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New methods of transplutonium element separation and determination

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Abstract

Some recently developed new methods of separation and determination of transplutonium elements (TPEs) are described. The solvent extraction of TPE^{III} by bidentate organophosphorus reagents from strongly acidic, salt-containing media and their extraction from alkaline solution by various reagents as well as isolation of TPEs in "unusual" oxidation states are discussed. Stabilization of americium as Am^{IV}, Am^{V}, Am^{VI} and berkelium as Bk^{IV} is considered. The separation of actinides and rare earth elements can be carried out by countercurrent chromatography which is based on the retention of the organic phase in a rotating column of a planetary centrifuge under the action of centrifugal forces while the stationary phase is continuously pumped through. It has been shown that TPEs can be successfully separated by this technique. Attention has been paid mainly to consideration of contemporary methods for determination of actinides, special distinction of such methods being low limits of determination, high precision and selectivity. A large number of coulometric methods for determination of americium and berkelium characterized by high precision and selectivity as well as luminescence methods have been developed.

1. Introduction

The recent development of the chemistry of transplutonium elements (TPEs) is mainly connected with continuous growth of nuclear energetics and great interest with respect to the problem of environmental protection. Furthermore, there is a substantial scientific interest in the elements, the chemical and physical properties of which have not been studied in detail.

The most comprehensive survey on the chemistry and technology of TPEs is given in the second edition of the monograph *The Chemistry of the Actinide Elements* [1] and the survey in ref. 2.

2. Methods of transplutonium element isolation and concentration

It is well known that the production of TPEs is associated with the processing of highly radioactive materials containing a mixture of several elements formed in nuclear reactors as a result of neutron irradiation of plutonium and heavier elements. High degrees of purification from radioactive isotopes and inert admixtures are necessary when isolating TPEs from various natural objects and highly radioactive materials, including technological solutions for their subsequent determination. The choice of methods of TPE isolation and separation is determined by the chemical composition of the analysed solution and by the purpose of the work.

2.1. *Extraction of actinides by bidentate neutral organophosphorus compounds*

The most hazardous among the probable sources of continuing inflow of radionuclides in the biosphere are disposals of highly radioactive wastes (HRWs). The potential biological danger of these wastes is retained for hundreds of thousands of years, if they contain TPEs, mainly americium and curium accumulated in waste solutions when spent fuel elements of atomic power stations are processed in order to regenerate the fuel. Hence long-lived Am and Cm isotopes should be isolated from such solutions before disposal. To solve this problem solvent extraction methods are basically used. Among all currently known types of extractants bidentate neutral organophosphorus compounds (BNOCs) are the most effective extractants capable of extracting TPEs in any oxidation states from acid solutions of complex compositions.

The most intensive work with these reagents is carried out in Russia at our institute and in the USA (the Argonne National Laboratory); recently several papers on this subject have appeared from Japan, France and

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India [3]. More than 100 phosphorus- and phosphorus–nitrogen-containing bi- and polydentate neutral reagents of two types have been studied: tetraalkyl(aryl)alkylene(arylene)diphosphine dioxides (DOs) [4] $R_2P(O)–X–P(O)R_2$ and dialkyl(diaryl)[dialkylcarbamoylmethyl]phosphine oxides ("carbamoyls", CMPOs) [5, 6] $R_2P(O)–X–C(O)NR'_2$, where R and R′ are alkyl or aryl and X is alkyl or aryl. Further in the text DOs are represented as 4R and CMPOs, containing two radicals, one being substituent at the phosphorus atom and the other at the nitrogen atom, as $R_2R'_2$.

Wide possibilities of varying the structures of these compounds enabled us to change both extractive power and selectivity of these reagents together with their compatibility with solvents. Thus, the radical nature at the phosphorus atom sufficiently influences the extraction capacity of a reagent. As seen from Fig. 1, the aryl-substituted reagents have the highest extraction capacity with respect to Am^{III} as well as to U^{VI} and Pu^{IV}.

The most interesting feature of these reagents is the so-called "anomalous aryl effect". This lies in the fact that, contrary to the rule known for monodentate analogues, the extractive power of BNOCs increases significantly (by several orders of magnitude in some cases) when alkyl radicals at phosphorus atoms are replaced by more electronegative aryl radicals. This effect was first detected in extraction process by DOs and was confirmed subsequently for CMPOs. The nature of this phenomenon is not completely clear yet. The anomalous aryl effect may be caused by strengthening of a complex by delocalization of electron density from phenyl rings into the cycle formed with a metal and by formation of a system of conjugated bounds in a cycle, increase in the solvation number accompanied by an increase in the complex distribution ratio due to the formation of a "hard" hydrophobic shell composed of phenyl rings or peculiarities in the conformational behaviour of aryl-substituted reagents. A conformational isomer could exist with a spatial distribution of P=O groups favourable for cycle closure stabilized in some cases by stacking–interaction of phenyl rings. Owing to this effect aryl-substituted BNOCs were found to be the most promising for isolation of transuranium elements (TUEs) owing to their high extractive power with respect to only these elements, unlike acids for which the anomalous aryl effect was not observed. Furthermore, different intensities of this effect on extractions of different metals provide some selectivity of TPE isolations, *e.g.* with respect to alkali and alkaline earth metals, iron, nickel and some other metals.

