

Rapid extraction and separation of indium(III) with a high molecular weight amine

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Received 2 January 2007; revised 11 February 2008

The liquid-liquid extraction of indium(III) from sodium succinate media using *n*-octylaniline in toluene as an extractant was studied. Quantitative extraction of indium(III) was observed in the range of 0.004-0.0075 M sodium succinate at pH 3.8-6.0 with 4% *n*-octylaniline in toluene. Indium(III) was completely stripped from the metal loaded organic phase of the extractant with water and determined complexometrically. The stoichiometry of the extracted species was determined on the basis of slope analysis. The extraction was found to proceed by a ion-pair mechanism with the extracted species being $[RNH_3^+In(succinate)_2^-]_{org}$. Separation of indium(III) was carried out from some associated metals like Tl(I), Mg(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Ge(IV), Sb(III), Bi(III). The selectivity of the extraction of indium(III) can also be achieved by use of a suitable masking agent for estimation and determination from the synthetic mixture corresponding to alloy to show the practical utility of the extractant.

Keywords: Indium(III), *n*-Octylaniline, Solvent extraction, Separation, Succinate

Abundance of indium in the earth's crust is about 0.24 ppm. It is found in minute amounts (0.1–2.8% w/w) in many minerals. It is generally found in zinc-blend, chalcopyrite, galena etc¹. Indium has extensive use in bearing alloys. Recently mixed tin-indium oxides along with In-P semiconductors have become increasingly popular in new Hi-tech devices. In alloys with lead, copper, aluminium and zinc, the hardening and strengthening of indium as well as its corrosion resistance property increases. Indium is sensitive to neutron radiation so it is used in safety monitoring badges to radiation exposure. It is effectively used in radio engineering and semiconductor technology.

In view of the above uses, and to meet high purity requirement of the indium, solvent extraction offers an attractive alternative for clear cut separation and determination of indium(III) from associated metal ions. Several extractants, such as di(2-ethylhexyl) phosphoric acid (D2EHPA)²⁻⁶, tributyl phosphate (TBP) and trioctylamine (TOA)^{7,8}, trioctylphosphine oxide (TOPO) and TBP⁹ have been used for the liquid-liquid extraction of indium(III). However, these methods suffer from limitations, such as multistage extraction^{2,4}, strong interference of iron⁵, higher acidity^{7,8}, etc.

Amines are good extractants for indium(III). Extractants such as trioctylamine (TOA) and trioctyl methyl ammonium chloride (TOMAC)^{10,11}, trialkyl

amine ADOGEN 364¹², Aliquat 336S¹³, *n*-octylaniline¹⁴, and *N-n*-octylaniline¹⁵ have been reported for the extraction of indium(III). *n*-Octylaniline extracts indium(III) from hydrochloric acid media but suffers from strong interference by Tl(III), Ga(III), Fe(II) and Fe(III)¹⁴.

The extractive separation and determination of indium(III) has been studied by using trioctylamine from iodide medium at different concentrations of H₂SO₄. The β -activity of ¹¹⁴In was measured by liquid scintillation counting. The method was applied to determine indium(III) in rock samples, calcium oxide, zinc ore, silicon wafer, zinc metal and stream sediments. However, co-extraction of many ions required the use of appropriate masking agent¹⁶. A rapid and selective method for extraction of indium(III) using ¹¹⁴In as a tracer has been developed by using quinaldic acid into isoamylalcohol as an extractant. This technique is applicable in nuclear medicine significantly for aid infection diagnosis, including imaging with ¹¹¹In-oxine¹⁷.

