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Solvent Extraction Separation of Germanium with Aliquat 336S from Citric Acid Solutions

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Germanium was quantitatively extracted with 0.1 mol dm^{-3} Aliquat 336S in xylene from 1×10^{-3} mol dm^{-3} citric acid solution adjusted to pH 3.5. It was stripped with 0.5 mol dm^{-3} hydrochloric acid and determined spectrophotometrically at 530 nm as the complex with phenylfluorone. It was effectively separated from binary as well as ternary mixtures by taking advantage of the difference in the stability of the citrate complexes with metal ions in mineral acids. The method was applied to the determination of germanium in coal fly ash.

Germanium was extracted with carbon tetrachloride.[1] Tributyl phosphate in toluene could extract germanium in the presence of salting out agent.[2] The extraction was not quantitative with diisopropyl ether.[1] Trioctylamine in butanol[3] or with oxine[4] in chloroform was also used for extraction of germanium. Germanium was separated from tin and lead with Amberlite LA-1 in xylene.[5] Trioctylamine in kerosene was used for the extraction of germanium from oxalic acid,[6,7] however germanium was not separated from associated elements.

This paper describes, therefore, a systematic investigation on the solvent extraction of germanium with Aliquat 336S from citric acid solutions. Novel methods are developed for the separation of commonly interfering ions. The method is applied to the determination of germanium in a standard coal fly-ash sample.

Experimental

Apparatus and Reagents. Spectrophotometer GS866C (ECIL, India) with matched Corex glass cells, Orion Research Microprocessor ion analyzer/901 (Orion Ltd., USA), with glass and calomel electrodes and Wrist action flask shaker (Toshniwal, India) were used.

A stock solution of germanium was prepared as follows: About 0.32 g of germanium dioxide was fused with equal amount of sodium hydroxide in a platinum crucible. The cooled mass was extracted with water and the solution was neutralized with hydrochloric acid. It was then made up to 100 cm^3 with water and standardized gravimetrically.[8] It contained 2.2 mg cm^{-3} of germanium. The working solution containing 22 μg cm^{-3} of germanium was prepared by exact dilution with water. Phenylfluorone (BDH, AnalR) (0.05% ethanolic solution), Gelatin (1% aqueous solution), Amberlite LA-1, Amberlite LA-2 (Rohm and Hass, Co. USA), Aliquat 336S (General Mills Ltd., England) and TOA (Riedel-Haen, Germany) were used without further purification. The extractant was converted into the citrate form as described earlier.[9]

General Procedure. To an aliquot of solution containing 22 μg of germanium, 5 cm^3 of 0.01 mol dm^{-3} citric acid was added. The pH of the solution was adjusted to 3.5 with 0.01 mol dm^{-3} sodium hydroxide or citric acid. The total volume of the aqueous phase was made up to 10 cm^3 and the solution was transferred to a separatory funnel. It was equilibrated with 10 cm^3 of 0.1 mol dm^{-3} Aliquat 336S in xylene for 5 min on wrist action flask shaker. After allowing the phases to settle and separate the aqueous phase was discarded and the organic phase was shaken with 10 cm^3 of 0.5 mol dm^{-3} hydrochloric acid to strip germanium. To the solution thus obtained 1 cm^3 of 1% gelatin and 2 cm^3 of 0.05% phenylfluorone in ethanol were added and the volume was made up to 25 cm^3 with distilled water. The absorbance of the yellow orange colored complex was measured at 530 nm against the reagent blank. The concentration of germanium was obtained from a calibration curve.[10]

Results and Discussion

Effect of pH. The pH for the quantitative extraction was ascertained by carrying out extractions between pH 1.0 and 8.0 with various liquid anion exchangers (Fig. 1). The extraction of germanium

