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Liquid–liquid extraction and recovery of gallium(III) from acid media with 2-octylaminopyridine in chloroform: analysis of bauxite ore

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Abstract: The liquid–liquid extraction of gallium(III) from hydrochloric acid solution using 2-octylaminopyridine (2-OAP) in chloroform was investigated. The extraction of gallium(III) from 6.0–9.0 mol dm^{-3} hydrochloric acid was found to be quantitative using 0.033 mol dm^{-3} 2-OAP in chloroform. The effect of the reagent concentration and other parameters on the extraction of gallium(III) was also studied. The stoichiometry of the extracted species of gallium(III) was determined based on the slope analysis method. The extraction reaction proceeded *via* the anion exchange mechanism from hydrochloric acid and the extracted species was $[RR'NH_2^+GaCl_4^-]_{org}$. The extraction of gallium(III) was performed in the presence of various ions to ascertain the tolerance limit to individual ions. The temperature dependence of the extraction equilibrium constants was examined to estimate the apparent thermodynamic functions (ΔH, ΔS and ΔG) for the extraction reaction. Gallium(III) was successfully separated from commonly associated metal ions, such as Zn(II), Pb(II), Cd(II), Hg(II), Bi(III), Al(III), Se(IV), Sb(III), Sn(IV), In(III), Tl(I) and Tl(III). However, gallium(III) was separated from Fe(III) from weak organic acid media. The procedure was also extended to the determination of gallium(III) in bauxite ore by the standard addition method.

Keywords: liquid–liquid extraction; gallium(III); 2-OAP; recovery of gallium from bauxite.

INTRODUCTION

Gallium is widely spread in nature, although minerals rich in gallium are rare. Owing to this, gallium is usually obtained as a by-product of the processing of other minerals (bauxite, sphalerite). The most important commercial source of gallium is bauxite and sodium aluminate from the Bayer process, its main raw

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material.[1–3] Hence, the separation of gallium from aluminium is of practical importance.

The earliest applications of solvent extraction of gallium were in analytical procedures established before a significant commercial demand for this metal existed. Gallium is used primarily in electronic devices because of the specific band structure of its crystalline compounds (mostly gallium arsenide). Such a structure provides for efficient optical transitions as well as high electron mobilities. Interest in the development of recovery processes of gallium increased in the late 1970s due to the potential of much faster computer chips made of gallium arsenide in place of silicon. In the following years, however, the manufacture of GaAs-based integrated circuits (IC) on a large scale and at low cost proved to be more difficult than initially thought, which led to the role of GaAs in the computer industry being redefined. Today, the sale of GaAs-IC is rising fast.[4] Other than digital circuits, GaAs is finding increasing application in optoelectronics: for light emitting diodes (LED), semiconductor lasers, solar cells and optical computing in analogue microware devices.[5]

Gallium is present in very small amounts compared to common or similar metals. Thus, its recovery is a difficult task in which solvent extraction plays a significant role. Organophosphorus acid reagents are known to be generally suitable for gallium(III) extraction from either mineral acid media or weak organic acid media. Di-2-ethylhexylphosphoric acid (D2EHPA),[6] divinylbenzene homopolymeric microcapsules containing di-2-ethylhexylphosphoric acid, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester,[7] cyanex-921,[8] cyanex-923,[9] cyanex-301,[10] cyanex-272,[11] and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A)[12] are reported as effective extractants for gallium(III). However, Fe(III), Ru(III), Os(VIII), Pt(IV), Au(I) interfere in the extraction.[8]

Oxygen-containing extractants play important role in the extraction of gallium(III). 8-Quinolinol and its derivatives, under the trade name kelex-100, are the most famous reagents used for the extraction of metal ions. Using 1-octanol/octane mixed solvent systems, the extraction of gallium(III) with 8-quinolinol was realized at 25 °C. The shaking time required for gallium(III) extraction was 2 h.[13] Gallium(III) was extracted from aqueous solution with 5-amylthio-8-quinolinol into the organic phase,[14] however, a 3-hour equilibrium time was needed. Alkylsubstituted-8-hydroxyquinoline (LIX-26) chelating reagents in *n*-decanol are good extractants for gallium(III) in the higher pH range.[15] They extract gallium(III) in 30 min at pH 9.2 and the reactions were exothermic. The extraction kinetics of gallium(III) with 5-chloro-8-quinolinol diluted in toluene was examined and clarified by Kondo and *et al.*[16,17] The extraction of gallium(III) was found to be 80 % after 3 h equilibration. The fundamental extraction kinetics with the pure kerosene/kelex 100 system and a method of selective re-extraction boosted by possible chloro-complex formation in HCl media was proposed by

