

interactions with living organisms are largely passive and they have no known biological function.

Transuranic elements are transported through the different compartments of marine ecosystems mainly by means of physical and chemical processes. Adsorption on suspended particulate material plays an important role in determining their accumulation in bottom sediments, which ultimately represent the storage reservoir. Subsequent remobilization is largely dependent upon geological processes. Benthic organisms have a minor role, usually through their own movements causing a rearrangement of upper sediment layers.

Biota are exposed to transuranic elements mainly through surface contact and ingestion (filter-feeding organisms). Transfer to man through the food chains is not relevant: biomagnification phenomena do not occur and concentration factors generally decrease with trophic level. Within the past years, concentration factors for Np, Pu, Am, and Cm have been determined in several species, but most data have been obtained for Pu-239. In algae and invertebrates, concentration factors for this radionuclide are in the range 100–10,000, while in vertebrate tissues lower values ranging from 1 to 100 have been observed.

Transuranic nuclides are of particular concern for the assessment of the radiological impact associated with the disposal of high-level radioactive wastes. Research on the long-term environmental behaviour of these man-made elements is considered with high priority in radiation protection programmes.

## E29

### Use of Higher Oxidation States of Trans-Plutonium Elements for Their Determination

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Besides the main oxidation state +3, transplutonium elements (TPE) possess a much more rich range

of oxidation states than analogous lanthanides. Lately Am(VII), Cm(VI), Cf(IV) and Cf(V), Md(I) have been added to the known Am(IV), Am(V), Am(VI), Cm(IV), Bk(IV), Md(II) and No(II). The number of practical methods for obtaining and stabilizing such forms as Am(IV), Am(V), Am(VI), Bk(IV), Fm(II) and Md(I) have been elaborated during systematic investigations of unusual oxidation states of TPE. This permitted to spread their use in technology and analytical practice.

The use of Am(V) gives a great effect at americium isolation from other TPE. They usually obtain Am(V) in two steps: at first Am(III) is oxidized to Am(VI) and then Am(VI) is reduced to Am(V). Persulphate ions are often used as oxidizer with heating. We have elaborated more suitable methods of oxidation: by the mixture of  $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{AgNO}_3$  without heating and electrochemically. In the latter case Am(III) is oxidized on platinum anode at potential of 2 V in a slight acidic solution (0.02–0.1 M  $\text{HClO}_4$ ,  $\leq 0.01$  M  $\text{H}_3\text{PO}_4$ ). It is easy to reduce Am(VI) to Am(V) by lowering the anode potential to 1.27 V. However, there is often no necessity to reduce specially Am(VI) since the extractant or the sorbent can act as reducer.

Am(V) extraction by several extractants: 1-phenyl-3-methyl-4-benzoylpyrasolone-5 (PMBP), di-2-ethylhexylphosphoric acid (HDEHP), ammonium pyrrolidinedithiocarbamate ( $\text{NH}_4\text{PDTC}$ ), mixture of PMBP and tri-n-octylphosphine oxide (TOPO), pycrolonic acid (PA), from different solutions has been studied (Table I).

Am(V) is extracted by different extractants from solutions with pH = 5, while extraction of trivalent actinides can be suppressed by complexing agents—acetate ions or  $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$ (PW). The separation coefficient ( $K_s$ ) of Am(V) and Cm(III) in these conditions during one-fold extraction cycle reaches  $5 \times 10^3$ . On the contrary, trivalent actinides can be separated by extraction from 0.1 M  $\text{HClO}_4$  or  $\text{HNO}_3$  if complexing agents are absent.

Reagent  $\text{NH}_4\text{PDTC}$  can be used also for Am(V) separation from tri- and hexavalent actinide ions by the precipitation method. More than 99% of Am(V) coprecipitates with PDTC at pH = 5, while copre-

TABLE I.

Aqueous phase	Organic phase	Distribution coef.	
		AM(V)	ME(III)
0.01 M $\text{NH}_4\text{NO}_3$ , pH = 5 (acetate buffer)	0.06 M $\text{NH}_4\text{PDTC}$ in the mixture of i-pentanol and ethanol	30	0.02*
0.1 M $\text{NH}_4\text{NO}_3$ , pH = 5 (acetate buffer)	0.05 M PMBP in i-butanol	11.6	50
the same + 0.001 M PW	the same	12.7	0.002
the same + 0.001 M PW	0.5 M HDEHP in octane	30	0.01
0.1 M $\text{HClO}_4$ + 0.01 M $\text{H}_3\text{PO}_4$	0.05 M PMBP + 0.025 M TOPO in cyclohexane	0.02	900
0.1 M $\text{HNO}_3$	0.16 M PA in methyl-i-butyl-ketone	0.26	194

precipitation of Me(III) and Me(VI) does not exceed a few percents.

