Journal of the Serbian Chemical Society
eVersion electronic
JSCS@tmf.bg.ac.yu • www.shd.org.yu/JSCS
www.shd.org.yu

J. Serb. Chem. Soc. *73* (4) 435–451 (2008) UDC 66.061.35:546.683.3+547.412.123:544.032.4
JSCS–3726 *Original scientific paper*

Rapid liquid–liquid extraction of thallium(III) from succinate media with 2-octylaminopyridine in chloroform as the extractant

SANDIP V. MAHAMUNI, PRAKASH P. WADGAONKAR[1] and MANSING A. ANUSE*

Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur – 416 004 and [1]Polymer Science and Engineering Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune – 411 008, India

(Received 28 May 2007)

Abstract: A simple solvent extraction study of thallium(III) was conducted. Selective and quantitative extraction of thallium(III) by 2-octylaminopyridine (2-OAP) in chloroform occurred from aqueous sodium succinate medium (0.0075 M) at pH 3.0. Thallium(III) was back extracted with acetate buffer (pH 4.63). The effect of the concentration of succinate and 2-OAP, the role of various diluents, stripping agents, loading capacity of 2-OAP, equilibrium time and aqueous:organic volume ratio on the extraction of thallium(III) was studied. The stoichiometry of the extracted species was determined based on the slope analysis method and found to be 1: 2: 1 (metal:acid:extractant). The temperature dependence of the extraction equilibrium constant was also examined to estimate the apparent thermodynamic functions ΔH, ΔG and ΔS for the extraction reaction. The method is free from interference of a large number of cations and anions. The method was used for the selective extraction of thallium(III) from its binary mixture with Zn(II), Cd(II), Hg(II), Bi(III), Pb(II), Se(IV), Te(IV), Sb(III), Ga(III), In(III), Al(III), Tl(I) and Fe(III). The proposed method was applied to the synthetic mixtures and alloys. It is simple, selective, rapid and eco-friendly.

Keywords: liquid–liquid extraction; thallium(III); succinate media; 2-OAP; temperature effect.

INTRODUCTION

Thallium is a trace element that occurs mostly in sulphur containing ores.[1] It is a by-product metal recovered in some countries from flue dusts and residues collected in the smelting of copper, zinc and lead ores. Thallium(III) is usually present in lead(II), cadmium(II), indium(III) or zinc(II) compounds as a trace constituent.[2] Consumption of thallium metal and thallium compounds continues for most of its established end uses, such as an additive in glass to increase its refractive index and density, a catalyst or intermediate in the synthesis of organic

---

* Corresponding author. E-mail: mansinganuse@yahoo.co.in

doi: 10.2298/JSC0804435M

compounds and a component in high-density liquids for sink-float separation of minerals.[3] Thallium is a highly toxic element and Tl(I) is known to replace potassium ions in the activation of enzymes.[4] The contamination of the environment with thallium mainly results from non-ferrous mines, coal combustion and cement plants.[5] Hence, bearing all this in mind, the separation of thallium from other metal ions has been a subject of great analytical interest.

There are a few research papers on the extraction and separation of thallium(III) from associated elements. The extraction of thallium(III) and thallium(I) by solutions of carboxylic acids, such as naphthenic acid (NA), *sec*-octylphenoxy acid (CA-12) and *sec*-nonylphenoxy acetic acid (CA-100) dissolved in kerosene and acidic aqueous chloride media has been reported by X. Zhang *et. al.*[6] Various organophosphorus compounds, such as Cyanex 921,[7] Cyanex 923,[8] Cyanex 925,[9] tributyl phosphate (TBP)[10] have been found to be useful for the extraction of thallium(III). Studies on the thermodynamics of solvent extraction of thallium(I) with diethylhexylmonothiophosphoric acid (D2EHMTPA)[11] and di(2-ethylhexyl)dithiophosphoric acid[12] were conducted at an ionic strength of 0.1 mol g^{-1} in the aqueous phase containing sodium sulphate as a supporting electrolyte and at a constant initial molality of the extractant in the organic phase at temperatures from 278.15 to 303.15 K. The standard extraction constants K_0 at various temperatures were obtained by the extrapolation and the polynomial approximation methods.