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Kekesi.[18] The steric effect of 3,5-bis(trifluoro)methyl phenol (BTMP) as a hydrogen-bond donor on the outer-sphere complexation in the synergistic extraction of gallium(III) with 2,4-pentanedione was investigated.[19] The chelate extraction behaviour of gallium(III) with the tripod quadridentate phenolic ligand, tris(2--hydroxy-3,5-dimethylbenzyl)amine (H_3tdmba) was studied by Hirayama *et. al.*[20]

Extraction behaviour and mechanism of gallium(III) with naphthenic acid (NA), *sec*-octylphenoxyacetic acid (CA-12) and *sec*-nonylphenoxyacetic acid (CA-100) dissolved in kerosene from hydrochloric acid solution was investigated.[21,22] A study was conducted on the solvent extraction of gallium(III) from hydrochloric acid media with 3-chlorinated organic solvents containing a non--ionic surfactant, polyoxyethylene nonyl phenyl ether (PONPE) as the extractant.[23] Gallium(III) could be separated from flue dust residues from aluminium production plants using a poly-ether type polyurethane foam from 3 mol dm^{-3} sulphuric acid and 3 mol dm^{-3} sodium chloride solutions with at least 92 % efficiency of the total recovery. The interference of iron was minimized by its reduction.[24]

Katiyar *et al*.,[25] and Vibhute and Khopkar,[26] determined the amount of gallium(III) in bauxite ore by neutron activation analysis and solvent extraction methods, respectively.

High molecular weight amines (HMWAs) have emerged as powerful extractants for many elements. The distribution equilibria of 0.01 mol dm^{-3} gallium(III) from 1–2 mol dm^{-3} hydrochloric acid media were studied using a commercial trialkyl amine, ADOGEN 364, dissolved in kerosene as the extractant.[27] Trioctyl amine (TOA) in benzene was investigated as an extractant for trivalent gallium from aqueous solutions containing hydrochloric acid and/or lithium chloride.[28] Recently *n*-octylaniline was used for quantitative extraction of gallium(III) from succinate media.[29] 2-Octylaminopyridine[30] was superior to *n*-octylaniline for the following reasons: *i*) *n*-octylaniline is commercially available but it is more expensive; *ii*) the synthesis of *n*-octylaniline by the Pohlandt method[31] in laboratory is tedious and time consuming; *iii*) 2-octylaminopyridine is a sensitive extractant as a lower concentration is required for the extraction of gallium(III) (0.033 mol dm^{-3}) as compared with *n*-octylaniline (0.29 mol dm^{-3}); *iv*) difficulties in phase separation arise when toluene is used as the diluent for *n*-octylaniline and *v*) *n*-octylaniline is effective only when it is freshly synthesized and used after distillation, otherwise the immediate formation of a solid phase occurs during the extraction.

In the present study, the extraction of gallium(III) from mineral acid media and weak organic acid media using a solution of 2-octylaminopyridine (2-OAP) in chloroform was investigated. The method permits the separation of gallium(III) from commonly associated metals and was used to separate and determine gallium(III) in bauxite ores.

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EXPERIMENTAL

Apparatus

An Elico digital spectrophotometer model SL–171 with 1 cm quartz cells was used for the absorbance measurements. The pH measurements were realised using an Elico digital pH meter model LI–120. A constant temperature (±0.1 °C) water bath MIC-66 A (Modern Scientific Instrument Company, Mumbai, India) was used for the temperature controlled studies.

Reagents

Gallium(III) solution. A standard stock solution of gallium(III) was prepared by dissolving 0.898 g of gallium trichloride in 6.0 mol dm^{-3} hydrochloric acid and diluted to 250 mL with distilled water and standardized complexometrically.[32] The solution contains 1.42 mg mL^{-1}, of gallium(III). The working solution was prepared by appropriate dilution of the stock solution with distilled water.

Thorium (IV) nitrate solution. A standard water solution of thorium nitrate (0.010 mol dm^{-3}) was prepared by dissolving 5.881 g thorium nitrate (AR) and diluted to 1 L with distilled water and standardized against a standard zinc(II) solution.[33]

EDTA solution. A standard solution of EDTA disodium salt (0.010 mol dm^{-3}) was prepared by dissolving 3.722 g disodium salt of EDTA in 1 L of distilled water.

2-Octylaminopyridine (2-OAP) solution. A 0.033 mol dm^{-3} solution of 2-octylaminopyridine[30] was prepared by dissolving in chloroform.

All the chemicals used were of analytical grade. Double distilled water was used throughout the experiments.

