Chem. Anal. (Warsaw), 38, 469 (1993)

Liquid–Liquid Extraction of Gallium with High Molecular Weight Amines from Ascorbate Solutions

by M. A. Karve and S. M. Khopkar*

Department of Chemistry, Indian Institute of Technology, Bombay – 400 076, India

Key words: gallium, liquid–liquid extraction, spectrophotometry

Gallium was extracted at pH 4–6 with 0.1 mol l^{-1} Aliquat 336S in xylene as anionic ascorbate complex. It was stripped from the organic phase with 1 mol l^{-1} nitric acid and was determined by spectrophotometry at 510 nm as a complex with 4-(2-pyridylazo)resorcinol. Gallium was separated not only from aluminium, indium, thallium(III) but also from iron(II), vanadium(IV) and scandium which metals are generally associated with it in minerals and alloys. The method was extended for analysis of gallium in high purity aluminium.

Ekstrakcję galu w postaci anionowego askorbinianowego kompleksu prowadzono przy pH 4–6, używając 0.1 mol l^{-1} roztworu Aliquatu 336S w ksylenie. Z fazy organicznej odzyskiwano go kwasem azotowym o stężeniu 1 mol l^{-1}. Gal oznaczano spektrofotometrycznie przy długości fali 510 nm po uprzednim skompleksowaniu go 4-(2-pirydyloazo)rezorcynolem. Gal z powodzeniem oddzielano od Al(III), In(III), Tl(III), Fe(II), V(IV) i Sc(III), które to metale zwykle występują razem z nim w minerałach. Opracowany sposób rozdzielania wykorzystano do oznacznia Ga w wysokiej czystości metalicznym glinie.

Although anionic complexes of gallium with haloacids were extracted with high molecular weight amines [1], very limited efforts were made to extract its anionic complexes with organic acids. The sequential separation of gallium, indium and thallium was done with liquid anion exchangers from malonate, oxalate [2–4] and citrate media [5]. With trioctylamine, gallium was extracted from succinate [6] and

---

* Present address: Department of Chemical Technology, University of Bombay, Bombay – 400 019, India.

tartrate media [7]. However these methods suffered from several limitations, namely the extraction was possible only over a narrow pH range [1, 2]. It was necessary to use high reagent concentration [6] and it was not possible to separate gallium from thallium [4]. An endeavour is made to present in this paper a systematic investigation on solvent extraction separation of gallium from associated elements with Aliquat 336S from ascorbic acid solution.

EXPERIMENTAL

Apparatus and reagents

The following instruments were used: an ECIL pH-meter with a glass- and a calomel electrode; GS8660 spectrophotometer with matched 10-mm corex glass cuvettes; a wrist action flask shaker (Toshniwal, India).

The solution of gallium was prepared by dissolving 0.50 g of powdered metal in 20 ml of hot concentrated hydrochloric acid. The solution was evaporated almost to dryness and the residue was dissolved in 2 ml of concentrated hydrochloric acid. It was made up to 250 ml with distilled water, and was standardised complexometrically with EDTA [8]. A diluted solution containing 15 μg ml^{-1} of gallium was prepared by appropriate dilution.

Aliquat 336S (General Mills Ltd.), Amberlite LA-1 and LA-2, Primene JMT (Rohn and Hass Co., Philadelphia, USA), and trioctylamine (Riedel-de Haen, Germany) were used without further purification. Liquid anion exchangers were converted into the ascorbate form by equilibration with ascorbic acid.

4-(2-Pyridylazo)resorcinol (PAR) (BDH Chemicals, Analar) was used as 0.1 % aqueous solution.

General procedure

An aliquot of solution containing (15 μg) gallium was taken. Then 0.01 mol l^{-1} ascorbic acid was added to it. The pH of the resulting solution was adjusted to 5.0 with either 0.01 mol l^{-1} ascorbic acid or ammonia. The total volume was made up to 10 ml with distilled water. The solution was transferred into separatory funnel and 10 ml of 0.1 mol l^{-1} Aliquat 336S in xylene was added to it. It was shaken with a wrist action flask shaker for ten minutes. The two layers were allowed to settle and separate. From the organic phase gallium was stripped with 1 mol l^{-1} nitric acid. After dry ashing, to eliminate organic matter, gallium was determined spectrophotometrically as its complex with PAR [9].