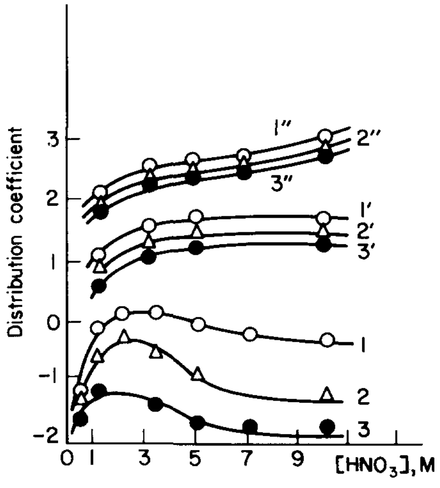

Fig. 1. Extraction of Am^{III} (curves 1–3), U^{VI} (curves 1′–3′) and Pu^{IV} (curves 1″–3″) by 0.05 M dichloroethane solutions of reagents Ph_2Et_2 (curves 1, 1′, 1″), $(PhBu)Et_2$ (curves 2, 2′, 2″) and Bu_2Et_2 (curves 3, 3′, 3″) from HNO_3 solutions.

The change in the substituent nature at phosphorus atoms influences not only a reagent's extraction capacity but also its solubility in both phases. Thus, tolyl-substituted reagents are much more compatible with a wide range of diluents than phenyl-substituted reagents; aryl-substituted reagents are less soluble in water and in HNO_3 than alkyl-substituted reagents.

The nature of the substituents at nitrogen atoms in CMPOs influences mainly their solubility in organic and water phases: butyl-substituted reagents are much more compatible with diluents than ethyl-substituted and more soluble in HNO_3 than octyl-substituted reagents.

Changes in the bridge structure between functional groups influences reagent extraction capacity. Thus, the reagents with a methylene bridge between functional groups have the highest extraction capacity; the increase in linear bridge length results in a decrease in reagent extraction capacity.

Aryl-substituted reagents with a methylene bridge (phenyl and tolyl) can be used for quantitative TUEs extraction and preconcentration from nitric solutions containing salts–nitrates (Table 1).

When possibilities of isolating TPEs from various media have been studied, an unusually high efficiency of extraction from perchloric acid media has been established by aryl-substituted CMPOs caused by a substantial amplification of the anomalous aryl effect in these media [7]. The efficiency of extraction is so high that addition of very small amounts of perchloric acid to solutions of other acids or complexing agents results in a formidable increase in the efficiencies of extraction of TPEs, rare earth elements (REEs), U^{VI}, Pu^{IV} and makes it possible to concentrate these elements from various solutions. Figure 2 represents the effect of perchloric acid on Am^{III} extraction from HNO_3 and U^{VI} extraction from H_3PO_4 solutions by CMPOs. It is shown that Am extraction is sufficiently increased; addition of a small amount of $HClO_4$ allows U^{VI} to

TABLE 1. Extraction of Am^{III} from nitric acid and salt solutions by 4Ph dioxide and Ph_2Bu_2 carbamoyl for 3 min

Reagent	Solvent	Concentration of reagent (M)	$V_{org.}:V_{aq.}$	Extraction of Am^{III} (%)		
				$[HNO_3]=3$ M	$[HNO_3]=1$ M	
					$[Al(NO_3)_3]=1$ M	$[Al(NO_3)_3]=1.8$ M
Dioxide, 4Ph	$CHCl_3$	0.1	1:10	–	–	99.9
			1:50	98.5	97.0	–
			1:100	98.0	93.0	90.0
Carbamoyl, Ph_2Bu_2	1,3,4-trichlorbenzene (TCB)	0.5	1:20	90.0	–	98.5
	o-dichlorbenzene	0.5	1:50	84.8	–	92.0
			1:100	76.0		90.0
		1.0	1:100	95.0	–	–

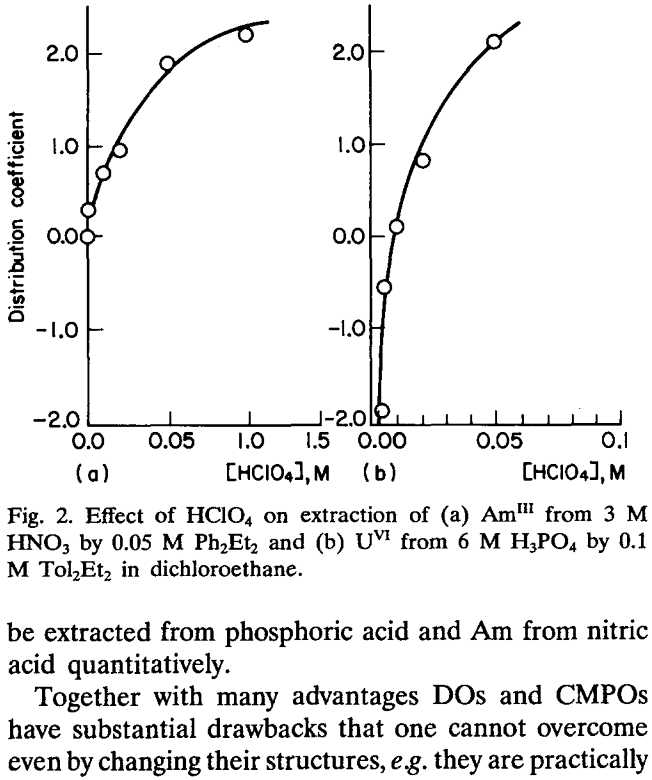

Fig. 2. Effect of $HClO_4$ on extraction of (a) Am^{III} from 3 M HNO_3 by 0.05 M Ph_2Et_2 and (b) U^{VI} from 6 M H_3PO_4 by 0.1 M Tol_2Et_2 in dichloroethane.

be extracted from phosphoric acid and Am from nitric acid quantitatively.

