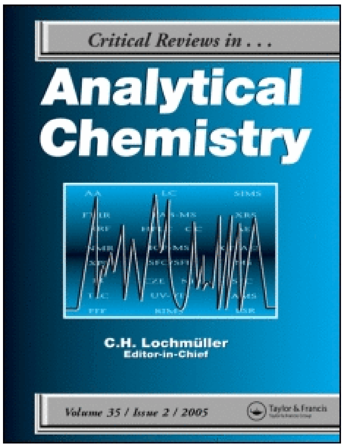

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Separation and Determination of Transplutonium Elements

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SEPARATION AND DETERMINATION OF TRANSPLUTONIUM ELEMENTS

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I. INTRODUCTION

The transplutonium elements (TPE) apportionment in a separate group of actinide series is conditioned by several reasons. In chemical relation TPE strongly differ from light actinides by the stability of +3 oxidation state in aqueous solutions[1,2] and demonstrate a considerable likeness with the elements of the first half of lanthanide series.[3] The half-lives of the most available TPE isotopes are considerably smaller than those of light actinides and the great radioactivity of TPE solutions arouses specific troubles at chemical processes. At last, from the point of practicality, using scale TPE for the present is inferior to light actinides and consequently (and also because of their smaller availability) their chemical properties are studied much less, than, e.g., those of uranium and plutonium.

TPE likeness with lanthanides, brilliantly proved by Seaborg in his "actinide hypothesis", was the basis of the classic methods of TPE isolation. In the first works concerning the synthesis of these elements carried out from 1944 to 1955, the coprecipitation of trivalent ions with lanthanum fluoride and their ion-exchange separation on cationite with the use of solutions of ammonium citrate or hydroxy-i-butyrate were used for TPE isolation.[4,5] Later on a number of effective methods, mainly extraction and ion exchange, for the group isolation and separation of TPE in 3+ oxidation state, were elaborated.

However, the separation of TPE in trivalent state and their isolation from lanthanides of the similar properties are connected with great troubles due to the closeness of properties of M^{3+} ions of f-elements. Separation and determination methods, based on different oxidation states of separated elements, possess greater selectivity. As is seen from Table 1, almost all of the TPE (except Lr) can exist in solution, except in the "usual" +3 oxidation state, and in the "unusual" oxidation states (+1, +2, +4, +5, +6, +7). The possibility of oxidation or reduction of M^{3+} ion to higher or to lower oxidation state and its stability in solution are known to be determined by the value of oxidation potential of corresponding redox couple. The values of standard oxidation potential E°[2,3,6] given in Table 1 show that in diluted solutions of mineral acids it is quite easy to obtain such ions, as Am(V) and Am(VI), Bk(IV), Md(II), No(II). In other cases the values of potentials of M(IV)/M(III) couples are too great and those of M(III)/M(II) are too small, and the oxidation and reduction are impossible. But in presence of strongly complexing reagents which form the more stable complexes with M^{4+} ions, the oxidation potential of the M(IV)/M(III) redox couple decreases to such an extent that the oxidation becomes possible. Thus, Am(III) can be oxidized to Am(IV) in aqueous and acetonitrile phosphoric acid solutions,[7-9] potassium phosphotungstate $K_{10}P_2W_{17}O_{61}$ solutions,[10] and alkaline metals carbonate solutions.[11,12] Decreasing of oxidation potentials depending on media composition is illustrated by the values of formal potentials, given in Table 2. M(III) reduction to M(II) in a number of cases is reached at the use of nonaqueous media-acetonitrile or alcoholic-aqueous solutions, and chloride melts.[3]

The possibility of the practical use of TPE in "unusual" oxidation states for the isolation and determination is mainly dependent on the stability of these oxidation

Table 1
OXIDATION STATES AND STANDARD REDOX POTENTIALS OF TPE

Oxidation state	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
+7									
+6	+								
	+1.7								
+5	+								
	+1.1								
+4	+	±	+	±	±				
	+2.45	+3.1	+1.67	+3.1	+4.5				
+3	⊕	⊕	⊕	⊕	⊕	⊕	⊕	+	⊕
	−2.6	−3.8	−2.8	−1.7	−1.2	−0.65	−0.15	+1.45	
+2	±	±	±	±	±	±	+	⊕	
+1							±		

Note: O — The most stable oxidation state in aqueous solutions. + — Relatively stable oxidation state. ± — Unstable oxidation state. Redox potentials are in volts (vs. normal hydrogen electrode) and belong to neighboring (in vertical) couple of ions.

states in solutions. Thermodynamic stability of M^{z+} ions in aqueous solutions is determined in the first place by the direction and intensity of these ions and solution components (H_2O, H^+, OH^-) redox reactions proceeding. Such reactions can be attributed the following:

Reduction with water:

$$M^{Z+} + 0.5\ H_2O = M^{(Z-1)+} + H^+ + 0.25\ O_2 \tag{1}$$

Oxidation by water:

$$M^{Z+} + H_2O = M^{(Z+1)+} + OH^- + 0.5\ H_2 \tag{2}$$

Oxidation by H^+ ions:

$$M^{Z+} + H^+ = M^{(Z+1)+} + 0.5\ H_2 \tag{3}$$

The disproportionation:

$$M^{Z+} + M^{Z+} = M^{(Z+1)+} + M^{(Z-1)+} \tag{4}$$

The general method of such reaction equilibrium estimation is based on the application of fundamental thermodynamic parameters of ions in aqueous solutions — standard Gibbs energy of formation ΔG°_f; standard enthalpy of formation (ΔH°_f), and standard entropy (S°) — or connected with these values of oxidation potentials. Such an approach permits not only the evaluation of the stability of known ions, but also those which are not found or investigated. A number of mutually correlated values of ΔG°_f, ΔH_f, and S° for aqueous TPE ions in oxidation states from +2 to +5 (and partially +1), which we evaluated, going from several experimental data, obtained by other authors, and found by us regularities existed for 5f-elements, are presented in Table 3.[6,34-36]

Table 2
THE FORMAL REDOX POTENTIALS (IN VOLTS) OF TPE REVERSIBLE ELECTROCHEMICAL COUPLES (VS. NHE)

Solution	Americium IV/III	Americium VI/V	Americium VII/VI	Curium IV/III	Berkelium IV/III	Californium III/II
H_2SO_4	—	—	—	—	1.4—1.33 (0.05—10 *M*[13-16]	−1.9 (0.001 *M*)[17]
H_3PO_4 (aqueous)	1.79—1.75 (10—15 *M*)[18,19]	1.58—1.45 (1—5 *M*)[18,20]	—	—	1.12—1.06 (3—10 *M*)[21,22]	—
H_3PO_4 (acetonitrile)	2.0—1.7 (0.3—2 *M*)[9]	—	—	—	—	—
$K_{10}P_2W_{17}O_{61}$	1.65—1.40 (6—13 m*M*, pH = 0—6)[23,24]	1.52 (0.016 *M*, pH = 0.7)[25]	—	2.1—2.3[24]	0.85—0.64 (6 m*M*, pH = 0—6)[24]	—
$NaCH_3COO$	1.9—2.0[26]	—	—	—	—	—
K_2CO_3	0.86 (1 *M*)[27]	0.97—0.77 (0.1—2.7 *M*)[28,29]	—	1.6 (1 *M*)[27]	0.26 (2 *M*)[21]	—
Na_2CO_3	0.89 (1.3—2 *M*, pH = 10)[12]	0.9—0.93 (0.2—2.1 *M*)[12,29]	—	—	—	—
NaOH	0.25—0.18 (1—10 *M*)[30]	0.68—0.63 (1—10 *M*)[30,31]	1.05 (1 *M*)[32,33]	—	—	—

Note: Values in parentheses are the solution concentration.

Table 3

STANDARD THERMODYNAMIC QUANTITIES FOR TPE AQUEOUS IONS

[ΔG°_f and ΔH°_f IN kJ/mol, S° IN J/(K·mol)]

	M^+	M^{2+}			M^{3+}			M^{4+}			MO_2^+		
Element	$-S^\circ$	$-\Delta G^\circ_f$	$-\Delta H^\circ_f$	$-S^\circ$	$-\Delta G^\circ_f$	$-\Delta H^\circ_f$	$-S^\circ$	$-\Delta G^\circ_f$	$-\Delta H^\circ_f$	$-S^\circ$	$-\Delta G^\circ_f$	$-\Delta H^\circ_f$	$-S^\circ$
Am	—	380.0	382.0	82.8	598.1	616.7[a]	203.3	361.7	418.7	398.0	741.0[a]	805.2	21[a]
Cm	—	221.5	228.2	81.2	588.2	607.2[b]	187.8	289.0	355.4	411.6	682.3	756.2	36.1
Bk	—	301.0	309.2	82.0	566.3	586.1	186.0	405.7	467.8[a]	393.0	796.9	877.1	53.0
Cf	—	429.4	439.0	84.9	581.8	602.5[c]	187.4	282.7	343.7	387.7	682.3	758.6	38.5
Es	—	427.5	438.1	87.9	577.0	598.3[c]	189.0	133.2	193.3	384.6	—	—	—
Fm	38.4	453.1	468.8	92.5	564.1	590[c]	191.9	52.7	116.1	382.8	—	—	—
Md	44.4	499.6	516.3	99.6	514.0	540[c]	195.9	-64.9	-2.93	381.9	—	—	—
No	58.6	541.9	557.7	118.8	402.0	423[c]	201.4	-244.4	-189.0	382.1	—	—	—
Lr	—	—	—	—	583.2	607[c]	220.5	-275.5	-222.2	384.7	—	—	—

[a] Reference 38.
[b] Reference 37.
[c] References 39 and 40.

Table 4
KINDS OF INSTABILITY OF TPE IONS IN ACIDIC AQUEOUS SOLUTION
($\mu = 0$, 298 K)

Ion	Am	Cm	Bk	Cf	Es	Fm	Md	No
M^{2+}	ox; d	ox; d	ox; d	ox	ox	ox	ox	
M^{3+}								red
M^{4+}	red; d	red; d	red; d	red; d	red	red	red	red
MO_2^{2+}		?	?		?	?	?	?
MO	red	red	?	?	?	?	?	?

Note: ox, oxidation by water; red, reduction by water; d, disproportionation (in case of M^{2+} ions with formation of M^{3+} and M°); ?, estimation of stability is impossible because of deficiency of data.

Based on these data, we evaluated thermodynamic stability of TPE ions, such as M^{2+}, M^{3+}, M^{4+}, MO_2^{2+}, and MO_2^{2+} in aqueous solution (Table 4). It has been admitted that ions are considered stable if at equilibrium, and the admixture of other ions does not exceed 10%. At such a condition in acid aqueous solution, those M^{z+} ions will be stable, $M^{z+}/M^{z-1)+}$, and couple the oxidation potential which does not exceed +1.11 V (is not reduced by water), and those ions $M^{z-1)+}$, the potential of which is greater than 0.16 V (is not oxidized by water). Stable to disproportionation are those that the highest valency couple oxidation potential of which is greater than those of the lowest ones. From Table 4 it is seen that in diluted acidic aqueous solutions, MO_2^+, M^{3+} ions (except No^{3+}) and No^{2+} are stable. In solution, containing anions, which form strong complexes, the stability of M^{4+} and MO_2^{2+} ions considerably increases, as the values of oxidation potentials M^{4+}/M^{3+} and MO_2^{2+}/MO_2^+ couples decrease. At the same time considerable complex formation and acidity increasingly decrease MO_2^+ ions stability, which began appreciably disproportionate, and those of M^{2+}. In order to increase the stability of the latters it is necessary to use specific complex-forming compounds, which would give with these ions more stable complexes than with M^{3+} ions. Knowledge of all these regularities permits one to choose conditions in which the usage of "unusual" oxidation states of TPE for their separation and determination become possible.

In the present work, the authors do not attempt to give an exhaustive analysis of the whole literature concerning the methods of TPE isolation and determination. The works of the last 50 to 70 years are quite fully elucidated in the reviews and monographs.[41-44] On the other hand, in the last 5 to 7 years, a number of new and efficient methods for isolation and determination and new extractants and eluants are elaborated and widely adopted in practice. In analytical chemistry of TPE, the "unusual" oxidation states begin to be used, which considerably expands the possibilities of methods. The instrumental methods of analysis, the efficiency of which considerably increases due to the usage of modern automatic devices and new methods (e.g., laser spectrophotometry), have developed intensively in recent years. So the works of recent years, especially concerning the usage of "unusual" oxidation states are mainly elucidated in this review. Most attention is paid to the works of Soviet authors which are not as well known to foreign readers due to the language barrier. As the main direction of the review is the analytical chemistry of TPE, there is no consideration of separation methods having only a technological application.

II. METHODS OF TRANSPLUTONIUM ELEMENTS (TPE) SEPARATION

It is known that TPE production is connected with the treatment of high radioactive materials, containing the mixture of several elements, and formed at plutonium or more heavy elements irradiation in special reactors. The modern methods of TPE recovery and separation are based usually on a small difference in properties of these elements in the most stable +3 oxidation state. They more often use both in technology and in analytical chemistry the extraction and ion exchange methods. The methods of precipitation, coprecipitation, electrochemical, and the methods of sublimation are used mainly as analytical ones. Extraction chromatography, combining advantages, and most importantly the selectivity, of extraction methods with convenience execution on the column, is widely used not only for its analytical purposes, but for purification and recovery of milligram quantities of transplutonium elements.

The choice of the method of TPE isolation and separation is conditioned by the chemical content of the analyzed solution and by the aim of the work. The methods of precipitation and extraction are used more often for TPE isolation from different materials, including their preconcentration, and the methods of ion exchange, solvent extraction, and extraction chromatography are used for TPE separation. It is necessary to take into account the great specific radioactivity of many TPE isotopes. Thus, the used extractants and sorbents must be resistant to radiation, and the methods used are both effective and expressive enough.

The high degree of purification not only from radioactive isotopes but from inert admixtures is necessary, as a rule at TPE isolation from different natural materials and high radioactive samples, including technological solutions for the purposes of their following determination. They use repeated separation, as well as combining of different methods of purification in order to reach this aim. Elaborated for these purposes the methods are summarized in monographs.[2,41-44] However, the separation methods, based on different TPE oxidation states, are the most effective. The new data obtained recently concerning TPE separation and concentrating on tetravalent oxidation state with the use of new extractants, sorbents, complex-forming media, as well as the methods based on the use of penta- and hexavalent americium, tetravalent berkelium, and divalent mendelevium, are discussed below.

A. Extraction Methods

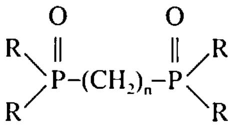
Extraction methods of TPE isolation and separation are widely adopted both in the analytical chemistry of these elements, and in the technology of their production. Their main advantage is the rapidity and efficiency of separation. The selectivity of extraction is conditioned by the choice of reagent and its concentration and diluent, by the introduction of complex-forming reagents in the aqueous phase, and by the adjustment of its acidity. In order to increase the efficiency of elements separation, repeated extraction or extraction chromatography is used.

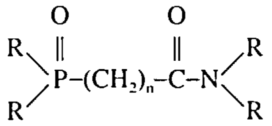
The extractants of different classes are applied for TPE extraction isolation and separation: organophosphorus compounds, amines, chelate-forming reagents, etc., and also their mixtures (synergetic extraction). Recently, Shoun and McDowell[45] have given an excellent review of extractants used in TPE separation methods. The application of bidentate organophosphorus reagents and alkaline solutions, as well as the use of penta- and hexavalent americium and tetravalent berkelium, open up new possibilities for extraction isolation and concentration and separation of these elements.