General extraction and determination procedure for gallium(III)

An aliquot of solution containing 0.500 mg of gallium(III) was mixed with a sufficient quantity of hydrochloric acid to make its concentration 7.0 mol dm^{-3} in a total volume of 25 mL of solution. The solution was then transferred to a 125 mL separation funnel, 10 mL of 0.033 mol dm^{-3} 2-OAP in chloroform was added, which was then shaken gently for about 2 min. The layers were allowed to separate and the aqueous layer was carefully withdrawn. Gallium(III) from the organic phase was stripped with 1.0 mol dm^{-3} hydrochloric acid (2×10 mL). The back extracts were evaporated almost to dryness and the residue was extracted with distilled water with warming.

The aqueous solution was then transferred into a 125 mL conical flask, followed by addition of 10 mL 1.0 mol m^{-3} EDTA solution. The excess of EDTA solution was titrated against a standard 1.0 mol m^{-3} solution of thorium nitrate using xylenol orange as the indicator. The end point was the yellow to pink red colour transition.[32] The percentage extraction, E, was calculated using Expression (1):

$$\%E = (\text{metal extracted}/\text{metal taken})\times 100 \quad (1)$$

and the distribution ratio, D, was calculated using Expression (2):

$$D = (\%E / (100 - \%E))\times \text{Volume aqueous phase}/\text{Volume organic phase} \quad (2)$$

RESULTS AND DISCUSSION

Effect of acidity

The extraction of 0.500 mg of gallium(III) from different acid media was performed with 0.033 mol dm^{-3} 2-OAP in chloroform at a constant aqueous:or-

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ganic volume ratio of 2.5:1.0. The extraction was found to be quantitative from hydrochloric acid (Table I), while there is no extraction from sulphuric, nitric, perchloric and hydrobromic acid media. The extraction of gallium(III) starts at 4.0 mol dm^{-3} hydrochloric acid and becomes quantitative in the range of 6.0–9.0 mol dm^{-3} hydrochloric acid, after which there is decrease of extraction. This may be due to the formation of the stable hydrochloride of 2-OAP. Thus, hydrochloric acid concentration of 7.0 mol dm^{-3} was used for the further extraction experiments.

TABLE I. Extraction behaviour of gallium(III) as a function of hydrochloric acid concentration. Gallium(III) = 0.500 mg, 2-OAP = 10 mL of 0.033 mol dm^{-3} in chloroform, aqueous:organic ratio = 2.5:1, equilibrium time = 2 min, strippant = 1.0 mol dm^{-3} hydrochloric acid (2×10 mL)

HCl Concentration, mol dm^{-3}	Amount of Ga(III) extracted, %	*D*
1.0	0.0	–
2.0	0.0	–
3.0	0.0	–
4.0	14.9	0.43
5.0	50.0	2.50
5.5	98.6	176.07
6.0	100.0	∞
6.5	100.0	∞
7.0[a]	100.0	∞
8.0	100.0	∞
9.0	100.0	∞
10.0	85.1	14.27

[a]Recommended for general extraction procedure

Extraction as a function of 2-octylaminopyridine concentration

The concentration of 2-OAP in chloroform was varied from 0.0004 to 1.0 mol dm^{-3} in 7.0 mol dm^{-3} hydrochloric acid. It was found that 10 mL 0.029 mol dm^{-3} 2–OAP in chloroform was required for quantitative recovery of gallium(III). However, 0.033 mol dm^{-3} 2-OAP was used for the further studies in order to ensure complete extraction. There was no adverse effect if an excess of 2-OAP was used.

Extraction with various diluents

Extractions of gallium(III) were performed from 7.0 mol dm^{-3} hydrochloric acid medium using 10 mL of 0.033 mol dm^{-3} 2-OAP in various solvents as diluents. The extraction of gallium(III) was quantitative with chloroform, xylene and amyl acetate because the ion-pair complex had a high distribution ratio in these solvents. The extraction was incomplete in benzene, toluene, methyl isobutyl ketone (MIBK), amyl alcohol, 1,2-dichloroethane and kerosene (Table II).

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There was no extraction in carbon tetrachloride. Hence, chloroform was used for the further extractions.