Recently, *isomethyl* butyl ketone (MIBK) containing TOMAC^{18,19}, 8-quinolinol (Hq)²⁰, triphenyl arsine oxide (TPASO)²¹, 4-isopropyltropolone (Hipt)²², 2,4-pentane dione (Hacac)²³, were used as extractants for indium(III). These methods have limitations such as strong interference from Bi(III), Pb(II), Sn(II) and Cu(II)¹⁸, hydration of complex²⁰ and

use of synergist^{20,23}. Some other extractants reported for extraction of indium(III) are β -hydroxynaphthaldoxime²⁴, 2-theonyltrifluoroacetone (Htta)²⁵, 1-phenyl-3-methyl-4-benzoyl-5-pyrozolone (PMBP)²⁶, and 3-phenyl-4-benzoyl isoxazol-5-one (HPBI)²⁷.

n-Octylaniline has been explored as extractant for Pb(II)²⁸, Tl(III)²⁹, and Al(III)³⁰ from this laboratory. The study has now been extended for the extraction separation of indium(III) from associated ions. The proposed method permits determination of indium(III) from synthetic mixture corresponding to alloy. The method is simple, rapid and extraction takes place at room temperature.

Experimental Procedure

Apparatus

An Elico digital spectrophotometer model SL-171 with 1 cm quartz cells was used for absorbance measurements. *pH* measurements were carried out using an Elico digital *pH* meter model LI-120.

Reagents

Standard solution of indium(III) was prepared by dissolving 6.566 g indium trichloride tetrahydrate (Fluka A.G.) in dilute hydrochloric acid and the solution diluted to 500 mL and standardised complexometrically³¹. The solution contains 5.142 mg In(III) per mL. The stock solution containing 1.0 mg/mL indium(III) was prepared by appropriate dilution with distilled water.

Standard solution of thorium nitrate (0.01 M) was prepared by dissolving 5.881 g thorium nitrate (A.R.) and diluted to 1.0 L with distilled water and standardised against standard zinc solution³².

Standard solution of EDTA (0.01 M) was prepared by dissolving 3.722 g disodium salt of EDTA in 1.0 L of distilled water and standardised complexometrically³².

n-Octylaniline was prepared by the Pohlandt method³³ and its solution 4% *v/v* (0.18 M) was prepared in toluene.

All solutions were prepared from analytical grade reagents. Aqueous solutions were prepared with doubly distilled water.

Extraction and determination procedure for indium(III)

An aliquot of solution containing 1.0 mg of indium(III) was mixed with 0.035 mg of sodium succinate to make its concentration 0.005 M in a total volume 25 mL of the solution. The *pH* of the solution was adjusted to 5.0 using dilute hydrochloric acid and

sodium hydroxide solution. The solution was then transferred to a 125 mL separatory funnel, 10 mL of 4% *v/v* *n*-octylaniline in toluene was added and it was shaken gently for about 1 min. The layers were allowed to separate and the aqueous layer was carefully withdrawn. Indium(III) from the organic phase was stripped with water (2 \times 25 mL).

The back extracts were mixed with an excess of EDTA solution (20 mL of 0.001 M), the *pH* adjusted to 2.5 and titrated against 0.001 M thorium nitrate using seven drops of 0.1% *w/v* xylenol orange as an indicator. The end point was yellow to red violet³¹.

Results and Discussion

Extraction of indium(III) as a function of *pH*

The extraction of indium(III) was carried out at various *pH* (1-10). Quantitative extraction of indium(III) was observed in the *pH* range of 3.8-6.0 from 0.005 M sodium succinate media (Fig. 1). At higher *pH* of extraction there is possibility of hydrolysis of ion pair complex. This indirectly promotes competing equilibria with the formation of ion pair complex, resulting in a decrease in extraction with increase in *pH*. In the proposed method *pH* 5.0 was maintained for quantitative extraction of indium(III).

