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Extraction and separation studies of Ga(III), In(III) and Tl(III) using the neutral organophosphorous extractant, Cyanex-923

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Abstract: The neutral extractant, Cyanes-923 has been used for the extraction and separation of gallium(III), indium(III) and thallium(III) from acidic solution. These metal ions were found to be quantitatively extracted with Cyanex-923 in toluene in the pH range 4.5–5.5, 5.0–6.5 and 1.5–3.0, respectively, and from the organic phase they can be stripped with 2.0 mol dm^{-3} HNO_3, 3.0 mol dm^{-3} HNO_3 and 3.0 mol dm^{-3} HCl, respectively. The effect of pH equilibration period, diluents, diverse ions and stripping agents on the extraction of Ga(III), In(III) and Tl(III) has been studied. The stroichiometry of the extracted species of these metal ions was determined on the basis of the slope analysis method. The reaction proceed by solvation and the probable extracted species found were [MCl_3. 3Cyanex-923] [where M = Ga(III) or In(III)] and [$HTlCl_4$. 3Cyanex-923]. Based on these results a sequential procedure for the separation of Ga(III), In(III) and Tl(III) from each other was developed.

Keywords: solvent extraction, Cyanex-923, Ga(III), In(III), Tl(III), stripping, separation.

INTRODUCTION

Gallium is mainly used in the electronic industry for the manufacturing of gallium arsenate laser diodes, semiconductors, gallium-gadolinium garnets and magnetic bubble memories. Indium is also used in electronic devices as indium phosphide semiconductor and indium solar batteries. In addition to this, compounds of indium are used for coloring glasses, paints, fluorescent lightening, *etc*. Compounds of thallium are poisonous and are used in the control of rodents, anti-exterminators, optical glasses, treatment of ring worm and against mildew growth in textile fabrics. Hence, bearing all this in mind, a study of an effective solvent extraction method of these metal ions was undertaken.

Ga(III) and In(III) have been extracted with various reagents such as octylphenyl phosphoric acid, 3,5-dibromosalicylaldehyde acylhydrazone, acidic organophosphorous extractants, alkyl carbonyl substituted *N*-phenyl hydroxyl amines and 4-acyl-3-phenyl-5-isoazolones.[1–5] Among the organophosphorous compounds, tributyl phosphate (TBP) has been

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studied in detail for the extraction and separation of these metal ions.[6] However, these methods require long extraction period, high reagent concentrations and salting out agents. Ion-pair extraction of gallium(III) from HCl and NaOH solutions was also studied with methoxy-substituted triaryl phosphines and 2,3-dihydroxy naphthalene, respectively.[7–9] Recently, the equilibrium and kinetics of the extraction of Ga(III) from NaOH with Kelex-100 and LIX-54 from hydrochloric acid solution have also been studied.[10–11]

Neutral organophosphorous compounds, such as triphenyl phosphine oxide (TPPO), tributyl phsphine (TBPO) and trioctyl phosphine oxide (TOPO), have been used for the extraction of In(III) from hydrochloric acid media, but a lengthy extraction time of 12 hours are required.[12] In(III) has been extracted with 8-hydroxyl quinoline and 0.02 mol dm^{-3} 18-crown-6-ether in HBr media.[13,14] Disodium sulphate and ascorbic acid have been used for the extraction of In(III) with 2-ethyl hexyl phosphoric acid mono (2-ethyl hexyl) ester and Aliquat 336S, respectively.[15,16] In(III) was also extracted with 1-(4-alkyl phenyl)-3-hydroxy-2-methyl-4-pyridones and its derivatives.[17,18] Bis-(2-ethyl hexyl) phosphate was used for the extraction of In(III) from 1.0 mol dm^{-3} $HClO_4$ / $NaClO_4$ solutions.[19]

An extraction mechanism of Tl(III) by di(2-ethyl hexyl) sulfoxide has been reported by Feng etal.[20] The addition of butanol to the chloroform phase containing pyrazolone was found to increase the extraction of Tl(III) chloride.[21] A selective separation of Tl(III) from some metal ions on sodium impregnated silica gel layers using a formic acid – butanol system has been studied.[22] The extraction equalibria of Ga(III) and Tl(III) with dihexyl sulfide from HCl solution was also studied.[23] Mulik *et al.* studied the separation and extraction of In(III) and Ti(III) from hydroxhloric acid media.[24] Cyanex-921 and bis (2-ethyl hexyl) phosphinic acid in toluene have been used recently for the extraction of Ga(III) and In(III).[25–28]

