}Am ratio. However, in this case the result is based only on one parent/daughter ratio, and in the case of residual americium the result will be positively biased. Other methods for the age determination of bulk material are Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Thermal Ionization Mass Spectrometry (TIMS), where the latter requires chemical separation (Wallenius and Mayer, 2000; Nygren *et al.*, 2007; Zhang *et al.*, 2008). For particle analysis, Secondary Ion Mass Spectrometry (SIMS) is the method of choice. However, the ^{241}Pu/^{241}Am ratio suffers from isobaric interferences due to a limited mass-resolving power. As a chemical separation cannot be performed prior to the analysis by SIMS the ^{241}Pu/^{241}Am ratio cannot be used. Another drawback of the method is caused by the different ionization efficiencies of uranium and plutonium. This difference must be quantified using standards of known age, and subsequent measurement results must be corrected using the so-called relative sensitivity factor (Wallenius *et al.*, 2001).

(d)   Materials characterisation by microscope techniques

The analysis of nuclear forensics samples is a field where TEM (see Section 36.4.5) is among the key characterization tools to provide a fingerprint on materials seized by legal authorities and to provide clues on the source of the material. The technique has proven so far to bring invaluable information on the materials seized (homogeneity, crystallite size, structure, etc). In the case of powder samples, SEM can firstly provide information on the morphology of the constituents, i.e. whether there is a single type of grains or more heterogeneous particle types. In parallel, EDX can give a quick overview on the elemental composition of the powder constituents. In cases where fissile elements (uranium, plutonium) might be present in the form of dispersed particles (typically micrometer sized), the SEM can help to search for them by being operated in backscattered mode. In this mode the image contrast is proportional to the atomic number of the elements hit by the electrons: the heavier the element, the larger the backscattering and the brighter the signal. In Fig. 36.17 this effect is illustrated for a plutonium particle on a swipe sample.

The search for elements with high atomic numbers is particularly suited for this technique originally developed for the conventional forensics and better known as gunshot residues (GSR) analyses (Tillman, 1987).The combination of SEM, TEM and EDX has also proven to be efficient to obtain a "fingerprint"
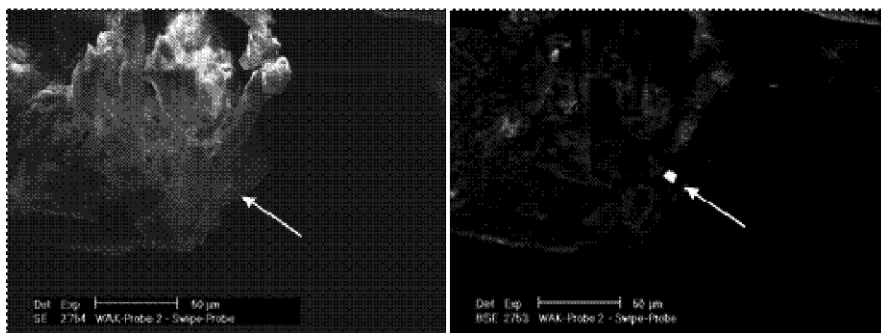
Fig. 36.17 *Secondary electron image of a swipe sample suspected to carry plutonium particles* (*left*). *The backscattered image* (*right*) *gives evidence of a particle showing a contrast typical of a high atomic number. The EDX* (*not shown here*) *confirmed it is a pure plutonium dioxide particle* (*copyright European Communities*).

of a given material. In Fig. 36.18 it is shown that plutonium particles from a seized material were found by SEM to be almost identical to a reference material whereas the TEM microstructure analysis showed that the grain size (at the nanometric level) was completely different. This fine microstructure is a clear signature, which can only be modified by reprocessing (annealing, refabrication). Therefore, it can be used to assess a potential origin (fabrication process) of a material (Ray *et al.*, 2002).

(e) Case studies

The first seizures of nuclear material took place in Switzerland where low enriched uranium was found and in Italy where a small amount of plutonium was seized in 1991. The seizures made during the last two decades include the whole spectrum of nuclear material, from depleted uranium to highly enriched uranium and plutonium, and from small particles to kilogram quantities. Investigations of some cases involving plutonium are discussed below (Wallenius *et al.*, 2007).