Together with many advantages DOs and CMPOs have substantial drawbacks that one cannot overcome even by changing their structures, *e.g.* they are practically not dissolved in aliphatic diluents. One means of eliminating these drawbacks is to add, to solutions of bidentate reagents, modifiers such as TBP that are highly compatible with many organic solvents. The addition of TBP not only results in elimination of the third phase but also provides a non-additive increase in distribution coefficients of TPEs (synergistic effect). Addition of TBP allowed the application of aliphatic hydrocarbons, widely used in radiochemical industries, as solvents for CMPOs [8].

One of the alternatives was also the study of principally new diluent classes such as, for example, fluoroethers and fluoro derivatives of some other compounds. These diluents have a good compatibility with reagents and their complexes, high density and boiling temperature (130–230 °C), are poorly soluble in water and have high chemical and radiation stability [9].

We suggested BNOC solutions in a solvating diluent ("Fluoropol-732") to isolate actinides from strongly acidic HRW solutions. Such systems have the advantage of the possibility of using readily available efficient carbamoyl reagents and of avoiding the addition of solvating TBP. The extraction of TPE and accompanying elements from model acidic HRW solutions (2.5 M HNO_3) by Ph_2Bu_2 in Fluoropol-732 was studied. It was shown that REEs and Zr^{IV} are extracted as effectively as TPEs; Mo^{VI} and Fe^{III} are extracted to a lesser extent than TPEs while alkali and alkaline earth metals and Cr, Co, Ni are not extracted at all. Mo^{VI}, Fe^{III}, Zr^{IV} can be separated from TPEs and REEs bu multiple stripping of organic phase by acetohydroxamic acid (AHA).

The technological scheme of actinide and lanthanide isolation using an 18-step set of centrifuge extractors with a CMPO (diphenyl[dibutylcarbamoylmethyl]-phosphine oxide, Ph_2Bu_2) in Fluoropol-732 and with AHA as a stripping reagent has been tested. With a model HRW containing more than 13 g l^{-1} of lanthanides and actinides and up to 5 M HNO_3 the possibility has been demonstrated of isolating more than 99.5% lanthanides and actinides as well as of purifying them from Fe, Zr and Mo ($K_{pur.}>50$) and transferring them to a weakly acidic extract with concentration by a factor of 4–6.

The back extract of TPEs and REEs contains as little as 0.02–0.04 M HNO_3, which makes it possible to choose any other aqueous system for group separation of these elements.

However, the tests have revealed large losses of extractant owing to its high water solubility to be the main disadvantage of this extraction system. To eliminate this disadvantage use of BNOC with iso-amyl and *n*-

octyl substituents at the nitrogen atom has been suggested. The solubility in water of these extractants is 3–5 times lower than that of Ph_2Bu_2, while the extractivity is practically the same. Therefore, solutions of diphenyl[diisoamyl (or dioctyl) carbamoylmethyl]-phosphine oxides in solvating Fluoropol-732 diluent may be used to isolate actinides from radioactive wastes of various compositions.

2.2 Extraction from alkaline solution

The application of alkaline solutions is worthwhile for TPE group isolation and concentration. The extraction of metals from such solutions had not been studied until recently. Our investigations have shown that TPEs and many other elements can be extracted from alkaline solutions in the presence of complex-forming reagents by extractants of various classes: quaternary ammonium bases, amines, alkylpyrocatechols (DOP), alkyl derivatives of aminealcohols (AAs) and β-diketones [10]. Some of the extractants studied, especially alkylpyrocatechols and α-oxy-5-alkylbenzyldiethanolamine, are characterized by a high extraction capacity in relation to TPEs, since with their help it is possible to isolate effectively those elements from the alkaline and carbonate solutions with a concentration of the order of 5–6 M (Fig. 3).

The efficiency of the extraction isolation of TPEs depends on the nature of the complex-forming reagents capable of keeping elements in alkaline solutions in a soluble form. Depending on the conditions, the elements may be extracted from alkaline and carbonate solutions in the form of ion associates, the anionic part of which contains either hydroxocomplexes of the corresponding metals or their compounds with the complexforming ligand, while the cationic part is the extractant. They can also be extracted in the form of the coordinatively saturated and hydrolysed β-diketonates.