1. Bidentate Organophosphorus Extractants

It is known[42] that monofunctional organophosphorus reagents, such as tributylphosphate (TBP), di-2-ethylhexylphosphoric acid (HDEHP), and phosphine oxides (trioctylphosphine-oxide-TOPO), do not permit isolation of trivalent TPE from acids solutions, as the acids themselves are well extracted by these reagents. Bidentate neutral organophosphorus reagents, containing either two ≡P=O groups, or one ≡P=O group and one =C=O group, possessed much greater extractability towards these elements, as was shown for the first time by Siddall.[46,47]

The properties of these reagents:





for the extraction of different metals were considered in reviews[48,49] and recently in detail by Schulz and Navratil.[50] TPE extraction by reagents of the first group, named diphosphine dioxides,[49,50] is widely investigated in the works of the Soviet authors. The influence of dioxide structure, nature of substituents at phosphorus atoms, nature and structure of the bridge between phosphorus atoms on extraction capacity, and selectivity towards TPE have been studied (Table 5). It has been determined[53,54] that the augmentation of a number of methylene groups between P=O groups from 1 to 3 (reagents MPhDPO, EPhDPO, PPhDPO — Table 5) leads to a considerable increase (about four orders) of distribution coefficients of Am, Cm, Bk, and Cf. Substitution of the ethylene bridge by the vinylene bridge arrests the P=O group in the *cis*-position (VPhDPO-*cis*, VTDPO-*cis*) and brings about a thousand-fold increase in the distribution coefficient of trivalent TPE in comparison with dioxides with the ethylene bridge (EPhDPO).[55-57] There is a decreased extraction of TPE, if the hydrogen atom in the methylene bridge MPhDPO is replaced for Cl^-, allyl, *n*-dodecyl, or vinylidene, the other conditions being equal.[57] The nature of substituents at phosphorus atoms strongly influences the capacity of dioxides extraction. The basicity of dioxides decreases and extraction capacity towards trivalent TPE and the stability of forming complexes increase if alkyl radicals (MBDPO, MOCDPO — electronegativity X = 2) are replaced for more negative phenyl ones (MPhDPO — electronegativity X = 2.27).[53,55,59-61] The same effect exists at the extraction from perchloric acid solutions.[63,64] Tetraphenylmethylenediphosphine dioxide (MPhDPO) has the most extraction capacity towards TPE among the studied reagents of the first group (Table 5). This reagent is dissolved badly in nitric acid solution; dissolved enough in chloroform (0.4 *M*) it has a good radiation resistance[66] and allows quantitative isolation and concentration of TPE from nitric acid solutions of various concentrations in the presence of great amounts of salting-out agents. Thus, during one extraction cycle americium isolates practically quantitatively by 0.1 *M* solution of MPhDPO at aqueous and organic phase ratios equal to 100:1, and from 3 *M* HNO_3 and 1 *M* HNO_3 solutions in the presence of 1.8 *M* $Al(NO_3)_3$. As the reagent is badly dissolved in aqueous phase, so its solutions can be used for the repeated extraction. Thus, e.g., after threefold use of 0.1 *M* MPhDPO chloroform solution for americium extraction from 3 *M* HNO_3, alternated with reextraction by 10% $(NH_4)_2CO_3$ solution, americium extracts by these solutions at 99.6%.[65]

The selectivity of all studied reagents (Table 5) towards TPE depends on HNO_3 concentration: during the extraction from 0.5 to 4 *M* HNO_3 separation factors are very

Table 5
IMPORTANT DIPHOSPHINE OXIDE FOR EXTRACTION OF TPE

Compound	Acronym[a]	Extractable species	Aqueous system	Ref.
$(Ph)_2(O)P\text{-}CH_2\text{-}P(O)(Ph)_2$	MPhDPO	Am	1—7 *M* HNO_3	51
		Am	0.1—12 *M* HNO_3	52, 53
		Am, Cm, Bk, Cf	1—15 *M* HNO_3	54, 55, 57, 58, 65
		Am	0.1—8.6 *M* $HClO_4$	63, 64
$(Ph)_2(O)P\text{-}(CH_2)_2\text{-}P(O)(Ph)_2$	EPhDPO	Am	0.1—12 *M* HNO_3	52, 53
		Am, Cm, Bk, Cf	1—15 *M* HNO_3	54, 55, 57, 58
		Am	0.1—8.6 *M* $HClO_4$	63, 64
$(Ph)_2(O)P\text{-}(CH_2)_3\text{-}P(O)(Ph)_2$	PPhDPO	Am	0.1—12 *M* HNO_3	52, 53
$(H)_2(O)P\text{-}CH_2\text{-}P(O)(H)_2$	MHDPO	Am	2 *M* $NaNO_3$—0.01 *M* HNO_3	62
$(CH)_2(O)P\text{-}(CH_2)_4\text{-}P(O)(H)_2$	B(CH)HDPO	Am	2 *M* $NaNO_3$—0.01 *M* HNO_3	62
$(CH_2)_2(O)P\text{-}(CH_2)_5\text{-}P(O)(H)_2$	A(CH)HDPO	Am, Cm	2 *M* $NaNO_3$—0.01 *M* HNO_3	62
$(Ph)_2(O)P\text{-}CH{=}CH\text{-}P(O)(Ph)_2$-*cis*	VPhDPO-*cis*	Am	0.1—11 *M* HNO_3	56
		Am, Cm, Bk, Cf	1—15 *M* HNO_3	54, 55, 57
$(Ph)_2(O)P\text{-}CH{=}CH\text{-}P(O)(Ph)_2$-*trans*	VPhDPO-*trans*	Am, Cm, Bk, Cf	1—15 *M* HNO_3	57, 58
$(Ph)_2(O)P\text{-}C{\equiv}C\text{-}P(O)(Ph)_2$	AcPhDPO	Am, Cm, Bk, Cf	1—15 *M* HNO_3	57, 58
$(Ph)_2(O)P\text{-}CH(n)^{b}\text{-}P(O)(Ph)_2$		Am, Cm, Bk, Cf	1—15 *M* HNO_3	57, 58
$(T)_2(O)P\text{-}CH{=}CH\text{-}P(O)(T)_2$-*cis*	VTDPO-*cis*	Am	0.1—11 *M* HNO_3	56
		Am, Cm, Bk, Cf	1—15 *M* HNO_3	57, 58
$(Bu)_2(O)P\text{-}CH_2P(O)(Bu)_2$	MBuDPO	Am	0.1—12 *M* HNO_3	52, 53
$(Oc)_2(O)P\text{-}CH_2\text{-}P(O)(Oc)_2$	MOcDPO	Am	0.1—12 *M* HNO_3	52, 53
		Am	0.1—8.6 *M* $HClO_4$	63, 64

Table 5 (continued)
IMPORTANT DIPHOSPHINE OXIDE FOR EXTRACTION OF TPE

Compound	Acronym[a]	Extractable species	Aqueous system	Ref.
$(Oc)_2(O)P\text{-}CH_2P(O)(Ph)_2$	MOcPhDPO	Am	0.1—12 *M* HNO_3	52, 53
		Am	0.1—8.6 *M* $HClO_4$	63, 64
$(Bu)_2(O)P\text{-}(CH_2)_2P(O)(Oc)_2$	EBuOcDPO	Am	0.1—8.6 *M* $HClO_4$	63, 64

[a] DPO, diphosphine oxide; A, amylene; Ac, acetylene; B, butylene; Bu, butyl; (CH), cyclohexyl; E, ethylene; H, hexyl; M, methylene; Oc, octyl; P, propylene; Ph, phenyl; T, tolyl; V, vinylene.

[b] n = Cl, allyl; dodecyl; vinylidene.

small and reach maximum value in 15.7 *M* HNO_3. Reagent selectivity and the degree of TPE separation by them are mainly determined by the structure of bridge, binding P=O groups.[54-57] Thus, the reagents with alkylene bridge (MPhDPO, EPhDPO) provide great enough separation factor of Am and Cf (to 25), and with vinylene one (VPhDPO-*cis*) of Cm and Bk (~10).[55] There is a considerable increase of TPE separation factors during the extraction from ammonium thiocyanate solutions in the presence of complex-forming reagents in aqueous phase.[67]

A new group of organophosphorus reagents — poly (diphenylphosphinylmethyl) arenes[68,69] — has recently been studied as extractants for TPE isolation.

Poor solubility of diphosphine dioxides in aromatic hydrocarbons is one main obstacle for their practical application for TPE isolation and preconcentration from different materials. Dioxide solutions of 0.01 to 0.1 *M* in such diluents as CCl_4, $CHCl_3$, and dichlorobenzene are employed in most of cases. It has been also found that 0.05 *M* MPhDPO solutions in the mixture of chloroform and xylene in the ratio of 1:10 extract americium with the same distribution coefficients as in the case of chloroform application as diluent.[65]

The second group of reagents, containing phosphorus and nitrogen atoms, is investigated for the purpose of TPE isolation from strong acid solutions, including solutions after treatment of fuels. Depending on the nature of the substituents at phosphorus atoms — $(RO)_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N(R)_2$ or $(R)_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N(R)_2$ they are called — dialkyl-*N,N*-dialkylcarbamoylmethylphosphonates (CMP) or dialkyl-*N,N*-dialkylcarbamoylmethyl phosphine oxides (CMPO), respectively. These reagents are inferior to alkylene (vinylene) diphosphine dioxides in extraction capacity, but they possess several advantages, in particular, a more simple method of synthesis and a better solubility in organic diluents. The data about trivalent TPE extraction by some of these extractants has been summarized in the literature.[48-50] Lately Myasoedov and Chmutova[70-72] in the U.S.S.R. and Schulz and McIsaac[73-75] and Horwitz et al.,[76-81] in the U.S. synthesized great groups of this class of reagents and studied their extraction capacity towards TPE and some fission elements (Table 6). It has been found that the extraction capacity of these reagents is mainly determined by the nature of radicals at phosphorus atoms. The replacement of alkoxy substituents for alkyl or aryl ones considerably increases reagent extraction capacity. Thus, the replacement of butoxy substituents at phosphorus atoms (DBDECMP) for butyl (DBDECMPO) or phenyl (DPhDECMPO) ones leads to an americium distribution coefficient increase at its extraction from 3 *M* HNO_3 with 0.1 *M* 1,2-dichloroethane solution of these reagents by factors of $4 \cdot 10^1$ and 10^3, correspondingly. The replacement of one of the phenyl radicals in reagent DPhDECMPO for the ethyl one (EPhDECMPO), on the contrary, leads to the decrease of K^{Am}_d almost on two orders.[72] Thus, the extraction capacity of the extractant with one phosphoryl group increases on two orders[70] if at the replacement of alkyl substituents at phosphorus atom for more electronegative phenyl ones, as in the case of diphosphines dioxides.[53,55,59-61] Basicity increase of substituent at phosphorus atom in the range: $(C_6H_{13}O)_2$ phosphate-(DHDECMP); $(C_6H_{13}O)$, (C_6H_{13})-phosphinate-(HHDECMP); $(C_6H_{13})_2$, phosphine oxide-(DHDECMPO) leads to considerable increasing of Kd^{Am} at its extraction from 0.1 to 1 *M* HNO_3 too. However, the selectivity of TPE isolation deteriorates. Thus, separation factor of americium from iron (K^{Am}_d/Kd^{Fe}) decreases from $5.1 \cdot 10^3$ for DHDECMP to $2.6 \cdot 10^2$ and 6.1 for HHDECMP and DHDECMPO, respectively, during the extraction from 0.5 *M* HNO_3 with 0.5 *M* p-diisopropylbenzene solutions of these reagents.[77] Introducing as substituents at phosphorus atoms parallel with phenyl: hexyl-(HPhDECMPO), octyl-[OPhD(IB)CMPO], and 6-methyl heptyl-[6MHPhD(IB)CMPO], i.e., substituents, decreasing P=O group basicity permits to synthesize reagents possessing high extraction properties towards TPE during extraction from 1 to 6 *M* HNO_3 and at the same time does satisfactory

Table 6
IMPORTANT CARBAMOYLMETHYLPHOSPHONATES AND CARBAMOYLMETHYL PHOSPHINE OXIDES FOR EXTRACTION OF TPE

Compound	Acronym*	Extractable species	Aqueous system	Ref.
$(C_6H_{13}O\text{-})_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N(\text{-}C_2H_5)_2$	DHDECMP	Am, Cm, Bk, Cf, Es, Fm	0.5—5 *M* HNO_3	74, 77, 82
		Am, Cm, Bk, Cf, Es, Fm	0.5—5 *M* $LiNO_3$	76
$(C_4H_9O\text{-})_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N(\text{-}C_2H_5)_2$	DBDECMP	Am	0.01—0.1 *M* NH_4SCN	78
		Am	0.1—10 *M* HNO_3	74, 82
$(C_4H_9O\text{-})_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N(\text{-}C_4H_9)_2$	DBDBCMP	Am	0.1—10 *M* HNO_3	74, 82
$(C_6H_{13}O\text{-})_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N(\text{-}C_4H_9)_2$	DHDBCMP			74, 75
$(C_6H_{13}O\text{-})_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N(\text{-}C_4H_9)_2$	DHD(IB)CMP	Am	0.1—10 *M* HNO_3	74, 82
		Am	0.01—0.1 *M* NH_4SCN	78
$(C_8H_{17}O\text{-}_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N(\text{-}C_4H_9)_2$	D(EH)D(IB)CMP	Am	0.1—10 *M* HNO_3	74, 82
$(C_6H_{13}O\text{-})_2(O)P\text{-}(CH_2)_2\text{-}C(O)\text{-}N(\text{-}C_2H_5)_2$	DHDECEP	Am	0.5—5 *M* $LiNO_3$	76
		Am	0.5—5 *M* HNO_3	76
		Am	0.01—0.1 *M* NH_4SCN	78
$(C_6H_{13}O\text{-})(C_6H_{13})(O)P\text{-}CH_2\text{-}C(O)\text{-}N(\text{-}C_2H_5)_2$	HHDECMP	Am	0.01—1 *M* HNO_3	77
		Am, Cm	0.1—6 *M* HNO_3	79, 80
$(C_6H_{13})_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N(\text{-}C_2H_5)_2$	DHDECMPO	Am	0.01—1 *M* HNO_3	77
		Am, Cm	0.1—6 *M* HNO_3	79, 80
$(C_6H_{13})(O)P\text{-}CH_2\text{-}C(O)\text{-}N(\text{-}C_4H_9)_2$	DHDBCMPO	Am	0.01—1 *M* HNO_3	77
$(C_6H_{13})_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N[\text{-}CH_2CH(CH_3)_2]_2$	DHD(IB)CMPO	Am	0.01—1 *M* HNO_3	77, 81
$(C_6H_{13})_2(O)P\text{-}CH_20C(O)\text{-}N[\text{-}CH(CH_3)C_2H_5)]_2$	DHD(SB)CMPO	Am	0.01—1 *M* HNO_3	77
$(C_6H_{13})(C_6H_5)(O)P\text{-}CH_2\text{-}C(O)\text{-}N(\text{-}C_2H_5)_2$	HPhDECMPO	Am	0.1—6 *M* HNO_3	79
$[(CH_3)_2CH(CH_2)_5](C_6H_5)(O)P\text{-}CH_20C(O)\text{-}N(\text{-}C_2H_5)_2$	6-MHPhDECMPO	Am	0.1—6 *M* HNO_3	79
$(C_8H_{17})(C_6H_5)(O)P\text{-}CH_2\text{-}C(O)\text{-}N[\text{-}CH_2\text{-}CH(CH_3)_2]_2$	OPhD(IB)CMPO	Am	0.1—6 *M* HNO_3	79—81
$[(CH_3)_2CH(CH_2)_5](C_6H_5)O)P\text{-}CH_2\text{-}C(O)N[\text{-}CH_2\text{-}CH(CH_3)_2]_2$	6-MHPhD(IB)CMPO	Am	0.1—6 *M* HNO_3	79
$[C_4H_9(C_2H_5)CHCH_2](C_6H_5)(O)P\text{-}CH_2\text{-}C(O)N[CH_2CH(CH_3)_2]_2$	2-EHPhD(IB)CMPO	Am	0.1—6 *M* HNO_3	79
$(C_6H_5)_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N[\text{-}CH_2CH(CH_3)_2]_2$	DPhD(IB)CMPO	Am	0.1—6 *M* HNO_3	81
$(C_6H_5)_2(O)P\text{-}CH_20C(O)\text{-}N(C_2H_5)_2$	DPhDECMPO	Am, Cm, Bk, Cf	1—15 *M* HNO_3	70—72
$(C_6H_5)_2(O)P\text{-}CH_2\text{-}C(O)\text{-}N(C_4H_9)_2$	DPhDBCMPO	Am, Cm, Bk, Cf	1—15 *M* HNO_3	70—72
$(C_6H_{11})_2\text{cyclo}(O)P\text{-}CH_2\text{-}C(O)\text{-}N(C_2H_5)_2$	DH(cyclo)DECMPO	Am, Cm, Bk, Cf	1—15 *M* HNO_3	70—72
$(C_4H_9)_2(O)P\text{-}CH_2\text{-}(C(O)\text{-}N(C_2H_5)_2$	DBDECMPO	Am, Cm, Bk, Cf	1—15 *M* HNO_3	70—72
$(C_2H_5)(C_6H_5)(O)P\text{-}CH_2\text{-}C(O)\text{-}N(C_2H_5)_2$	EPhDECMPO	Am, Cm, Bk, Cf	1—15 *M* HNO_3	70, 72