According to the manufacturer, Cytec Industries Inc. Canada, Cyanex-923 extractant comprises a mixture of four trialkyl phosphine oxides, with the general formula R_3PO (14 %), $R_2R'PO$ (42 %), PR'_2PO (31 %) and R'_3PO (8 %) in which R denote *n*-octyl and R' for *n*-hexyl group.[14] In the present work, the extraction of gallium(III), indium(III) and thallium(III) with neutral phosphine oxide, *i.e.*, Cyanex-923, diluted in toluene was studied in detail. Ga(III), In(III) and Tl(III) are typical class 'a' metals, according to Hard Soft Acid Base (HSAB) principle, hence they have a strong tendency to be extracted with chelating agents which coordinate through oxygen, nitrogen or sulphur donor atoms. Since Cyanex-923 possesses 'O' as donor atom, extraction of these metal ions was possible from the aqueous to the organic phase.

EXPERIMENTAL

Reagents

The extractant, Cyanex-923 supplied by Cytec Industries Inc. Canada was used without further purification. Stock solutions of Ga(III) and In(III) were prepared by dissolving known amounts of gallium trichloride and indium trichloride separately in a the minimum quantity of hydrochloric acid and diluted to 1 litre with double distilled water and standardized by the EDTA method.[29,30] The stock solution of Tl(I) was prepared by dissolving a known amount of thallium(I) nitrate in the minimum amount of nitric acid. The Tl(I) was oxidized to Tl(III) by adding a few drops of bromine water and warming to remove excess bromine. This solution was standardized by a known method.[30] All other chemicals used were of analytical grade. An Elico

model LI-120 pH meter with a combined electrode was used for H^+ ion concentration studies and a GBC UV-Visible 911A spectrophotometer with 10 mm cortex quartz cuvettes for absorbance measurements.

Procedure

Aliquots of solution containing either gallium (5 μg), indium (20 μg) or thallium (50 μg) were taken, diluted to 10 ml and equilibrated separately with an equal volume of Cyanex-923 in toluene for the required shaking time (5 min), after the pH of the aqueous solutions had teen adjusted 5.0, 5.5 and 2.0, respectively. The organic phase containing the extracted metal species was then stripped with different stripping agents, such as HCl, HNO_3, H_2SO_4 and $HClO_4$. It was found that Ga(III), In(III) and Tl(III) were stripped quantitatively from the organic phases of Cyanex-923 with 2.0 mol dm^{-3} HNO_3, 3.0 mol dm^{-3} HNO_3 and 3.0 mol dm^{-3} HCl solutions. They were then determined spectrophotometrically using the 4-(2-pyridylazo)-resorcinol method.[11] All experiments were carried out at a room temperature except when the effect of temperature was to be studied.

RESULTS AND DISCUSSION

Effect of pH and reagent concentration on the extraction of Ga(III), In(III) and Tl(III)

The effect of pH on the percent extraction of Ga(III) and Tl(III) with Cyanex-923 in toluene was studied in the pH range from 0.1 – 6.0. Quantitative extraction of Ga(III), In(III) and Tl(III) into the organic phase was observed in the pH range 4.5–5.5, 5.0–6.0 and 1.5–3.0, respectively.

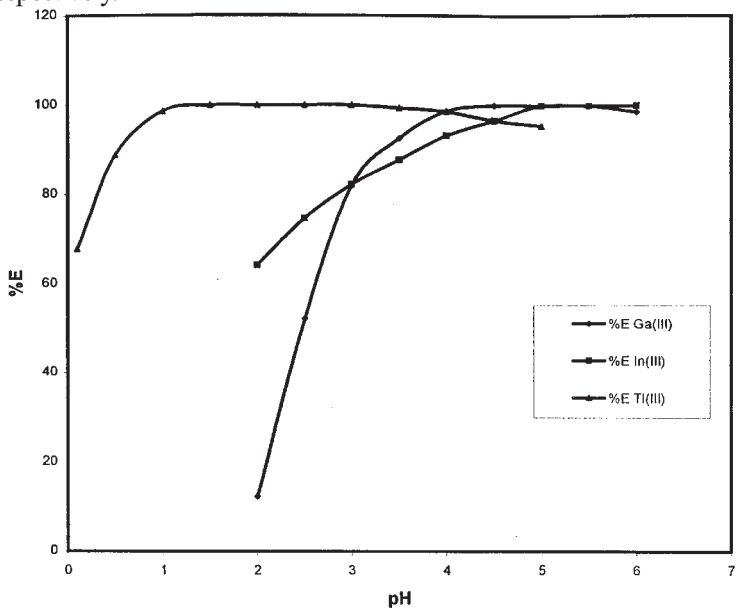


Fig. 1. Effect of pH on the percentage extraction of Ga(III), In(III) and Tl(III) with Cyanex-923 in toluene.