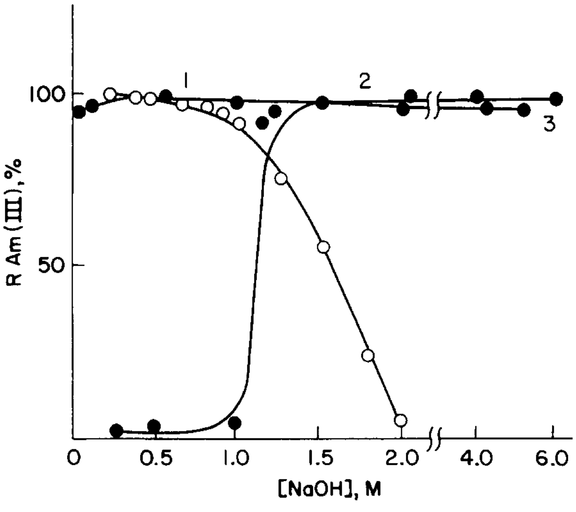

Fig. 3. Extraction of Am^{III} by 0.2 M Aliquat-336·OH in xylene (curve 1), 0.04 M DOP in toluene (curve 2) and 0.1 M AA in hexane (curve 3) in the presence of 0.025 M tartaric acid as a function of the NaOH concentration.

Methods of extraction and extraction chromatography in alkaline and carbonate solutions are used to solve a number of practical tasks. First, under certain conditions with the help of all the extractants studied, one can quantitatively isolate and concentrate the elements capable of existing in alkaline solutions in the form of various complex compounds. Secondly, the group concentration of tervalent TPEs is achieved in these systems with simultaneous isolation from the elements in other oxidation states as well as from iron (separation factors: $Am^{III}:U^{VI}$, 2×10^2; $Pu^{IV}:Am^{III}$, 1×10^2; $Ce^{IV}:Am^{III}$, 3×10^2; $Fe^{III}:Am^{III}$, 1×10^3, $Am^{III}:Cs^{I}$, 2×10^3). The selectivity of extraction may be improved by varying the alkali concentration and the time of phase contact. That will allow separation of TPEs from some rare earth fission products (Ce:Am, 3×10^2; Eu:Am, 70) and the intragroup separation of the TPEs (Bk:Am, 4×10^2).

2.3. Extraction in two-phase water–poly(ethylene glycol) salt systems

A liquid–liquid extraction system based on water-soluble polymers such as poly(ethylene glycol) (PEG) has been suggested for the concentration, separation and extraction of actinides from various salt solutions [11]. These systems are of interest from a practical point of view, since they contain no organic solvents, which are usually volatile, explosive and toxic, and they make it possible to use well-known water-soluble reagents. Extraction of actinides from sulphate, carbonate, phosphate, rodanide and nitrate solutions in the presence of different complexing agents has been investigated. Conditions have been found for quantitative group extraction on the TPEs and for separation of these elements from U, Th and lanthanides. Figure 4 shows the extraction of the complexes of actinides and lanthanides with (curve 1) and without (curve 2) arsenazo III as a function of equilibrium salt phase pH. The distribution of elements in the absence of arsenazo III was less than 10% into the PEG-enriched phase. The quantitative extraction of actinides takes place only in the presence of arsenazo III, which is connected with metals complexing with the reagent. The distribution coefficients of elements increase with increasing arsenazo III concentration.

A high degree of separation of trivalent actinides from neptunium(V) in the system PEG–potassium phosphotungstate (PW) has made it possible to develop a method for separation of ^{243}Am from the daughter ^{239}Np and to work out an isotope generator of ^{239}Np. In Fig. 5 are shown γ spectra of the initial americium solution and a solution of ammonium sulphate and PEG after extraction with PW.

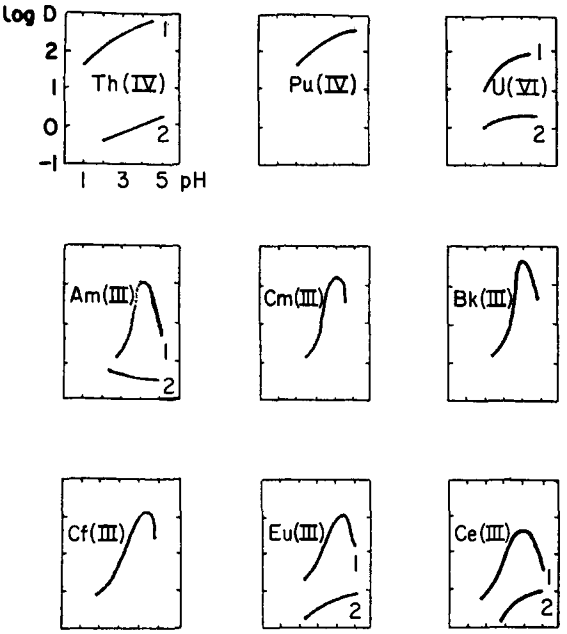

Fig. 4. Dependence of distribution coefficients of different metals on pH in the system PEG–$(NH_4)_2SO_4$–H_2O: curves 1, with arsenazo III; curves 2, without arsenazo III.

