cipitation 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 $(NH_4)_2S_2O_8$ and $AgNO_3$ oxidizes rapidly Bk(III) to Bk(IV) at room temperature in HNO_3 and H_2SO_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 CCl_4 from 6–10 *M* HNO_3 solutions containing 0.2 *M* $K_2Cr_2O_7$ as oxidizer (D = 20). 30% solution of Aliquat-336 in CCl_4 is a good extractant for Bk(IV) at 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 H_2SO_4 solutions by a solution of decylamine in 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* 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 3×10^3.

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 H_3PO_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 H_3PO_4 solutions, but it forms on electrochemical oxidation of Am(III) in 0.3–2 *M* solutions of H_3PO_4 in acetonitrile.

The conditions of coulometric determination of Am are presented in Table II. It is possible to determine 5 μg Am (and more) with precision of 1–2%. Pu, Cm, lanthanides(III) and actinides(III) do not interfere in the determination of americium. Ce interferes in phosphoric acid aqueous solution and does not interfere in PW solution.

TABLE II.

Electro-chem. pair	Solution	Anode potential, V, and time of oxid.	
		Oxidation	Reduction
Am(VI)/ Am(V)	2 M H_3PO_4 + 0.1 M $HClO_4$(aq)	2.0(1.5 h)	1.3
Am(IV)/ Am(III)	0.006 M PW + 0.1 M $HClO_4$(aq)	1.7(15 m)	1.2
Am(IV)/ Am(III)	0.5 M H_3PO_4 (acetonitr.)	2.0(30 m)	1.2

A spectrophotometric method of americium determination by measuring the light absorption at 500 nm (ε = 1227) in 0.004 *M* PW solution has been elaborated. The mixture of 0.2 *M* $(NH_4)_2S_2O_8$ + 0.003 *M* AgNO 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 μg/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.

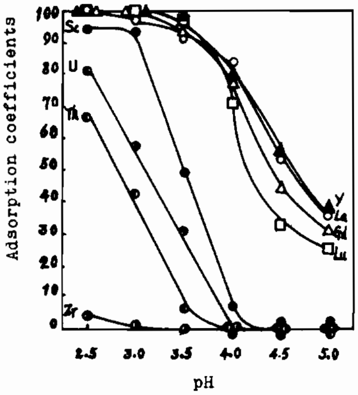

Fig. 1. Adsorption coefficients of Zr, Th, Sc, U, Y, La, Gd, Lu in Arsenazo M solution (HAc–NaAc medium). Liq. phase: 6.62×10^{-4} *M* Arsenazo M solution (HAc–NaAc medium). Solid phase: Macroreticular resin, a sulfonate of polystyrene divinylbenzene (Na^+ form), 150–180 mesh.

The ion exchange behaviour of U, Th, Zr, Y, La, Gd and Lu on the strong acidic cation exchange resin in Arsenazo M in various media (aqueous, acetic acid–sodium acetate and hydrochloric acid–sodium acetate buffer solution) has been investigated by equilibrium. The adsorption coefficients of the above metals have been measured. From the experimental results the acetic acid–sodium acetate buffer solution is favourable for the metals (Fig. 1).

The mechanism of the effects of the media has been studied, with La as a representation, because the media greatly affect the adsorption coefficients of the metals. When the Arsenazo M solution contains some single bonded ligands such as Ac^-, we found that the shape and peak place of the absorption spectra of the complexes formed with La change distinctly (as shown in Fig. 2). It is clear that Lanthamum has formed a ternary complex, acetate–metal ion–Arsenazo M. Thus, the adsorption coefficients of La are much smaller in the Arsenazo M solution containing Ac^- medium than in that containing no Ac^- medium. The results for the other elements (Th, Sc, *etc.*) are similar to La.

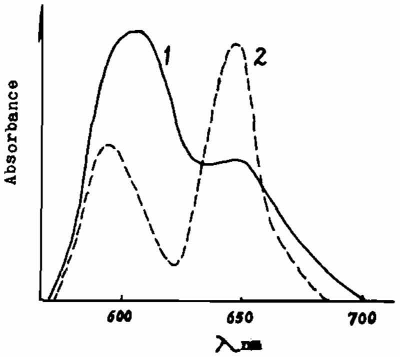

Fig. 2. Absorption spectra of La complexes in various media (reference: reagent blank). 1) HAc–NaAc; 2) aqueous.

TABLE I. Results for Separation and Determination of Mixtures.