These metal ions were extracted with varying concentrations of Cyanex-923 in toluene from $1.0 \times 10^{-4} – 1.0 \times 10^{-1}$ mol dm^{-3}, keeping the other parameter, like pH, period of equilibration and temperature constant. The extraction was found to increase with increasing reagent concentration. The extraction of Ga(III), In(III) and Tl(III) was quantitative with 2.5×10^{-3} mol dm^{-3}, 1.0×10^{-3} mol dm^{-3} and 1.25×10^{-3} mol dm^{-3} Cyanex-923 in toluene, respectively.

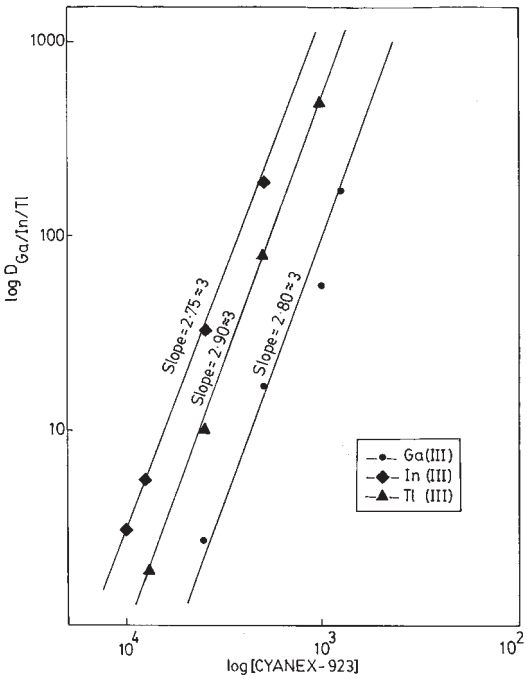


Fig. 2. Effect of Cyanex-923 concentration on the percentage extraction of Ga(III), In(III) and Tl(III).

Effect of stripping agents

The metal ions were stripped out from the organic phases of Cyanex-923 with different strengths of acids, such as HCl, HNO_3, H_2SO_4 and $HClO_4$. Complete recovery of Ga(III) from the organic phase of Cyanex-923 was observed with 2.0–3.0 mol dm^{-3} HNO_3 and 1.5–2.0 mol dm^{-3} H_2SO_4 solution. In(III) was stipped quantitatively with 6.0–7.0 mol dm^{-3} HCl, 3.0 mol dm^{-3} HNO_3 and 1.0–1.5 mol dm^{-3} H_2SO_4 and 3.0–4.0 mol dm^{-3} $HClO_4$. While Tl(III) was stipped with 3.0–4.0 mol dm^{-3} HCl and 2.0–4.0 mol dm^{-3} $HClO_4$ (Table I).

TABLE I. Effect of stripping agents on the percentage recovery of Ga(III), In(III) and Tl(III) from metal loaded organic phases of Cyanex-923 in toluene

	Percentage recovery (% R) of gallium(III)							
Acids/mol dm^{-3}	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
HCl	86.1	74.4	60.0	52.2	45.2	10.6	1.2	1.2
HNO_3	97.0	99.9	99.9	86.2	60.2	51.2	35.3	16.8
H_2SO_4	47.9	99.9	–	–	–	–	–	–
$HClO_4$	82.8	76.2	69.5	49.1	–	–	–	–
	Percentage recovery (% R) of indium(III)							
Acids/mol dm^{-3}	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
HCl	25.0	29.2	36.4	46.9	83.4	99.9	99.9	91.0
HNO_3	24.8	68.3	99.9	89.9	70.8	69.5	60.9	55.2