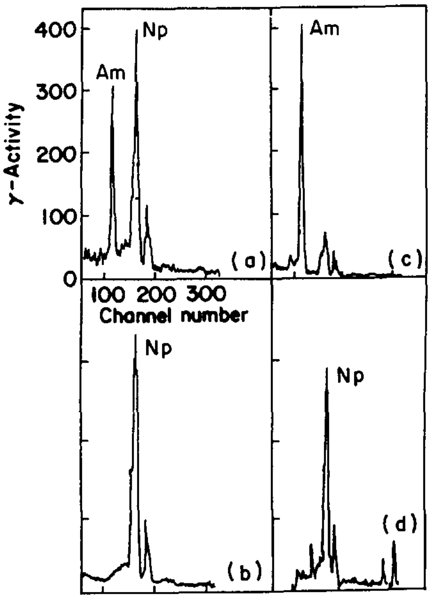

Fig. 5. Separation of ^{243}Am and ^{239}Np in the system PEG–$(NH_4)_2SO_4$–H_2O–KPW: γ spectra of americium initial solution (spectrum a), salt phase after extraction (spectrum b), PEG phase after extraction (spectrum c), ammonium sulphate solution with accumulated ^{239}Np back extracted from the PEG phase (spectrum d).

From γ spectra analysis it follows that it is only americium that passes into the PEG phase while all the neptunium remains in the salt phase. ^{239}Np accumulated in the PEG phase may be washed out from the PEG solution by any salt solution that makes up a heterogeneous system with the PEG and no complexing agent.

3. Methods of transplutonium element separation

To determine reliably various radionuclides in natural objects simple and effective methods are very necessary to isolate them in a radiochemically pure state. Modern separation methods for TPEs are usually based on small differences in the properties of these in the +3 oxidation state, which is the most stable. The best separation of TPEs is obtained by using methods based on the various oxidation states of the separated elements. Almost all the transplutonium elements (except Lr) can exist in solution in "unusual" oxidation states, from +1 up to +7. Systematic investigation of TPE properties in solution has resulted in the creation of quite a large number of practically convenient methods for the preparation and stabilization of Am^{IV} and Bk^{IV}, Am^{V} and Am^{VI} [2]. This has expanded their application in analytical practice and technology, and primarily in the extraction methods of isolation and separation of those elements.

The separation of actinides and lanthanides can be carried out by countercurrent chromatography (CCC).

3.1. Separation of americium, curium and berkelium

Until recently Am^{IV} was considered to exist in concentrated solutions of fluoride ions only. Nowadays a number of methods of americium stabilization in the tervalent state has been developed (Table 2).

Americium(IV) is so stable in the presence of PW that the conditions of its quantitative extraction from solutions of rather concentrated sulphuric and nitric acids by solutions of dioctylamine in dichloroethane were found. Under these conditions, extraction of americium(III) did not exceed 5% and a high degree of americium (both micro and macro amounts) separation from curium and other trivalent elements was achieved.

A number of extraction methods of americium separation from other TPEs and fission products based on the use of Am^{V} and Am^{VI} have been developed. Such methods are especially promising for the isolation of americium(V) traces for subsequent determination. The conditions for quantitative extraction of Am^{V} with thenoyltrifluoroacetone (TTA), 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP), di(2-ethylhexyl)-phosphoric acid (HDEHP) and ammonium pyrrolidinedithiocarbamate (PDTC) have been found. Table 3 shows that Am^{V} is extracted well by different extractants at pH 5 while the extraction of tervalent actinide ions may be suppressed by complexing agents, such as acetate and potassium PW. Am^{V} (both micro and macro amounts) can be extracted by HDEHP from acetate buffer at pH 4–5, with a distribution coefficient as high as 30. The separation factor of Am from Cm by extraction of Am^{V} with PMBP or HDEHP is $(3–6)\times 10^3$. Pentavalent americium can be separated

TABLE 2. Methods of production and stabilization of Am^{IV} in solutions

Medium	Oxidation method	Conditions of oxidation	Year
Aqueous solutions of phosphoric acid	Electrochemical: $E_a = 1.75$ V	10–12 M H_3PO_4; oxidation time, 1–1.5 h; $t = 20$ °C	1973
Acetonitrilic solutions of phosphoric acid	Electrochemical: $E_a = 2.07$ V	0.5–2 M H_3PO_4; oxidation time, 1 h; $t = 20$ °C	1983
Aqueous solutions of potassium PW	Electrochemical: $E_a = 1.77$ V	0.5–3.5 M H_2SO_4, 10^{-2} M $K_{10}P_2W_{17}O_{61}$; oxidation time, 0.5–1 h; $t = 25$ °C	1983
	Chemical: 0.05 M $(NH_4)_2S_2O_8$ + 0.01 M Ag^+	0.1–3 M H_2SO_4, HNO_3, 5×10^{-3} M $K_{10}P_2W_{17}O_{61}$; $t = 20$ °C	1985
Aqueous solutions of potassium hydrocarbonate	Electrochemical: $E_a = 1.0$ V	3 M $KHCO_3$, pH = 9; oxidation time, 0.5–1 h; $t = 25$ °C	1986
Aqueous solutions of linear condensed phosphates	Electrochemical: $E_a = 1.8$ V	0.1–1 M $Na_4P_2O_7$ or $Na_5P_3O_{10}$, pH < 2; oxidation time, 1 h; $t = 25$ °C	1987
Aqueous solutions of ring condensed phosphates	Chemical: 0.1 M $Na_2S_2O_8$	0.5 M $Na_3P_3O_9$ or $Na_6P_2O_{18}$, pH 1–2; oxidation time, 10 min; $t = 90$ °C	1988

