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Reversed Phase Extraction Chromatographic Separation of Germanium with Aliquat 336S from Citric Acid

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Germanium was extracted from 0.005 mol dm^{-3} citric acid at a pH between 2.5 and 6.5 on a column of silica gel coated with Aliquat 336S as the stationary phase. Germanium was then stripped with 0.5 mol dm^{-3} hydrochloric acid and determined spectrophotometrically as its complex with phenylfluorone. Germanium was separated from alkali and alkaline earths, manganese, iron, cobalt, nickel, copper, and zinc in binary mixtures by the exploitation of difference in pH for formation of citrato complexes. It was separated from antimony, bismuth, tin, gallium, indium, and thallium by taking advantage of stability of chloro and sulfato complexes. This method was applied to the determination of germanium in coal fly ash.

The solvent extraction methods for the separation of germanium with liquid anion exchangers as extractants are limited. Germanium has been separated from tin and lead with Amberlite LA-1.[1] Trioctylamine in kerosine was used for the extraction of germanium from oxalic acid.[2,3] The separation of germanium from cobalt and copper by extraction chromatography was carried out with trioctylamine.[4] However, germanium was not separated from associated elements. In continuation of our work with citric acid[5] as the complexing media, extraction chromatographic studies were extended for the separation of germanium on a column of silica gel coated with Aliquat 336S as the stationary phase. This paper describes the separation of germanium from associated elements.

Experimental

Apparatus and Reagents. Spectrophotometer GS 886C (ECIL, India) with matched corex glass cells and Orion Research Microprocessor Ionalyser 901 (Orion, USA) were used.

A stock solution of germanium (3.976 mg cm^{-3}) was prepared by fusing 0.573 g of germanium oxide (ExcelaR grade, Qualigens, India) with 0.5 g of sodium hydroxide in a platinum crucible, neutralizing the residue with hydrochloric acid and diluting to 100 cm^3 with distilled water, and standardized gravimetrically.[6] A solution containing 15 μg cm^{-3} of germanium was prepared by appropriate dilution.

Aliquat 336S (trialkylmethylammonium chloride) was obtained from Fluka and used without further purification.

The silica gel (100—200 mesh) was dried at 120 °C for 2 h, and then packed in a U-tube. A stream of dry nitrogen was passed for 3 h through a small Drechsel bottle containing 25 cm^3 of dimethyldichlorosilane, and then through U-tube containing the silica gel, to convert the surface silanol groups to silyl ether groups. The silica gel was then washed with anhydrous methanol to form methoxyl groups from the unreacted hydroxyl groups, as well as to remove hydrochloric acid from the silica gel. The treated silica gel was then dried at 100 °C. In routine work 1 cm^3 of dimethyldichlorosilane is adequate to render 10 g of silica gel hydrophobic.

A solution of 1 cm^3 of Aliquat 336S in benzene was prepared and transferred into a flask containing 4 g of the hydrophobic silica gel. The benzene was slowly removed from the suspension, in a rotary vacuum evaporator, until dry silica gel was obtained; a low vacuum was applied to remove air from the micropores and to accelerate evaporation of benzene. The silica gel coated with Aliquat 336S was then slurried with citric acid solution and poured into a column having a bed dimension of 10×0.8 cm, where 4 g of the coated silica gel was sufficient to give a bed height of 8 cm which was used for the column studies. The column is not affected with use of strong acids or alkalies as stripping agents.