RESULTS AND DISCUSSION

Extraction as the function of pH

Gallium was extracted with various liquid anion exchangers in the pH region 1.0–9.0. The phase volume ratio was maintained as 1:1. The extraction was quantitative only with Aliquat 336S at pH = 4.0–6.0, while extractions with all other liquid anion exchangers were not quantitative. Finally, 0.1 mol l^{-1} Aliquat 336S is recommended for quantitative extraction (Fig. 1).

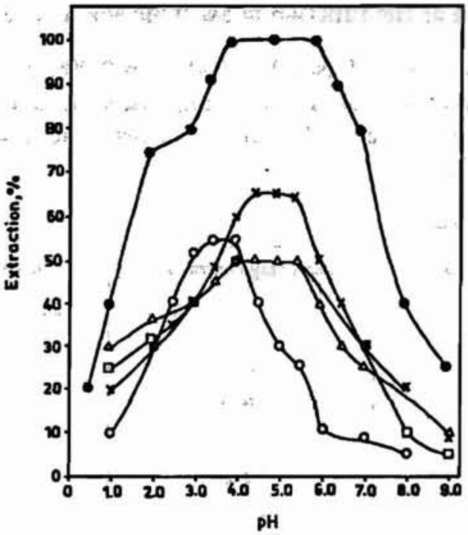

Figure 1. Extraction of gallium as a function of pH with various liquid anion exchangers: ● Aliquat 336S, o Amberlite LA-1, Δ Amberlite LA-2, × trioctylamine, ❑ Primene JMT

Extraction as the function of Aliquat 336S concentration

When extraction was carried out with varying (0.025–0.1 mol l^{-1}) concentration of Aliquat 336S, it was found that the extraction was quantitative for concentrations higher than 0.08 mol l^{-1} (Table 1). Therefore 0.1 mol l^{-1} Aliquat 336S in xylene was used subsequently.

Table 1. Effect of Aliquat 336S concentration

Aliquat 336S mol l^{-1}	Percentage extraction %	Distribution ratio (*D*)
0.025	10.0	0.11
0.050	25.0	0.33
0.01	50.0	1.0
0.02	55.0	1.2
0.03	62.0	1.6
0.04	74.0	2.3
0.05	85.0	5.6
0.06	95.0	19.0
0.07	98.0	49.0
0.08–0.10	99.6	249.0

Extraction as the function of ascorbic acid concentration

Varying the concentration of ascorbic acid from 0.00025 to 0.01 mol l^{-1}, it was found that the extraction was quantitative for the ascorbic acid concentration higher than 0.007 mol l^{-1}, therefore 0.01 mol l^{-1} ascorbic acid was used for further complexation (Table 2).

Table 2. Effect of ascorbic acid concentration

Ascorbic acid mol l^{-1}	Percentage extraction %	Distribution ratio (D)
0.00025	25.0	0.33
0.00050	38.0	0.61
0.0010	55.0	1.2
0.0020	70.0	2.3
0.0030	86.0	6.1
0.0040	90.0	9.0
0.0050	98.0	49.0
0.0060	99.0	99.0
0.007–0.010	99.6	249.0

Effect of diluent

When extraction was carried out with nonpolar solvents as the diluents, it was observed that with xylene and toluene extraction was quantitative. However with cyclohexane (95 %), hexane (91 %), benzene (90 %), chloroform (85 %), carbon tetrachloride (76 %) and nitrobenzene (65 %) extraction was incomplete (recovery is given in parenthesis). As xylene is not toxic, and as it offers the better phase separation it was preferred as the diluent.

Period of equilibration

Gallium was extracted after varying time of shaking which ranged from 2.5 to 20 min. The extraction efficiencies were 86 %, 95 %, 99 %, 99.6 % and 99.6 % for 2.5, 5, 7.5, 10 and 20 min of shaking, respectively. Thus with a ten-minute period of equilibration the extraction was quantitative.

Nature of extracted species

The composition of the extracted species was ascertained from graphs of log$D$ *vs.* log[Aliquat 336S], when 0.01 mol l^{-1} ascorbic acid was used, and from log$D$ *vs.* log[ascorbic acid] when 0.1 mol l^{-1} Aliquat 336S in xylene was used. The slopes were 3.0 and 2.70, respectively. Therefore the nature of the extracted species is $[(R_4N)_3Ga(asc)_3]$ [1].