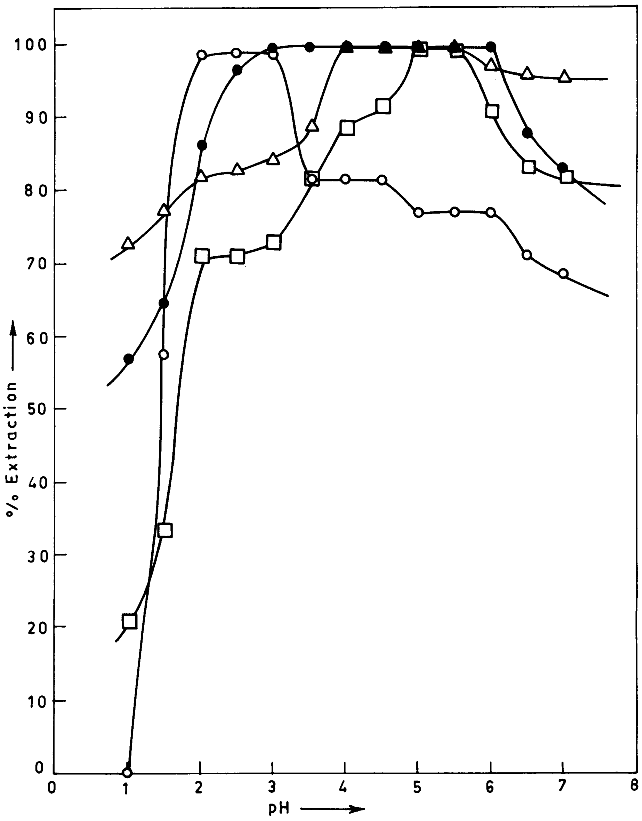

Fig. 1. Extraction of germanium with liquid anion exchangers.
●: Aliquat 336S (0.1M), ○: Amberlite LA-2 (0.08M), □: Amberlite LA-1 (0.1M), △: TOA (0.1M).

Table 1. Effect of Aliquat 336S Concentration
Ge=22 μg; pH=3.5

Concentration of Aliquat 336S 10^{-2} mol dm^{-3}	Extraction/%	Distribution ratio
1.00	59.3	1.5
1.25	64.3	1.8
2.50	86.0	6.1
3.75	88.9	8.0
5.00	93.1	13.5
6.25	96.6	29.5
7.50	99.9	999.0
8.75—10.0	99.9	999.0

Table 2. Effect of Citric Acid Concentration
Ge=22 μg; pH=3.5

Concentration of citric acid 10^{-4} mol dm^{-3}	Extraction/%	Distribution ratio
1	56.0	1.3
2	74.5	2.9
3	79.6	4.9
4	85.8	6.0
5	91.0	10.1
6	98.1	51.6
7	99.3	141.9
8-10	99.9	999.0

into xylene commenced below pH 1.0 for all the extractants except Amberlite LA-2. The extraction was quantitative from pH 3.0 to 6.0 with Aliquat 336S, pH 2.0 to 3.0 with Amberlite LA-2, pH 5.0 to 5.5 with Amberlite LA-1, and pH 4.0 to 4.5 with TOA in xylene. As the optimum pH range for the extraction was fairly broad. Aliquat 336S was used in further investigation. On the contrary the pH was quite broad (pH 3.0—6.0) with Aliquat 336S. Therefore Aliquat 336S was selected for further work.

Effect of Aliquat 336S Concentration. Germanium was extracted with varying concentrations of Aliquat 336S (1×10^{-2}—10^{-1} mol dm^{-3}) in xylene, while other factors were held at constant (Table 1). The extraction was almost quantitative when more than 7.5×10^{-2} mol dm^{-3} Aliquat 336S was used. Therefore 1×10^{-1} mol dm^{-3} Aliquat 336S was preferred throughout this investigation.

Effect of Citric Acid Concentration. The optimum concentration for the complete extraction was ascertained by extracting germanium from aqueous solution containing 1×10^{-4} to 10×10^{-3} mol dm^{-3} citrate. The extraction was incomplete below 5×10^{-4} mol dm^{-3} but quantitative above 7×10^{-4} mol dm^{-3} citrate (Table 2).

Effect of Various Diluents. A solution of 0.1 mol dm^{-3} Aliquat 336S was used in various diluents, such as, benzene, toluene, xylene, *n*-hexane, cyclohexane, carbon tetrachloride, chloroform, or nitrobenzene. The organic to aqueous phase volume ratio was maintained at 1:1. As shown in Table 3 chloroform and nitrobenzene are not effective as diluents perhaps due to their high polarities. The extraction was almost quantitative when xylene, *n*-hexane, cyclohexane, and carbon tetrachloride were used as diluents.