(i) *MOX powder*

In August 1994, three men were stopped at Munich airport in Germany carrying a suitcase containing 560 g plutonium and uranium oxide powder. The powder consisted of 64.9 wt% plutonium and 21.7 wt% uranium. The ^{239}Pu enrichment was about of weapons grade quality, whereas uranium had a low ^{235}U enrichment only (Table 36.7). The MOX powder consisted of three different particle types: PuO_2-platelets, rod-shaped PuO_2 and hexagonal U_3O_8 (Fig. 36.19). In addition to the MOX powder, the seizure contained a 210-g piece of lithium metal that was enriched to 89.4 % in ^{6}Li .
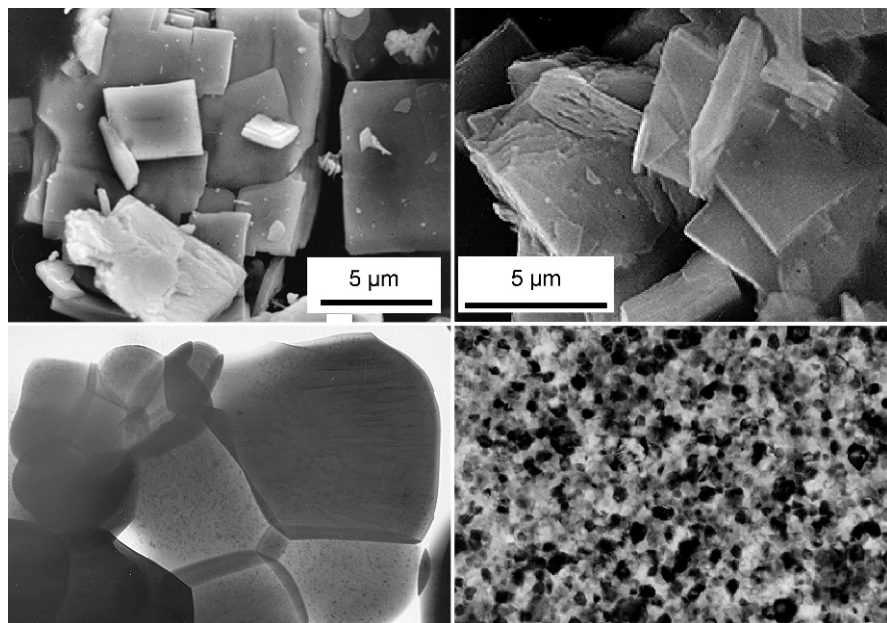
Fig. 36.18 *SEM* (*top*) *and TEM* (*bottom*) *micrographs showing two plutonium oxide samples of a reference material* (*left*) *and a seized material* (*right*). *The two TEM images have the same magnification and highlight the very different grain sizes of particles that have almost the same morphology and size as seen in SEM at lower magnification* (*copyright European Communities*).

Table 36.7 *Isotopic composition of plutonium and uranium in the MOX powder seized at Munich airport, Germany in* 1994.

Sample composition				Simulated mixture[a]	
Pu	wt% ± 1σ	U	wt% ± 1σ	Pu	wt%
238	0.170 ± 0.003	234	0.021 ± 0.001	238	0.11
239	87.58 ± 0.16	235	1.606 ± 0.001	239	87.15
240	10.78 ± 0.04	236	0.049 ± 0.001	240	10.69
241	0.809 ± 0.005	238	98.32 ± 0.01	241	1.15
242	0.658 ± 0.004			242	0.90

[a] Decay corrected with the age of the material.