TABLE 3. Conditions for Am^V separation from transplutonium elements [2]

Aqueous phase composition	Organic phase composition	Distribution ratio		Separation factor, Am^V:Me^{III}
		Am^V	Me^{III}	
0.01 M NH_4NO_3, pH 5	0.06 M NH_4PDTC in isopentanol–ethanol mixture	30	0.02	1.5×10^3
0.1 M NH_4NO_3, pH5 (acetate buffer 0.001 M potassium PW)	0.05 M PMBP in isopentanol	12.7	0.002	6.4×10^3
0.1 M NH_4NO_3, pH5 (acetate buffer 0.001 M potassium PW)	0.5 M HDEHP in octane	30	0.01	3.0×10^3
0.1 M $HClO_4$ + 0.01 M H_3PO_4	0.05 M PMBP + 0.025 M TOPO in cyclohexane	0.02	900	4.5×10^4[a]
0.1 M HNO_3	0.16 M PA in methyl isobutyl ketone	0.26	194	7.3×10^2

[a] Me(III):Am(V).

from other actinides and lanthanides by extraction with mixtures of picrolonic acid (PA) and sulphoxides in methyl isobutyl ketone from nitric acid since Am^V is extracted significantly under these conditions.

Finding conditions for the oxidation and stabilization of TPEs in different oxidation states gave a basis for the development of a number of isolation methods for TPEs from solutions of complex compositions, such as the effective methods of separation of weighable amounts of Am and Cm. Americium preliminarily oxidized to the hexavalent state reduces on extraction to the pentavalent state and stays in the aqueous phase. A mixture of extractants (such as TTA and TOPO as donor enhancer) is used to increase the isolation factor of curium. Under these conditions the separation factor of Am and Cm reaches 10^3 in a single extraction cycle.

TABLE 4. Separation of Am and Cm from 0.1 M pyrophosphate solution at pH 10 by extraction with 0.1 M solution of PMBP in chloroform [12]

Element	Taken		Found in aqueous phase		Found in organic phase		
	Oxidation state	Amount (μg)	Oxidation state	Amount (μg)	Oxidation state	Amount (μg)	Proportion (%)
Am	VI	241.2	V	227.0	III	14.2	5.8
Cm	III	25	III	0.04	III	25	98.4

An americium sample of about 1 g with a curium content of 10^{-6}% has been obtained by this method.

Trivalent curium can be separated from americium by PMBP extraction after electrochemical oxidation of the latter to the hexavalent state in sodium pyrophosphate solution with pH 10. The coefficient of curium separation from americium during one extraction cycle was about 10^3 (Table 4).

A number of extraction methods for $\mathrm{Bk^{IV}}$ have been developed for selective isolation of berkelium. TOPO and TBPO solutions extract $\mathrm{Bk^{IV}}$ quantitatively from 1–12 M nitric acid and TBP solutions extract it from 8–12 M nitric acid. The berkelium(IV) can be efficiently separated from trivalent americium and curium, rare earths and some fission products using TOPO and TBP as extractants.

The use of the high molecular weight amines to extract berkelium is most promising. By extraction of berkelium with 30% Aliquat solution in carbon tetrachloride from 10–12 M nitric acid after oxidation with dichromate, a separation from the other TPEs and the lanthanides is achieved. In the presence of heteropoly acid anions, $\mathrm{Bk^{IV}}$ is quantitatively extracted from nitric acid and sulphuric acid by primary, secondary or tertiary amines and quaternary ammonium bases. Table 5 shows the distribution coefficients of some elements and separation factors of $\mathrm{Bk^{IV}}$ from other metals in extraction with amines from nitric acid.

3.2. Separation of actinides and lanthanides

The separation of actinides and REEs together with commonly used techniques can be carried out by CCC which is based on the retention of the organic phase in a rotating column of a planetary centrifuge under the action of centrifugal forces while the aqueous phase is continuously pumped through. A number of BNOCs have been tested as extractants. These reagents are not selective and cannot be used for the separation of TPE from trivalent REEs. There are two possibilities for increasing the separation factors for the elements in BNOC-based systems: (1) improvement of reagent selectivity by changing the reagent structure, mainly by introduction of "hard" bridge fragments (arresting the arrangement of the donor atoms) into the extractant molecule; (2) addition of selective complex-forming agents to the aqueous phase. However, neither the first nor the second means enables one stage separation of TPEs from REEs as they have very similar properties. Multistage extraction separation is required to separate TPEs and REEs.

Such separations can be carried out by CCC. Investigations were made on a device consisting of a planetary centrifuge with a vertical column drum developed in the Institute of Analytical Instrumentation, St. Petersburg, a peristaltic pump and a fraction collector. The column of the device rotated around its axis and at the same time revolved around the central axis of the device. The rotation and revolution speeds were equal (350 rev $\mathrm{min^{-1}}$). The planetary centrifuge model had the following design parameters: revolution radius $R = 140$ mm, rotation radius $r = 50$ mm. The column was made of a Teflon tube with an inner diameter of 1.5 mm and a wall thickness 0.75 mm. The total inner capacity of the column was 20 ml.