Table 3. Effect of Various Diluents
Ge=22 μg, Citrate concentration=0.001 mol dm^{-3}, pH=3.5

Diluent	Dielectric constant	Extraction %	Distribution ratio
Benzene	2.28	94.0	15.6
Toluene	2.38	95.6	21.7
Xylene	2.30	99.9	999.0
Hexane	1.89	99.0	99.0
Cyclohexane	2.05	99.3	141.8
Carbon tetrachloride	2.24	98.3	57.8
Chloroform	4.8	45.6	0.6
Nitrobenzene	35.5	88.1	7.4

Effect of Stripping Agents. Germanium was stripped, after extraction, with 10 cm^3 of various concentrations of mineral acids and alkalis. Hydrochloric acid (0.5—4.0 mol dm^{-3}) and nitric, sulfuric, and hydrobromic acids (0.5—8 mol dm^{-3}) were capable of stripping germanium quantitatively. Similarly sodium hydroxide (0.1—2.0 mol dm^{-3}) or sodium carbonate (0.5—2.01 mol dm^{-3}) was also effective stripping agents. Hydrochloric acid was selected as a stripping agent considering its use in the separation and determination of germanium (Table 4).

Nature of Extracted Species. The composition of the extracted species was investigated by plotting the logarithm of the distribution ratio of germanium against the logarithm of the concentration of Aliquat 336S at a constant citric acid concentration and the logarithm of the distribution ratio against the logarithm of the citric acid concentration at a constant concentration of Aliquat 336S. Linear relationship were obtained with slopes of 1.32 and 1.27, respectively. It is probable that the extracted species is $[R_4N^+\{Ge(OH)_2(Cit)^-\}]$. This postulation is supported by the observation of Pozhariskii et al.[12] who used trioctylamine in the extraction of germanium from citric and tartaric acid media.

Separation of Germanium from Foreign Metal Ions. Methods for the separation of germanium from foreign metal ions were investigated in the light of the difference in their complex forming abilities with citrate. Metal ions forming no complex or very weak complexes with citrate were not extracted and readily separated from germanium. A few metal ions forming weak complexes with citrate were readily removed from the organic extractant by washing with distilled water before stripping of germanium. Some metal ions forming stable complexes with citrate were strongly retained in the organic phase but these were effectively separated from germanium by using suitable stripping agents. Examples of the separation of germanium

Table 4. Effect of Different Stripping Agents Ge=22 μg

Stripping agents /mol dm^{-3}	Back stripping/%								
	0.1	0.25	0.5	1.0	2.5	4.0	5.0	6.0	8.0
HCl	0.0	94.0	99.9	99.9	99.8	99.7	10.5	0.0	0.0
HNO_3	67.8	99.9	99.9	100.0	99.9	99.1	100.0	99.8	99.8
H_2SO_4	20.3	99.0	99.9	99.1	100.1	100.0	99.8	99.9	99.8
HBr	0.0	99.7	99.9	99.9	99.9	99.9	100.0	99.0	0.0
Aqueous NH_3	50.0	62.7	69.5	70.0	—	—	—	—	—
NaOH	99.3	99.4	99.9	99.9	—	—	—	—	—
Na_2CO_3	76.3	99.3	99.8	99.5	—	—	—	—	—