- CMP, carbamoylmethylphosphonate; CEP, carbamoylethylphosphonate; CMPO-carbamoylmethyl phosphine oxide; DB, dibutyl; DE, diethyl; DH, dihexyl; DH(cyclo), dihexyl (cyclo); D(EH), di(2-ethylhexyl); D(iB), di(isobutyl); DPh, diphenyl; D(SB), di(sec-butyl); 6-MH, 6-methylheptyl; 2-EH, 2-ethylhexyl; E, ethyl; H, hexyl; Ph, phenyl; O, octyl.

selectivity.[79] Branching of substituents at phosphorus atoms [reagents DHDECMPO and D(EB)DECMPO] leads to a significant decrease of reagent extraction capacity, but its selectivity keeps on the same level.[77] The nature of substituents at nitrogen atom does not affect extraction properties of reagent, but tells on its solubility. Thus, reagents DPhDECMPO and DPhDBCMPO,[70] as well as DHD(SB)CMPO, DHDBCMPO, and DHD(IB)CMPO,[77] having the same substituents at P, but different at *N*(ethyl, butyl, and *sec*-butyl, butyl, isobutyl, respectively), differ negligibly by their extraction properties towards TPE, but differ considerably by solubility in organic diluents. Reagent DPhDBCMPO is well dissolved in $CHCl_3$, dichloroethane, 1,2,4-trichlorbenzene (TCB), *o*-dichlorbenzene (O-DCB), benzene, CCl_4, perchloroethylene, diethylbenzene, *o*-xylene, and methylisobutylketone, and reagent DPhDECMPO in only $CHCl_3$ and dichloroethane. Chmutova et al.[72] have shown, that for quantitative americium isolation from 3 $M\,HNO_3$, it is necessary to use DPhDBCMPO solutions in organic diluents of the following concentrations: 0.3 *M*, O-DCB; 0.4 *M*, CCl_4; 0.5 *M*, TCB; 0.6 *M*, $CHCl_3$ and *o*-xylene. DBDECMP and DHDECMP are the most often used extractants for practical purposes among those presented in Table 6, mainly for trivalent TPE isolation from acidic high active waste of fuel elements treatment.[73-75,83-87] However, these reagents have some disadvantages: the former is well dissolved in diluted acids, which leads to its substantial waste; on the contrary, the latter is badly dissolved in acids, but its purification from acid admixtures, keeping TPE in organic phase during the reextraction, is quite complicated. So, lately, the possibility of using for group isolation of U, Np, Pu, Am, and Cm from high radioactive liquid solution after Purex process of 0.4 *M* OPhD(IB)CMPO diethylbenzene solution is being studied. It is important to note that in this case there is no necessity to stabilize plutonium in +4 oxidation state, since tri- and hexavalent actinides are extracted with enough great distribution coefficients too.[80] Yamada et al.[88] have elaborated on the method of americium isolation and purification from the waste, forming in the process of plutonium recovery. They use the extraction chromatography, when extractant was sorbed on inert support Amberlite-XAD-4. The method arranges Am separation from Al, Ca, Cu, Fe, Pb, Mg, Pu, K, Na, Zn, and Cl,F ions.

Bidentate organophosphorus compounds have been studied as donor-active admixtures in a number of works. Thus, Myasoedov et al.[89,90] have investigated synergetic extraction of Am from 0.1 $\div$ 1 $M\,HNO_3$, using the chelate-forming reagent 1-phenyl-3-methyl-4- benzoylpyrazolene-5 (PMBP) and some diphosphine dioxides as donor-active additives. A considerable synergetic effect equal to 10^4 has been found for VPhDPO-*cis* and to 10^3 for MPhDPO. The usage of the mixture of PMBP with VPhDPO-*cis* or MPhDPO in chloroform permits the carrying out of quantitative Am isolation from 0.1 to 1 $M\,HNO_3$. Navratil et al.[91-94] have studied a synergetic americium extraction from 0.35 and 7 $M\,HNO_3$ by the mixture of reagents: tri-*n*-butyl phosphate (TBP), trioctylphosphine oxide (TOPO), dibutyl-butylphosphinate (DBBP), and dibutylphosphonate (DBP) in the presence of some carbamoylphosphonates (DHDECMP, DBDECMP) and carbamoylphosphine oxide [OPh(IB)CMPO]. Though the synergetic effect found in this system has not been very high, the application of extractant mixture permits carry out of TPE extraction using smaller concentrations of expensive bidentate organophosphorus reagents, and above all, to use as solvents kerosene and *n*-dodecane as diluents. They have proposed to use the mixture of reagents DPhD(IB)CMPO and TBP in decalin for the group isolation of U, Np, Pu, Am, and fission products from high acidic solutions (5 $M\,HNO_3$) after Purex process in the variant of extraction chromatography. Americium isolation is equal to 99.8%.[81]

2. *Extraction from Alkaline Solutions*

Alkaline solutions are widely adopted in the process of metal isolation from various materials and in a number of cases provide more complete, in comparison with acid decomposition, transport of them in solution. So, the task of isolation, separation, and concentration of elements, including actinides, from alkaline media is very important.

Extraction from basic media is complicated by formation of slightly soluble precipitates. On the other hand, many elements can exist in alkaline solutions in the form of stable soluble complexes, which under appropriate conditions may be transferred into an organic phase. Myasoedov and Karalova[58,95-98] have found that it is possible to extract many metals from very alkaline media using quaternary ammonium bases and 4(α,α-dioctylethyl)pyrocatechol (DOP). It has been found that the chemism of extraction strongly depends on the nature of the extractant. Aliquat 336 extracts metals into organic phase in the form of an ion associate, the anionic part of which is the hydroxocomplex of the metals or metal compound with complex-forming ligand, and the cationic part is the extractant. α-Hydroxycarboxylic or aminopolyacetic acids as complex-forming agents are used to keep the hydrolyzable elements in aqueous phase in soluble form in alkaline solutions. Alkylpyrocatechol extracts actinides and lanthanides from alkaline solutions in the form of chelates.[97]

Since TPE in a trivalent state form hydroxocomplexes of various composition in solution depends on OH-ions concentration, and hydrolyzed forms demonstrate less reaction capacity, their extraction by Aliquat 336 with alkaline concentration increasing usually decreases.[96] At the same time DOP isolates quite completely microquantities of noticed elements even in the absence of complex-forming reagents in aqueous phase, but only from just prepared alkaline solutions.[98] In order to suppress hydrolysis and to increase the selectivity of elements extractive isolation, different complex-forming reagents, presented in Table 7, are employed. In this table the conditions of americium and europium maximum extraction by different extractants are also reported.[97,99]

It is seen from these data that the nature of complex-forming ligands considerably influences americium and europium extraction from alkaline solutions. Undoubtedly, DOP is a more effective extractant than Aliquat 336, since it permits not only displacement of the extraction in the high basic area, but increases considerably the selectivity of the isolation of these elements, especially the usage of DTPA[98] and DTPMP[99] as complex-forming ligands. TPE and REE with most noticed reagents form quite stable compounds, which do not change under prolonged storage of alkaline solutions.

Extraction from alkaline solution solves some practical problems. With the use of Aliquat 336, it is possible to perform group concentration of actinides and lanthanides in a trivalent state, as well as the separation of these elements in different oxidation states. During Ac, Th, Pa, U, Np, Pu, Am, and Cm extraction with Aliquat 336 from alkaline solution in the presence of tartaric acid, as well as other complex-forming reagents, the following order of elements extraction is established: Me(III) > Me(IV) > Me(V) > Me(VI).[97] Since hexa-, penta-, and tetravalent elements are extracted less than trivalent ones, it is possible to obtain in these systems significant separation factors of pairs Am(III)-U(VI) ($\approx$100), Ac(III)-U(VI) (100), and Am(III)-Pu(IV) (75).

As far as trivalent TPE and REE separation are concerned, alkylpyrocatechol has an advantage,[100] since in the system of Aliquat 336, the separation factor of europium and americium does not exceed 4.[95,101] Increase of alkaline concentration in the solution does not adequately affect trivalent TPE and REE extraction by alkylpyrocatechol. Distribution coefficients of americium and curium increase slowly with alkaline concentration increases, when those of REE increase very sharply.[100] Maximum separation factor of the Eu-Am pair, equal to 70, is obtained in the system NaOH-DOP-DTPP.[99]

Table 7
COMPLEX-FORMING REAGENTS USED IN EXTRACTION OF THE ELEMENTS FROM ALKALINE SOLUTION[97,99]

Reagents	Concentration of NaOH, M, for max. extraction of Am and Eu	Extractants
Glyceric acid	<0.25	Aliquat 336
Gluconic acid	<0.25	Aliquat 336
Tartaric acid	0.1—0.5	Aliquat 336
	1.0—8.0	DOP
Trioxyglutaric acid	0.05—0.6	Aliquat 336
Hydroxyethyliminodiacetic acid (OEIDA)	0.1	Aliquat 336
Hydroxyethylethylendiaminotriacetic acid (OEDTA)	0.05	Aliquat 336
Hydroxyethyldiethylenetriaminetetraacetic acid (OEDTTA)	0.05	Aliquat 336
Hydroxydiaminepropanetetraacetic acid (ODPTA)	0.05—0.8	Aliquat 336
Dihydroxydiaminebuthanetetraacetic acid (DOBTA)	0.05—1.0	Aliquat 336
Hydroxyphenyliminodiacetic acid (OPIDA)	0.05—1.0	Aliquat 336
Diethylenetriaminepentaacetic acid (DTPA)	Eu: <0.2	Aliquat 336
	Am: 4.0—8.0	DOP
	Eu: 2.0—8.0	DOP
Ethylenediaminetetramethylphosphonic acid (EDTMPA)	0.05—0.6	Aliquat 336
	Eu: 2.0	DOP
	Am: 4.0	DOP
Ethylenediaminetetraacetic acid (EDTA)	<0.5	Aliquat 336
	>2.0	DOP
Diethylenetriaminepentamethylphosphonic acid (DTPMP)	0.05—0.6	Aliquat 336
	Am: >4.0	DOP
	Eu: <2.0	DOP

The investigation of TPE behavior during extraction from DTPA alkaline solutions shows that distribution coefficients decrease in the row of Bk > Cf > Am > Cm, americium and curium being extracted worse from NaOH solution of concentration >2 *M* than REE, and berkelium, on the contrary, better. It is worth mentioning that distribution coefficients of berkelium, like those of cerium, are very close to distribution coefficients of tetravalent plutonium.

Besides TPE, Fe(III), Ru(III), Zr(IV), Th(IV), Pu(IV), Pa(V), Nb(V), U(VI), and Cs(I) extraction with DOP from alkaline solutions are also studied. In contrast to TPE and REE, iron (III) both as indicator, and in macroquantities, extracts with very high distribution coefficients in the whole range of studied NaOH concentration. Tetravalent elements in the concentration interval from 0.5 to 3 *M* have much higher distribution coefficients than trivalent Am and Cm. Penta- and hexavalent elements are extracted with smaller distribution coefficients than tetravalent ones, and the extent of its isolation is not practically dependent upon alkaline concentration. The difference in Pa(V), Nb(V), U(VI), and Am(III) extraction becomes significant at alkaline concentrations more than 4 *M*, i.e., in conditions of maximum TPE isolation. Cesium which in the whole studied interval of alkaline concentration is negligibly extracted with DOP solution, behaves analogously. The data obtained permit a conclusion to be drawn, that actinides are extracted with DOP solution in the following consequence: Me(IV) > Me(III) > Me(V) > Me(VI).[100]

Extraction from alkaline solutions with DOP is very perspective for the separation of many elements. In particular, there is a satisfactory separation of TPE from rare-earth elements — fission products: separation factor of the most extractable of REE-cerium and the less extractable of TPE-curium are equal to ∼ 300. It is also possible to obtain in this system a good separation of Am-Cm and transcurium elements. For example, separation factor of berkelium and curium exceeds 400. Further increase of TPE purification from admixtures is expected to take place during repeated separation operations. DOP permits the separation of other elements, in particular zirconium and niobium. Extraction with DOP is used successfully for americium and plutonium isolation from salt solutions, as well as on the stage of deep purification of americium from iron (separation factor of Fe-Am is equal to n (·) 10^4). It is worth adding that during americium isolation from alkaline salt solution by DOP, there is not only its separation from accompanying elements, but absolute concentration also takes place.[102]

3. *Extraction of Am(V, VI) and Bk(IV)*

The greatest effect of extraction methods of TPE separation takes place at the use of unusual oxidation states of some of these elements, in particular americium and berkelium. Several methods of preparing Am(V) in solutions are known and are described in the literature.[2,42] A convenient method of electrochemical production of Am(V) by reduction of Am(VI) in 1 to 10 *M* NaOH at an anode potential of 0.2 V,[30] in 1 *M* K_2CO_3 at a potential of 0.54 V,[28] and in diluted $HClO_4$ + H_3PO_4 solutions[105] has been worked out. Americium (V) is stable in diluted H_3PO_4 solutions and reduced slowly to americium (III) by radiolysis products with a rate of about 0.2%/hr. In weak acid solutions, Am(V) is generally more stable than Am (VI)[106-110] but with increasing acidity, the stability of Am(V) falls due to the increasing disproportionation rate (the same effect is observed with increasing PO^{3-}_4 ion concentration.[111] Trace amounts of Am(V) are reduced quickly in the presence of CH_3COO^-, SO_4^{2+}, Cl^-, BrO_3^-, I^-, SO^{2-}_3 ions and H_2O_2.[110]

A number of extraction methods of americium separation from other TPE and fission products, based on the utilization of the Am(V) chemical properties, have been developed. Such methods are especially promising for the separation of americium (V) tracers for further determination.[112,113] Am(V) can be recovered from aqueous solutions by the extraction with thenoyltrifluoroacetone (TTA),[114] 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP),[115] HDEHP,[116] and with pyrrolidinethiocarbaminate.[117] Am(V) extraction with HDEHP (both trace and marco Am quantities) is carried out from the acetate solutions with pH = 5 to 6 ($K^{Am(V)}_d$ ∼30). The separation factor of Am(V) and Cm(III) during the extraction with PMBP or HDEHP is about $2.5 \cdot 10^3$.[116,118] Am(V) can be separated from actinide and lanthanide elements by extractions with mixtures of picrolonic acid and sulfoxides from nitric acid solutions, as Am(V) extraction is negligible in such conditions.[119]

Recently, the following new methods producing Am(VI) have been worked out: in HNO_3 solutions by oxidation with sodium bismuthate;[120] in phosphoric acid media by the electrochemical method[8,122] and oxidation with the mixture of Ag_3PO_4 + $(NH_4)_2S_2O_8$;[123-125] in $HClO_4$ solutions with a small addition of H_3PO_4 by electrochemical oxidation;[105] in HNO_3 solutions with an addition of $K_{10}P_2W_{17}O_{61}$ — by the mixture of $AgNO_3$ + $(NH_4)_2S_2O_8$[126] or by $Na_2S_2O_8$ at heating;[127] in 5 *M* NaOH solutions;[30] and in acetic solutions[26] by electrochemical oxidation.