Effect of stripping agents

After extraction, gallium was stripped with hydrochloric, nitric, sulphuric and hydrobromic acids of concentration in the range 0.1–6 mol l^{-1} (Fig. 2). The stripping was quantitative with hydrochloric (0.5–1.0 mol l^{-1}), nitric (05.–4.0 mol l^{-1}) and hydrobromic (1.0–3.0 mol l^{-1}) acids. Other acids proved to be poor stripping agents (Fig. 2).

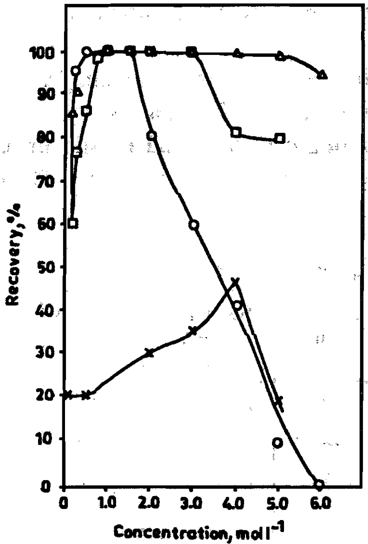

Figure 2. Effect of stripping agents: o HCl, Δ HNO_3, × H_2SO_4, □ HBr

Separation from binary mixtures

When gallium was extracted in the presence of several diverse ions from binary mixtures, it was noted that alkali- and alkaline-earth metals, aluminium, lead, tin(IV) and thallium(I,III) were tolerated in the ratio 1:100, while iron(II), copper and manganese were tolerated in the ratio 1:50. The transition metals like scandium, titanium(IV), zirconium(IV), hafnium(IV), thorium(IV), vanadium(IV) and niobium(V) were tolerated in the ratio 1:20. During separations all these metals were stripped first (with 6 mol l^{-1} hydrochloric acid), which was followed by stripping of gallium with 1 mol l^{-1} nitric acid. In the separation of antimony(III) and bismuth(III) these metals were also stripped first (with 1 mol l^{-1} hydrochloric acid), then gallium was stripped with 0.5 mol l^{-1} nitric acid.

Separation from multicomponent mixtures

Gallium, vanadium(IV) and aluminium(III) were separated after extraction by stripping vanadium(IV) with 6 mol l^{-1} hydrochloric acid, and gallium with 1 mol l^{-1} nitric acid. Aluminium was not extracted.

Scandium, gallium and copper(II) were separated by stripping first scandium with 6 mol l^{-1} hydrochloric, then gallium with 1 mol l^{-1} nitric acid. Copper(II) was not extracted.

Gallium, thorium and iron(II) were separated by stripping gallium with 6 mol l^{-1} nitric acid, then thorium was stripped with 2 mol l^{-1} hydrochloric acid. Iron(II) was not extracted.

Gallium was separated from antimony(V) and thallium(III) by stripping gallium with 1 mol l^{-1} hydrochloric acid, then antimony(V) with 0.5 mol l^{-1} nitric acid. Thallium(III) was not extracted.

The quaternary mixture of gallium, thorium(IV), uranium(VI) and aluminium(III) was separated by stripping first gallium with 6 mol l^{-1} nitric acid, then thorium with 8 mol l^{-1} hydrochloric acid and finally uranium(VI) with 0.5 mol l^{-1} sodium hydroxide. Aluminium(III) was not extracted (Table 3).

Table 3. Separations from multicomponent mixtures

SN	Element	Amount taken µg	Amount found µg	Stripping agent, mol l^{-1}	Recovery %	Chromogenic ligand	λ_{max} nm
1	V(IV)	100	99.0	HCl, 6	99.0	Xylenol orange	535
	Ga	15	14.94	HNO_3, 1	99.6	PAR	510
	Al(III)	200	199.2	not extr.	99.6	Alizarin Red S	520
2	Sc	100	99.6	HCl, 6	99.6	Arsenazo III	670
	Ga	15	14.8	HNO_3, 1	99.1	PAR	510
	Cu(II)	200	199.2	not extr.	99.6	Diethyldithiocarbamate	435
3	Ga	15	14.8	HNO_3, 6	99.1	PAR	510
	Th(IV)	50	49.8	HCl, 2	99.6	Arsenazo III	650
	Fe(II)	40	39.8	not extr.	99.6	1,10-phenanthroline	540
4	Ga	15	14.8	HCl, 1	99.6	PAR	510
	Sb	400	392	HNO_3, 0.5	98.0	phenylfluorone	555
	Tl(III)	200	199.2	not extr.	99.6	Crystal violet	610
5	Ga	15	14.8	HNO_3, 6	99.1	PAR	510
	Th(IV)	50	49.8	HCl, 8	99.6	Arsenazo III	650
	UO_2^{2+}	100	99.6	NaOH, 0.5	99.6	Arsenazo III	665
	Al(III)	100	99.0	not extr.	99.0	Alizarin Red S	520