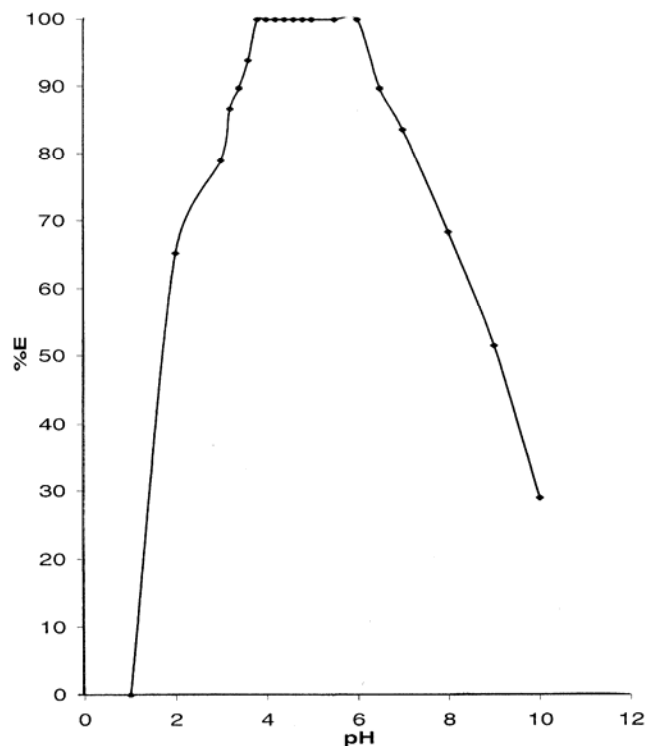


Fig. 1—Extraction behaviour of In(III) as a function of *pH* from 0.005 M sodium succinate with 4% *v/v* *n*-octylaniline in toluene.

Extraction of indium(III) as a function of *n*-octylaniline concentration

Toluene solutions of *n*-octylaniline with varying concentrations (1-10% *v/v*) were employed to optimize the extraction conditions for indium(III). It was found that 10 mL of 2% *v/v* *n*-octylaniline in toluene was sufficient for quantitative extraction of indium(III) (1.0 mg) from 0.005 M sodium succinate but in recommended procedure 4% *v/v* *n*-octylaniline in toluene was used to ensure the complete extraction of metal ion. The excess of reagent showed no adverse effect.

Extraction of indium(III) as a function of weak organic acid concentration

The extraction of indium(III) was carried out at pH 5.0 with 4% *v/v* *n*-octylaniline in toluene in the presence of varying concentrations of sodium succinate, sodium malonate and sodium salicylate as weak acid media. The extraction of indium(III) was found to be quantitative in the concentration range of 0.0040 to 0.0075 M sodium succinate. With increased concentration of sodium succinate there was a decrease in the extraction of indium(III) (Fig. 2). The decrease in extraction at high acid concentration is presumably due to preferential formation of the succinate of the *n*-octylaniline. Therefore, 0.005 M concentration of sodium succinate was used

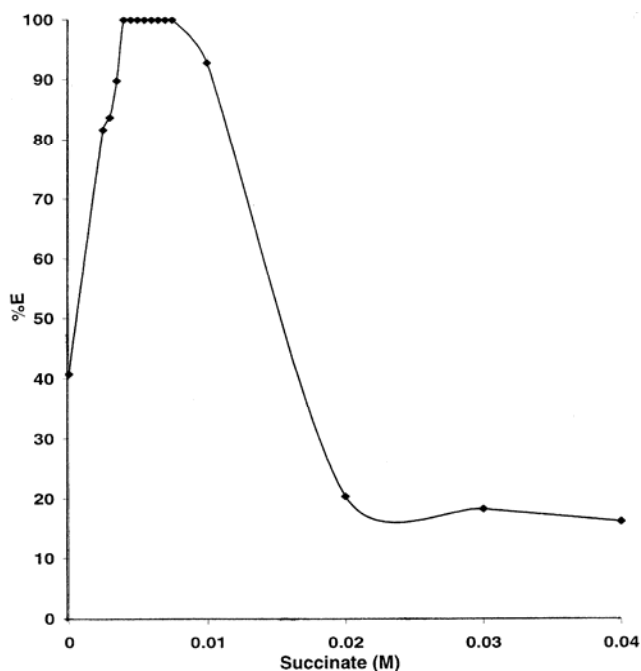


Fig. 2—Extraction behaviour of In(III) as a function of sodium succinate concentration with 4% *v/v* *n*-octylaniline in toluene at pH 5.0.

throughout this work. However, there was incomplete extraction of indium(III) from sodium salicylate (83.67%) while no extraction was observed from sodium malonate medium.