The oxidation of americium to Am(VI) is used in the methods of its separation from other elements and determination. When concentration of the hexavalent americium is ≥2 mg/m*l*, it can be extracted by solutions of HDEHP,[129-132] TOPO,[132] di-(2,6-dimethyl-4-heptyl) phosphoric acid,[133] and by mixture of HDEHP and TBP[134] or TOPO in cyclohexane.[135,136] Using mixtures of PMBP and TOPO[113] and TTA and TOPO[135] in cyclohexane as extractants, Am and Cm can be efficiently separated. Americium is previously oxidized up to the hexavalent state: during extraction it reduces to the unextracted pentavalent state, and curium and other trivalent elements with a high distribution coefficient transfer into organic phase. The method provides quantitative extraction of americium and a high degree of its purification from curium ($>10^3$) and fission products.[113] Using electrochemical oxidation of americium instead of oxidation by persulfate ions, the radiometric determination of americium becomes more exact.[105]

Recently, some new methods of Bk(III) oxidation have been suggested, many of which have been tested on large quantities of Bk. Berkelium can be oxidized by ozone in HNO_3,[137-139] K_2CO_3,[138] and H_2SO_4[140] media; by $KBrO_3$ on heating or without heating in HNO_3, H_2SO_4, and HCl solutions (not completely);[137,141,142] by AgO or the mixture of $AgNO_3 + (NH_4)_2S_2O_8$ in solutions of HNO_3[143-146] and H_2SO_4;[147] by $(NH_4)_2S_2O_8$ on heating; by $K_2Cr_2O_7$, $NaBiO_3$ and PbO_2 in HNO_3 solutions;[142,145] by the electrochemical method in HNO_3 solutions,[21,139,148,150] K_2CO_3,[21] H_2SO_4,[16] and $K_{10}P_2W_{17}O_{61}$.[24] In acidic solutions in the presence of such oxidizers as $KBrO_3$, $(NH_4)_2S_2O_8$, ozone, Bk(IV) is stable during several days[139,141,143] and in pure solutions of HNO_3 and H_2SO_4 it reduces as a result of its interaction with radiolysis products and water at the rate of 15 to 20%/hr.[16,139]

Lately, for the selective isolation of berkelium, a number of effective methods based on the extraction of berkelium in the tetravalent state have been elaborated. The conditions of tetravalent berkelium extraction by HDEHP[137,144,145,153,154,157,158] and its reextraction from the organic phase have been studied in detail.[157] Trioctylphosphine oxide and triphenylphosphine oxide (TPPO) solutions extract Bk(IV) quantitatively from 1 to 12 *M* HNO_3,[158,159] as well as TBP solutions from 2 to 16 *M* HNO_3.[160,161] The extraction of Bk(IV) by TOPO from sulfuric acid solutions is less efficient, and TBP solutions practically do not extract Bk(IV) at all.

The high molecular amines are also used for Bk(IV) extraction. Milyukova et al. have studied the influence of the concentration of acids and the nature of the oxidizer and the diluent on the completeness of Bk(IV) extraction by trioctylamine (TOA)[147,162] and by Aliquat 336.[163] Potassium bromate and bichromate as well as the mixture of silver nitrate and ammonium persulfate[143] have been used as oxidizers in those works. The quantitative extraction of berkelium after its oxidation by bichromate ions of 0.4 *M* TOA in CCl_4 takes place in 10 *M* HNO_3. The use of the mixture of silver nitrate and persulfate ions for the extraction by TOA makes it possible to separate berkelium from cerium, as in these conditions berkelium reduces to the trivalent state and remains in the aqueous phase. During the extraction of berkelium by 30% Aliquat in CCl_4 from 10 to 12 *M* HNO_3, after its oxidation by bichromate ions, a separation from TPE and lanthanides is achieved.[163]

In the presence of heteropolianions, Bk(IV) is quantitatively extracted from nitric acid solutions by the primary, secondary, and tertiary amines and the quaternary ammonium bases. Heteropolianions not only stabilize the tetravalent berkelium, but also enter the composition of the extracted compounds.

Various reducing agents are used to reduce Bk(IV) to Bk(III) for Bk(IV) reextraction from HDEHP solutions: hydrogen peroxide,[137,142] hydroxylamine, ascorbic acid[137] in HNO_3 solutions, and hydrazine-nitrate.[157]

B. Sorption Methods

Sorption methods are widely employed for TPE isolation, recovery from irradiated materials, and their separation from fission products and miscellaneous impurity in order to obtain highly pure samples of these elements reserved for medical purposes and physics investigations, as well as to separate TPE from different natural objects with the purpose of their quantitative determination. These methods possess a number of advantages. It is worth noting first of all their effectiveness of TPE separation, the simplicity of the carrying out of the process at a distance with high radioactive samples in shielded hot boxes and cells.

TPE behavior on organic ion exchangers, both anion and cation exchange resin, is most carefully studied. Inorganic sorbents attract researchers' attention first of all by their high radiation and thermal stability. Paper and thin-layer chromatography, as well as chelate sorbents and solid extractants (TVEX), are less employed for the purposes of TPE separation and concentration.

The data, available in literature, are concerned in general with the sorption and separation of TPE in the trivalent state. The behavior of these elements in unusual oxidation states has not been studied enough at present.

1. Ion-Exchange Chromatography

The method of ion-exchange chromatography is known to have played an important role in TPE discovery, since their isolation and identification have been carried out by beforehand-predicted positions on elution curves. Great amounts of data, concerning TPE behavior on cation and anion exchangers in inorganic acids solutions in the presence of different complex-forming substances, as well as the application of these systems for the resolution of many practical problems, have been summarized before in known monographs.[2,42] Recently, the interesting data concerning chromatography usage for isolation, concentration, and separation of great quantities of TPE in conditions of high radioactivity, have been published.[86,92,165-171] The application of mixed organic-aqueous solutions as eluents and high pressure effective chromatography open up new possibilities in employment of these methods.

The replacement of part water for organic diluents has a strong influence on ion state in solutions and the state of ion-exchanger, which permits the separation and isolation of elements in more optimum conditions. Besides, alcohol application as organic additives leads to suppression of solution radiolysis which has a great importance at TPE isolation, since they are α-emitters with a great specific activity. Behavior of Am, Cm, Bk, Cf, and some other elements on cation and anion exchangers in aqueous-alcohol solutions of inorganic acids, as well in solutions of salts and complex-forming reagents, is systematically studied.[172-188] The most effective results have been obtained in the system anionite-alcohol solutions of nitric acid.

Transplutonium elements are known to not be practically sorbed by anion exchangers from aqueous solutions of acids. A significant sorption is observed only in concentrated solutions of hydrochloric acid (≥ 11 *M*), lithium chloride, and nitrate salts.[42] TPE distribution coefficients reach the values of 10^2 to 10^3 in solutions containing 80 to 90% alcohol at acid concentrations of 0.1 to 1 *M*. Effectiveness of TPE sorption from diluted solutions of nitric acid increases with the growth of alcohol content in the solution, as well as with the augmentation of alcohol hydrocarbon chains. Am, Cm, Bk, and Cf sorption at constant alcohol content increases with the growth of concentration of nitric acid and nitrate salts, as well as divinylbenzene (DVB) content in resin.[192] In the row of TPE, the sorption decreases with the increase of ordinal number of elements. Macroquantities of sorbed elements affect suppressively the sorption; however, the effectiveness of separation does not decrease, if the amount of macrocomponent does not exceed 2% of the total capacity of anion exchanger.[187,188] It is better to carry out Am and Cm separation on the anionites with a small content of DVB ($\sim$4%) by 0.5 to 0.75 *M* HNO_3 solutions in the presence of 80% CH_3OH, and their preconcentration on the resins, containing 8% of DVB from HNO_3 solution ≥ 0.5 *M*, with alcohol content $\geq$90%.[182]

During the sorption on anion exchangers from 0.5 to 1 *M* HNO_3 solutions in 90%

alcohol TPE easily separate from elements, which are badly sorbed in these conditions (the elements with $Z < 56$, as well as Hf, Ta, Re, U, Np(V)). TPE separation from fission rare-earth elements can be carried out at column washing by 0.5 *M* NH_4SCN solution in 80% alcohol,[178,181,186] and the separation of TPE remaining on the resin is performed by 0.5 *M* HNO_3 solution in the presence of 85% alcohol. The system of anion exchanger-alcohol solutions of nitric acid is successfully employed for the isolation of separate TPE in a highly pure state,[183,185] as well as for their isolation from different natural objects with the aim of the following radiometric determination.[183,184]

The combination of several methods is used in a number of works in order to isolate TPE in a chemically and radiochemically pure state enough for alpha spectrometric analysis. Thus, Yamato,[195] after transferring analyzed samples in solution, carried out the precipitation of TPE on calcium oxalate, then on $Fe(OH)_3$ precipitate, and finished the isolation of Am and Cm on anionite with the use of water-alcohol solutions. Fukai et al.[196,197] from the Monaco oceanographic museum suggested the method of Am and Cm determination in environment objects. In this method they used two columns with anion and cation exchangers with water-alcohol eluents and preliminary extraction of Am and Cm with HDEHP and dibutyl-*N,N*-diethylcarbamoylphosphonate. The method of Am determination in natural objects of small weight samples (~2 g), based on Am isolation on cation exchanger in HCl solution and then on anion exchanger in water-alcohol solution of nitric acid with the following electrodeposition of isolated Am and spectrometric analysis, provides 80% recovery of analyzed americium.[198]

They obtain high separation factors of Am-Cm and Cm-Cf, equal to 6 and 4, respectively, by α-hydroxyisobutyric acid introduction in water-alcohol solutions of nitric acid.[189-191] High extent of berkelium purification from cerium can be achieved on anion exchanger with the use as eluent of 0.25 to 0.75 *M* HNO_3 solution, containing 80% of methyl or ethyl alcohol.[195]

TPE *preconcentration from* 2 *to* 6 *M* HCl *solutions in the presence of more than* 40% of alcohol can be performed on cation exchangers with high content of DVB. Group separation of TPE from REE on cation exchanger is carried out in 8 to 10 *M* HCl solutions, containing 60 or 40% of alcohol, respectively.[180]

The use of high pressure effective chromatography is the essence of the other direction of the augmentation of effectiveness of ion-exchange elements separation. This method, originally suggested for the separation of very close properties in biological substances, beginning since 1967, is successfully employed for TPE separation. Recently, Campbell has summarized the achievements in this branch.[200] The advantage of this method is the following: due to very small dimensions of resin fraction (20 to 40 μm), the separation is carried out under the pressure at very high rates of eluents (5 to 25 mℓ $cm^{-2}min^{-1}$) on the columns with a diameter of ~2.5 cm and of 1.2-m long. The time necessary for TPE separation from Am to Fm reduces by 10 to 100 times in comparison with ordinal chromatography. This permits the successful use of high pressure effective chromatography for the separation of great quantities of high radioactive isotopes Am, Cm, Bk, Cf, Es, and Fm,[201-205] including short-life isotopes ^{242}Cm and ^{252}Cf, possessing high specific radioactivity. The influence of different factors on the effectiveness of TPE separation by high pressure effective chromatography is discussed in References 206 and 207.

2. *Inorganic Sorbents*

There are a few number of works concerning the application of different inorganic sorbents for TPE sorption and separation from inorganic acid and salts solutions. These works are summarized in reviews of Barsukova and Myasoedov[208] and Schulz et al.[209] The use of unusual oxidation states of these elements proves to be the best perspective for TPE separation on inorganic sorbents.

Moore[210] has used zirconium phosphate for the elaboration of a new method of americium separation from curium and accompanying elements in nitric acid solutions. The method is based on negligible Am(V) sorption on zirconium phosphate from diluted nitric acid solutions, while curium and other actinides and lanthanides, as well as cesium, are quantitatively sorbed in these conditions. The author has obtained the following coefficients of purification of Am from: Cs $> 5.5 \cdot 10^5$; Eu $> 2 \cdot 10^5$, U $\sim 3 \cdot 10^2$; Pu ~ 8.5; Cm $\sim 2.5 \cdot 10^5$; Bk $- 2.1 \cdot 10^2$; Cf $> 4.5 \cdot 10^5$.

Shafiev et al.[211] have applied zirconium phosphate for the separation of Am(V,VI) and Cm(III)-Pm(III) in nitric acid solutions with pH = 1.5 to 2.5. In these conditions Am passes through the column, and Cm(III)-Pm(III) are sorbed by zirconium phosphate. Cm(III)-Pm(III) are eluated by 1 *M* nitric acid solution. The application of zirconium phosphate for the separation of milligram quantities of americium and curium is described in the literature.[212] Shafiev et al. have oxidized Am(III) to Am(VI) in 0.1 *M* nitric acid solution by 0.2 to 0.4 *M* ammonium persulfate at 90 ± 1°C. Am(VI) has been completely reduced to Am(V) during solution cooling until reaching room temperature after which solution acidity has been adjusted to pH = 2.5 by acetate buffer. This solution has passed through the column, with zirconium phosphate Am(V) overtraveling through the column, and then Cm being desorbed by 1 *M* HNO_3 solution. Curium content in americium fraction has consisted from 0.01 to 0.5 wt %; americium content in curium fraction has been somewhat higher — from 0.2 to 1.0 wt %— and this has been conditioned to the authors' opinion by autoreduction of Am(V) to Am(III). Radiochemical purity of isolated americium has reached more than 99%; curium has been polluted by americium in a higher degree. The simple and effective method of berkelium isolation from a complex mixture of other TPE and fission elements,[213] and of continuous isolation of isotopical pure ^{249}Cf, a product of ^{249}Bk decay,[214] with the use of zirconium phosphate, has been suggested.

The possibility of Am(III) separation from Am(V) by sorption on zirconium hydroxide from weak acid solutions has been demonstrated in the literature.[216] The same authors have performed the separation of the pairs U-Pu, U-Am and Np-Pu, Np-Am on iron hydroxide from 1 *M* ammonium nitrate solutions in 0.2 *M* hydrogen peroxide at pH > 12.5 and 13.0, respectively. Separation of americium and curium is possible at Cm(III) and Am(V,VI) sorption on zirconium hydroxide from 1 *M* ammonium nitrate solution in pH intervals equal to 5.3 ÷ 5.8. Purification factors of the elements staying in the solution are equal to 10^2 to 10^3, and those of the elements taken by precipitate are equal to 20 to 30.

Shulz et al.[209] have used calcium hydroxyapatite and sodium titanate for the purification of waste solution from radioactive impurities. The possibility of Am and Cm separation from lanthanides on sodium titanate, niobate, and zirconate has been studied in the same work.

3. Separation on Chelate Sorbents and TVEX

They introduce different chelate groups in order to increase sorbents selectivity. Myasoedov and Molochnikova[218] have investigated the possibility of the application of chelate resin, obtained on the base of aminopolystyrene and arsenazo-I, for Am and Cm isolation from HCl, HNO_3, and H_2SO_4 solutions. Practically complete sorption of studied elements ($Kd \geqslant 10^3$) takes place at acid concentration <1 *M*, which permits TPE concentration from large volumes. The separation of TPE from Fe, Cs, and Ru takes place during their sorption on chelate resin from HNO_3 solutions; other elements — Zr, Nb, and Pu — are sorbed with TPE. TPE separation from Zr, Nb, and Pu is carried out during resin washing by 0.5 *M* $H_2C_2O_4$ solution. Other types of chelate resins, including phosphorus-containing resins, have been investigated for TPE isolation.[219] Separation of Am(V) and Cm(III) on DOWEX-A1x8 has been studied in the literature.[136] It has been proved that Am and Cm separation coefficients strongly increase with pH augmentation from 2.5 to 3.2, with temperature decreasing and the increasing of resin weight.

The new type of sorbent, obtained by extractant introducing in polymer matrix during the synthesis, has recently been suggested in the U.S.S.R.[221] The sorbents have been named solid extractants (TVEX) and have been employed for isolation from solutions of some elements, including actinides.[222] The possibility of TVEX application for isolation and separation of transuranium elements from the solution with high salt background has been investigated. These TVEX have contained the following organophosphorus compounds: TBP, HDEHP, TBP + HDEHP (1:1), and others. The conditions of group separation of TPE and REE in ammonium thiocyanate solution (8 *M*) in the presence of complexones on TVEX-HDEHP have been found.[223] Bk separation from Cf and Am and Cm and REE is possible in 1 *M* aluminum nitrate solution on TVEX.[224]

C. Methods of Extraction Chromatography

Distribution (extraction) chromatography is one of the perspective and simple method of separation of close in properties elements. This method is widely adopted for TPE isolation, especially for their separation. This method successfully combines the advantages of extraction and chromatography. The separation is based on the difference in ion distribution between two immiscible liquids, one of which is mobile, and the other fixed on carrier. TBP, alkylphosphoric acids, in particular HDEHP, tertiary and quaternary ammonium salts, and a mixture of extractants are used as organic phase during TPE isolation and separation. Siliconized silica gel, fine dispers Teflon®, kieselguhr, diatomite, and glass are used as carriers. Inorganic acids and their salt solutions are used as eluents during TPE separation, and ammonium thiocyanate solutions are used during group separation from rare-earth elements. The data on TPE separation are summarized in the monographs.[42,225]

HDEHP is the most often used extractant. With this extractant usage, applied on different carriers, different methods of americium and curium separation have been elaborated,[235,236] as well as of berkelium (IV)-selective isolation.[237,238] Separation factor of Am(VI) from Cm has formed 2.10^2, and those of Cm from Am 10^2. With pentavalent americium usage, the purification from Cm has been equal to $\sim 5.10^3$; Cm purification from Am being worse, has made up ~ 60.[236] The column with HDEHP sorbed on a granular porous glass support (BiO-Class 500) has been used for ^{248}Cm and ^{252}Cf separation, purification factor of curium being $\geqslant 10^6$.[239] Erin et al.[240] have investigated the effect of some cations (Fe, Co, Cr, Ni, Ti, Zr) on the effectiveness of Cm and Cf separation in the same system and on the extent of their purification.

