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TRIS(2-ETHYLHEXYL)PHOSPHATE AS AN EXTRACTANT FOR TRIVALENT GALLIUM, INDIUM AND THALLIUM

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Summary—A systematic study of solvent extraction behaviour of gallium(III), indium(III) and thallium(III) with tris(2-ethylhexyl)phosphate from salicylate media has been undertaken and a scheme for their separation is proposed. The optimum extraction conditions are evaluated and described. The method is applicable to the analysis of standard aluminium and aluminium alloys samples. The results obtained are reproducible and accurate.

Various methods for solvent extraction of gallium(III), indium(III) and thallium(III) have been summarized by different authors,[1–5] but the existing methods suffer from drawbacks such as pre-equilibration of phase, multiple extractions, multiple scrubbing and co-extraction of a large number of ions. Of the neutral organophosphorus compounds De and Sen[6] have reported, there is a solvent extraction method for gallium(III), indium(III) and thallium(III) using tributyl phosphate as extractant. The method reports extraction at milligram level with 100% tributyl phosphate as extractant. The method also requires long extraction period, use of salting out agents and scrubbing. The method does not report the analysis of real samples. Pfeifer[7] has reported extraction of gallium(III) with mixed acid solution with tributyl phosphate. Levin and Balakireva[8] has reported separation of gallium(III) and aluminium(III) by synergic extraction with mono(2-ethylhexyl)phosphoric acid and tributyl phosphate. Levin *et al.*[9] has reported use of alkylphosphoric acids for solvent extraction of gallium(III) and other elements from hydrohalic acid media. Neutral organophosphorous compounds[10] such as triphenylphosphine oxide, tributylphosphine oxide and trioctylphosphine oxide were used for extraction of indium(III) from hydrochloric acid media, but extraction time is 12 hr at 20°C. Michell and Riley[11] reported sub-stoicheiometric extraction of gallium(III), indium(III) and thallium(III) from hydrochloride media in the presence of strong 'O' donors.

The methods involving use of other neutral organophosphorous compounds, however, have many limitations. In contrast tris(2-ethylhexyl) phosphate allows quantitative extraction of gallium(III), indium(III) and thallium(III) in a single extraction with only 30 to 40 sec shaking time, additionally the method does not require scrubbing or use of salting out agents. The method is free from interference from commonly associated elements and permits mutual separation of gallium(III), indium(III) and thallium(III) with greater accuracy and precision.

EXPERIMENTAL

Absorbance measurements were made on a Spectronic D-20 (Milton Roy and Co) using quartz cells. pH values were recorded on a Controlled Dynamics digital pH meter with combination glass electrode.

Stock solutions of gallium(III) and indium(III) were prepared by dissolving 7.7 and 4.2 g of gallium trichloride and indium trichloride (Aldrich), respectively, in 250 ml of distilled water containing $0.5M$ hydrochloric acid. A stock standard solution of thallium(I) was prepared by dissolving 6.5 g thallium nitrate (BDH) in 500 ml of distilled water containing $1M$ nitric acid. The solutions were standardized by known methods[12,13] and diluted further as required.

In the test solution, thallium(I) was oxidized to thallium(III) by adding a few drops of

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Table 1. Optimum extraction conditions for gallium(III), indium(III) and thallium(III)

Metal ions (μg)	Aqueous phase salicylate concentration (M)	pH	Organic phase	Extraction period (*sec*)	Stripping solution
Ga(III), 30	3.5×10^{-2}–6.5×10^{-2}	5.0–6.5	10*ml* of 35% T2EHP in toluene	30	2 × 5 *ml* water
In(III), 20	7.5×10^{-2}–1.3×10^{-1}	3.5–4.5	10 *ml* of 50% T2EHP in toluene	40	2 × 5 *ml* water
Tl(III), 50	1.3×10^{-3}–3.1×10^{-3}	2.8–3.8	10 *ml* of 45% T2EHP in toluene	35	2 × 5 *ml* acetate buffer

bromine water, warmed to remove excess of bromine, cooled and used for extraction.