TABLE I. Continued

H_2SO_4	99.9	68.3	–	–	–	–	–	–
$HClO_4$	68.8	80.8	99.9	99.9	–	–	–	–
	Percentage recovery (% R) of thallium(III)							
Acids/mol dm^{-3}	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
HCl	50.7	72.9	99.9	99.9	–	–	–	–
HNO_3	21.2	6.1	12.1	13.6	–	–	–	–
H_2SO_4	19.7	27.3	16.6	14.2-	–	–	–	–
$HClO_4$	70.9	99.9	99.9	99.9	–	–	–	–

Effect of various diluents and period of equilibration

The extraction of Ga(III), In(III) and Tl(III) was performed with Cyanex-923 using various aromatic and aliphatic organic diluents, such as toluene, xylene, benzene, *n*-hexane, carbon tetrachloride, cyclohexane and chloroform. Quantitative extraction of Ga(III) was found with toluene, xylene and *n*-hexane. In cases of In(III) and Tl(III) the extraction was quantitative with toluene, xylene and cyclohexane. The other solvents such as chloroform, carbon tetrachloride and benzene showed poor extraction. Toluene was preferred as the best diluent for the extraction of Ga(III), In(III) and Tl(III) since it provided better phase separation (Table II).

TABLE II. Effect of solvent on the percentage extraction of Ga(III), In(III) and Tl(III) with Cyanex-923 in toluene

	Percentage extraction (% E)		
Dilunets	**Ga(III)**	**In(III)**	**Tl(III)**
Toluene	99.9	99.9	99.9
Benzene	85.7	84.8	84.3
Xylene	89.6	99.9	99.9
Cyclohexane	99.3	99.9	99.9
Chloroform	75.8	62.1	51.0
Carbon tetrachloride	88.2	84.2	82.1
n-Hexane	99.9	82.7	53.3

The extraction equilibrium was studied for different periods of shaking ranging from 1–20 min. It was observed that 5 min shaking was sufficient for the quantitative extraction of Ga(III), In(III) and Tl(III) with Cyanex-923, and there was no adverse effect on increasing the extraction period up to 20 min.

Nature of the extracted species

It was necessary to evaluate the distribution coeffcient (*D*) while varying the extractant concentration to ascertain the nature of the extracted species. The probable

nature of the extracted species was established by plotting a graph of log $D_{Ga/In/Tl}$ *versus* log [Cyanex-923] at the fixed pH values of 5.0, 5.5 and 2.0. The slope obtained were 2.8, 2.75 and 2.9, respectively, for Ga(III), In(III) and Tl(III) metal ions, indicating that three moles of ligands reacts with one mole of Ga(III), In(III) and Tl(III) ions. Hence the probable composition of the extracted species is in ratio 1:3 for all the three metal ions, which is similar to earlier reported results with Cyanex-923.[35] Therefore, the probable species formed in the organic phase are [$GaCl_3$ · 3Cyanex-923], [$InCl_3$ · 3Cyanex-923] and [$HTlCl_4$ · Cyanex-923], which are similar to those earlier reported with TOPO[36] and ethyl acetate.[37]

Effect of temperature

Extraction of Ga(III), In(III) and Tl(III) with 2.5×10^{-3} mol dm^{-3}, 1.0×10^{-3} mol dm^{-3} and 1.25×10^{-3} mol dm^{-3} Cyanex-923 in toluene, respectively, was carried out in the temperature range of 303–343 K at pH 3.0, 3.0 and 0.5, for Ga(III), In(III) and Tl(III), respectively. The extraction of these metal ions increases with increasing temperature (Table III).

TABLE III. Effect of temperature on the distribution ratio of Ga(III), In(III) and Tl(III) with Cyanex-923 in toluene, Ga(III) 5 μg, pH 3.0; In(III) = 20 μg, pH 3.0; Tl(III) = 50 μg, pH 0.5.

Temperature /K	D_{Ga}	D_{In}	D_{Tl}
303	4.46	4.57	7.93
313	6.92	7.05	11.48
323	10.71	10.23	17.38
333	16.21	14.79	25.70
343	25.11	21.38	38.02

$$\log D_{Ga/In/Tl} = -\frac{\Delta H}{2.303\,RT} + C$$

where $D_{Ga/In/Tl}$ represent the distribution ratio, ΔH is the enthalpy change for the reaction and C is a constant. The slopes obtained from the plot of log D *versus* $1000/T$ were –1.87, –1.66 and –1.73 for Ga(III), In(III) and Tl(III) metal ions, respectively. The ΔH values obtained are 35.80 kJ/mol, 31.78 kJ/mol and 33.12 kJ/mol, respectively, indicating that the three extraction reactions are endothermic in nature.