Effect of diluents

Indium(III) was extracted with 10 mL of 4% *n*-octylaniline in various diluents. The extraction of indium(III) was quantitative with toluene and methyl isobutyl ketone (MIBK). Benzene (16.3%), xylene (25.5%), carbon tetrachloride (13.3%), chloroform (90.8%), amyl acetate (5.1%), amyl alcohol (7.1%), *n*-butanol (67.3%) and 1,2 dichloroethane (93.9%) were found to be poor solvents.

Nature of extracted species

Attempts were made to ascertain the nature of the extracted complex species using log *D* – log *C* plots. The graphs of log *D*_[In(III)] against log *C*_[*n*-octylaniline] at fixed sodium succinate concentration (0.005 M) were found to be linear, having slopes of 0.98, 1.01 and 0.99 at pH 3.5, 6.5 and 6.8, respectively (Fig. 3). Also, plots of log *D*_[In(III)] against log *C*_[succinate] at fixed *n*-octylaniline concentration (4% *v/v*), were linear and slope values were found to be 1.89, 1.76 and 1.74 at

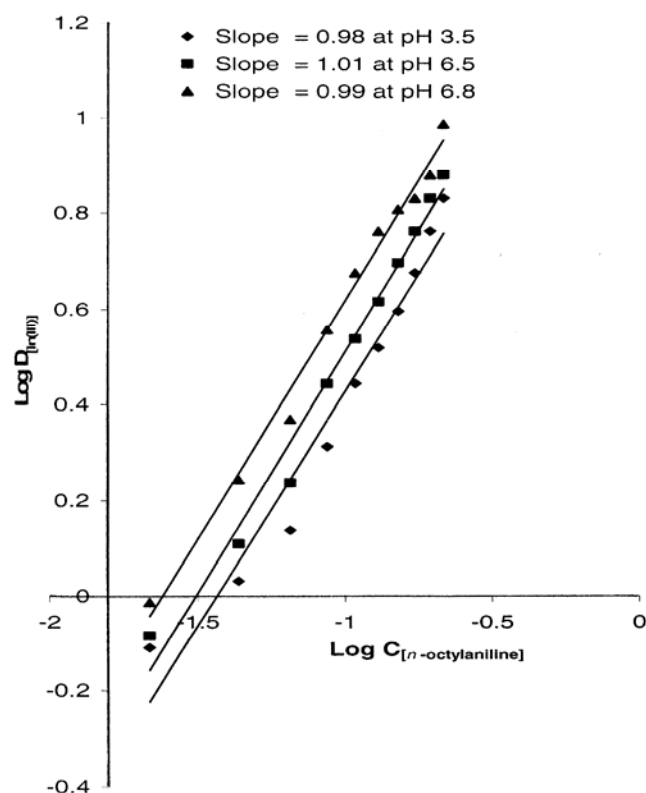
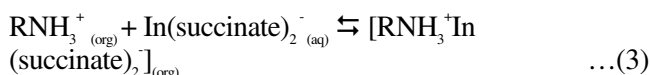
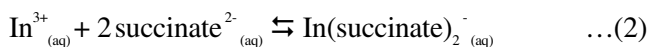
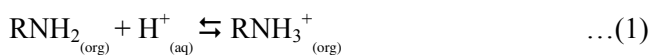


Fig. 3—Log-log plot of distribution ratio Log *D*_[In(III)] versus Log *C*_[*n*-octylaniline] at 0.005 M sodium succinate.

pH 3.5, 6.5 and 6.8, respectively (Fig. 4). The probable composition of the extracted species is calculated to be 1:2:1 (metal : acid : extractant). The possible mechanism of extracted species appears to be protonated *n*-octylaniline which forms cationic species as RNH_3^+ , while succinate combines with indium(III) to form anionic species as $\text{In}(\text{succinate})_2^-$, and both of them associate to form ion pairs of the type $[\text{RNH}_3^+\text{In}(\text{succinate})_2^-]_{\text{org}}$, which being neutral constitutes extractable species. The mechanism of formation of ion-pair complex may be represented as