TABLE II. Extraction behaviour of gallium(III) as a function of the diluent. Gallium(III) = = 0.500 mg, hydrochloric acid = 7.0 mol dm^{-3}, 2-OAP = 10 mL 0.033 mol dm^{-3}, aqueous:organic ratio = 2.5:1, equilibrium time = 2 min, strippant = 1.0 mol dm^{-3} hydrochloric acid (2×10 mL)

Diluent	Relative permittivity, ε_r	Amount of Ga(III) extracted, %	D
Benzene	2.28	11.5	0.32
Xylene	2.30	100.0	∞
Toluene	2.38	1.3	0.03
Chloroform[a]	4.40	100.0	∞
Carbon tetrachloride	2.24	0.0	–
MIBK	13.10	41.0	1.73
Amyl alcohol	13.90	14.1	0.41
Amyl acetate	4.80	100.0	∞
1,2-Dichloroethane	10.50	85.8	15.10
Kerosene	1.80	71.7	6.33

[a]Recommended for general extraction procedure

Nature of the extracted species

Attempts were made to ascertain the nature of the extracted complex species using log D–log c plots. A graph of log $D_{[Ga(III)]}$ *versus* log $c_{[2\text{-OAP}]}$ at 4.5 and 5.0 mol dm^{-3} hydrochloric acid concentration gave slopes of 1.21 and 1.22, respectively (Fig. 1). The possible mechanism of the extraction appears to be protonation of 2-OAP, which forms cationic species, such as $[RR'NH_2^+Cl^-]_{(org)}$, while the chloride ions combines with gallium(III) to form anionic species such as $[GaCl_4^-]_{(aq.)}$, both of which associate to form an ion-pair of the type $[RR'NH_2^+GaCl_4^-]_{(org)}$, which being neutral, constitutes the extractable species. The mechanism of formation of the ion-pair complex is:

$$[RR'NH]_{(org)} + HCl_{(aq)} \leftrightarrows [RR'NH_2^+Cl^-]_{(org)} \quad (3)$$

$$GaCl_{3(aq)} + Cl^-_{(aq)} \leftrightarrows [GaCl_4^-]_{(aq)} \quad (4)$$

$$[RR'NH_2^+Cl^-]_{(org)} + [GaCl_4^-]_{(aq.)} \leftrightarrows [RR'NH_2^+GaCl_4^-]_{(org)} + Cl^-_{(aq)} \quad (5)$$

where R = $-C_5H_4N$ and R' = $-CH_2(CH_2)_6CH_3$.

The influence of equilibrium time

Variation of the shaking time from 10 s to 20 min showed that a 1-min equilibrium time was adequate for the quantitative extraction of gallium(III) from chloride media. However, for the general procedure a 2-min equilibrium time is recommended in order to ensure the complete extraction of the metal ion. Nevertheless, prolonged shaking up to 20 min had no adverse effect on the extraction.

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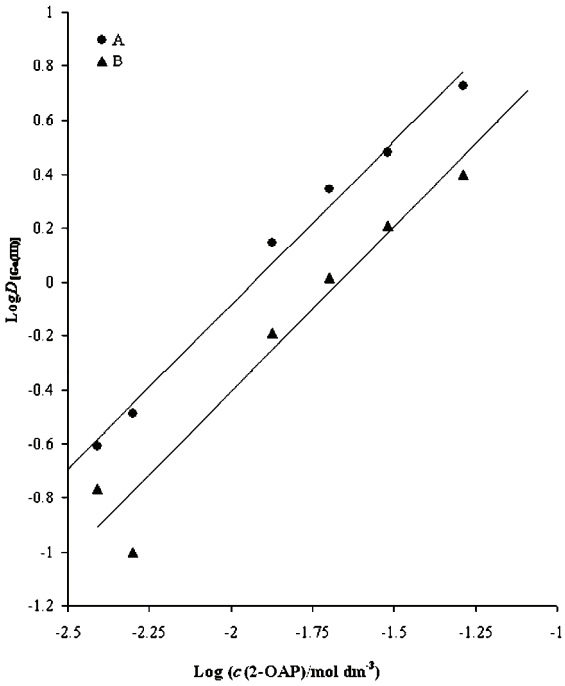

Fig. 1. Log–log plot of the distribution ratio, $D_{[Ga(III)]}$, *vs.* $c_{[2\text{-OAP}]}$ at 4.5 mol dm^{-3} (A, slope = 1.21) and at 5.0 mol dm^{-3} hydrochloric acid (B, slope = 1.22).

Loading capacity of 2-OAP

The loading capacity of the extractant was determined by repeated contact of the organic phase with a fresh feed solution of the metal at the same concentration. For 10 mL of a 0.033 mol dm^{-3} solution of 2–OAP in chloroform at 7.0 mol dm^{-3} concentration of hydrochloric acid, the maximum loading capacity for gallium(III) was found to be 2.0 mg at 300 K.

Effect of aqueous to organic volume ratio

The results of contacting different volume ratios of aqueous to organic phase were investigated. The study indicated that the preferred aqueous to organic phase ratio is 5:1 or less. This is evident from the sharp increase in the separation efficiency as well as the distribution ratio of gallium(III) when phase ratio was changed from 20:1 to 5:1. This may simply due to the non-availability of the reagent for metal extraction, so that a crowding effect occurred at low phase ratios. However, in the recommended procedure the phase ratio was maintained at 2.5:1 in order to avoid a large consumption of hydrochloric acid.