The mixture of extractants has been used in a number of works in order to increase the effectiveness of TPE separation by the method of extraction chromatography. Thus, the mixture of TTA and dibutyldiethylcarbamoylphosphonate has been used for Cm and Cf separation in the works.[241,242] Gusev et al.[243] have studied the behavior of Am, Cm, Bk, and Cf on the column with silica gel, the mixtures of TBP with TOA or TBP with quaternary ammonium base being applied on it. The mixture of TTA and TBP, as a fixed phase sorbed on a porous Teflon®,[245,246] has been used for the separation of a complex mixture of elements, including Am, Cm, Cf, U, Th, and others, as well as for express (5 min) separation of Am and Eu.[244]

D. Separation in the Gaseous Phase

The obtaining of TPE volatile compounds and their application are some of the interesting and important directions in TPE chemistry. Separation and recovery of elements (especially in trace quantities) for preparatory and analytical purposes, development of gaseous radiochromatographic and mass spectrometric methods of their determination, separation of isotopes, and obtaining metal and oxide films and covers for creation of neutron and other radioactive sources are some of the radiochemical tasks which can be solved on the basis of the application of the volatile TPE compounds. Common TPE compounds such as chlorides and fluorides are not convenient, since they are not very volatile. Perspective is the usage of β-diketonate and metalorganic TPE compounds which are distinguished by their high volatility, i.e., by the essential values of the pressure of the saturated vapor (0.1 to 1 kPa) at moderate temperatures (150 to 250°C). Besides, the β-diketonate complexes are relatively easily synthesized with a quantitative yield, and are less subjected to alterations under the action of oxygen and moisture than the volatile halides, hydrids, carbonyles, metalorganic, and other compounds.

In the recent decade, papers have been published (mainly by Soviet and Japanese authors) in which the obtaining and study of the properties of the volatile β-diketonate TPE complexes are described.[247-257]

In the 3+ oxidation state, transplutonium elements as well as lanthanides form complexes with three bidentate β-diketonate ligands, filling the remained vacancies in the coordination sphere by the molecules of water and compounds with the properties of the Lewis bases.

Though the synthesis of β-diketonates seems to be easy, it presents a rather delicate preparatory task. Therefore, the complications connected with hydrolysis and other complex-forming processes should be considered when the optimal synthesis conditions are being chosen (especially concerning the microamounts of radionuclide compounds).

One of the most widely used methods of synthesis of metal β-diketonates is based on the interaction of salts of metals (acetates, nitrates, chlorides, oxalates) with β-diketonates or their ammonium salts in aqueous or aqua-ethanol solutions. According to the well-known methods of Eisentraut and Sievers,[258] milligram quantities of americium dipivaloylmethanate (4 mg ^{243}Am) were synthesized. After separation of the oily product from the 50% ethanole solution and separation of the excess of dipivaloylmethane (HDPM) by sublimation in vacuum at room temperature, red crystals of Am $(DPM)_3$ were obtained. The analogous compounds of ^{241}Am and ^{252}Cf (the tracer quantities) were obtained with the use of lanthanum and praseodimum as carriers.[248]

Most β-diketonates of TPE and lanthanides are hardly extracted by the nonpolar organic solvents due to the formation of hydrates. Therefore the extraction method, which is especially perspective for the obtaining of microamounts of radionuclide compounds, can be recommended only for synthesis of the adducts of β-diketonates of TPE and lanthanides with donor-active compounds, which are extracted into the most organic solvents with high distribution coefficients.

Adducts of americium (III) hexafluoroacetylacetonates (HFA), TTA, and pivaloyltrifluoroacetonates (PTFA) with TBP, TBPO, TOPO, and dipropylsulfoxides (DPSO), and adducts of curium (III) and berkelium (III) hexafluoroacetylacetonates with TBP have been synthesized with the help of the extraction method.[249-251]

Recently, a new method of synthesis of volatile aqualess metal β-diketonates has been suggested, based on the interaction of different metal compounds (such as the nonvolatile acetylacetonates and tenoyltrifluoroacetonates of TPE and lanthanides chlorides, oxychlorides, nitrates, and hydroxides in the hydrated and the aqualess forms) with β-diketonate vapors.[252,253] This reaction, carried out at high temperatures, allows the synthesis of the volatile compounds and the transfer of them (in most cases quantitatively) into the gaseous phase. Table 8 contains the data on synthesis of volatile β-diketonates, including those for the tracer and microgram quantities of such elements as americium, berkelium, neptunium, and europium. The presence of the ligand vapors in the gaseous phase disturbs the thermic disintegration of metal β-diketonates and

Table 8
CONDITIONS OF SYNTHESIS OF VOLATILE METAL β-DIKETONATES

Element	Amount of element	Initial compound	β-diketone	Temperature (°C) Of saturation of inert gas by β-diketone vapors	Temperature (°C) Of transition of the formed β-diketonates into the volatile phase	Rate of temperature increase (°C/min)	Duration of synthesis (min)	Yield of volatile β-diketonates (%)
^{241}Am (III)	5 μg	TTA	HHFA	50	180•	—	65	98
^{249}Bk (III)	Tracer	TTA	HHFA	45	180—220	3	60	95.5
^{249}Bk (IV)	Tracer	TTA	HHFA	40	180—230	4	55	100
Eu (III)	20 μg	TTA	HHFA	30—50	160—180	5	50	96—100
		AA	HHFA	30—50	160—180	5	40	80
			HPTFA	50—70	180—220	5	60	90
		Oxychloride	HHFA	30—50	160—180	6	90	45
		Hydroxide	HHFA	30—50	160—180	6	90	96
^{239}Np(IV)	Tracer	TTA	HHFA	50	180•	—	65	98
Cu (II)	0.4 mg	Hydroxide	HAA	95	160—210	4	40	80
	0.066 ng	TTA	HAA	95	150—190	4	40	100
Zn (II)	4 mg	Hydroxide	HHFA	50	160—210	4	40	40
^{95}Zr (IV)	Tracer	TTA	HHFA	50	110—140	4	20	100
Fe (III)	0.5 μg	Hydroxide	HHFA	50	150—190	4	50	100
Cr (III)	2.5 mg	Hydroxide	HHFA	50	110—160	4	30	100

• *The synthesis and the transition into the volatile state were conducted at the constant temperature of 180°C.*

allows to quantitatively keep and transport the tracer amounts of radionuclide β-diketonate, which is practically impossible in usual conditions.

TPE β-diketonates, formed by extraction in the hydrated form, have a low thermic stability. Thus, for instance, americium hexafluoroacetylacetonates and pivaloyltrifluoroacetonates transferred into the volatile form in the absence of the donor active admixture, though they undergo considerable disintegration with the formation of the nonvolatile products.[249]

The thermodiagrams of the adducts of americium (III), curium (III), berkelium (III) hexafluoroacetylacetonates indicate the high thermic stability of those compounds. The degree of disintegration of the adducts of americium (III) β-diketonates with TBP increases in the row: $\mathrm{Am\ (HFA)_3 \cdot 2TBP < Am\ (TFA)_3 \cdot 2TBP < Am\ (PTFA)_3 \cdot 2\ TBP}$. Among the studied adducts of americium (III) β-diketonates with TOPO, only $\mathrm{Am\ (HFA)_3 \cdot 2\ TOPO}$ is characterized by a outstanding thermic stability at the temperatures of intensive vaporizing.

The dependence of $\mathrm{Am\ (HFA)_3 \cdot 2TBP}$ stability on americium concentration and the period of time during which the solution was kept in cyclohexane has been studied in the process of its transfer into the volatile phase. It has been established that when ^{241}Am concentration is equal to 0.5 g/*l*, solutions of the compound are stable for 16 days (the dose of the α-radiation being equal to $\sim 5 \cdot 10^{20}$eV), and the radiolytic disintegration is not essential.[250]

Data on the dependence of the pressure of the americium β-diketonate complexes saturated vapor (Psat) upon temperature, taken from the literature, are given in Table 9. The Knudsen effusion method is used for determination of the values of americium dipivaloylmethanates Psat[247] and the flow method with temperature programming was used for the adducts of the americium fluorine-containing β-diketonates with the donor-active compounds.[254]

The sublimation temperature of some actinides, including Am, Cm, and Cf with 2,2,6,6-tetramethyl-3,5-heptahedione, was determined in the literature.[256] The influence of the amount of sample (in trace or in milligram scale) on its sublimation temperature was examined. The sublimation zone temperatures of the actinide chelates were found to be in the following sequence: $\mathrm{UO_2^{2+}}$ > Am(III) Cm (III) > Th(IV), Np(IV), Pu(IV) > Cf(III).

In the row of americium β-diketonate adducts with TBP, the volatility is decreased in the following sequence: $\mathrm{Am\ (HFA)_3 \cdot 2TBP > Am\ (PTFA)_3 \cdot 2\ TBP > Am(TFA)_3 \cdot 2TBP}$, although the compound with hexafluoroacetylacetone is not very volatile. Pivaloyltrifluoroacetone, which contains the tret-butyl and the $\mathrm{CF_3}$ groups, forms a less volatile compound in comparison with hexafluoroacetylacetone and a more volatile compound in comparison with trifluoroacetylacetone.[254]

It was observed on the example of the adduct of americium hexafluoroacetylacetonate with phosphorusorganic compounds that the volatility and the thermic stability of the compounds are decreased with the increase in the electronic-donor ability of the neutral ligands in the row: $\mathrm{Am\ (HFA)_3 \cdot 2TBP > Am\ (HFA)_3 \cdot 2TBPO\ Am\ (HFA)_3 \cdot 2TOPO}$. Among the studied compounds, $\mathrm{Am\ (HFA)_3 \cdot 2DPSO}$ is the most volatile one.

As a result of the study of the behavior of the actinide (and rare-earth) elements β-diketonates in the process of thermogas-adsorption chromatography, the method of ^{243}Am and ^{239}Np separation was suggested, based on the different behavior of americium (III) and neptunium (IV) hexafluoroacetylacetonates, formed by the interaction of tenoyltrifluoroacetonates of those elements with HHFA vapors.

Americium (III) and neptunium (IV) hexafluoroacetylacetonates are precipitated in the column at temperature ranges of 125 to 95 and 90 to 70°C, respectively. Mutual pollution of fractions makes less than 0.1%. The developed method can be recommended for determination of neptunium in americium.

Table 9
THERMODYNAMIC CHARACTERISTICS OF THE PROCESS OF EVAPORATION OF ADDUCTS OF AMERICIUM β-DIKETONATES[247,254,255]

	$1g\,P_{Pa} = B-$				
Compound	B	A	Temperature range (°C)	ΔH (kJ/mol)	ΔS (J/mol.K)
Am $(DPM)_3$	19.884 ± 0.036	8.407 ± 0.494	90—130	160.84 ± 9.44	
Am $(HFA)_3 \cdot 2TBP$	16.06 ± 0.28	6.99 ± 0.10	140—240	133.97 ± 16.74	288.88 ± 4.18
Am $(HFA)_3 \cdot 2TBPO$	19.00 ± 1.66	8.80 ± 0.78	160—220	168.72 ± 15.07	364.25 ± 32.23
Am $(HFA)_3 \cdot 2TOPO$	14.20 ± 0.79	7.72 ± 0.43	240—290	147.79 ± 7.95	274.23 ± 15.07
Am $(HFA)_3 \cdot 2$ DPSO	14.61 ± 1.32	6.22 ± 0.53	105—160	119.32 ± 10.04	293.49 ± 24.70
Am $(PTFA)_3$	13.25 ± 0.37	5.81 ± 0.15	130—175	116.36 ± 2.93	261.67 ± 6.28
Am $(PTFA)_3 \cdot 2TBP$	14.00 ± 2.32	6.27 ± 1.22	165—220	120.16 ± 2.34	257.90 ± 49.82
Am $(TFA)_3 \cdot 2TBP$	21.99 ± 3.25	11.62 ± 1.72	235—282	222.73 ± 29.30	420.35 ± 55.26

Reference 248 contains the data on ^{140}La, ^{241}Am, and ^{252}Cf separation by sublimation of their dipivaloylmethanates in vacuum ($\sim 10^{-4}$ kPa) at 180°C with the subsequent precipitation in the column with temperature gradient. The indicated elements are precipitated in different temperature zones, thus being separated. ^{152}Eu and ^{241}Am dipivaloylmethanates, as well as the adducts of their hexafluoroacetylacetonates with TBP,[250] are precipitated in the neighboring zones and are not separated by the given method.

Practical application of the method of gas-liquid chromatography for separation of microamounts of actinide and lanthanide β-diketonate complexes is limited by a number of difficulties related to the thermic disintegration and the essential sorption of the chromatographed compounds in column. The sorption degree of compounds in column considerably depends on the amount of the injected compound, its concentration in the injected solution, the nature and content of the liquid phase, the nature of the solid support and the temperature. It is shown that the sorption of the compounds partially has a reversible character. When the nonpolar liquid phases are used, the chelate sorption is lower than that in the case of the polar phases, though it still remains quite essential.[255,257,258]

The lowering of the sorption of β-diketonates of metals and their adducts with donor-active compounds in chromatographic column is achieved by the insertion of the isotopic and nonisotopic carriers in it in the form of the corresponding compounds. The application of the gas-carried containing HHFA vapors[260,261] has proved to be more efficient, since it provides for the eluation of microamounts (hundredth parts of a microgram) of compounds from the column. In the conditions of gas-liquid radiochromatography in the helium flow, which contains HHFA vapors, the reproduced chromatograms of the right form of the adducts of americium and curium hexafluoroacetylacetonates with TBP have been obtained for the first time.[255,257] Full separation of ^{241}Am and ^{243}Cm from ^{176}Lu is achieved by chromatographic processing of ^{241}Am, ^{243}Cm, and ^{176}Lu mixtures in the form of $M(HFA)_3 \cdot 2TBP$ in HHFA vapors. Such separations as ^{152}Eu-^{176}Lu and ^{160}Tb-^{176}Lu are also conducted in the same conditions.[255,257]

One more important aspect of β-diketonate complexes application should be mentioned, i.e., their termic nonstability. Thermodestruction of metal β-diketonates lies in the basis of one of the perspective methods of obtaining metal and oxide films. This method can probably be used for plotting of radionuclide layers as well, e.g., ^{152}Cf in the technology of preparation of radioactive sources for different purposes.

Among metalorganic TPE compounds, cyclopentadienyl compounds are characterized by the greatest chemical and termic stability as well as volatility.[262-269] Microamounts of TPE triscyclopentadienyles were obtained by the reaction of the melted berillium biscyclopentadienyle with aqualess metal chlorides: $2MCl_3 + 3Be(C_5H_5)_2 \xrightarrow{65\ C} 2M(C_5H_5)_3 + 3BeCl_2$ where M = Pu, Am, Cm, Bk, Cf.

TPE and lanthanide triscyclopentadienyle compounds are rather sensitive to the oxygen in air and to moisture, and they are destroyed by water, alcohols, and chlorine-containing solvents. The compounds are dissolved in such polar solvents as tetrahydrofuran (THF), benzene and melted berillium and magnium cyclopentadienyles. One of the characteristic properties of cyclopentadienyl compounds of f-elements is in the formation of adducts with Lewis bases (THF, NH_3, $P(C_6H_5)_3$,$C_6H_{11}NC$, etc.).

The metal-carbon bond in f-element cyclopentadienyles being highly ionic is distinguished unlike the corresponding d-element compounds and the covalent character reveals in actinide compounds to a greater degree than it does in lanthanide complexes. It has been fixed in the row of TPE and lanthanides that the increase in covalency of the metal-carbon bond (and chemical stability) is connected with the increase in the degree of oxidation of the central atom. Thus, ytterbium and europium biscyclopentadienyles are immediately destroyed by water, while americium tricyclopentadienyle is slowly destroyed, and cerium tetracyclopentadienyle is stable to hydrolysis.