Effect of time of equilibrium

The period of equilibration was varied from 10 s - 10 min. However, it was found that prolonged shaking (>2 min) had adverse effect on the extraction

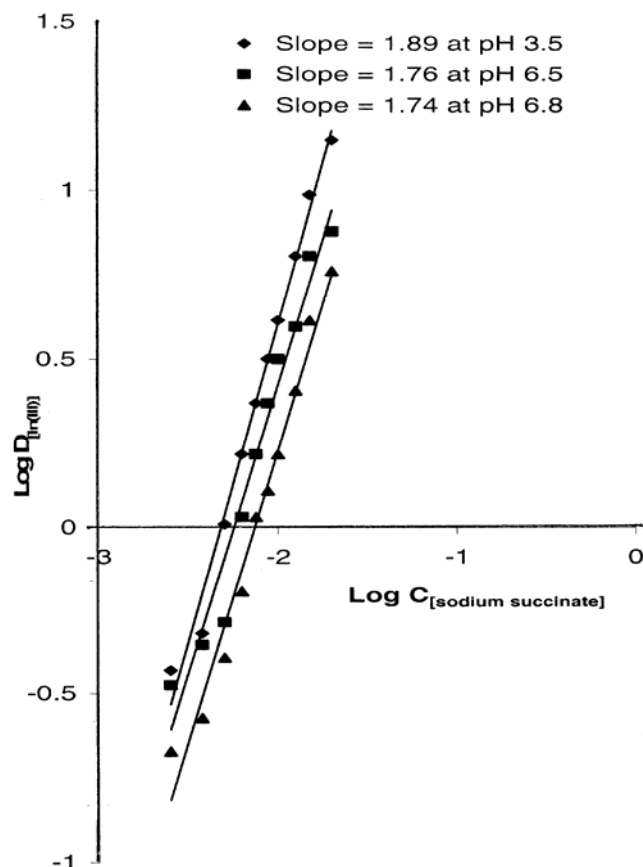


Fig. 4—Log-log plot of distribution ratio $\text{Log } D_{[\text{In(III)}]}$ versus $\text{Log } C_{[\text{sodium succinate}]}$ at 4% v/v *n*-octylaniline in toluene.

of the metal ion and it should be avoided. The decrease in the extraction of indium(III) with shaking was due to dissociation of the ion pair complex. The optimum extraction of indium(III) was found in the range of 20 s - 2 min. Hence, 1 min time was recommended for general procedure.

Effect of various stripping agents

Indium(III) from organic phase was stripped with two 10 mL portions of various stripping agents at different concentrations like mineral acids, alkali and buffer solutions. The recovery percentage of indium(III) from organic phase was found to be incomplete with hydrochloric acid (81.8%), nitric acid (70.4%), perchloric acid (73.5%), sulphuric acid (44.9%), sodium hydroxide (18.6%) and ammonium hydroxide (8.6%). Indium(III) is not stripped with sodium nitrate. However, indium(III) is quantitatively stripped with water as well as acetate buffer (pH 4.70). Water is a suitable strippant for quantitative recovery of indium(III) from the organic phase. In the recommended procedure, two 25 mL portions of water were used for the complete recovery of indium(III).

Effect of aqueous to organic volume ratio on extraction of indium(III)

The result of contacting different volume ratios of aqueous to organic phase have been studied. The results indicate that a preferred aqueous/organic (A/O) phase ratio in this study was found to be 10:1 or less. This is evident from the sharp increase in the separation efficiency as well as the distribution ratio of indium(III) when phase ratio (A/O) changed from 20:1 to 10:1. This may simply be due to the unavailability of reagent for metal extraction and so a crowding effect occurs at low phase ratio. However, in the recommended procedure the phase ratio is maintained as 2.5:1 so as to avoid the large consumption of the sodium succinate.

Loading capacity of *n*-octylaniline on extraction of indium(III)

Varying concentrations of indium(III) (1-15 mg) were extracted with 10 mL 4% v/v *n*-octylaniline in toluene from 0.005 M sodium succinate media. It was observed that extraction of indium(III) was quantitative upto 10 mg.