The ability of berkelium to be oxidized to Bk(IV) is often used for its isolation from trivalent TPE and lanthanides. The mixture of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{AgNO}_3$  oxidizes rapidly Bk(III) to Bk(IV) at room temperature in  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  solutions. Different amines and neutral phosphorus-organic compounds (tributylphosphate, TBP, trioctyl- and triphenylphosphine oxides, TOPO, TPPO) have been investigated as extractants of Bk(IV). It has been established that Bk(IV) can be extracted by 0.4 M solution of trioctylamine in  $\text{CCl}_4$  from 6–10 M  $\text{HNO}_3$  solutions containing 0.2 M  $\text{K}_2\text{Cr}_2\text{O}_7$  as oxidizer ( $D = 20$ ). 30% solution of Aliquat-336 in  $\text{CCl}_4$  is a good extractant for Bk(IV) at  $\text{HNO}_3$  concentrations 10–12 M: 95% of Bk(IV) is extracted for one-fold extraction, it is possible to separate berkelium from other TPE and rare-earths. Bk(IV) is extracted from  $\text{H}_2\text{SO}_4$  solutions by a solution of decylamine in  $\text{CCl}_4$ , and from nitric, hydrochloric and sulphuric acids by solutions of TBP, TOPO and TPPO.

Berkelium(IV) is strongly adsorbed by zirconium phosphate–silicate sorbent from 1 M  $\text{HNO}_3$ . Berkelium isolation from all TPE and other elements is based on this phenomenon, the separation coefficient of Bk from Am, Cm and Cf being more than  $3 \times 10^3$ .

The existence of reversible electrochemical pairs Am(VI)/Am(V) and Am(IV)/Am(III) has permitted to elaborate coulometric methods of Am determination. These methods possess high sensitivity and accuracy. The possibility of electrochemical oxidation of Am(III) to Am(IV) and Am(VI) and the great stability of higher oxidation states of americium in  $\text{H}_3\text{PO}_4$  and PW solutions are the basis of these methods. Particularly, we have established that stable Am(IV) exists not only in 10–15 M aqueous  $\text{H}_3\text{PO}_4$  solutions, but it forms on electrochemical oxidation of Am(III) in 0.3–2 M solutions of  $\text{H}_3\text{PO}_4$  in acetonitrile.

The conditions of coulometric determination of Am are presented in Table II. It is possible to determine 5  $\mu\text{g}$  Am (and more) with precision of 1–2%. Pu, Cm, lanthanides(III) and actinides(III)

TABLE II.

Electro-chem. pair	Solution	Anode potential, V, and time of oxid.	
		Oxidation	Reduction
Am(VI)/Am(V)	2 M $\text{H}_3\text{PO}_4$ + 0.1 M $\text{HClO}_4(\text{aq})$	2.0(1.5 h)	1.3
Am(IV)/Am(III)	0.006 M PW + 0.1 M $\text{HClO}_4(\text{aq})$	1.7(15 m)	1.2
Am(IV)/Am(III)	0.5 M $\text{H}_3\text{PO}_4$ (acetonitr.)	2.0(30 m)	1.2

do not interfere in the determination of americium. Ce interferes in phosphoric acid aqueous solution and does not interfere in PW solution.

A spectrophotometric method of americium determination by measuring the light absorption at 500 nm ( $\epsilon = 1227$ ) in 0.004 M PW solution has been elaborated. The mixture of 0.2 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  + 0.003 M  $\text{AgNO}_3$  is used to oxidize Am(III) to Am(IV), oxidation time at room temperature being 5 min. The limit of detection is equal to 10  $\mu\text{g}/\text{ml}$  Am, with precision of about 2%. Curium, lanthanides and some other elements do not interfere in the Am determination.

## E30

### Cation-exchange Separation of Thorium(Zirconium), Scandium(Uranium) and Rare Earth with Arsenazo M as the Eluant

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Strong inorganic acids [1, 2] and organic complexing agents [3, 4] have been usually used as eluants for cation-exchange separation of U(VI), Th, Zr, Sc and RE. However, the elution volume of strong inorganic acid is large, the organic complexing agents always interfere the determination of metals in the effluent. In this paper Arsenazo M has been developed as an eluant, the effluent may be used for direct spectrophotometric determination. The simple and rapid methods for cation-exchange and direct spectrophotometric determination of Zr/Sc/RE, Zr/U/RE, Th/Sc/RE mixture have been proposed.

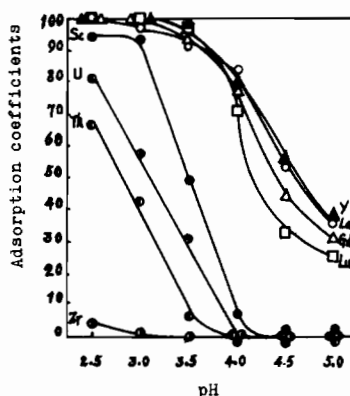


Fig. 1. Adsorption coefficients of Zr, Th, Sc, U, Y, La, Gd, Lu in Arsenazo M solution ( $\text{HAc-NaAc}$  medium). Liq. phase:  $6.62 \times 10^{-4}$  M Arsenazo M solution ( $\text{HAc-NaAc}$  medium). Solid phase: Macroreticular resin, a sulfonate of polystyrene divinylbenzene ( $\text{Na}^+$  form), 150–180 mesh.