For example, a method has been suggested for group separation of TPEs from weighed amounts of REEs in a tetraphenylmethylenediphosphine dioxide–$\mathrm{CHCl_3}$–$\mathrm{NH_4SCN}$–HCl system [14]. Figure 6 illustrates the separation of TPEs from 10 mg of REEs. First a REE fraction containing 95.4% of REEs and no TPEs is eluted with $\mathrm{NH_4SCN}$–HCl solution, then 97.5% TPEs without REEs are stripped out with hydroxyethylidene diphosphonic acid (HEDPA) solution in water. The separation takes 20 min.

4. Methods of transplutonium element determination

The recent development of TPE determination methods follows two main trends. The first consists in methods of analysis with record low determination limits that have been developed to solve problems in the analysis of natural objects and in studies of heavy TPEs (Md, No, Lr). Until recently, the determination of trace amounts of TPEs was almost exclusively carried out by radiometric methods (by α, β, γ and neutron radiation) in conjunction with preliminary chemical isolation and concentration. However, nowadays a number

TABLE 5. Distribution coefficients D and separation factors S of berkelium(IV) and several metals during the extraction with amines from 1 M nitric acid containing 4×10^{-5} M $K_{10}P_2W_{17}O_{61}$ [13]

Metal	Extractant					
	3% decylamine in chloroform[a]		TOA in carbon tetrachloride		5% Aliquate-33 in carbon tetrachloride	
	D	S	D	S	D	S
^{249}Bk	305.5[b]		23.4		30.9	
^{241}Am	0.014	2.2×10^4	0.0045	5.2×10^3	0.0035	8.8×10^3
^{243}Cm	0.017	1.8×10^4	0.014	1.7×10^3	0.0045	6.9×10^3
^{144}Ce	49	6.2	4.5	5.3	15.4	2.0
$^{152-154}$Eu	0.006	5.1×10^4	0.006	3.9×10^3	0.0015	2.1×10^4
^{137}Cs	0.007	4.4×10^4	0.0016	1.5×10^4	0.0033	9.4×10^3
^{106}Ru	0.055	5.6×10^3	0.044	534	0.064	483
^{90}Sr	0.020	1.5×10^4	0.003	7.8×10^3	0.0025	1.2×10^4

[a] Extraction from 6 M HNO_3.
[b] ^{250}Bk was used.

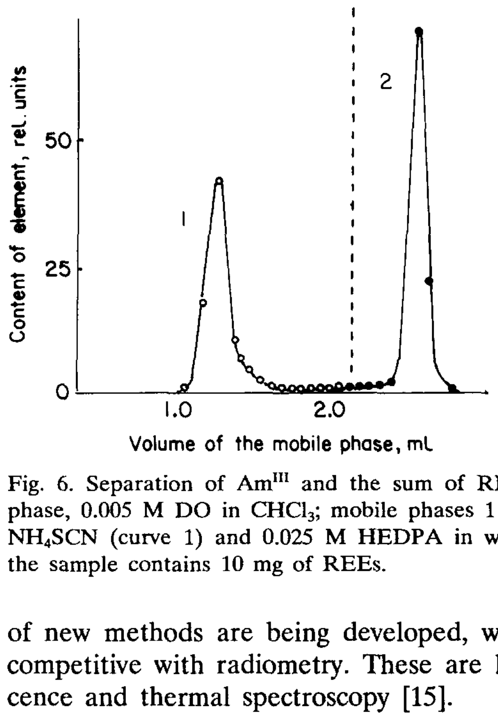

Fig. 6. Separation of Am^{III} and the sum of REEs: stationary phase, 0.005 M DO in $CHCl_3$; mobile phases 1 M HCl–0.5 M NH_4SCN (curve 1) and 0.025 M HEDPA in water (curve 2); the sample contains 10 mg of REEs.

of new methods are being developed, which may be competitive with radiometry. These are laser fluorescence and thermal spectroscopy [15].

Another trend is the development of simple and reliable, precise and selective techniques for determination of the elemental and nuclide composition of irradiated targets and technological solutions and products, on the basis of various analytical methods. There are coulometry, spectrophotometry, titrimetry, mass spectrometry, X-ray fluorescence analysis, neutron activation analysis and the others. The use of such a variety of methods is dictated by their different capabilities and by the diversity of analysed samples. For the last few years the development of methods to analyse macro amounts of TPEs has been aimed at increasing selectivity and rapidity of analysis and at decreasing determination limits.

A detailed description of TPE determination methods was given in ref. 2. Therefore only two methods of TPE determination are discussed here, *i.e.* luminescence and coulometry.

4.1. Luminescence methods

Luminescence methods are remarkable for their very high sensitivity. However, only recently have these methods been developed enough to be used in TPE and TUE determination. It was established that luminescence of phosphor crystals based on fluorides, molybdates or tungstates doped with uranium, plutonium and americium or curium may be used to determine quantitatively nanogram amounts of these elements, first of all in natural objects. The excitation of U, Np, and Pu luminescence in phosphor crystals was carried out by UV light at 337–365 nm wavelength and of americium at 511 nm [16]. The luminescence spectra of activated phosphor crystals comprise several broad bands in the visible and IR region of the spectrum and do not depend on the oxidation state of the element activator introduced into the phosphor crystals.