Table 5. Separation from Binary Mixtures

Foreign ion	Added as	Tolerance limit/μg	Stripping agent†	Foreign ion	Added as	Tolerance limit/μg	Stripping agent†
Li^+	$Li_2SO_4 \cdot H_2O$	4500	Not extracted	Pb^{2+}	$Pb(NO_3)_2$	1850	H_2O
Na^+	NaCl	4400	Not extracted	Tl^+	Tl_2SO_4	1850	H_2O
K^+	KCl	4500	Not extracted	Ga	$GaCl_3$	275	0.5M HCL[b]
Rb^+	RbCl	4500	Not extracted	In	$InCl_3$	350	0.5M HCl[b]
Be^{2+}	$Be(NO_3)_2$	400	Not extracted	Tl^{3+}	$TlCl_3$	520	0.5M $HClO_4$[b]
Mg^{2+}	$MgSO_4 \cdot 7H_2O$	3200	Not extracted	Sn^{4+}	$SnCl_2$	325	0.5M H_2SO_4[b]
Ca^{2+}	$CaCl_2 \cdot 6H_2O$	3200	Not extracted	Sb^{3+}	$Sb(NO_3)_3$	410	0.5M H_2SO_4[b]
Sr^{2+}	$Sr(NO_3)_2 \cdot 2H_2O$	3200	Not extracted	Bi^{3+}	$Bi(NO_3)_3 \cdot 5H_2O$	130	0.5M H_2SO_4[b]
Ba^{2+}	$Ba(NO_3)_2 \cdot 4H_2O$	3000	Not extracted	Hg^{2+}	$HgCl_2$	240	0.1M NaOH[b]
Mn^{2+}	$MnSO_4 \cdot 7H_2O$	1000	H_2O	Sc^{3+}	$Sc(NO_3)_3$	200	5M HCl[a]
Fe^{2+}	$FeSO_4 \cdot 7H_2O$	1700	H_2O	Ti^{4+}	$Ti(SO_4)_2$	234	5M HCl[a]
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	970	H_2O	Zr^{4+}	$Zr(NO_3)_4 \cdot 4H_2O$	290	5M HCl[a]
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	1050	H_2O	Hf^{4+}	$Hf(SO_4)_2$	210	5M HCl[a]
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	890	H_2O	V^{4+}	NH_4VO_3	320	5M HCl[a]
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	950	H_2O	U^{6+}	$UO_2(NO_3)_2 \cdot 6H_2O$	275	0.5M HCl[b]
Ag^+	$AgNO_3$	1650	H_2O	Th^{4+}	$Th(NO_3)_4 \cdot 4H_2O$	150	5M HCl[a]
Cd^{2+}	$3Cd(NO_3)_2 \cdot 8H_2O$	990	H_2O	Au^{3+}	$AuCl_3$	225	0.5M NaOH[b]
As^{3+}	$AsCl_3$	980	H_2O	pt^{4+}	$PtCl_4$	265	0.5M NaOH[b]
Al^{3+}	$Al(NO_3)_3$	1100	H_2O	Pd^{2+}	$PdCl_2$	435	5M HCl[a]

† 1M=1 mol dm^{-3}.

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

from synthetic binary and ternary mixtures are given in Tables 5 and 6.

Application for the Determination of Germanium in Coal Fly Ash. About 0.5 g of a standard coal fly ash sample was dissolved in a mixture (10 ml cm^{-3}) of aqua regia and hydrofluoric acid (1:1) in a Teflon beaker. After removal of the excessive acids the content was dissolved in dilute hydrochloric acid and the solution was made up to 50 cm^3[11] with distilled water. An aliquot of this solution was equilibrated with 10 cm^3 of 0.1 mol dm^{-3} Aliquat 336S in xylene as described above. Copper, cadmium, zinc, and cobalt were also extracted but these metals were readily removed by washing the extract with distilled water; thorium was then stripped with 6 mol dm^{-3} hydrochloric acid and finally germanium with 3 mol dm^{-3} hydrochloric acid. With duplicate determinations, the amount of germanium found was 18.7 and 18.5 ppm against the standard value of 19.0 ppm.

The separation of germanium from copper, zinc, lead, and antimony is interesting, as these elements are usually associated with each other in minerals. Similarly the separation of germanium from gallium, indium, and thallium is important because of their

Table 6. Separation of Germanium from Ternary Mixtures

S. No.	Mixture	Taken	Found	Recovery	Stripping agents†
		μg	μg	%	
1	As(III)	210.5	210.4	99.9	H_2O
	Ge	22.4	22.3	99.5	4M HCl
	Hg	100.1	100.0	99.9	0.5M NaOH
2	Pb	314.2	314.0	99.9	H_2O
	Ge	22.4	22.4	100.0	3M HCl
	Sn	78.7	78.6	99.8	0.5M H_2SO_4
3	Al	278.0	277.5	99.6	H_2O
	Ge	22.4	22.2	99.1	3M HCl
	Bi	101.3	101.3	100.0	1M H_2SO_4
	Tl(III)	59.4	59.4	100.0	1M $HClO_4$
4	Ag/Zn	579.4	579.2	99.9	H_2O
	Ge	22.4	22.3	99.5	3M HCl
	Au	100.4	100.3	99.3	1M NaOH
5	Ge	22.4	22.3	99.5	4M HCl
	Sb	135.4	135.2	99.6	5M HNO_3
	In	100.0	99.8	99.8	0.5M HCl
6	Ge	22.4	22.2	99.1	3M HCl
	Bi	220.0	219.9	99.5	6M HCl
	Ga	125.0	124.8	99.8	0.5M HCl

† 1 M=1 mol dm^{-3}.

significant use in semiconductors. The proposed method is simple, rapid, and reproducible. The time required for complete separation and determination is 2 h. The standard deviation was 1.1% for 22 μg of germanium.

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