E. Methods of Precipitation and Coprecipitation

Those methods were widely used during the first stages of TPE research, when their properties were studied for their separation and preconcentration from different materials and for separation of the impurities.[2,42]

Nowadays precipitation and coprecipitation methods are applied usually for TPE separation in different oxidation states. The study of Am (III,V,VI) coprecipitation on sediments of lanthanum, thorium and cerium fluorides, and on bismuth and zirconium phosphates,[270] has proved that all the sediments studied, except as zirconium phosphate, fully capture Am(III), and Am(VI) remains in the solution. Am(V) is partially captured by the sediments of lanthanum and thorium fluorides. Another method of americium separation in different oxidation states has been used to study its stability in the presence of oxidizers.[108] The pentavalent americium can be separated from Am(III) and Am(VI) in acetate solutions by coprecipitation with the sediment of pyrrolidinedithiocarbaminate,[272] and Am(V) can be separated from Am(III) with the sediment of zirconium hydroxide.[216,217] Americium(III) coprecipitation with metal cupferrates was studied.[273] It was found that Am coprecipitates quantitatively with cupferrates of the rare-earth elements and scandium, whereas it does only partially with cupferrates of the further studied elements [Fe(III), Cu(II), Al, In(III), Pb(II), Bi(III)]. Raghuraman, K. et al.[274] discusses the possibility of using nickel for americium (III) coprecipitation in the form of hydroxide from large volumes of the diluted acidic solutions containing ^{239}Pu and oxalate ions. Am separation from Ni is carried out by precipitation of americium hydroxide by ammonia. The coefficients of purification of nickel from americium are higher than 1000.

To separate large quantities of americium from strongly radioactive waste, its precipitation is used in the form of oxalate.[85,275,276] Consequent plutonium and americium precipitation in the form of their oxalates and their coprecipitation with lead oxalate are used for purification of aqueous solutions from radioactivity. The final Pu and Am separation was carried out by the ion-exchange method.[277,278]

The conditions of precipitation of americium (V) oxalate and its properties have been studied in the literature.[279]

For the separation of fermium from Cf, Es, and lanthanide, an efficient method has been suggested, which is based on the cocrystallization of Fm, reduced in the presence of Yb(II), with sodium chloride from aqueous ethanolic solutions. When a practically quantitative extraction of Fm is going on, the degree of purification from most attendant elements achieves 10^3 to 10^4.[280] In the presence of divalent europium Md(I) is fully recovered, with sediments of chlorides K or Na; the purification from the other actinides and lanthanides reaches $\sim 5 \cdot 10^2$.[281]

III. METHODS OF TPE DETERMINATION

A. General

Methods of TPE determination are being developed in two directions. The first direction is connected with the determination of trace amounts of TPE and uses, exclusively, almost radiometrical methods of analysis. As is known, all the TPE isotopes are radioactive and disintegrate with the emission of α- (mainly) and β-particles, in a number of cases -neutrons. Disintegration is always followed by the emission of specific X-rays and almost always γ-quanta. The registration of those types of radiation lies in the basis of the methods of TPE determination, which are selective and have extremely low limits of detection. Usually, radiometric methods are considered to make relatively high errors. However, recent works on half-life revision, perfection of measuring technique, and automatizing of the results processing have drawn the radiometric methods to precision methods level. Values of half-life of several commonly used TPE isotopes and the specific activities are given in Table 10. Those data are partially taken from the review,[103] and partially obtained from statistic processing of the data from original papers of recent years. As is shown in Table 10, the error (average-quadratic deviation) of half-life values for some nuclides do not exceed 1%. The specific activities of TPE isotopes (10^5 to 10^{16} Bq/mg) correspond to the limits of detection 10^{-11} to 10^{-22}g. More detailed considerations on nuclear-physical properties of TPE isotopes are given in our review.[103]

The other direction, the development of which is mainly stimulated by the increasing practical application of TPE, is determination of TPE macroquantities by the methods used in the analytical chemistry of common (nonactive) elements, i.e., coulometry, spectrophotometry and titrimetry, mass spectrometry and X-ray fluorescence analysis, neutron activation, etc. Such a variety is caused by the different possibilities of the methods and by a variety of the analyzed objects. Thus, coulometry, which is less sensitive than other methods, can guarantee a high precision of determination. Spectrophotometric methods allow identification and the ability to determine separate oxidation states of TPE. Mass spectrometric and emission spectroscopy methods are often used to determine admixtures in TPE, since they allow determination of a large number of elements simultaneously with a high sensitivity. In special cases it is worthwhile to use X-ray fluorescence or neutron activation methods which allow conducting of nondestructive analysis or that determine such elements as berkelium. During recent years, the development of methods of TPE macroamounts analysis is directed to the heightening of selectivity, express analyzing, and lowering of limits of detection.

B. Radiometric Methods

1. Measuring of Alpha-Activity

The greatest majority of TPE isotopes disintegrate with the emission of α-particles with the energy lying in the range of 4.9 to 7.2 MeV. The total yield of α-particles is near to 100% per decay in most cases, therefore measuring total α-activity is a convenient and a sensitive method of quantitative determination of many TPE. Since most samples contain a mixture of radionuclides, it is preferable to use α-spectrometer for

Table 10
HALF-LIVES AND SPECIFIC ACTIVITIES OF SOME TPE ISOTOPES

Nuclide	Half-life	Specific activity (Bq/mg)	Neutron activity [n/(sec·mg)]	Ref.
^{241}Am	432.6 ± 0.4 years	$(1.268 \pm 0.001)\cdot 10^{8}$	0.0012	103
^{243}Am	7369 ± 11 years	$(7.38 \pm 0.01)\cdot 10^{6}$	0.0043	104, 121, 128
^{242}Cm	162.8 ± 0.3 days	$(1.226 \pm 0.003)\cdot 10^{11}$	$2.1\cdot 10^{4}$	149, 151, 152, 155, 156
^{244}Cm	18.11 ± 0.02 years	$(2.992 \pm 0.003)\cdot 10^{9}$	$1.1\cdot 10^{4}$	103
^{248}Cm	$3.32\cdot 10^{5}$ years	$(1.61 \pm 0.03)\cdot 10^{5}$	$4.1\cdot 10^{4}$	164, 177, 215
^{249}Bk	323 ± 8 days	$(6.00 \pm 0.15)\cdot 10^{10}$	94.6	226—228
^{249}Cf	357 ± 7 years	$(1.49 \pm 0.03)\cdot 10^{8}$	2.68	164, 229—231
^{252}Cf	2.633 ± 0.01 years	$(1.993 \pm 0.008)\cdot 10^{10}$	$2.3\cdot 10^{9}$	103, 237
^{253}Es	20.4 ± 0.3 days	$(9.36 \pm 0.14)\cdot 10^{11}$	$3.2\cdot 10^{5}$	232—235
^{254}Es	276 days	$6.89\cdot 10^{10}$	—	103
^{256}Fm	2.63 hr	1.72 ± 10^{14}	$5.9\cdot 10^{14}$	103
^{257}Fm	100.5 days	$1.87\cdot 10^{11}$	$1.5\cdot 10^{9}$	103
^{257}Md	5.0 hr	$9.02\cdot 10^{13}$	—	103
^{258}Md	56 days	$3.34\cdot 10^{11}$	—	103
^{255}No	3.1 min	$8.8\cdot 10^{15}$	—	103
^{256}Lr	27 sec	$6.0\cdot 10^{16}$	—	103

measurements. The modern α-spectrometer with semiconductor detector (SCD) of 1 to 3 cm² area reveals 50% efficiency and the limit of detection equal to ~10^{-3} Bq.[193.271] The efficiency of the α-spectrometry was heightened up to 85% with the use of two detectors.[282]

The error of α-spectrometric measurements depends on the resolution of the spectrometer, i.e., on the possibility to distinguish α-particles with similar energy. Modern silicon SCD have resolution of 20 to 30 keV, which allows analysis of mixtures containing almost any TPE isotopes. [Mixtures: ^{242}Cm(E_α = 6.089 MeV) + ^{252}Cf(E_α = 6.111 MeV), ^{244}Cm(E_α = 5.80 MeV) + ^{249}Cf(E_α = 5.82 MeV) make an exclusion.] However, the spectrometer resolution depends also on the quality of the electronic technique and the presence of macroadmixtures in samples. To prepare a sample ("a target") for measuring α-spectrum of macroadmixture, a layer of substance is created which leads to an essential widening of spectral peaks. Therefore, α-spectrometric targets are usually prepared by the method of electrodeposition, which makes TPE selectively precipitate on the target-cathode macroadmixtures remaining in the solution. Quite a number of methods of electrodeposition of TPE from aqueous solutions[283-286] or organic solutions[282.287-290] have been developed; they secure a thin uniform coating on target and a high resolution of α-spectral lines, the substance being practically completely separated from the solution. The choice of method depends on the composition of the solution and the chemical properties of admixtures, from which elements should be separated. Precipitation from nonaqueous solutions (mainly alcoholic ones) can be rather selective, though it needs high voltage (600 V or higher). Aqueous solutions need less voltage, but the current strength appearing at electrolysis needs an intensive cooling of the solution.

There are some other methods of target preparation for α-spectrometry, which are still more simple. It has been suggested[291] to coprecipitate TPE with a small amount of $Ce(OH)_3$ with the subsequent separation of the sediment on a fine membrane filter with the size of the pores of 0.1 μm, the filter then being dried and used as target. Disks of sulfurated polystyrole, which sorb TPE from diluted nitric acid solution, can be used as targets.[292] In both cases more than 95% of TPE is separated.

If a sample contains only one α-active nuclide or one α-active element with a certain isotopic composition, or if the task is to determine the total α-activity, the methods of integral α-counting are used. The most sensitive methods are those in which the active sample is placed into the detector: for dry targets, a flow proportional counter with the geometry of 2π or 4π is used, for solutions, a liquid-scintillation counter (LS) is used. The proportional counters usually have a count efficiency of 50% and a very low background ($\sim 10^{-3}$ c/sec), are able to carry out measurements of the absolute α-activity with the error to 0.3%.[293] LS counters have a much higher background, however, they are also widely used for measuring α-activity of TPE isotopes. The advantages of the LS method are in the high efficiency of counting (~100%) as well as the possibility of avoiding the complex stage of preparation of the dry sample for measuring. There are two methods of samples preparation for LS measuring: directly adding the aqueous or organic solution of sample to LS, and extraction of the radionuclide under determination from the sample by LS. In the latter case an extractant is added to the LS solution. To determine TPE, mixtures are suggested containing 5 g/*l* *p*-terphenyl and 0.05 g/*l* POPOP as scintillating substances, and 20%-di-2-ethylhexylphosphoric acid (HDEHP)[294] or 43.5%-nonylphosphate[295] (diluent-toluene) as extractants. Such LS with the added extractant makes it possible to concentrate the element under determination and to separate it from impurities. This LS extracts Am, Cm, and Cf from solutions with low acidity separating them from anions.[294] LS with nonylphosphate can completely extract Am and Cm from HNO_3 solutions up to 2 *M*; the methods of the analysis of americium and curium content in biological samples with the help of this LS are characterized by the limit of detection to 3.10^{-3} Bq/m*l*.[295]

Historically, one of the first devices used for measuring intensity of α-radiation was a counter with solid inorganic scintillation detector ZnS.[296] Nowadays, the application of such counters in α-radiometry is limited, since they have characteristics worse than SCD, LS, and proportional counters. In addition, the application of solid scintillators for determination of absolute intensity of α-radiation is not convenient, as its counting coefficient depends on the energy of α-particles. However, in some cases the usage of solid scintillators is expedient and can give a positive effect, e.g., for determination of small amounts of americium and curium in aqueous solutions. It was suggested to coprecipitate those elements with lanthanum hydroxide in the presence of a solid scintillator (ZnS, activated Ag).[297] The glass with a thin layer of sediment on the bottom in which the radionuclides are fully mixed with the scintillator put on the photocathode of the photomultiplier and the rate of counting is measured. The efficiency of counting reaches 80%, the limit of detection 4.10^{-5} Bq/m*l* (the volume of the sample being equal to 1*l*).

The methods of α-counting described above are distinguished by extremely low limits of detection. They are used mainly for measuring α-activity in samples with small TPE content. However, the error of measuring samples with low activity is sufficiently high even at the low level of the background. (As is known, due to the statistical character of the decay, the error of the radiation intensity measurements depends on both the signal-to-noise ratio and the absolute value of the signal.) When highly active samples are measured, the error of radiometric determination can be lowered to shares of a percent. To measure α-activity of samples with a large content of TPE, it is expedient to use the methods of α-counting, which are not highly sensitive, but have other priorities, i.e., they are simple, express, and highly precise. For example, it is possible to use a counting device with a small solid angle, which lowers the counting coefficient, thus excluding the necessity to dilute the solution before determination. One such device,

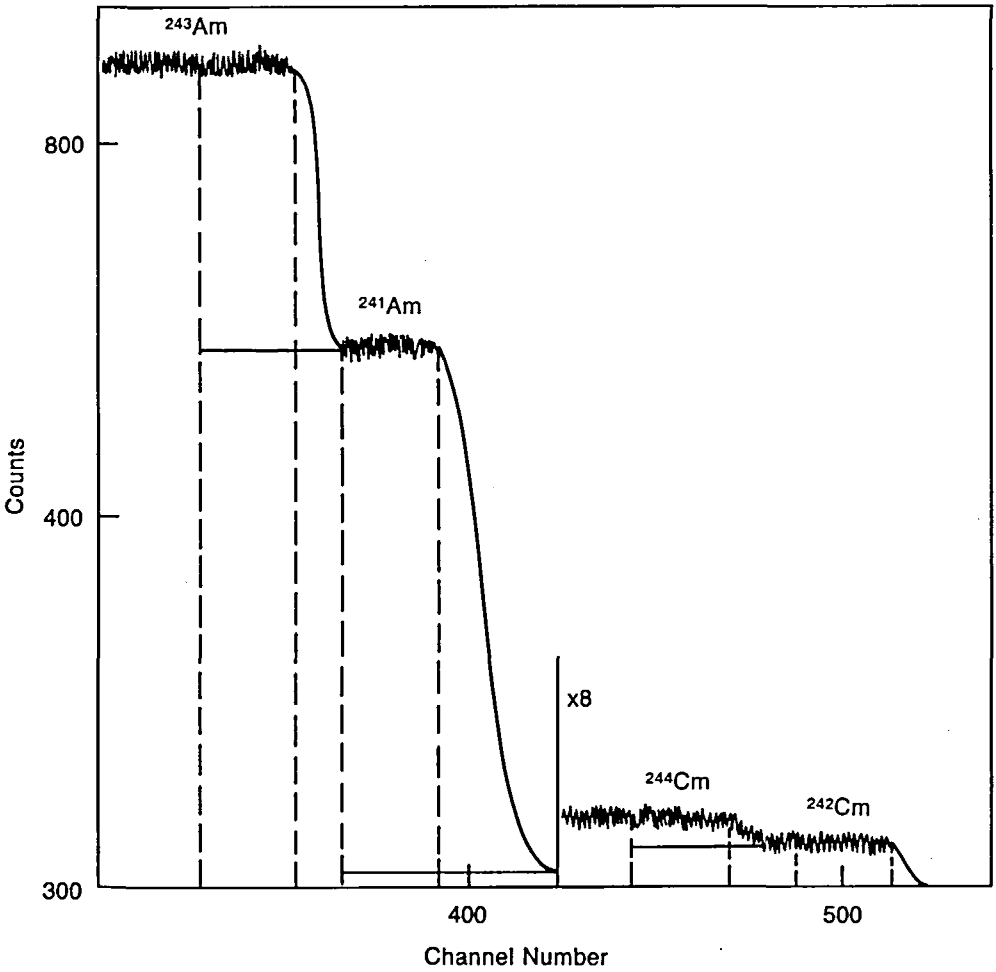


FIGURE 1. Alpha-spectrum of Am + Cm mixture, being measured by "immersed" detector.

described in the literature,[298] with the SCD sensor, allows determination of ^{241}Am, when its content in solution is ~10^{-4} mg/ml, the precision being equal to ~0.3%.