Sequential separation of gallium, indium, thallium and aluminium

After extraction of gallium and indium from the mixture, gallium was stripped from the organic phase with 2 mol l^{-1} hydrobromic acid, then indium was stripped with 1 mol l^{-1} nitric acid while thallium and aluminium were not extracted. From the aqueous phase containing 0.1–0.5 mol l^{-1} HBr, thallium was extracted with 0.5 % Amberlite LA-1 while aluminium was not extracted. Thus it was possible to separate all four elements from each other at the ratios ranging from 1:1 to 1:6 (Table 4). All metals were determined by spectrophotometry [9].

Table 4. Sequential separation of gallium, indium, thallium and aluminium

SN	Element	Amount taken µg	Amount found µg	Stripping agent, mol l^{-1}	Chromogenic ligand	λ_{max} nm
1	Ga	15	14.8	HBr, 2	PAR	510
	In	45	45.0	HNO_3, 1	PAN	540
	Tl	90	89.1	HNO_3, 4	Crystal violet	610
	Al	90	89.0	not extr.	Alizarin Red S	520
2	Ga	15	14.8	HBr, 2	PAR	510
	In	15	14.8	HNO_3, 1	PAN	540
	Tl	15	14.0	HNO_3, 4	Crystal Violet	610
	Al	15	14.0	not extr.	Alizarin Red S	520
3	Ga	15	14.8	HBr, 2	PAR	510
	In	60	59.1	HNO_3, 1	PAN	540
	Tl	60	59.1	HNO_3, 4	Crystal violet	610
	Al	60	59.0	not extr.	Alizarin Red S	510
4	Ga	15	14.8	HBr, 2	PAR	510
	In	30	29.1	HNO_3, 1	PAN	540
	Tl	30	29.2	HNO_3, 4	Crystal violet	610
	Al	90	89.0	not extr.	Alizarin Red S	520

Determination of gallium in high purity aluminium

A known mass of pure metal was dissolved in concentrated hydrochloric acid and was made to known volume. Gallium was extracted as per the general procedure. It was noted that the amount of gallium found in the high purity sample is 0.008 % against the standard value of 0.009 %.

The proposed method is simple, rapid and selective. It is applicable at microgram concentration. The sequential separation of aluminium and gallium from indium and thallium is of significance as they belong to the same group of classification. The separation of gallium from vanadium(IV), antimony(V), iron(II) and scandium is useful as they are generally associated in alloys and minerals.

Acknowledgement

The authors are thankful to the Council of the Scientific and Industrial Research (New Delhi) for sponsoring this project and awarding fellowship to one of us (MAK).

REFERENCES

1. Rao R. R. and Khopkar S. M., *J. Ind. Chem. Soc.*, **12**, 620 (1985).
2. Takabe K., Kato H. and Minami S., *J. Inorg. Nucl. Chem.*, **39**, 871 (1977).
3. Bol'shova T. A., Ershova N. I. and Kaplunova A. M., *Zh.Neorg.Khim.*, **31**, 1803 (1986).
4. Yakabe K., Koichi I. and Shirchi M., *Nippon Kagakukaichi*, **1**, 119 (1987).
5. Vibhute C. P. and Khopkar S. M., *Analyst*, **111**, 435 (1986).
6. Shete S. D. and Shinde V. M., *Analyst*, **107**, 225 (1982).
7. Kaplunova A. M., Ershova N. I. and Bol'shova T. A., *Zh.Anal.Khim.*, **33**, 1940 (1978).
8. Welcher F. J., *The Analytical Uses of Ethylenediamine Tetraacetic Acid*, Van Nostrand, Princeton 1958.
9. Snell F.D., *Photometric and Fluorometric Methods of Analysis*, Wiley–Interscience, New York 1978, Part I and II.

Received November 1992
Accepted May 1993