A buffer solution was prepared by dissolving 27.2 g of sodium acetate trihydrate in 400 ml of distilled water, adding 17 ml of glacial acetic acid, and diluting to 1 l. (pH 4–5).

Tris(2-ethylhexyl)phosphate (T2EHP) (Fluka) dissolved in toluene was used for extraction without further purification.

All other chemicals used were of analytical reagent grade.

General extraction procedure

An aliquot of solution containing gallium(III), indium(III) and thallium(III) in sodium salicylate was taken in a total volume of 10 ml. (The optimum extraction conditions are reported in Table 1). The solution was transferred into a separatory funnel and equilibrated with tris(2-ethylhexyl)phosphate (dissolved in toluene) for the required shaking time. After phase separation, the metal ions were stripped from the organic layer with appropriate stripping solutions and were subsequently determined in aqueous phase spectrophotometrically with 4-(2-pyridylazo)-resorcinol (PAR) as follows.

For gallium(III), 1.0 ml of 0.05% aqueous solution of PAR was added, the pH adjusted to 4.8–5.8 with dilute sodium hydroxide or hydrochloric acid and the absorbance measured at 510 nm against a reagent blank prepared in the same way.

For indium(III), 1 ml of 0.1% aqueous PAR solution was added, the pH adjusted to 6.5–8.5 with dilute sodium hydroxide or hydrochloric acid and the absorbance measured at 535 nm against a reagent blank prepared in the same way.

Similarly for thallium(III), 0.5 ml of aqueous 0.1% PAR solution was added, the pH adjusted to 2.1–2.5 with dilute sodium hydroxide or hydrochloric acid and the absorbance measured at 530 nm against a reagent blank prepared analogously.

The complete analysis from extraction to determination took about 15 min.

RESULTS AND DISCUSSION

Extraction conditions

The extraction of gallium(III), indium(III) and thallium(III) was studied at various pH (adjusted with dilute sodium hydroxide and hydrochloric acid solutions), sodium salicylate concentrations (1.0×10^{-3}–$1.0 \times 10^{-1}M$) and tris(2-ethylhexyl)phosphate concentration (10–50%) using toluene as the diluent. The extraction commenced at pH 2 and became quantitative at pH 5–6.5, 3.5–4 and 2.8 to 3.8 for gallium(III), indium(III) and thallium(III), respectively, when extracted from $3.5 \times 10^{-2}M$–$6.5 \times 10^{-2}M$ $7.5 \times 10^{-2}M$–$1.3 \times 10^{-1}M$ and 1.3×10^{-3}–$3.1 \times 10^{-3}M$ sodium salicylate solution with 10 ml of 35, 50 and 45% tris(2-ethylhexyl)phosphate in toluene, respectively. Figure 1 shows that the extraction depended on pH because the metals form a chelate with salicylate ions. The probable nature of extracted species was established by plotting log of distribution ratio vs. log of tris(2-ethylhexyl)phosphate concentrations (at fixed pH and sodium salicylate concentration) for gallium(III), indium(III) and thallium(III). It gave slopes of 1.9, 1.79 and 1.73, respectively

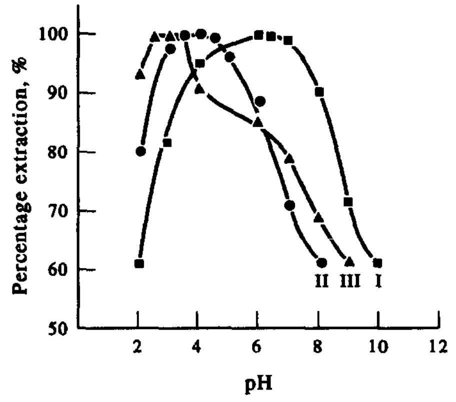

Fig. 1.