Luminescence spectra of phosphor crystals doped with Np, Pu and Am are shown in Fig. 7. Luminescence intensity (proportional to concentration) was measured in the IR region where there was no interference caused by other elements. Hence, the luminescence method turned out to be highly selective, and applicable to simultaneous determinations of Np, Pu, Am and, in some cases, U in the same sample. Using lead molybdate as the matrix of the phosphor crystals it is possible to determine 0.01 ng of Np ($\lambda=1713$ nm), 0.5 ng of Pu ($\lambda=1986$ nm) and 0.5 ng of U ($\lambda=507$ nm). Determination of 0.1 ng of Am ($\lambda=696$ nm) can be undertaken with an $NaBi(WO_4)_2$ crystallophosphor. This method is being used to determine U, Np, Pu and Am in waste

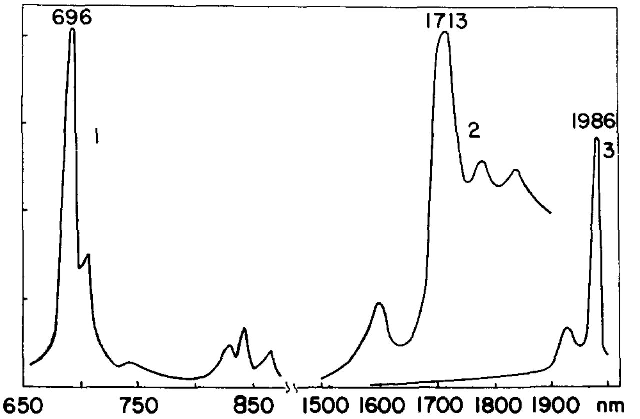

Fig. 7. Luminescence spectra of Np (spectrum 2) and Pu (spectrum 3) in $PbMoO_4$ and Am (spectrum 1) in $NaBi(WO_4)_2$.

solutions of radiochemical products and in natural objects without preliminary isolation of the elements to be determined and independently of the isotopic compositions thereof. A simple filter photometer has been constructed at the Vernadsky Institute to determine actinide elements by luminescence in natural objects and to control areas occupied by radiochemical products. When necessary the sensitivity of neptunium determination in environmental samples can be increased by more than two orders of magnitude if a selective membrane preconcentration technique is used.

Luminescence in solution is a unique feature of the Cm^{III} ion. Luminescence bands in the 593–615 nm region are observed on laser excitation [17] or mercury discharge lamp excitation [18]. The determination limit of Cm is less than 10^{-4} $\mu g\ ml^{-1}$, in both organic and aqueous solutions. Unfortunately, luminescence of other TPE ions is much weaker and it is observed in the IR region, thus resulting in a much poorer determination sensitivity [19].

4.2. Coulometry

Coulometry is one of the few absolute analytical methods which does not demand the use of standards to calculate the quantity of a substance determined. Furthermore, controlled-potential coulometry provides TUE determinations with very low errors of several hundredths of a per cent [20]. The following redox couples are now used for TUE determinations: Np^{VI}/Np^{V}, Pu^{IV}/Pu^{III}, Am^{VI}/Am^{V}, Am^{VI}/Am^{III}, Bk^{IV}/Bk^{III}. There is a theoretical possibility that Cm^{IV}/Cm^{III}, Cf^{IV}/Cf^{III}, Md^{III}/Md^{II}, No^{III}/No^{II} redox couples could also be used. Although controlled-potential coulometry provides the highest precision of determination, coulometry with a scanning voltage is also being developed successfully. Recently, the latter method was used to determine Np and Pu; detection limits were 10^{-7}–10^{-6} mol l^{-1} [21].

The coulometric methods of americium determination that use the Am^{IV}/Am^{III} redox couple are extremely selective. Such a determination can be carried out in aqueous solutions of potassium PW ($K_{10}P_2W_{17}O_{61}$) and sodium carbonate, and in acetonitrilic solutions of phosphoric acid where Am^{III} can be readily oxidized to Am^{IV} by electrolysis. Am^{IV} is especially stable in PW solutions. Therefore, in this case even a ten-fold excess of curium does not affect the results of an americium determination. Many other elements which are oxidized under these conditions (including Pu and Ce) do not influence the results either, because they are not reduced when reduction of Am^{IV} takes place at an anode potential of +1.17 V.

Coulometric determination of berkelium can best of all be carried out in a 1 M HNO_3+0.1 M H_2SO_4 solution [22]. In this case the detection limit is the lowest, and the error for ^{249}Bk is lower than that of radiometric determination by α-activity of the daughter ^{249}Cf.

The above-mentioned methods of separation and analysis are widely used to determine TUEs in nuclear fuel and products of its recovery [23–26], as well as in natural objects (soils, sediments, natural waters, air, gas blow out etc.) [27–32]. Modern methods of TUE determination provide very low determination limits. This allows reliable control of TUE contents in natural objects. For example, the detection limits of TUEs were 0.037 Bq kg^{-1} in soils, 1.8×10^{-5} Bq l^{-1} in natural waters, and 3.7×10^{-3} Bq kg^{-1} in biological materials [33], while the background Pu content in soils was 0.07–0.7 Bq kg^{-1} and up to 5×10^{-5} Bq l^{-1} in water. Recent investigations have been directed to further reductions in detection limits and increased precision of these analyses.

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