Effect of various diverse ions

The effect of various diverse ions on the extraction of Ga(III), In(III) and Tl(III) was studied at pH 5.0, 5.5 and 2.0, respectively, with Cyanex-923 in toluene. The tolerance limit was set at not more than ± 2.0 % in the recovery of all the three metal ions. Alkali metals like Na^+, K^+, Li^+, Rb^+ were highly tolerated while Fe^{3+}, Ru^{3+}, Os^{8+}, Pt^{4+}, Au^+ and EDTA were found to interfere strongly with the extraction of all three metals (Table IV).

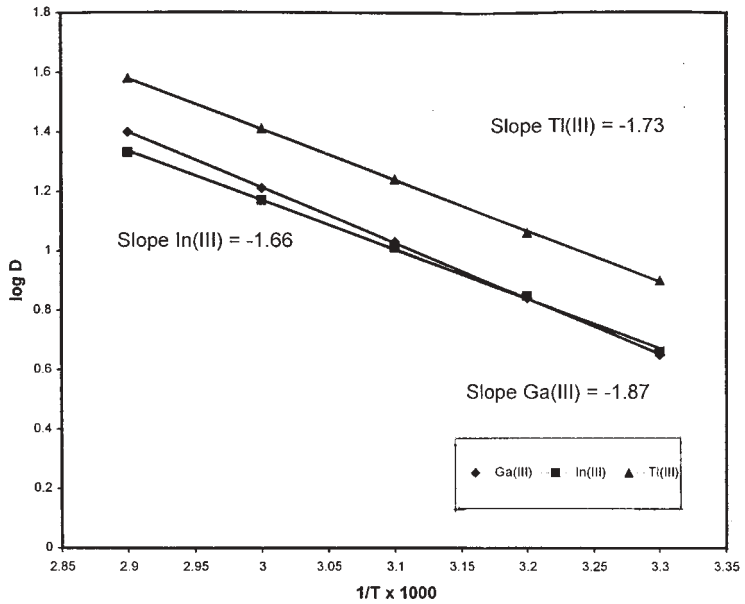


Fig. 3. Effect of temperature on the percentage extraction of Ga(III), In(III) and Tl(III) with Cyanex-923 in toluene.

TABLE IV. Effect of various diverse ions on the percentage extraction of Ga(III), In(III) and Tl(III) with Cyanex-923 in toluene

		Gallium(III)/5 μg : diverse ion	
1:30	1:15	1:5	Strongly interfere
Na^+; Li^+; Rb^+; K^+	Bi^{3+}; Mg^{2+}; Sr^{2+}	In^{3+}; Cr^{6+}; Ca^{2+}	Fe^{3+}; Ru^{3+}; Os^{8+}
Cs^+; Cl^-	Zn^{2+}; Ba^{2+}; Hg^{2+}	Mn^{2+}; Co^{2+}; Ni^{2+}	Pt^{4+}; Au^+; EDTA
	Pb^{2+}; SO_3^{2-}; SCN^-	Cu^{2+}; Ag^+; Cd^{2+}	
		Tl^{3+}	
		Indium(III)/20 μg : diverse ion	
1:25	1:18	1:5	Strongly interfere
Na^+; Li^+; Rb^+; K^+	Bi^{3+}; Mg^{2+}; Sr^{2+}	Zn^{2+}; Cr^{6+}; Ca^{2+}	Fe^{3+}; Ru^{3+}; Os^{8+}
Cs^+; Cl^-; SO_3^{2-}	Ba^{2+}; Hg^{2+}; Pb^{2+}	Mn^{2+}; Co^{2+}; Ni^{2+}	Pt^{4+}; Au^+; EDTA
		Cu^{2+}; Ag^+; Cd^{2+}	
		Tl^{3+}	
		Thallium(III)/50 μg : diverse ion	
1:22	1:12	1:5	Strongly interfere
Na^+; Li^+; Rb^+; K^+	Bi^{3+}; Mg^{2+}; Sr^{2+}	Zn^{2+}; Cr^{6+}; Ca^{2+}	Fe^{3+}; Ru^{3+}; Os^{8+}
Cs^+; NO_3^-; Cl^-; SO_3^{2-}	Ba^{2+}; Hg^{2+}; Pb^{2+}	Mn^{2+}; Co^{2+}; Ni^{2+}	Pt^{4+}; Au^+; EDTA
		Cu^{2+}; Ag^+; Cd^{2+}	
		In^{3+}; Ga^{3+}	