indicating a molar ratio of 1:2 with respect to the extractant. Similarly a plot of log of distribution ratio vs. log of sodium salicylate concentrations [at fixed pH and concentration of tris(2-ethylhexyl)phosphate] gave slopes of 2.1, 2.05 and 1.96 for gallium(III), indium(III) and thallium(III), respectively, indicating a molar ratio of 1:2 with respect to salicylate ions. (Figs 2 and 3). The extraction mechanism involves solvation by tris(2-ethylhexyl)phosphate of ion-associated compound formed with salicylate as follows:

$$M^{3+} + Sal^{2-} \rightleftharpoons Msal^{+} \qquad (1)$$

$$MSal^{+} + Hsal^{-} \rightleftharpoons [Msal^{+}, Hsal^{-}] \qquad (2)$$

$$[Msal^{+}, Hsal^{-}]2H_2O$$

$$+ T2EHP\ [Msal^{+}, Hsal^{-}] . 2T2EHP, \qquad (3)$$

where M is gallium(III), indium(III) and thallium(III), sal is salicylate and T2EHP is tris(2-ethylhexyl)phosphate.

The third step involving the solvation of ion pair compound rendered the species hydrophobic and made the extraction quantitative. The optimum extraction conditions are reported in Table 1.

The suitability of diluents was investigated using solvents such as benzene, toluene, xylene carbon tetrachloride and chloroform. The extraction was between 89–95% with other diluents, the only suitable diluent was toluene.

The method permitted quantitative extraction for gallium(III), indium(III) and thallium(III) between 30 and 40 sec. Prolonged shaking gave emulsion and phase separation was difficult.

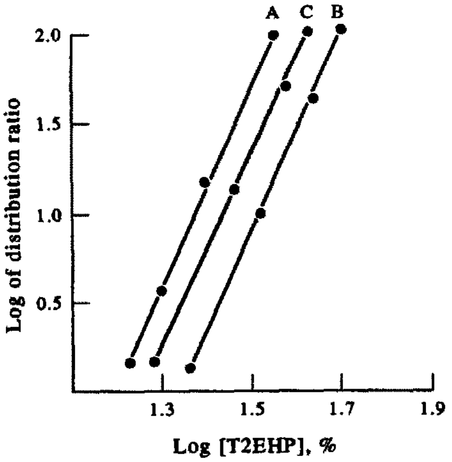

Fig. 2.

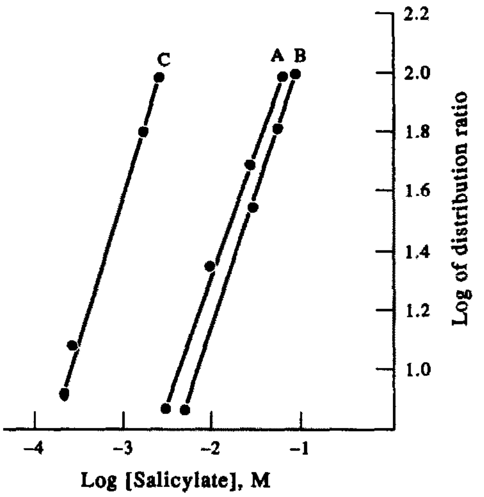

Fig. 3.

Various stripping agents such as water, mineral acids and sodium hydroxide were tried, for back extraction of gallium(III), indium(III) and thallium(III) from tris(2-ethylhexyl)phosphate phase. Water stripped gallium(III) and indium(III) quantitatively, whereas stripping of thallium(III) was possible only with acetate buffer.

Effect of diverse ions

An interference study showed that zinc(II) (800 μg), manganese(II) (1000 μg), magnesium(II) (500 μg), aluminium(III) (1000 μg), titanium(IV) (1000 μg), vanadium(V) (150 μg), molybdenum(VI) (650 μg), tungsten(VI) (200 μg), chromium(VI) (100 μg), tartrate (400 μg), citrate (150 μg), thiocynate (150 μg), oxalate (200 μg), phosphate (500 μg) and thiosulphate (350 μg) did not interfere in the extraction of 30 μg of gallium(III) when extracted from $5.6 \times 10^{-2} M$ sodium salicylate solution adjusted to pH 6.5 with 10 ml 35% tris(2-ethylhexyl)phosphate dissolved in toluene.