Recently, it has been suggested to use the "immersive" SCD for determination of α-activity of highly active solutions.[299-303] A silicon semiconductor detector in a stainless-steel cover[303] or in a glass tube[300] is inserted directly into a solution containing TPE. The detector registers α-particles contained in the thin layer of the solution adjoined to its surface, the thickness of the layer being determined by a range of α-particles. For a certain solution the volume, from which α-particles are registered, is constant, therefore the value of counting is proportional to the concentration of the substance with α-radiation. Thus, the possibility of an error in measuring the volume of a sample is excluded and the measurements become much simpler. The counting efficiency of such a detector does not exceed 1%. Such an efficiency combined with modern electronic apparatus allows measurements to be carried out directly in technological solutions containing macroamounts of americium, curium, and other TPE. If the signal of the detector is given to the multichannel analyzer, a specific α-spectrum of the solution can be obtained (Figure 1), on which the value of each step is proportional to the intensity of α-particles with a certain energy. The energy resolution of such an α-spectrometer can reach 20 keV,[301] i.e., not worse than that of a common α-spectrometer with a SCD.

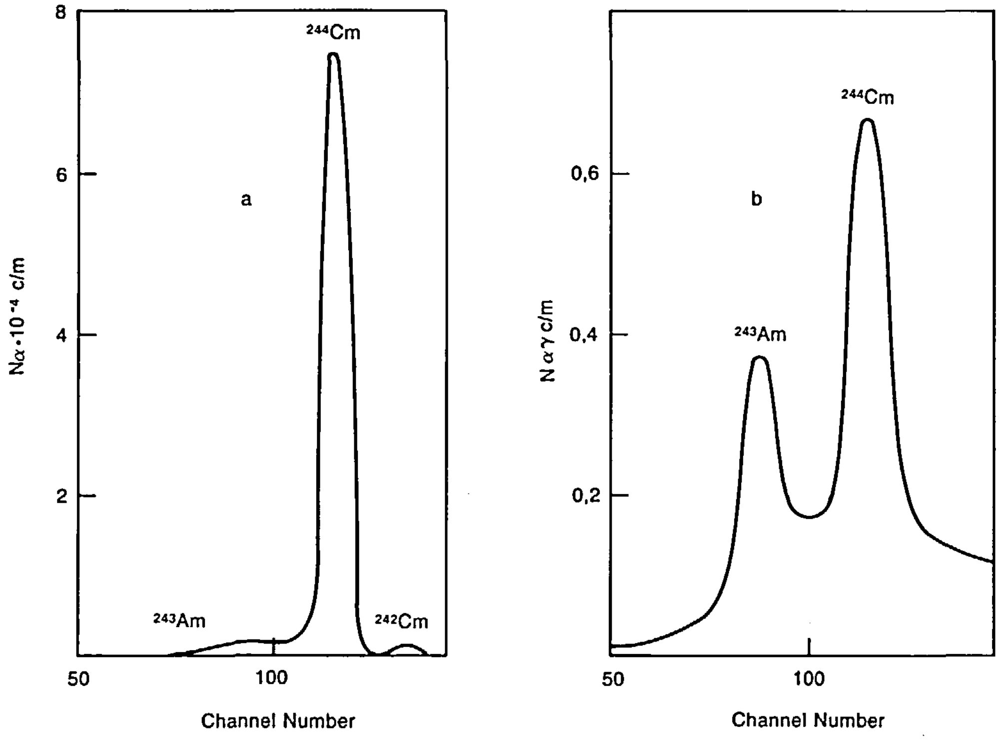


FIGURE 2. Alpha-spectrum of the Am + Cm mixture, being measured by ordinary alpha-spectrometer (a) and by alpha-gamma-concidence spectrometer (b). The Am to Cm ratio is equal to $1 \cdot 10^{-4}$.

The presence of nonvolatile macroadmixtures in a solution practically does not effect the measurements with the immersed detector: thus, it is possible to determine americium and curium if they are both present in solutions containing $NaNO_3$ up to 7 *M.*[303]

In the case of highly radioactive solutions, the usage of the method of α-γ-coincidences, which allows neutralization of the disturbing influence of the nuclide with a great activity or with a close energy of α-particles, is possible. The spectrometer of α-γ-coincidences has an additional detector of γ-radiation, which "allows" registration of those α-particles, which are emitted simultaneously with γ-quanta of a certain energy. As a result, the counting of the α-radiation of the disturbing nuclide is essentially suppressed (e.g., when the content of ^{243}Am is measured, the counting of α-radiation of ^{244}Cm is suppressed) (Figure 2).[304] If this method is used to measure the absolute α-activity of a pure TPE isotope, the error can reach 0.1 to 0.2%.[293,298]

2. *Measuring of Beta-Activity*

Among the usual TPE isotopes, only ^{249}Bk disintegrates with the emission of mainly β-particles (the branch of α-decay of ^{249}Bk makes only $1.45 \cdot 10^{-3}\%$). Measuring of soft β-radiation of berkelium (E_β = 124 keV) presents a serious problem, especially in the presence of admixtures. To measure pure ^{249}Bk preparations, a proportional flow counter or an LS meter is often used, the limit of detection being equal to several Bq in a sample. However, the use of an LS counter is complicated by the fact that most substances quench relatively weak scintillations induced by β-particles of ^{249}Bk. That is why it is necessary to make a preliminary determination of the dependence of the count coefficient on the composition of a solution.[305] When the berkelium concentration is high, the "immersed" silicon detector can be used, which allows to count the total β-activity and to measure the β-spectrum. The limit of detection of ^{249}Bk in solution by the immersed SCD is equal to ~2.10^4 Bq/m*l*.[301] Due to the difficulties in ^{249}Bk determination through β-activity, the α-spectrometry is often used for that purpose (by measuring the berkelium α-activity or the α-activity of daughter ^{249}Cf), as well as other methods (see below).

3. Determination of TPE by Gamma- and Neutron Radiation Measurements

Gamma-spectrometric analysis of radioactive substances has become widespread due to the creation of semiconductor detectors of high resolution and multichannel analyzers with the automatic processing of the spectrum. The efficiency of this method depends on several conditions. γ-Spectrometry is worthwhile for determination of nuclides with a high yield of γ-quanta such as ^{241}Am, ^{243}Am, ^{249}Cf, ^{257}Fm, etc. However, in technological solutions, determination of those nuclides through γ-radiation is often complicated by the presence of a great amount of γ-active fission products. The possibility of the nondestructive analysis of different objects is an important priority of γ-spectrometry. It is necessary to take into consideration the fact that the efficiency of registration of γ-quanta by semiconductor detector depends (nonlinearity) on the energy of radiation; therefore, thorough calibration is necessary for determination of absolute activity. On the whole, the γ-spectrometric method is convenient for express analyses in standard conditions, if precise determination is not necessary.

X-ray spectral TPE determination is a variant of γ-spectrometric analysis. A specific peculiarity of TPE, as well as that of other radioactive elements, is the presence in their γ-spectrum of the X-ray radiation, emitted by the excited atoms of the daughter elements (products of decay). The energy of such radiation lies in the range of 97 to 140 keV (K-line) and 14-27 keV (L-line);[103] for its registration the planar SCD with the resolution of 0.2 to 0.3 keV is used. Due to the complexity of X-ray spectra and the proximity of spectral lines, this method is not widespread, however, in some cases it can be efficient. For instance, X-ray determination of berkelium in californium according to the L_α-line (~15.5 keV) allows determination of up to 0.01 μg of ^{249}Bk in 1 μg of californium.[306]

Many TPE isotopes emit another type of the penetrating radiation, i.e., neutrons. Neutrons appear at spontaneous fission of heavy nuclei (especially the even-even ones). Thus, neutron radiation is a specific peculiarity of the elements in the end of the Periodic Chart, while strong neutron activity is a property of TPE isotopes (curium, californium, and more heavy elements). Unfortunately, efficiency of registration of simple neutron counters is not high,[296] therefore TPE determination of the neutron activity is not characterized by a high sensitivity. Besides, to analyze the TPE mixture it is necessary to take into consideration the influence of other α-active nuclides, which create an additional flow of neutrons by reactions of the (α, n) type on light nuclei. It was suggested to use counters of neutron-neutron coincidences.[307,308] They neutralize the background of (α, n) reactions and allow identification of separate neutron-active nuclides through their specific characteristic — the average number of neutrons per fission. In such a way, ^{244}Cm can be determined with the error of 1 to 2% and the limit of detection of 3.10^{-3} μg.[308]

C. Other Physical Methods

1. X-Ray Fluorescence

The fluorescence yields of K-level for TPE (Am-Es) are about 97.2%.[309] This radiation in the range of 100 to 140 keV can be used for TPE determination with the help of spectrometer with semiconductor detector, however, the γ-radiation of TPE and radioactive admixtures presents a serious hindrance. When the diffraction X-ray spectrometer is used, TPE are usually determined through the L-series (14 to 25 keV), but in this case the limits of detection are also high due to the background evoked by the source of spectrum excitement (the X-ray tube). Therefore, it was suggested[310] to use M-series for X-ray fluorescence determination of americium (from 3.4 to 3.6 keV), where the background from the X-ray tube is essentially lower. (The peak to background ratio of M_α-line is 30 times greater than that of L_α-line). Limit of detection of americium reaches 0.046 μg, if they use M-lines, while it is equal to 0.93 μg in the determination of L-lines.[310] The relative yields of X-rays of M-series for Am have been determined in the literature.[311]

Special spectrometers have been developed for X-ray fluorescence determination of heavy elements, including TPE, directly in solutions with a high content of radioactive substances (up to 4.10^{12} Bq/l). Two types of spectrometers are described: the crystal-diffraction spectrometer (LiF)[312,313] and the spectrometer with a semiconductor silicon detector.[314] Characteristic radiation of the determined elements is exited by the braking spectrum of the X-ray tube with a tungsten or a palladium anode. A special protection of the detector from both the diffused radiation of the source and the γ-radiation of the sample is used. The error of concentration determination does not exceed 1%, and the ratio between concentrations of the neighboring elements may reach 10.

2. Mass Spectrometry

The mass spectrometry method is used for determination of isotopic composition of TPE, and for the determination of the content of those elements in the analyzed materials. That is one of the most sensitive and selective methods, which demands, however, complex and expensive technique. The content of some other elements (actinides, lanthanides, etc.) is determined simultaneously with TPE, however, the quantitative interpretation of the results demands the knowledge of the ionization coefficients of the determined elements in certain concrete conditions.

Methods of TPE and other elements determination in samples of uranium, plutonium, americium, curium, berkelium, and californium have been developed.[315-318] When the MI-1311 mass spectrometer with a three-ribboned ion source is used, the mass of the analyzed sample makes 0.1 to 10 μg. The limits of detection of americium in curium, americium, and curium in berkelium and californium are equal to ~1 ng; the error of determination makes 10 to 20%. Simultaneously, lanthanide impurities (on the level of 0.1 ng) and their isotopic composition can be determined.

Mass spectrometric analysis of nanogram amounts of americium and curium can be carried out with the help of a special system of mass spectrum registration, based on counting of separate ions and multiple scanning.[319] This method is used for determination of isotopic composition of americium and curium in the irradiated nuclear fuel, where the content of those elements makes 10^{-1} to 10^{-3}%. However, it is necessary to preliminarily separate americium and curium from other actinides, since the presence of even relatively small quantities of heavy plutonium isotopes can strongly distort the result. The relative error of isotopic content determination makes 5 to 10%, the sample mass being equal to 0.01 to 0.1 ng, and 1 to 2%, the sample mass being equal to 1 to 10 ng.

3. Neutron Activation

The neutron activation analysis is known to be one of the most sensitive methods of the analysis. It is usually used to determine microimpurities of the nonactive elements through the γ-activity of the short-living isotopes, formed by (n,γ)-reactions during the irradiation of natural isotopes by a high flow of neutrons. However, it can be useful for determination of radioactive elements as well, if the neutron irradiation of the initial nuclides leads to the formation of short-living isotopes, characterized by an intensive γ-radiation. Thus, for instance, neutron activation methods of ^{238}U determination through daughter ^{239}U and ^{239}Np[320] or ^{237}Np determination through the daughter

^{238}Np[321,322] are well known. Due to the fact that neutron irradiation of heavy elements causes the formation of fission products, one of the main problems is the choice of the analytical γ-spectral line which is not affected by the disturbing lines of the fission product nuclides.

Among TPE, the neutron activation method was used for ^{249}Bk determination.[323] As it was indicated above, ^{249}Bk decay gives the emission of β-particles with a low energy, therefore it is impossible to radiometrically determine small quantities of berkelium in the mixture with other TPE, due to the disturbing influence of α-radiation. It is known, however, that neutron irradiation of ^{249}Bk forms ^{250}Bk, an isotope with the half-life of 3.32 hr and an intensive γ-radiation. The cross-section of the thermal neutrons capture of the ^{249}Bk isotope is quite great (1400—1700 barns), so this method is considered to be highly sensitive for berkelium. For ^{249}Bk determination in a mixture of curium, berkelium and californium, the measurements are carried out along the ^{249}Bk γ-line 989 keV, since in that area the disturbing influence of the fission products activity is the smallest. If the sample irradiation is carried out by the neutron flow of 1.10^{13} n/cm^2/sec for 3 hr, the limit of detection of ^{249}Bk is equal to 4 ng; the sample can contain hundreds multiple quantities of californium and curium.

4. Emission Spectroscopy

The method of emission spectroscopy is an express one, its sensitivity is similar to that of the mass spectroscopy method. In TPE analysis this method is used mainly for determination of the nonactive impurities. The direct spectrographic analysis (with the usage of the alternating current arc) allows determination of 16 contaminant elements (Al, Si, Cd, B, Na, Ca, Mg, Ni, Cr, Fe, Ce, Pr, Nd, Sm, Eu, Id) in americium, curium, berkelium, and californium samples on the level of 10^{-2} to 10^{-3}%, the sample mass being equal to 0.2 mg.[324] If the impurities are separated from TPE before determination, the limits of detection are 6 to 5 times lowered and it becomes possible to determine Li, K, Rb, Cs, Sr, Ba, Be, Y, La, Mn, and Co as well. The error of spectrographic determination makes 4 to 20%.

The method of emission spectroscopy is seldom used for determination of TPE themselves, though the emission spectra of americium, curium, and other TPE in macroamounts have been thoroughly studied in recent years.[325-328] In most cases other methods of analysis (radiometrical) are considered more sensitive and precise, therefore the development of the emission spectral methods does not seem advantageous. However, in some cases, for instance, for determination of microamounts of americium in curium, the application of the emission spectral method is expedient. The direct radiometrical determination of americium in curium is complicated by the essentially greater specific activity of curium isotopes (see Table 10), and it is necessary to either separate curium, or to use other method. One of such methods is spectrographic determination of americium with the help of a hot hollow cathode.[329] A nitric acid solution, containing to 100 μg of curium, is inserted into a carbonic hollow electrode and after drying the emission spectrum is taken in a helium atmosphere. Americium is determined according to the spectral line of 351. 013 nm. The limit of detection of americium is equal to 0.1 μg; the error does not exceed 25%. The shortcoming of the method is the dependence of the intensity of the americium line upon the curium content.

5. Luminescence

Methods of transuranium elements (neptunium, plutonium) determination with the help of luminescence in solid crystallophosphorus are distinguished by extremely low limits of detection (several nanograms) and by a high selectivity.[330-332] It was shown[333] that the luminescence of Cm^{3+} ions can be observed directly in solution, if laser serves an exciting source. The peak of Cm^{3+} luminescence is located in the visible part of the spectrum (593 nm); the quantum yield is equal to ~0.5 in D_2O and 0.03 in H_2O.[333] The authors have theoretically calculated that the minimum curium concentration detected in aqueous solution can reach 0.1 ng/m*l*, if luminescence is exited by a nanosecond laser and registration is carried out by counting the photons. A device of that type is described in the literature.[334] It is necessary to mention that this method is not useful for determination of the other TPE, since their luminescent radiation is located in the infrared part, and the sensitivity of determination is much lower.