Effect of stripping agents

Stripping is the reverse of extraction. Various stripping agents (2×10 mL), such as hydrochloric acid, sulphuric acid, perchloric acid, nitric acid, ammonia, potassium hydroxide, sodium hydroxide, ammonia buffer solution (pH 10.0),

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acetate buffer solution (pH 4.63) and water, were used for the recovery of gallium(III) from the organic phase. It was found that of all the stripping solutions examined, only hydrochloric acid (0.5–2.0 mol dm^{-3}) was effective in stripping gallium(III) from the organic phase. In the actual practice, two 10 mL portions of 1.0 mol dm^{-3} hydrochloric acid were used (Table III).

TABLE III. Extraction behaviour of gallium(III) as a function of the strippant. Gallium(III) = = 0.500 mg, hydrochloric acid = 7.0 mol dm^{-3}, 2-OAP = 10 mL 0.033 mol dm^{-3} in chloroform, aqueous:organic ratio = 2.5:1, equilibrium time = 2 min

c	Recovery, %						
mol dm^{-3}	HCl[b]	H_2SO_4[a]	$HClO_4$	HNO_3	KOH	NaOH	NH_3
0.1	98.1	98.4	98.5	94.5	26.1	19.1	60.7
0.5	100.0	95.5	97.0	63.9	16.4	0.0	60.7
1.0[b]	100.0	95.5	97.0	42.2	0.0	0.0	60.7
2.0	100.0	95.5	97.0	13.8	0.0	0.0	60.7
2.5	96.7	95.5	96.0	0.0	0.0	0.0	60.7
3.0	96.6	95.5	96.0	0.0	0.0	0.0	60.7
4.0	77.6	95.5	96.0	0.0	0.0	0.0	60.7
5.0	77.6	95.5	96.0	0.0	0.0	0.0	60.7

Strippant	Recovery, %
Ammonia buffer (pH 10)	21.8
Acetate buffer (pH 4.63)	75.2
Water	29.2

[a]Concentrations in normal; [b]recommended for general extraction procedure

Effect of temperature on the extraction of gallium(III)

The extraction of gallium(III) from 5.0 mol dm^{-3} hydrochloric acid using 0.033 mol dm^{-3} 2-OAP in chloroform at varying temperatures from 298 to 310 K gave the results presented in Table IV. It was found that in the extraction of gallium(III) by 2-OAP in chloroform, the distribution coefficient increased with increasing temperature.

TABLE IV. Effect of temperature on the extraction of gallium(III) with 2-OAP in chloroform. Gallium(III) = 0.500 mg, hydrochloric acid = 5.0 mol dm^{-3}, 2–OAP = 10 mL 0.033 mol dm^{-3}, aqueous:organic ratio = 2.5: 1, equilibrium time = 2 min, strippant =1.0 mol dm^{-3} HCl (2×10 mL)

T / K	Log K_{ex}	ΔG / kJ mol^{-1}	ΔS / J K mol^{-1}	ΔH / kJ mol^{-1}
298	0.2829	–10.9	237.2	59.73
301	0.3979	–14.4	246.3	
304	0.4436	–16.1	249.5	
307	0.5637	–21.5	264.6	
310	0.7075	–30.3	290.3	

The change in the extraction equilibrium constant, K_{ex}, with temperature is expressed by the van't Hoff Equation:

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$$d(\log K_{ex})/d(1/T) = -\Delta H/2.303R \quad (6)$$

The plot of log K_{ex} *vs.* $1/T$ was linear with a slope of –3.12 (Fig. 3) and the enthalpy change of the extraction realized at a hydrochloric acid concentration 5.0 mol dm^{-3} was evaluated as ΔH = 59.7 kJ mol^{-1}, which means that the extraction was an endothermic process. The change in Gibbs energy ΔG and entropy ΔS were calculated from Eqs. (7) and (8):

$$\Delta G = -2.303RT \log K_{ex} \quad (7)$$

$$\Delta S = \Delta H - \Delta G/T \quad (8)$$

The negative value of the Gibbs energy change implies that the reaction was spontaneous. The positive value of the enthalpy change indicates that the extraction of gallium(III) with 2-OAP in chloroform was more favourable with increasing temperature.