Effect of temperature

The extraction of indium(III) with *n*-octylaniline was carried out in the temperature range of 293 to 323 K. The extraction of indium(III) increases with temperature. Figure 5 shows the plot of $\log K_{ex}$

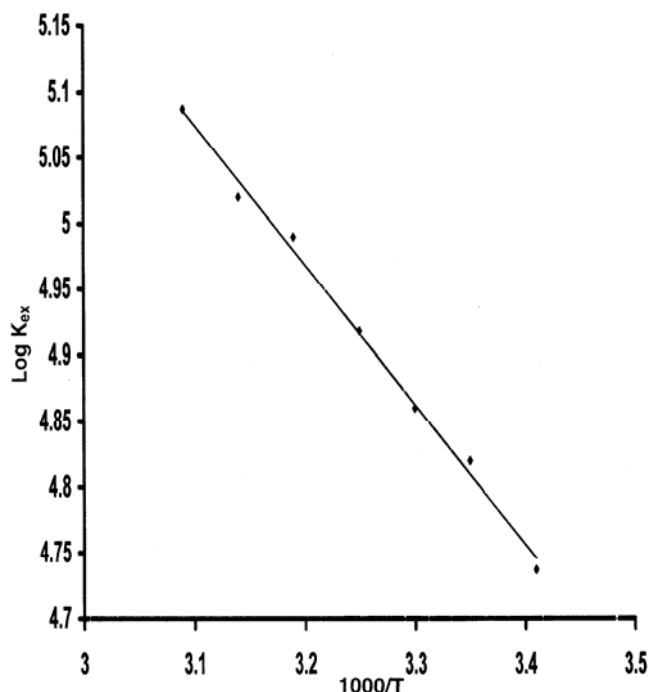


Fig. 5—Effect of temperature on the extraction of In(III) with 4% v/v *n*-octylaniline in toluene from 0.005 M sodium succinate.

against $1000/T$. The enthalpy change (ΔH) is evaluated from this plot by using equation(1)

$$\Delta H = - \{\text{slope}\} \times 2.303 \times R \quad \dots(1)$$

where $R = 8.314 \text{ KJmol}^{-1}$

The free energy change (ΔG) and entropy change (ΔS) at room temperature (T)(298 K) are calculated using Eqs (2) and (3), respectively.

$$\Delta G = - 2.303 RT. \log K_{ex} \quad \dots(2)$$

$$\text{where, } K_{ex} = \frac{D}{[\text{RNH}_2][\text{H}^+]}$$

where, $\text{RNH}_2 = n\text{-octylaniline}$
 $R = -\text{C}_6\text{H}_4\text{-CH}_2\text{-CH}_2\text{-CH}_3$

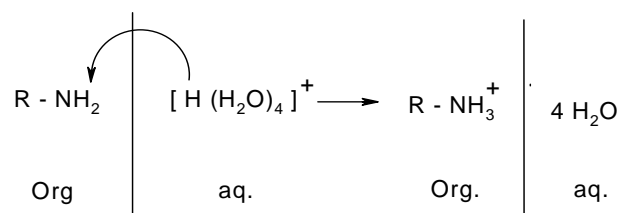
$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad \dots(3)$$

The activation parameters obtained for the solvent extraction of indium(III) are

$$\Delta G = - 27.50 \text{ KJ mol}^{-1}, \Delta H = - 25.52 \text{ KJ mol}^{-1}, \text{ and } \Delta S = 6.87 \text{ Jmol}^{-1}\text{K}^{-1}$$

The entropy of activation obtained is a low positive value. The loss or gain of translational and rotational

entropy is generally most important determinant of the entropy of activation. Most of the reactions loose translational degrees while forming a transition state leading to negative entropies. In the present study, the preliminary step of extraction is protonation of the reagent (*n*-octylaniline) followed by ion-pair formation with the anionic complex of indium(III). The small +ve value of ΔS is due to loss of translational and rotational entropy of the hydrogen cation in aqueous solution when it is attached to the reagent in organic liquid. The hydrogen cation is extensively hydrated, by at least four water molecules, but after protonation the reagent is not hydrated. Therefore, the release of hydration by the hydrogen cation may increase the entropy sufficiently to offset its loss of translational and rotational freedom which is shown in scheme given below.