Light water reactors (PWR, BWR and VVER) could be excluded as the origin of the plutonium. The isotopic composition of plutonium after a typical irradiation period of 3 years in these reactors would have been significantly different. Also, materials testing reactors using 36–90% enriched ^{235}U could be
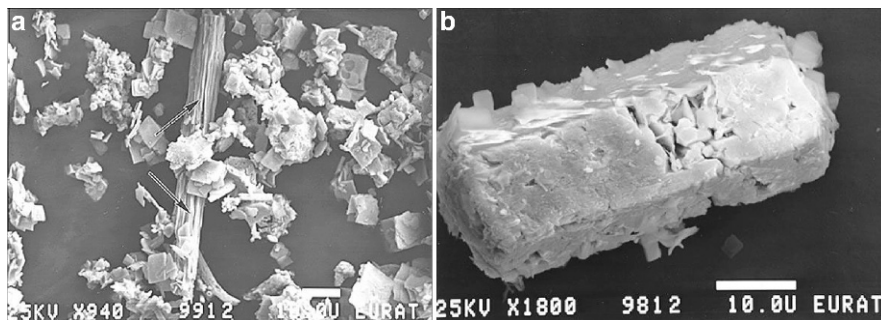
Fig. 36.19 *Seizure of nuclear material at Munich airport, Germany, 1994. (a) SEM micrograph of plutonium particles. (b) SEM micrograph of a uranium particle (copyright European Communities).*

excluded, because higher ^{238}Pu abundance would have been expected in this case. Most likely, a reactor type with a softer neutron spectrum (e.g. heavy water or graphite moderated reactors) was used for the production of the material. In this case, the nuclear reactor would have been operated with an initial ^{235}U enrichment of 1.8% to yield the uranium composition of Table 36.7, assuming that the uranium and plutonium originated from the same reactor. This scenario was also proposed by the isotopic correlation in Fig. 36.15. However, the ^{238}Pu and ^{242}Pu abundances in the seized material were too high to originate from a low burn-up spent fuel of a RBMK-1000 reactor. Thus, most probably, the plutonium was a mixture of different spent fuels (e.g. a low burn-up, i.e. weapons plutonium and a high burn-up fuel) and it had no direct connection with the uranium present. In order to simulate the isotopic composition of a mixed plutonium material mixing calculations were performed. The best fit to the investigated material was found with a mixture of 85–15% of low and high burn-up fuels from RBMK-1000 or Magnox (Table 36.7, last column). As the powder consisted of two different plutonium particle types, individual microparticles were analyzed by SIMS in order to determine if their isotopic compositions were identical or if the earlier determined isotopic composition for the bulk material was a result of mixing two different compositions. The ^{240}Pu/^{239}Pu ratios in platelets and rod-shape particles were slightly different being 0.1166 and 0.1230, respectively. However, the difference was too small to conclude that one plutonium particle type originated from weapons grade plutonium (^{240}Pu/^{239}Pu < 0.05) and the other type from high burn-up fuel (^{240}Pu/^{239}Pu ~ 0.4–0.7). Thus the mixing must have taken place before the particles were produced.

The age of the plutonium material was determined by gamma-spectrometry (bulk sample) and SIMS (both plutonium particles types). The adjacent uranium particles interfered in the SIMS measurements leading to biased results for the ^{238}Pu/^{234}U and the ^{239}Pu/^{235}U ratios (isobaric interferences for

^{238}U and ^{238}Pu, and for ^{235}U from uranium particles and ^{235}U from ^{239}Pu decay). As ^{236}U is a minor isotope in the uranium material, its interference with the ^{236}U that had grown-in from ^{240}Pu decay was negligible. The ages determined for different particle types from the ^{240}Pu/^{236}U ratio were similar (within the uncertainties) and they were consistent with the age obtained from the bulk measurement of the ^{241}Pu/^{241}Am ratio by gamma-spectrometry. Both methods gave a production time around the end of 1979 with an uncertainty of ± 0.5 years.

Even though the ^{239}Pu enrichment was somewhat too low for military purposes, it would not be impossible to produce a nuclear device with plutonium of this quality. With regard to the Li-metal, its high enrichment in ^{6}Li is noteworthy. One of the possible uses of ^{6}Li is its ability to generate energetic tritons via the ^{6}Li(n,α)^{3}T reaction. Such energetic tritons would then be able to initiate DT nuclear fusion in a thermonuclear device. Therefore it may not be a coincidence that plutonium and ^{6}Li were found together.