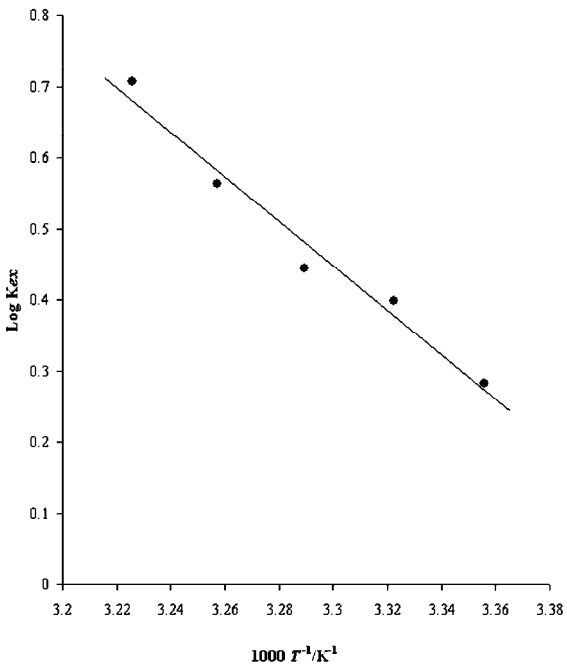

Fig. 2. Plot of log K_{ex} *vs.* T^{-1} at constant pH 4.0 (slope = –3.12) with 2-OAP in chloroform.

Effect of various foreign ions on percentage extraction of gallium(III)

The effect of large number of foreign ions on the extraction of 0.500 mg of gallium(III) by the proposed reagent was investigated following the recommended procedure. Initially the foreign ions were added to the gallium(III) solution in large excess, 100 mg for the tested anions and 25 mg for the tested cations. When interference was found to be intensive, the tests were repeated with successively smaller amounts of foreign ion. The tolerance was set at the amount of the fo-

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reign ion that could be present to give an error less than ±2 % in the recovery of gallium(III) (Table V). It was observed that the method was free from interference from a large number of cations and anions. However, interference due to Bi(III) and Tl(III) had to be eliminated by masking with 100 mg tartrate each. In addition, to mask Sn(II), Co(II) and Ge(IV), 10 mg citrate, 100 mg thiocyanate and 5 mg oxalate were used respectively for each metal. The method suffered from strong interference due to Fe(III), V(V) and Ni(II). Under the optimum extraction conditions for gallium(III), these metals were found to be co-extracted.

TABLE V. Effect of various foreign ions on percentage extraction of gallium(III). Gallium(III) = 0.500 mg, hydrochloric acid = 7.0 mol dm^{-3}, 2-OAP = 10 mL of 0.033 mol dm^{-3} in chloroform, aqueous: organic ratio = 2.5:1, equilibrium time = 2 min, strippant =1.0 mol dm^{-3} hydrochloric acid (2×10 mL)

Tolerance limit, mg	Foreign ion added
100	Bromide, iodide, acetate, thiourea, thiocyanate, salicylate, ascorbate, nitrate, nitrite, succinate, malonate, tartrate, phosphate
50	Fluoride
25	Cd(II), Ba(II), Cr(VI), Sr(II), Mn(VII), Mn(II)
15	Mo(VI)
10	Citrate, Pb(II), Al(III), Ca(II), W(VI), Sn(IV), Sn(II)[a], Se(IV), Sb(III)
5	Oxalate, Hg(II), Cu(II), Tl(I), Bi(III)[b]
2	Zn(II), Te(IV), Tl(III)[b]
1	Co(II)[c]
0.5	In(III), Ge(IV)[d]
0	Fe(III), V(V), Ni(II)

Masked with: [a]10 mg citrate, [b]100 mg tartrate; [c]100 mg thiocyanate and [d]5 mg oxalate

APPLICATIONS

Separation and determination of gallium(III) from binary mixtures

The suitability of the above-developed method was examined by applying it to the separation and determination of gallium(III) in a variety of binary mixtures, which are frequently in association (Table VI).

It was found that Zn(II), Pb(II), Cd(II), Hg(II), Al(III), Se(IV), Sb(III), Sn(IV), In(III) and Tl(I) remained unextracted under the optimum extraction conditions for gallium(III) using 7.0 mol dm^{-3} hydrochloric acid with 10 mL 0.033 mol dm^{-3} 2–OAP in chloroform. The loaded organic phase was stripped with 1.0 mol dm^{-3} hydrochloric acid (2×10 mL) and determined complexometrically, as recommended in the procedure. The raffinate containing the added metal ion was estimated by standard procedures.[32–34]

The proposed method was also extended to the separation of gallium(III) from Bi(III) and Tl(III) by masking with 100 mg tartrate. The masked metals remained quantitatively in the aqueous phase under the optimum extraction condi-

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tions of gallium(III). Gallium(III) was stripped with 1.0 mol dm^{-3} hydrochloric acid (2×10 mL) and estimated as in the recommended procedure.