TABLE V. Separation of Tl(III) from multicomponenet mixtures with Cyanex-923 in toluene

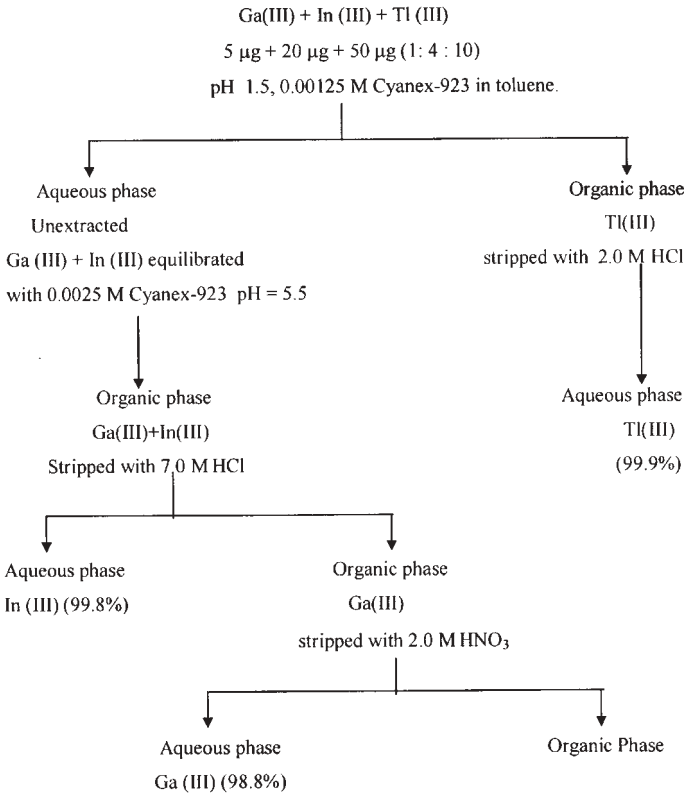
No.	Mixtures	Amount taken μg	pH/acidity	Extractant Cyanex-923	Stripping agents	Percentage recovery/%
1.	In(III)	20	5.5	0.001 M	7.0 M HCl	99.8
	Ga(III)	5	5.5	0.0025 M	2.0 M HNO_3	99.8
2	Tl(III)	50	1.5	0.00125	3.0 M HCl	99.9
	In(III)	20	1.5	0.00125	unextracted	99.7
3.	Tl(III)	50	1.5	0.00125	3.0 M HCl	99.9
	Ga(III)	5	1.5	0.00125	unextracted	99.8
4.	Ga(III)	5	4.5	0.0025 M	2.0 M HNO_3	99.5
	Zn(II)	20	8.0	0.01 M	1.0 M HCl	99.2
	Be(II)	15	8.0	0.01 M	0.5 M NaOH	99.4
	Fe(III)	50	8.0	0.01 M	unextracted	99.5
5.	In(III)	20	5.5	0.001 M	3.0 M HNO_3	99.8
	Zn(III)	20	8.0	0.01 M	1.0 M HCl	99.7
	Fe(III)	50	6.0 M HCl	0.005 M	water	99.2
	Hg(II)	50	6.0 M HCl	0.005 M	unextracted	99.1
6.	Tl(III)	50	1.5	0.00125	3.0 M HCl	99.8
	Zn(II)	20	8.0	0.005	3.0 M HNO_3	99.1
	Fe(III)	50	6.0 M HCl	0.005	water	99.4
	Ti(IV)	50	6.0 M HCl	0.005	unextracted	99.3