(ii)   *Theft of radioactive waste*

In July 2001, plutonium was found in a routine urine control of an employee who had been working in a decommissioned reprocessing plant in Karlsruhe, Germany (Höfer *et al.*, 2003). It was also noted that his car and his apartment were contaminated. In addition, his girlfriend had incorporated americium and cesium. The employee was arrested and he confessed that he had stolen two items, namely a plastic vial containing liquid and a swipe cloth. He had managed to get both items out of the reprocessing plant about half a year earlier. The analytical task was twofold: first confirm that the reprocessing plant in question was really the source of the material, and second, verify whether the two stolen items were the only sources of the contamination and the incorporation. Besides the two stolen items, analyzed samples included vacuum cleaner bags from three apartments showing signs of contamination, house-hold gloves used to handle the stolen items and pieces of clothing.

All samples were measured first by gamma spectrometry. The plastic vial contained ^{238,239,241}Pu, ^{241}Am, ^{134,137}Cs and ^{125}Sb. In addition to these elements, ^{154}Eu was also found in the swipe cloth. The other items contained the same nuclides in slightly lower activities. In order to quantify the uranium and plutonium isotopes, part of the samples was dissolved in nitric acid and measured by TIMS and ICP-MS.

The isotopic compositions of plutonium and uranium were similar in all samples and resembled the spent fuel last reprocessed in the plant before shutdown. The large amount of cesium ingested by the thief's girlfriend was difficult to explain from the activity found in the two stolen items. However, the items were most probably washed before having been transferred for the investigations. Because cesium is fairly soluble in water, most of the cesium might have been lost at this stage. The thief was sentenced to prison for breaking the

security regulations of the reprocessing plant and for unauthorized possession of radioactive material.

(iii)   *Plutonium round robin*

In 1998, six laboratories participated in a Plutonium Round Robin exercise launched by the International Technical Working Group on nuclear forensics (ITWG) (Dudder, 2001). The results from ITU Karlsruhe presented below were reported within three periods (24 hours, 1 week and 2 months after receipt of material), which is the recommended practice of the ITWG.

Twenty-four hours: The material is PuO_2 powder with an isotopic composition typical of spent fuel from the commercial fuel cycle (57 wt% ^{239}Pu, 26 wt% ^{240}Pu by gamma-spectrometry). The age is (4.7 $\pm$ 0.2) years determined from the ^{241}Pu/^{241}Am ratio. However, as the americium was noticed to be inhomogeneously distributed, the age needed to be confirmed with other techniques.

One week: The isotopic composition of plutonium was confirmed by TIMS. The plutonium content of 83.5 wt% indicates the presence of major impurities. The ^{241}Am content was determined to be 2.1 wt%. The material was likely to be used for MOX fuel production; however, due to the high americium content it is difficult to handle.

Two months: The ICP-MS analysis gave main impurities of gadolinium of natural composition and ^{237}Np. Electron microscopy investigations showed that the powder consists of PuO_2 platelets of 3.6 μm average size. This is typical for material produced by calcination of oxalates. The investigation also revealed that the gadolinium was not detectable in the plutonium platelets, but it appeared separately.

Conclusions: The plutonium originated from reprocessing of light-water reactor spent fuel. The reactor physics calculations indicate a burn-up of about 40 gigawatt day per metric ton in a PWR. The neptunium content is not typical for large commercial reprocessing plants in the European Union, but rather points to the shut-down pilot reprocessing plant WAK in Karlsruhe, Germany. The age determined from the ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U ratios was significantly lower than the one from the ^{241}Pu/^{241}Am ratio, indicating that the americium was partly coprecipitated when the material was produced. The time of the production was determined to be the second half of 1997 within $\pm$0.1 year. With additional information from a nuclear materials database (Dolgov *et al.*, 1997), the plutonium source was identified as the nuclear power plant at Stade (KKS), Germany.

(iv)   *Summary*

In the last two decades we have seen the emergence of a new and potentially hazardous form of smuggling, namely smuggling of nuclear and radioactive

materials. This has triggered the development of a new scientific discipline – nuclear forensics, where the main aim of the investigations is to find out the origin of the diverted nuclear material. Existing analytical techniques as used in material science, nuclear safeguards and environmental analysis, were adapted to the specific needs of nuclear forensic investigations. Additionally, new methodologies are being developed, aiming at identifying other useful "nuclear fingerprints" in order to reduce the ambiguities often remaining in the interpretation of the analytical results. The hazard involved with nuclear smuggling and the potential relation with nuclear terrorism are the driving forces for deploying and further improving this methodology.

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