TABLE VI. Separation of gallium(III) from binary mixtures in mineral acid media

Metal ions	Amount taken, mg	Average recovery[a], %	Method of estimation
Ga(III)	0.500	100.0	–
Zn(II)	0.500	100.0	EDTA[33]
Ga(III)	0.500	99.5	–
Pb(II)	0.500	100.0	EDTA[33]
Ga(III)	0.500	99.5	–
Cd(II)	0.500	100.0	EDTA[33]
Ga(III)	0.500	100.0	–
Hg(II)	1.0	99.5	EDTA[33]
Ga(III)	0.500	99.4	–
Bi(III)[b]	1.0	100.0	EDTA[32]
Ga(III)	0.500	99.4	–
Al(III)	1.0	100.0	EDTA[32]
Ga(III)	0.500	100.0	–
Se(IV)	0.500	100.0	Selenium sol[34]
Ga(III)	0.500	100.0	–
Sb(III)	0.500	100.0	Potassium iodide[34]
Ga(III)	0.500	99.8	–
Sn(IV)	0.05	100.0	Pyrocatechol violet[34]
Ga(III)	0.500	100.0	–
In(III)	0.500	100.0	EDTA[32]
Ga(III)	0.500	99.2	–
Tl(I)	0.500	99.1	EDTA[32]
Ga(III)	0.500	100.0	–
Tl(III)	0.500	100.0	EDTA[32]
Ga(III)[c]	0.500	100.0	–
Fe(III)[b]	0.500	99.3	Thiocyanate[34]

[a]Average of six determinations; [b]masked by 100 mg tartrate; [c]separation from sodium succinate media

It was found that there is co-extraction of iron(III) with gallium(III) from hydrochloric acid media. This is due to formation of ion-pair complex of both the metal ions according to Eq. (4). However, the separation can be achieved from weak organic acid media, such as sodium succinate. Gallium(III) was extracted at pH 4.0 from 5.0 mol m^{-3} sodium succinate solution into the organic phase. It was back extracted into 0.010 mol dm^{-3} EDTA (2×5 mL) or 1.0 mol dm^{-3} hydrochloric acid solution (2×10 mL). The back extracts were estimated using xylenol orange as the indicator and thorium(IV) nitrate as the titrant. Microlevels of gallium(III) can be estimated spectrophotometrically by the PAR method.[35]

An aqueous solution containing a mixture of 0.500 mg, each of gallium(III) and iron(III) in 5.0 mol m^{-3} sodium succinate at pH 4.0 was equilibrated for 2 min with 0.033 mol dm^{-3} 2-OAP in chloroform, whereby iron(III) was masked

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with 100 mg tartrate. It was found that only gallium(III) was extracted into organic phase while iron(III) remained unextracted in the aqueous phase. Gallium(III) from the organic phase was back extracted into 0.010 mol dm^{-3} EDTA (2×5 mL) or 1.0 mol dm^{-3} hydrochloric acid solution (2×10 mL). The back extracts were estimated using xylenol orange as the indicator and thorium(IV) nitrate as the titrant. The iron(III) from the aqueous phase was demasked with concentrated hydrochloric acid and estimated spectrophotometrically by the thiocyanate method.[34]

Determination of gallium(III) in a synthetic mixture

The proposed method was applied for the analysis of gallium(III) from a multi-component mixture (Table VII).

TABLE VII. Separation of gallium(III) in synthetic mixtures

Composition of multicomponent mixture, mg	Ga(III) found, mg	Recovery[a], %
Ga(III) 0.500,Tl(III) 0.500, Al(III) 0.500	0.499	99.8
Ga(III) 0.500, In(III) 0.500, Tl(III) 0.500	0.500	100.0
Ga(III) 0.500, Al(III)0.500, In(III) 0.500	0.500	100.0
Ga(III) 0.500, Pb(II) 0.500, Bi(III)[b] 0.500	0.496	99.3
Ga(III)[c] 0.500, Fe(III)[b] 0.500, Al(III) 0.500	0.496	99.3
Ga(III)[c] 0.500, Fe(III)[b] 0.500, Mn(VII) 0.500	0.500	100.0
Ga(III)[c] 0.500, Fe(III)[b] 0.500, Cu(II) 0.500	0.500	100.0

[a]Average of six determination; [b]masked by 100 mg tartrate; [c]separation from sodium succinate media

A solution containing 0.500 mg of gallium(III) was taken and known amounts of other metals were added. The extraction of gallium(III) was performed using the method developed herein. The results obtained were in good agreement with the amount added. The selectivity of the extraction of gallium(III) can be achieved by the use of suitable masking agent for the added metal ions.