General Procedure. An aliquot of solution containing 15 μg of germanium was mixed with 5 cm^3 of 0.005 mol dm^{-3} citric acid and the pH of the resulting solution was adjusted to 4.0 either with 0.005 mol dm^{-3} citric acid or sodium hydroxide. The solution was passed through the column at a flow rate of 1 cm^3 min^{-1} where germanium was extracted as its anionic citrato complex by Aliquat 336S. It was stripped with various mineral acids and alkalies. Eight 5 cm^3 fractions were collected. The amount of germanium from each fraction was determined spectrophotometrically as its complex with phenylfluorone at 530 nm.[7]

Results and Discussion

Germanium can be quantitatively extracted with 0.1 mol dm^{-3} Aliquat 336S in xylene from 0.01 mol dm^{-3} citric acid at a pH between 3.0 and 6.0 employing batch

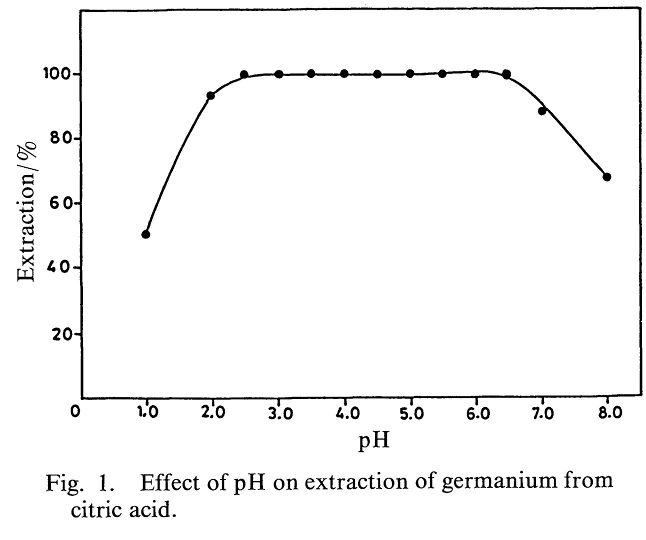

Fig. 1. Effect of pH on extraction of germanium from citric acid.

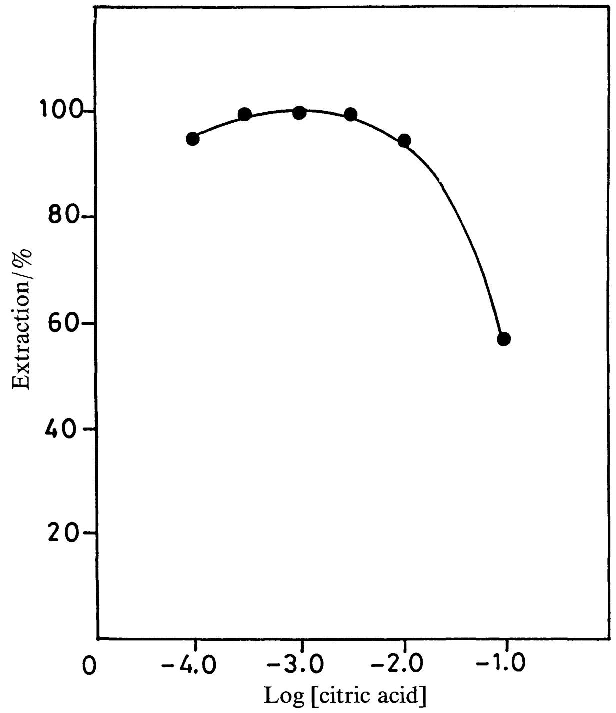

Fig. 2. Effect of citric acid concentration on extraction of germanium.

extraction.[8] However in the extraction chromatographic method, this procedure was modified. The study of extraction of germanium as a function of pH was carried out in the pH range of 1.0 to 8.0. The extraction commenced at pH 1.0 (51.4%) and was quantitative in the pH range of 2.5 to 6.5. Above pH 6.5 (96.2% extracted), the amount of germanium extracted decreased (Fig. 1). The optimum pH for the extraction of germanium used was 4.0 as it is intermediate between 2.5 to 6.0 where extraction was quantitative.