Similarly, zinc(II) (650 μg), manganese(II) (400 μg), magnesium(II) (650 μg), aluminium(III) (750 μg), titanium(IV) (400 μg), vanadium(V) (100 μg), molybdenum(VI) (150 μg), tungsten(VI) (300 μg), chromium(VI) (350 μg), tartrate (300 μg), citrate (100 μg), thiocyanate (200 μg), oxalate (500 μg), phosphate (350 μg) and thiosulphate (400 μg), did not interfere in the extraction of 20 μg of indium(III) when extracted from $8 \times 10^{-2} M$ sodium salicylate solution adjusted to pH 4 with 10 ml of 50% tris(2-ethylhexyl)phosphate in toluene.

Zinc(II) (500 μg), manganese(II) (300 μg), magnesium(II) (650 μg), aluminium(III)

Table 2. Results for analysis of standard aluminium alloys

Composition (%)	% recovery*			Standard deviation		
	Gallium(III)	Indium(III)	Thallium(III)	Gallium(III)	Indium(III)	Thallium(III)
Mg, 0.87; Si, 0.65; In, 0.14; Mn, 0.50; Ti, 0.65; Zn, 0.87; Al, 96.32 + 1 mg Tl	—	99.2	99.3	—	2.19×10^{-3}	1.67×10^{-3}
Mg, 0. 25; Si, 0.10; Ga, 0.05; Mn, 1.50; Ti, 1.50; Zn, 1.50; Al, 94.00 + 1 mg Tl	99.6	—	99.6	5×10^{-3}	—	2.1×10^{-3}

*Average of six determinations.

(750 μg), titanium (IV) (500 μg), vanadium (V) (200 μg), molybdenum (VI) (400 μg), tungsten (VI) (350 μg), chromium(VI) (500 μg), tartrate (100 μg), citrate (300 μg), thiocynate (600 μg), oxalate (350 μg) phosphate (250 μg) and thiosulphate (750 μg) did not interfere in the extraction of 50 μg of thallium(III) when extracted from $1.875 \times 10^{-3}M$ sodium salicylate solution adjusted to pH 3.5, with 10 ml of 45% tris(2-ethylhexyl)phosphate in toluene. Copper(II), nickel(II) and iron(III) interfered seriously.

Mutual separation of gallium (III), *indium* (III) *and thallium* (III)

The proposed method provides mutual separation of trivalent gallium(III), indium(III) and thallium(III) in tracer concentrations. A mixture of gallium(III) (10–30 μg), indium(III) (10–30 μg) and thallium(III) (20–50 μg) was taken in $1.875 \times 10^{-3}M$ sodium salicylate solution adjusted to pH 3.5 and extracted for 35 sec with 10 ml of 45% tris(2-ethylhexyl)phosphate in toluene. This transferred thallium(III) quantitatively into the tris(2-ethylhexyl)phosphate phase. It was stripped with 2 × 5 ml acetate buffer (pH 4–5) and determined spectrophotometrically with PAR. The aqueous phase was evaporated to incipient dryness, the residue was dissolved in distilled water, a sufficient amount of sodium salicylate was added to make the concentration $5.6 \times 10^{-3}M$, adjusted to pH 6.5 and extracted for 30 sec with 10 ml of 35% tris(2-ethylhexyl)phosphate in toluene. This transferred gallium into tris(2-ethylhexyl)phosphate phase and retained indium(III) in the aqueous phase where it was determined spectrophotometrically with PAR. Gallium(III) from tris(2-ethylhexyl)phosphate was stripped with 2 × 5 ml water and determined spectrophotometrically with PAR. The recoveries of gallium(III), indium(III) and thallium(III) from ternary mixture were ⩾99.2%. The significant figures were 99.46, 99.32 and 99.32 for gallium(III), indium(III) and thallium(III), respectively.

Analysis of aluminium and aluminium alloys

A 1 g amount of alloy was dissolved in 3 ml of aqua regia and diluted to 100 ml. An aliquot of 2 ml of solution was taken for extraction and determination of gallium(III) and indium(III) by the proposed method. The recovery was ⩾99.2% (Table 2). As thallium(III) was not present in standard samples, a known amount of thallium(III) was added to the alloy solution and recovered by the proposed method.

The method permitted the separation and determination of metal in about 20 min.

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