D. Chemical Methods

1. Coulometry

Coulometry is one of the most perspective methods of TPE determination. It is characterized by high selectivity, sensitivity, and precision. Coulometric methods are easily automatized and measurements can be carried out from a distance. Coulometry is one of the few absolute methods of analysis which do not demand standards for calculation of the quantity of the determined substance. One of the directions of this method, i.e., coulometry with a controlled potential, has been most successfully developed in the analytical chemistry of TPE. If the most perfect technique is used, the error in TPE determination can reach several hundredths of a percent.[335,336]

The coulometric determination demands the presence of reversible couples consisting of the ions of the given element in two different oxidation states. Nowadays such couples as Am(VI)/Am(V), Am(IV)/Am(III), and Bk(IV)/Bk(III) are used for coulometric determination of TPE. There are other couples which can also be used, i.e., Cm(IV)/Cm(III), Cf(IV)/Cf(III), Md(III)/Md(II), and No(III)/No(II). In addition, methods of indirect coulometry are being developed, where an electrochemical couple of ions of the element, which is not determined, is used, but which is equivalently substituted from the complex coupound by the ions of the element under determination. The indirect coulometry secures the high precision of determination, but it has no selectivity, since the substituting ability of any TPE ions of the same valency is similar.

The recently developed well-known methods of coulometric TPE determination are given in Table 11. If the direct coulometric determination is used, the error in the analysis considerably depends on the stability of the ion of the determined element in the highest oxidation state. In the case of TPE determination an additional error appears due to the formation of the products of solution radiolysis, which reduces a part of ions during electrochemical processes. To eliminate this error in the methods of berkelium[15] and americium[337] determination, special corrections were made, however, the general error in determination was rather high. Due to the same reason, americium determination using the Am(VI)/Am(V) couple in sulfuric acid solutions in the presence of curium is complicated.[337,338] This difficulty is eliminated when the determination is carried out in phosphoric acid solutions,[339] since the formation of the reducing products of the α-radiolysis in them is negligible.[345] Neither the hundreds-fold quantities of most of the stable elements, including lanthanides (except cerium), nor the commensurable quantities of other TPE and plutonium, interfere to determine americium in the phosphoric acid aqueous solution.

The coulometric methods of americium determination with the use of the Am(IV)/Am(III) couple are extremely selective.[9,341,342] This determination can be carried out in aqueous solutions of potassium phosphotungstate $K_{10}P_2W_{17}O_{61}$ (PW), sodium carbonate, and in phosphoric acid acetonitrile solution, where Am(III) is easily electrochemically oxidized to Am(IV). Am(IV) is especially stable in PW solutions, therefore, in this case even the tenfold excess of curium does not interfere to determine americium. Other elements (including Pu, Ce) oxidized in those conditions also do not interfere

Table 11
COULOMETRIC METHODS OF TPE DETERMINATION

Element	Electrochemical couple	Composition of solution	Limit of detection (μg)	Precision (%)	Interfering elements	Ref.
Am	Am(VI)/Am(V)	1.8 $M\,(NH_4)_2SO_4 + 0.1\,M\,H_2SO_4$	70	3	Cm, Ce	337
		0.05—0.2 $M\,HNO_3$	400	0.5	Cm	338
		2 $M\,H_3PO_4 + 0.1\,M\,HClO_4$	5	2	Ce	339
	Am(III)/Am(V)	0.05 $M\,Na_2CO_3 + 0.1\,M\,LiClO_4$	30	1.5	U, Np, Pu, etc.	340
	Am(IV)/Am(III)	0.006 $M\,K_{10}P_2W_{17}O_{61} + 0.1\,M\,HClO_4$	6—70	3	None	341
		0.5 $M\,H_3PO_4$ (in acetonitrile)	5	2		9
		1—2 $M\,Na_2CO_3$ (pH <10)	6	2.5		342
	Hg(II)/Hg(O)(ind)	0.01 M HgEDTA (pH = 5)	80	0.1	M^{3+}, M^{4+}, etc.	344
Cm	Hg(II)/Hg(O)(ind)	0.02 M EDTA	100	<1	M^{3+}, M^{4+}, etc.	215
Bk	Bk(IV)/Bk(III)	0.05 $M\,H_2SO_4$	5	5	Ce	15

since they are not reduced when Am(IV) is reduced at the anode potential 1.17 V. A shortcoming of this method is the necessary limitation of the amount of the determined americium (not more than 70 to 100 μg), connected with the limited solubility of the PW reagent. Therefore, other methods of americium determination with the use of the Am(IV)/Am(III) couple, given in Table 11, which are not yet thoroughly developed, seem to be rather perspective.

The indirect coulometric method of americium determination[343,344] is based on the substitution reaction of Hg^{2+} by americium from its complex with EDTA: Am^{3+} + Hg EDTA → Am EDTA + Hg^{2+}. Then the mercury ions are being reduced on the mercury cathode up to the state of metal, the spent amount of electricity being proportional to the amount of americium. However, the high precision of this method (0.1 to 0.2%) was obtained when relatively large amounts of americium were determined (300 to 800 μg). Many impurities interfere in the determination of americium, i.e., the ions of metals, which substitute mercury from its complex with EDTA (3- and 4-valent cations, several 2-valent cations, which form stable complexes with EDTA), and anions, which form stable complexes with Am^{3+} (citrate, fluoride, etc.). On the other hand, this method is universal and can be used for determination of any TPE, including those which do not have reversal electrochemical couples convenient for the direct coulometric determination. This method (with some variations) has been used for precise determination of the quantity of ^{248}Cm during the measuring of its half-life.[215]

2. *Spectrophotometry*

Spectrophotometric methods are traditionally used in analytical chemistry for determination of the content of elements in solutions. The determination methods, based on the measurement of the absorption spectra of the aqueous solution of mineral acids are more selective, especially in the case of TPE, with their characteristic narrow bands of the f-f transition. Another group of methods is based on the measuring of light absorption of the colored complex compounds, formed in the presence of the organic reagents. Those methods are usually characterized by very low limits of detection, but they are less selective, since the analytical absorption bands belong to the organic part of the complex.

The detailed data on the absorption spectra of TPE ions in various oxidation states in aqueous solutions are given in monograph.[42] The Am^{3+} ion absorption band, which lies in the area of 503 nm, is usually used for Am determination in solutions in the presence of curium and other TPE. The minimum concentration of americium detected by this method is equal to $\sim 2.10^{-5}$ M (when the usual laboratory spectrophotometers are used). The characteristic absorption bands of americium ions in other oxidation states are used for the study of the kinetics and the equilibrium of the redox reactions in solutions. The Am^{3+} and Cm^{3+} ions with the arsenazo III reagent form colored complexes with very high coefficients of extinction $\sim 10^5$ M^{-1} cm^{-1} in aqueous and alcoholic solutions, which correspond to the limit of detection equal to 10^{-7} M.[346]

Recently, new data has been obtained on the 3- and 4-valent TPE ion absorption spectra in H_3PO_4, PW solutions,[10,122,127,347] and in solutions of other inorganic acids.[127] which can be used for their quantitative determination. The use of phosphoric acid solutions for Am determination according to the absorption band of 503 nm of Am^{3+} is essentially more convenient than the use of HNO_3, H_2SO_4, or $HClO_4$ solution, since the extinction coefficient of Am^{3+} in H_3PO_4 solutions is considerably higher than that of solutions of other mineral acids (it is equal to 505 M^{-1} cm^{-1}) and does not depend on H_3PO_4 concentration in the range of 3 to 13 M.[122] The limit of detection of Am is considerably lowered, if the intensive Am^{4+}-ion absorption is used for its determination in the blue part of the spectrum.[8] Reference 349 gives the description of americium oxidation to Am(IV) in 1 M HNO_3 solution containing 0.004 M PW, with the help of the mixture of ammonium persulfate and silver nitrate, as well as the measurement of the optical density of the solution at 500 nm. The limit of americium detection is equal to 8.10^{-6} M (2 μg/mℓ); the error of determination of $\geq$20 μg/mℓ Am does not exceed 2% in the presence of the equal quantities of curium and the tenfold quantities of La, Ce, Eu, Zr, etc.

It should be mentioned that in recent years one more way of lowering the limits of detection of elements by spectrophotometric methods has been successfully developed. It is based on the improvement of the measuring technique. It is shown[350] that the use of a spectrophotometer with a low noise level and a high-quality detector permits measurement of ion concentrations with extinction coefficients of 50 to 300 M^{-1}cm^{-1} on the level of 10^{-6} to 10^{-7} M. In this case the limit of americium detection according to the absorption band of 503 nm of Am^{3+} in 3 to 13 M H_3PO_4 is equal to $\sim 1.10^{-7}$ M, and the limit of berkelium detection according to Bk(IV) absorption at 393 nm in HNO_3[348] is equal to 8.10^{-8} M. When the laser spectrophotometer combined with "thermal lenses" method is used, the limit of Am^{3+}-Cf^{3+} ions detection can be lowered to 2.10^{-9} to 10^{-7} M, according to Reference 333.

Colored reaction of Am^{3+} with arsenazo III is used for extraction-photometric americium determination.[351] Americium (III) is extracted by diisoamylsulfoxide from nitric acid solution and is determined directly in the organic phase adding arsenazo III. This method allows elimination of the interfering influence of some ions, including lanthanides (except europium). Americium to 0.1 μg can be determined with the error $\leq$2%.

3. *Titrimetry*

Usually two main types of titrimetric methods are used for TPE determination, i.e., the complexometric titration (the 3-valent ions) and the redox titration (the ions in the highest oxidation states). It has already been mentioned above that EDTA are used in indirect coulometric methods of americium and curium determination.[215,343,344] Up to 1 mg of americium and curium can be determined by the direct complexometric titration of Am^{3+} and Cm^{3+} with the EDTA solution, the error being equal to $\sim$1.4 μg.[352]

Methods of determination of microgram amounts of Am and Cm by titration with a solution of DTPA have been developed.[353,354] By potentiometric indication of end point, the determination error is $\sim$2%; by spectrophotometric indication it is 0.5%.[353] In another version of this method, an electrochemically generated complex of Fe(II) with DTPA serves as a titrant, permitting analysis with the help of an automatic coulometric titrator.[355] The determination error of 20 to 200 μg of americium is about 3 to 5%.[354]

The method of complexometric titration of 3-valent TPE is not selective, and in the case of a mixture of curium and americium, it gives a total content of both elements, and in the presence of lanthanides it helps determine the total quantity of TPE and RE. If TPE content is determined by any other method (e.g., radiometrically), the content of the nonactive impurities in the analyzed sample can be calculated from the difference. For instance, this method was used to determine the neodymium impurity in the solution of americium and curium with the error of 0.4%.[353]

Spectrophotometric titration is used for the quaitative determination of americium (VI,V,III) when they are jointly presented.[356] Titration is executed in nitric acid solution. First, Am(VI) is titrated with standard solution of $NaNO_2$, and the end of titration is detected by the change of optical density under 996 nm [Am(VI)] or 717 nm [Am(V)]. In this case Am(VI) is reduced to Am(V), which is stable in these conditions. The total amount of Am(V) is titrated by the solution of U(IV), which reduces Am(V) to Am(III), and from this content of Am(V) in the original sample is calculated. The americium (III) content at the end of titration is found from the optical density of 813 nm. The determination error is 2 to 3% if the americium concentration in the solutions is $\sim 6.10^{-3}$ M (1.5 mg/mℓ).

IV. DETERMINATION OF TPE IN SELECTED SAMPLES

A. Environmental Samples

Due to the nuclear weapons testing and the development of nuclear energetics, radioactive elements penetrate into environmental objects (natural waters, air, various living organisms, etc.). Among them are TPE isotopes, the most active ones being ^{241}Am, ^{242}Cm, and ^{244}Cm. However, the most dangerous are the long-living nuclides of ^{243}Am and the heavy curium isotopes, the relative activity of which is increased with the decay of the short-living nuclides.

The TPE content determination in the objects of the environment is a difficult task due to their low content and the interference of the other α-active nuclides (mainly plutonium isotopes). Recently, a number of schemes of americium and curium separation and determination have been developed, with the use of different methods of separation and concentration, such as ion exchange, extraction, and coprecipitation.[193,196,197,271,295,357,358] The final determination is carried out by the radiometric methods, mainly α-spectrometrically, though the liquid counting is also used.[295] The limits of detection of americium and curium with the use of those schemes usually make $\sim10^{-4}$ Bq/ℓ (or 1 g of the sample). The accuracy of determination of such methods does not exceed 10 to 15%, which is sufficient in the framework of the task. Three main tasks should be solved in TPE determination: (1) TPE preconcentration, (2) TPE separation from the interfering α-active nuclides, and (3) TPE separation from the nonactive impurities, which make the quality of α-spectrometric targets worse. Preconcentration is usually carried out with the help of the coprecipitating methods using precipitates of hydroxide,[193,196,197,271] bismuth phosphate,[358] barium sulfate,[357] and calcium oxalate.[197] The ion-exchange methods,[193,197,271,358] as well as the extraction methods,[197,295,357] are used for separation from radioactive impurities. HDEHP and TOPO are often used as extractants, and recently dibutyl-*N,N*-diethylcarbamoylphosphonate (DDCP) has been suggested for this purpose.[197] The efficient method of separation from the nonactive impurities, based on the selective elution of americium and curium from anionite by alcoholic HNO_3 or HCl solutions, has been used in a number of methods.[193,196,197]

Methods in which the lowest limits of detection are achieved include several stages of preconcentration and purification. For example, a method[197] combines coprecipitation with $Fe(OH)_3$ and CaC_2O_4, purification on cationite and anionite, extraction by DDCP, and final purification on anionite by HNO_3 solution in methanol. Total yield of americium and curium makes 70 to 100%, and the limit of detection for samples with the mass to 100 g or volume to 200 ℓ reaches $\sim10^{-6}$ Bq/ℓ.

If the TPE activity measurement is carried out not alpha-spectrometrically, but with the help of the liquid scintillator, the methods can be made considerably easier. Thus, it was suggested to use extraction LS containing nonylphosphate[295] for determination of total americium and curium content in biological samples. After the sample is decomposed and TPE are concentrated, plutonium is separated by HDEHP extraction, and then Am + Cm is extracted by LS and their activity is measured. The limit of detection in this method is $\sim10^{-4}$ Bq/g.

B. Nuclear Fuel

Americium and curium are formed in the nuclear fuel in very little quantities (about 0.1 mg/g) when atomic power stations work.[220] When the reprocessing of nuclear fuel is going on, americium and curium usually remain in the waste solutions, and the question of the expediency of the separation from those solutions is solved according to several factors, including their content. Besides, it is important to take into consideration the isotopic composition of americium and curium as well, since the danger of radioactive wastes at long storage depends on the content of the long-living nuclides (^{243}Am, ^{245}Cm, ^{246}Cm, etc.).

Usually, the α-spectrometric method is used for the analysis of nuclear fuel, which allows determination of ^{241}Am, ^{243}Am, ^{242}Cm, and ^{244}Cm. According to methods,[292] uranium and plutonium are separated by the double extraction of HDEHP from nitric acid solution, then TPE are sorbed on the disks of sulfurized polystyrole from the remaining aqueous phase, and the α-spectrum is measured. The error of determination makes $\sim$30%, the ^{244}Cm content in solution being equal to $\sim$0.6 ng/mℓ ($\sim 2 \cdot 10^3$ Bq/ℓ).

^{238}Pu influence on americium determination is most interfering. It emits α-particles with the same energy as ^{241}Am does. Reference 359 gives the comparison of four methods of ^{241}Am determination in the presence of plutonium: α-spectrometry, γ-spectrometry, isotopic dilution with α-spectrometric ending, and isotopic dilution with mass spectrometric ending. It is shown that the simple α-spectrometric method based on the comparison of the α-spectra of the initial solution and the purified plutonium gives the results which coincide with the results of other methods. The error of ^{241}Am α-spectrometric determination in the presence of plutonium makes $\sim$1%.

Mass spectrometric methods give the most complete information on the content of TPE isotopes in nuclear fuel, and the method of isotopic dilution with mass spectrometric ending is often used for the exact determination of the absolute content of elements (sometimes α-spectrometric data are involved). It is important that mass spectrometric analysis helps determine the content of heavy curium isotopes, which are not discovered by the α-spectrometric methods. One of the most sensitive methods[319] uses the system of mass spectrum registration, based on counting separate ions and multiple scanning. TPE are preliminarily separated from uranium, plutonium, and other elements present in nuclear fuel. The limit of detection of americium and curium isotopes is 0.01 mg, and the error of determination (on the level of the limit of detection) is equal to $\sim$10%. Such limit of detection for ^{245}Cm and ^{246}Cm isotopes corresponds to the activity of 0.05 to 0.1 Bq, which is comparable with the sensitivity of radiometrical methods.

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