The optimum concentration of citric acid for the complete extraction of germanium was ascertained by extracting from aqueous solution containing 1×10^{-4} to 1×10^{-2} mol dm^{-3} of citric acid. The extraction was incomplete below 1×10^{-4} mol dm^{-3} (Fig. 2). Above 1×10^{-2} mol dm^{-3} citric acid concentration the extraction decreased probably due to presence of competitive equilibria between anionic citrato complex of germanium and citrate anion of Aliquat 336S.

The germanium extracted was stripped from the stationary phase with various mineral acids and alkalies. Hydrochloric acid (0.5—4 mol dm^{-3}), nitric or sulfuric acid (0.25—8 mol dm^{-3}) was capable of stripping of germanium quantitatively. Similarly, 0.25—1.0 mol dm^{-3} of sodium hydroxide or sodium carbonate was also effective for stripping of germanium. At high concentration of hydrochloric acid (>6 mol dm^{-3}) germanium forms negatively charged chloro complex which in turn was reextracted on the column. Hydrochloric acid was selected as a stripping agent considering its use in the spectrophotometric determination of germanium (Table 1).

Separation of Germanium from Other Ions. Germanium was separated from several elements in binary mixtures by utilizing the differences in their capability to form anionic complexes. Thus, since alkali and alkaline earths, manganese, iron, cobalt, nickel, zinc, cadmium, aluminium, and lead can not form anionic citrato complexes they were not extracted and hence were separated from germanium. Some metal ions forming stable complexes with citrate were strongly retained on the column but these were effectively separated from germanium by using suitable stripping agents. Since germanium forms anionic chloro complexes at higher concentration of hydrochloric acid, it was possible to separate it from scandium, titanium, zirconium, hafnium, vanadium, thorium, and palladium as they can not form such complexes and were stripped out with 6 mol dm^{-3} hydrochloric acid. Germanium, which was retained in the form of anionic chloro complex on the liquid anion exchanger, was subsequently stripped with 0.5 mol dm^{-3} hydrochloric acid. Germanium has been separated from gallium, indium, thallium, tin, antimony, and bismuth in binary mixtures by the judicious choice of stripping agents. Germanium was stripped with 3 mol dm^{-3} hydrochloric acid when other elements were reextracted as chloro complexes and later stripped with specific eluents (Table 2). In all these separations, the elements were determined spectrophotometrically by using appropriate chromogenic reagents.[9] Examples of the separation of germanium from multicomponent mixtures are given in Table 3.

Analysis of Germanium in Fly Ash. A 0.5 g of fly ash was dissolved in a mixture (10 cm^3) of aqua regia and hydrofluoric acid (1 : 1) in a Teflon container[10] and evaporated to almost dryness. The residue was dis-

Table 1. Effect of Stripping Agents. Amount of Ge Taken, 15 µg

Stripping agent	Recovery/%									
mol dm^{-3}	0.1	0.25	0.5	1.0	2.0	3.0	4.0	5.0	6.0	8.0
HCl	0.0	92.4	100.1	100.1	100.1	100.1	100.1	14.5	0.0	0.0
HNO_3	65.5	99.8	99.9	99.8	99.8	99.9	99.8	99.9	99.8	99.8
H_2SO_4	24.4	99.9	99.9	99.8	99.8	99.9	99.9	99.8	99.9	99.9
NH_4OH	48.4	53.2	58.8	66.4						
NaOH	99.9	99.9	99.8	99.9						
Na_2CO_3	74.2	100.1	100.1	100.1						

Table 2. Separation of Germanium from Other Elements in Binary Mixtures
Amount of Germanium Taken, 15 μg