Mixtures	Ratios of metals	Taken (μg)		Found (μg)	Recovery (%)
Zr–Sc–RE	1000:1:1	Zr	2000	1967	98
		Sc	2.0	2.1	105
		RE	2.0	1.9	95
	2:1:60	Zr	10	10.3	103
		Sc	5.0	5.0	100
		RE	300	290	97
Zr–U–RE	500:5:1	Zr	1000	1000	100
		U	10	9.8	98
		RE	2.0	2.2	110
	5:200:1	Zr	10	9.7	97
		U	400	406	102
		RE	2.0	2.0	100
Th–Sc–RE	40:4:1	Th	200	188	94
		Sc	20	19	95
		RE	5.0	5.0	100
	1:3:10	Th	10	10	100
		Sc	30	31	103
		RE	100	95	95
Th–RE	2000:1	Th	4000	3900	98
		RE	2.0	2.2	110
	1:100	Th	5.0	5.1	102
		RE	500	500	100
U–RE	2000:1	U	4000	4100	102
		RE	2.0	1.9	95
	1:100	U	10	10	100
		RE	1000	935	94
Sc–RE	2000:1	Sc	4000	4125	103
		RE	2.0	2.1	105
	1:500	Sc	2.0	2.0	100
		RE	1000	975	98

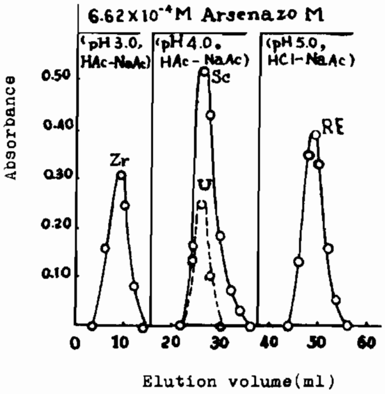

Fig. 3. Elution curve of Zr–Sc (or U–RE).

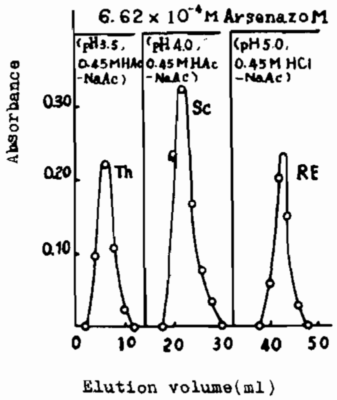

Fig. 4. Elution curve of Th–Sc–RE.

According to the experimental results the complete separation of the ternary mixtures may be achieved by a column (0.8 cm × 10 cm). The flow rate was 0.5–1.0 ml/min. The elution was carried out at room temperature.

Procedure of column separation: Solution of mixture of Zr/Sc(U)/RE (or Th/Sc/RE) added to the column. Elution was carried out with Arsenazo M in the different media and pH. Elution curves for these mixture are given in Fig. 3 and 4. The metals were directly determined by spectrophotometry. The spectrophotometric determination of each element is presented in the literature [5].

The results of percentage recovery are shown in Table I.

The method was applied to the analysis of Th (0.017–0.17%), Sc (0.005–0.13%), and RE (0.6–2.9%) in ore samples with satisfactory results

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E31

Thermochromatographic Studies of the Heaviest Actinides

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The latest Dubna studies on the thermochromatographic behaviour of lanthanide and actinide elements in metallic columns are reviewed. At a very low concentration of oxygen in the carrier gas (He, Ar) and in the column material, under certain conditions, lanthanides and actinides form adsorption zones at about 600 °C in Ti columns. The deposition temperature increases beyond 1200 °C with increasing oxygen content. No separation of the elements has practically been observed. The chemical transport of gaseous lower oxides seems to be responsible for the behaviour of the elements under study in the presence of just minute quantities of oxygen.

When oxygen is practically removed by the addition of some calcium vapours to the carrier gas, those lanthanides and actinides known to be divalent metals are deposited in Ti columns at 500–600 °C, at the same time as the trivalent metals—at considerably higher temperatures. This can be understood if the elements are present in the atomic state and their valency in the adsorbed state is the same as that of the metals [1]. These regularities offer some prospects for the experimental study of the metallic valency of element 102. The basic scheme of such an experiment with the short-lived $^{252}102$ ($T_{1/2} = 3s$, 30% SF) on a beam from a heavy ion accelerator is discussed. The necessary experimental conditions are chosen from experiments with some Yb tracers.

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E32

Determination of Trace Rare Earth Impurities in High-purity Yttrium Oxide by Using Ion-exchange Separation and Spectroscopic Method

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Since the sensitivity of direct emission spectroscopic method is not enough to analize rare earth impurities in high-purity rare earth oxides, a separation and pre-concentration step is always required. In the present paper, a cation exchange spectroscopic method is described. α-Hydroxyisobutyric acid is used as an efficient eluant to separate La, Ce, Pr, Nd,