Analysis of bauxite ore for its gallium(III) content by standard addition method

Owing to the trace amounts of gallium(III) present in bauxite ores, the standard addition method was followed for the analysis.

Bauxite ore or red mud sample (1 g) was fused with four times its weight of sodium hydroxide (4 g), which dissolves most of the alumina and gallia. The residue was leached with 0.50 mol dm^{-3} sodium hydroxide. The solution was diluted with a little distilled water and filtered by suction on a 7 cm Buchner funnel.[36] The residue left was again washed with 0.50 mol dm^{-3} sodium hydroxide. The obtained alkaline solution containing gallia was nearly neutralized and then made 7.0 mol dm^{-3} in concentrated hydrochloric acid. To this, 0.500 mg of standard gallium(III) solution was added and the solution was made up to 100 mL with 7.0 mol dm^{-3} hydrochloric acid. An aliquot of the solution was taken for

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extraction of gallium(III) and estimated spectrophotometrically using the PAR method (Table VIII).[33]

TABLE VIII. Analysis of gallium(III) in bauxite ore. Initial pH: 4.0, aqueous phase = 0.005 mol dm^{-3} sodium succinate, aqueous: organic ratio = 2.5:1, 2-OAP = 10 mL of 0.033 mol dm^{-3} in chloroform, equilibrium time = 2 min, strippant = 0.010 mol dm^{-3} EDTA (2×5 mL) or 1.0 mol dm^{-3} hydrochloric acid (2×10 mL)

Bauxite ore sample	Amount of gallium(III) found by AAS, μg/g	Amount[a] of gallium(III) found by proposed method, μg/g
1	90.5	90.0
2	93.0	92.0
3	91.2	91.0

[a]Average of six determinations

CONCLUSIONS

The important features of the method described herein are:

– it is very simple, selective, reproducible and rapid;

– it permits the selective separation of gallium(III) from other metals which are generally associated with it in real samples;

– gallium(III) is separated from iron(III) by use of a weak organic acid medium (sodium succinate) at pH 4.0 using 2-OAP;

– a very low reagent concentration (0.033 mol dm^{-3} 2-OAP) is required for the quantitative recovery of gallium(III);

– gallium(III) can be extracted both in mineral acid as well as weak organic acid media;

– the equilibrium constant and thermodynamic parameters ΔH, ΔS and ΔG in the extraction of gallium(III) with 2-OAP were evaluated. The extraction is an endothermic process. The extraction of gallium(III) increases with increasing temperature;

– the method is free from interference from a large number of foreign ions which are often associated with naturally occurring gallium(III);

– the time required for the extraction separation is very short. The very short extraction time indicates a high distribution ratio of the ion pair complex involved in the quantitative recovery of gallium(III);

– the developed method involves a one-stage extraction step;

– gallium(III) occurs in trace amount in bauxite ores; hence, the proposed method can be applied for the estimation of gallium(III) in bauxite ore.

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ИЗВОД

ТЕЧНО–ТЕЧНО ЕКСТРАКЦИЈА ГАЛИЈУМА(III) ИЗ КИСЕЛЕ СРЕДИНЕ ПОМОЋУ 2-ОКТИЛАМИНОПИРИДИНА У ХЛОРОФОРМУ: АНАЛИЗА РУДЕ БОКСИТА

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Испитиван је утицај концентрације реактаната и други параметри течно–течно екстракције галијума(III) из хлороводоничне киселине (6,0–9,0 mol dm^{-3}) коришћењем 0,033 mol dm^{-3} раствора 2-октиламинопиридина (2-OAP) у хлороформу и нађено је да је у овим условима екстракција квантитативна. Стехиометријски састав узорака галијума(III) одређен је методом анализе нагиба. Екстракција се одиграва по механизму измене анјона хлороводоничне киселине, а екстраховани узорак је $[RR'NH_2^+GaCl_4^-]_{org}$. Ради утврђивања границе толеранције екстракција галијума(III) рађена је уз присуство различитих јона. Испитана је температурна зависност равнотежне константе екстракције да би се одредиле привидне термодинамичке функције екстракције (ΔH, ΔS и ΔG). Галијум(III) је успешно одвојен од обично присутних металних јона као што су Zn(II), Pb(II), Cd(II), Hg(II), Bi(III), Al(III), Se(IV), Sb(III), Sn(IV), In(III), Tl(I) и Tl(III). Галијум(III) је, међутим, одвојен од Fe(III) из слабо киселе органске средине. Поступак је такође проширен на одређивање галијума(III) у руди боксита стандардном методом додавања.

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