Foreign ion	Added as	Amount of foreign ion added	Recovery of Ge	Stripping agent
		mg	%	mol dm^{-3}
Mn^{II}	$MnSO_4\cdot7H_2O$	1.2	98.7	H_2O
Co^{II}	$Co(NO_3)_2\cdot6H_2O$	1.2	99.1	H_2O
Ni^{II}	$Ni(NO_3)_2\cdot6H_2O$	1.1	99.8	H_2O
Cu^{II}	$CuSO_4\cdot5H_2O$	1.4	99.0	H_2O
Zn^{II}	$ZnSO_4\cdot7H_2O$	1.0	99.6	H_2O
Cd^{II}	$3CdSO_4\cdot8H_2O$	0.9	99.4	H_2O
Pb^{II}	$Pb(NO_3)_2$	1.75	99.6	H_2O
Al^{III}	$Al(NO_3)_3\cdot9H_2O$	1.05	99.2	H_2O
Ga^{III}	$GaCl_3$	0.5	99.4	0.5 HCl[b]
In^{III}	$In_2(SO_4)_3\cdot5H_2O$	0.35	99.8	0.5 HCl[b]
Tl^{III}	Tl_2O_3	0.5	100.1	1.0 $HClO_4$[b]
Sn^{IV}	SnO_2	0.5	98.8	0.5 H_2SO_4[b]
Sb^{III}	$SbCl_3$	0.4	99.2	0.5 H_2SO_4[b]
Bi^{III}	$Bi(NO_3)_3\cdot5H_2O$	0.2	99.4	0.5 H_2SO_4[b]
Au^{III}	$AuCl_3\cdot2H_2O$	0.15	99.2	0.5 NaOH[b]
Sc^{III}	$Sc(NO_3)_3$	0.4	98.4	6.0 HCl[a]
Ti^{IV}	$TiCl_4$	0.25	99.2	6.0 HCl[a]
Zr^{IV}	$Zr(NO_3)_4\cdot5H_2O$	0.4	98.2	6.0 HCl[a]
Hf^{IV}	$Hf(SO_4)_2$	0.5	99.1	6.0 HCl[a]
V^{IV}	$VOCl_2$	0.5	99.2	6.0 HCl[a]
U^{VI}	$UO_2(NO_3)_2\cdot6H_2O$	1.0	98.8	0.5 HCl[b]
Th^{IV}	$Th(NO_3)_4\cdot4H_2O$	0.4	99.2	6.0 HCl[a]

a) Before stripping of germanium. b) After stripping of germanium.

Table 3. Separation of Germanium from Multicomponent Mixtures

Mixture No.	Element	Stripping agent	Amount taken	Recovery
		mol dm^{-3}	μg	%
1.	Pb	H_2O	250.0	98.8
	Ge	3.0 HCl	15.0	99.4
	Sn	0.5 H_2SO_4	75.0	98.9
2.	Ag	H_2O	325.0	99.4
	Ge	3.0 HCl	15.0	98.9
	Au	1.0 NaOH	100.5	99.2
3.	Ge	4.0 HCl	15.0	99.8
	Fe	0.05 HCl	200.0	99.4
	Sb	5.0 HNO_3	150.0	98.7
	In	0.5 HCl	100.0	98.8
4.	Al	H_2O	150.0	99.4
	Bi	0.05 H_2SO_4	250.0	99.8
	Ge	1.0 H_2SO_4	15.0	99.8
	Tl	1.0 $HClO_4$	150.0	99.9

solved in dilute hydrochloric acid. An aliquot of solution containing germanium was passed through the column as described in General Procedure. Copper, cobalt, zinc, and cadmium were not retained and so they passed through column. Thorium was then stripped with 6 mol dm^{-3} hydrochloric acid and finally germanium with 3 mol dm^{-3} hydrochloric acid. The germanium content found was 18.8 ppm against the standard value of 19.0 ppm.

The advantages of the proposed method over solvent extraction method is that it couples the favorable features of solvent extraction and ion exchange. Multiple extractions are possible in a single column. In batch extractions, 10 cm^3 of 0.1 mol dm^{-3} Aliquat 336S is used for one extraction whereas in extraction chromatography same amount can be used for twenty extractions on a single column.

The proposed method is rapid and reasonably selective. The time required for complete separation and determination is 2 h.

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