Effect of foreign ions on percentage extraction of indium(III)

The effect of large number of foreign ions on the extraction of 1.0 mg of indium(III) with the proposed reagent was investigated by the recommended procedure. Initially the foreign ion was added to indium(III) solution in large excess; 150 mg for anions and 25 mg for cations. When interference was intensive, the tests were repeated with successively smaller amounts of foreign ion. The tolerance was set at the amount of the foreign ion that could be present to give an error less than $\pm 2\%$ in the recovery of indium(III) (Table 1). It was observed that the method is free from interference from a large number of cations and anions.

Applications

Separation and determination of indium(III) from binary mixture

The suitability of the above developed method was examined by applying it to the separation and determination of indium(III) in a variety of binary mixtures which are commonly associated with it.

It was found that Tl(I), Mg(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Ge(IV), Sb(III) and Bi(III) remained unextracted under optimum conditions with indium(III) using 0.005 M sodium

Table 1—Effect of foreign ions on the extraction of indium(III)

In (III) = 1.0 mg	Sodium succinate = 0.005 M
Initial pH = 5.0	Strippant = water (2×25 mL)
<i>n</i> -Octylaniline = 10 mL	4% v/v in toluene
Aqueous :	Equilibration time = 1 min
Organic = 2.5 : 1	
Tolerance limit, mg	Diverse ions added
100	Tartrate, Thiocyanate, Nitrate, Thiosulfate, Acetate, Malonate
50	Salicylate, Ascorbate, Fluoride, Iodide, Nitrite, EDTA, Thiourea oxalate
25	Citrate
20	Ca(II), Sr(II), Ba(II), Mg(II), Bi(III), Zn(II), Cd(II), Cr(VI), Mn(II), Fe(III), Ti(IV)
10	Be(II), Pb(II), Cr(III), Mn(VII), Fe(II), Co(II), Ga(III), Tl(I), Tl(III), Mo(VI)
7	Ge(IV)
5	Sn(II), Sn(IV), Sb(III), Cu(II), V(V), Al(III)
1	Ru(III), Os(VIII), Ir(III), Rh(III), Re(VII), Au(III)

succinate with 10 mL 4% v/v *n*-octylaniline in toluene. The pregnant organic phase was stripped with water (2×25 mL) and determined complexometrically as recommended in the procedure. The raffinate containing added metal ion was estimated by standard procedure.

The proposed method was also extended for separation of indium(III) from Ga(III) and Fe(III) by masking with tartrate (100 mg each), Al(III) and Tl(III) by masking with oxalate (50 mg each) and Sn(IV) by masking with fluoride (50 mg). The masked metal ion remained in the aqueous phase while indium(III) was extracted selectively into the organic phase with *n*-octylaniline in toluene. It was stripped from the organic phase with water and estimated as per the given procedure. The aqueous phase containing added metal ion was demasked and after reduction the volume of the aqueous phase estimated by standard procedure^{31,34} (Table 2).

Determination of indium(III) in a synthetic mixture

A solution containing 1.0 mg of indium(III) was taken and known amounts of other metals were added. Extraction of indium(III) was carried out using the recommended procedure. The results obtained were in good agreement with the amount added (Table 3). The method is also applicable for extraction and determination of indium(III) in synthetic mixture corresponding to alloy (Table 4).