Mutual separation of gallium(III), indium(III) and thallium(III) with Cyanex-923

The proposed method provides for the mutual separation of gallium(III), indium(III) and thallium(III) from their mixture. A mixture of gallium()III) (5 μg), indium(III) (20 μg) and thallium(III) (50 μg) in 10 ml water was taken and the pH of the solution was adjusted to 1.5. It was then equilibrated with an equal volume of 1.25×10^{-3} mol dm^{-3} Cyanex-923 in toluene by shaking it in a separating funnel for 5 min at room temperature. After allowing the two phases to separate, the aqueous phase containing unextracted Ga(III) and In(III) was put aside. The organic phase containing extracted Tl(III) was stripped with 3.0 mol dm^{-3} HCl. The pH of the aqueous solution containing Ga(III) and In(III) was adjusted to 5.5 and then again equilibrated with 2.5×10^{-3} mol dm^{-3} Cyanex-923 for 5 min, when both types of metal ions are extracted simultaneously. Taking advantage of the difference in the stripping agents both the metal ions were separated. In(III) was first stripped with 7.0 mol dm^{-3} HCl followed by that of Ga(III) with 2.0 M HNO_3 (Flow chart 1).

The proposed methods also enables the separation of each of these metals from multicomponent mixtures. The separation of Ga(III) from In(III), In(III) from Ga(III) and Ga(III) from Tl(III) was possible. In addition to these, Ga(III), In(III) and Tl(III) were separated from mixtures containing Be(II), Zn(II), Hg(II), Fe(III) and Ti(IV) (Table V).

Flow chart-1: Separation of Ga(III), In(III) and Tl(III) using Cyanex-923 in toluene.



CONCLUSIONS

1. The obtained results show that the extraction of gallium(III), indium(III) and thallium(III) is possible with Cyanex-923 dissolved in toluene at pH 5.0, 5.5 and 2.0, respectively. It requires a low reagent concentration, low stripping agent concentration and can tolerate large amounts of diverse ions.

2. The ΔH values calculated for Ga(III), In(III) and Tl(III) are 35.80 kJ/mol, 31.78 kJ/mol and 33.12 kJ/mol, respectively, indicating that all three extraction reactions are endothermic in nature.

3. The concentration of reagent required for the extraction of Ga(III), In(III) and Tl(III) is lower than that of TBP (100 %).

4. The extraction time required is less (5 min) as compared than that required when using TBP, TOPO, TPPO (12 hrs.) and 18-crown-6-ether (2 h).

5. The method does not require any masking agent as is required by *N*-phenylbenzylamine[32] in the extraction of Tl(III) and bis-(2-ethylhexyl) phosphate[33] the extraction of Ga(III).

6. Quantitative extraction of Ga(III), In(III) and Tl(III) is observed in the given pH range whereas in other cases, agents like ascorbic acid, disodium sulphate, sodium salicylate and butyl alcohol were used for quantitative extraction by the extractants, 2-ethyl hexyl phosphoric acid mono (2-ethyl hexyl) ester, Aliquat 336S, tris(2-ethylhexyl) phosphate[31] and pyrazolone, respectively.

7. The above method can be employed for the separation of Ga(III), In(III) and Tl(III) by exploiting various factors such as reagent concentration, pH or stripping agent.

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ИЗВОД

ПРОУЧАВАЊЕ ИЗДВАЈАЊА И РАЗДВАЈАЊА Ga(III), In(III) И Tl(III) КОРИШЋЕЊЕМ НЕУТРАЛНОГ ОРГАНОФОСФОРНОГ СРЕДСТВА ЗА ЕКСТРАКЦИЈУ, CYANEX-923

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Неутрално средство за екстракцију, Cyuanex-923 коришћено је за издвајање и раздвајање галијума(III), индијума(III) и талијума(III) из киселих раствора. Нађено је да се ови јони квантитативно екстрахују помоћу Cyanex-923 у толуену у областима pH 4,5–5,5; 5,0–6,5 и 1,5–3,0 по горе наведеном редоследу, док се из органске фазе по истом редоследу могу издвојити помоћу 2,0 mol dm^{-3} HNO_3, 3,0 mol dm^{-3} HNO_3, односно 3,0 mol dm^{-3} HCl. Проучаван је утицај pH, времена уравнотежења, средства за екстракцију, различитих јона, као и средстава за издвајање из органске фазе. Стехиометрија екстрахованих врста ових јона метала одређена је помоћу методе анализе нагиба. Реакције се одигравају солватацијом, а највероватније екстраховане врсте су [MCl_3 · 3Cyanex-923], (где су M = Ga(III) или In(III) и [$HTlCl_3$ · 3Cyanex-923]. На основу ових резул;тата развијена је процедура за међусобно раздвајање Ga(III), In(III) i Tl(III).

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