Table 2—Separation of indium(III) from binary mixture

Metal ion	Concentration, mg	Average % recovery*
In(III)	1.0	99.9
Al(III) ^b	1.0	99.8
In(III)	1.0	99.8
Ga(III) ^a	1.0	99.7
In(III)	1.0	99.7
Tl(I)	1.0	99.7
In(III)	1.0	99.8
Tl(III) ^b	1.0	99.7
In(III)	1.0	99.9
Mg(II)	1.0	99.7
In(III)	1.0	99.8
Fe(III) ^a	1.0	99.6
In(III)	1.0	99.7
Ni(II)	1.0	99.8
In(III)	1.0	99.8
Cu(II)	1.0	99.7
In(III)	1.0	99.7
Zn(II)	1.0	99.7
In(III)	1.0	99.8
Cd(II)	1.0	99.7
In(III)	1.0	99.9
Hg(II)	1.0	99.8
In(III)	1.0	99.7
Pb(II)	1.0	99.7
In(III)	1.0	99.8
Sn(IV) ^c	1.0	99.7
In(III)	1.0	99.7
Ge(IV)	1.0	99.7
In(III)	1.0	99.9
Sb(III)	1.0	99.8
In(III)	1.0	99.8
Bi(III)	1.0	99.7

* - Average of five determinations

^a - Masked by tartrate (100 mg)

^b - Masked by oxalate (50 mg)

^c - Masked by fluoride (50 mg)

Table 3—Separation of indium(III) from multicomponent mixture

Composition, mg	Indium(III) found ^a , mg	Recovery, %	R.S.D., %
In, 1.0; Al, 1.0; Fe ^a , 1.0	0.997	99.7	0.30
In, 1.0; Zn, 1.0; Ge, 1.0	0.998	99.8	0.20
In, 1.0; Pb, 1.0; Sb, 1.0	0.996	99.6	0.40
In, 1.0; Ni, 1.0; Cu, 1.0; Fe ^a , 1.0	0.997	99.7	0.30
In, 1.0; Mg, 1.0; Al ^b , 1.0; Zn, 1.0	0.998	99.8	0.20
In, 1.0; Sn ^c , 1.0; Pb, 1.0; Ge, 1.0	0.997	99.7	0.30
In, 1.0; Bi, 1.0; Sb, 1.0	0.999	99.9	0.10
In, 1.0; Tl ^b , 1.0; Cd, 1.0	0.997	99.7	0.30

* - Average of five determinations

^a - Masked by tartrate (100 mg)

^b - Masked by oxalate (50 mg)

^c - Masked by fluoride (50 mg)

Table 4—Separation of indium(III) from synthetic mixture corresponding to alloy.

Composition, %	Indium(III) taken, mg	Indium(III) found,* mg	Recovery, %	R.S.D., %
Lipowitz's alloy Bi, 50.1; Cd, 10.0; Pb, 26.6; Sn, 13.3; In, 18.3	1.0	0.997	99.7	0.3

* Average of five determinations

Conclusion

The important conclusions from the results of the study are:

- (i) It permits selective separation of indium(III) from other metals such as Al(III), Ga(III), Tl(I), Tl(III), Mg(II), Fe(III), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Sn(IV), Ge(IV), Sb(III) and Bi(III) which are generally associated with it.
- (ii) It is free of interferences from a large number of foreign ions which are associated with indium(III) in its natural occurrence.
- (iii) The time required for equilibration is very short (20 s).
- (iv) Low reagent concentration is required for quantitative recovery of indium(III).
- (v) *n*-Octylaniline extracts indium(III) in toluene from sodium succinate media by an anion exchange mechanism in which a ion pair complex of stiochiometric formula $[\text{RNH}_3^+\text{In}(\text{succinate})_2]_{\text{org}}$ is formed in the organic phase.
- (vi) The developed method is very simple, selective, rapid, reproducible, accurate and requires only 15–20 min for separation and determination of indium(III).

Acknowledgement

The authors express their gratitude to Hon'ble Vice Chancellor Prof M. M. Salunkhe, Shivaji University, Kolhapur for his constant encouragement during the research work.

Nomenclature

- D = Distribution ratio
 %E = Percentage extraction
 V_w = Volume of aqueous phase
 V_o = Volume of organic phase
 K_{ex} = Extraction equilibrium constant
 ΔG = Free energy change, kJ mole⁻¹
 ΔH = Enthalpy change, kJ mole⁻¹
 ΔS = Entropy change, Jmole⁻¹K⁻¹
 R = Gas constant, 8.314J (4.186 cal)

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