Trace amounts of thallium(III) were quantitatively extracted with hexa-acetyl calix(6)arene at pH 2.0 with toluene as the diluent. However, uranium, antimony, tin and lead showed strong interference.[13] Meso-tetraspirocyclohexylcalix(4)pyrrole (TSCC4P) in 20.6 % (v/v) tetrahydrofuran was found to be an effective complexing ligand for homogeneous liquid–liquid extraction and preconcentration of thallium(I) ions at pH 5.4. The reproducibility of method was at the most 3.4 %.[14]

Thallium(III) was separated by solvent extraction into methyl isobutyl ketone (MIBK) in hydrobromic acid medium from a sample digest of geological material.[15] The extraction equilibria for the determination of ultra trace amounts of thallium(III) in a water sample by ion-pairs of the methyl-2-naphthoate (2HNpH) complex and tetrabutylammonium ion in MIBK extraction was studied by Kim and co-workers.[16] However, the percentage extraction of thallium(III) as an ion pair was 73.5 % at pH 6.0. A method was proposed for extraction of trivalent thallium from salicylate media using triphenyl arsine oxide (TPASO) dissolved in toluene as the extractant.[17] The separation of thallium(I) and thallium(III) was achieved by the difference between the distribution coefficients of thio–oxime and PAN–thallium complexes. Heavy metals such as Mn(II), Fe(III), Ni(II), Cu(II), Zn(II) needed to be masked by EDTA.[18] The kinetics of the hydrolysis of tris(thenoyltrifluoroacetonate)thallium(III) in water was studied.[19] A method for the extraction of thallium(III) with isopentyl acetate from 10 M hydrochloric acid media was proposed, whereby co-extracted iron could be removed by its re-extraction from the organic phase with 4 M H_2SO_4.[20] Trivalent thallium can be extracted from aqueous solutions at 65 °C with 2,6-bis-(1′-phenyl-3′-methyl-5′-oxo-pyrazole-4′)pyridineacyl (H_2PMBPP or H_2A) using molten paraffin wax as a diluent.[21]

The influence of module arrangements on the solvent extraction of thallium(III) from sodium chloride–sulphuric acid solution into butyl acetate was studied using laboratory-made modules consisting of hydrophobic poly(vinylidine fluoride) (PVDF) and polypropylene (PP) hollow fibres.[22–25] The distribution coefficient of thallium(III) between butyl acetate and the aqueous phase was about 1000 when the extraction was carried out from 5.0 mol dm^{-3} sulphuric acid solution containing sodium chloride, providing the molar ratio between thallium(III) and Cl^- was not less than 1:4. From this solution, thallium(III) is extracted in the form of the $HTlCl_4$ complex.[24] The extraction was found to be dispersion free.[24,25]

Gas-stirred propylene carbonate (PC) extraction has proved to be highly useful for the separation and subsequent direct polarographic estimation of thallium(III). It can be seen that selective separation of thallium(III) from other metal ions was achieved by the extraction into PC from 0.03 M hydrochloric acid. However, Fe(III) was found to be partially co-extracted with thallium(III).[26] Chung *et al.* reported a selective extraction method for thallium(III) in the presence of gallium, indium, bismuth and antimony into 2-propanol by the salting out method using sodium chloride to induce phase separation.[27] The distribution behaviour of the ion association complexes of tetrahalogenatothallate(III) ions (TlX_4^- (X^- = chloride, bromide and iodide ions)) with quaternary ammonium cations (Q^+) between three organic phases (chloroform, chlorobenzene and benzene) and an aqueous phase was examined, and the extraction constants ($\log K_{ex}$) were determined.[28] Electrothermal atomic absorption spectrometry (ETAAS) has been used for the determination of thallium(III) in aqueous solution in conjunction with an enrichment technique such as solid-phase extraction.[29] Thallium(III) was quantitatively retained by 1,10-phenanthroline and tetraphenylborate onto benzophenone in the pH range 0–11.0 from a large volumes of aqueous solutions of various samples.[30] A selective method has been developed for extraction studies of thallium(III) with a high molecular weight carboxylic acid, SRS–100 (a liquid cation exchanger). Quantitative extraction of thallium(III) was achieved in the pH range 5.0–6.0 from acetic acid and sodium acetate solution.[31]

Solvent extractions of thallium(III) with high molecular weight amines have been investigated. A simple solvent extraction study for thallium was conducted based on the extraction of thallium as a chlorocomplex (tetrachlorothallate(III) anion) with tribenzylamine. The recovery of thallium was found to be 95 %.[32] Recently, a primary amine, *n*-octylaniline dissolved in toluene was reported to be an effective extractant for thallium(III) using salicylate media.[33]

Herein, a rapid and selective extraction procedure for thallium(III) with 2-octylaminopyridine is reported. The method permits the separation of thallium(III) from commonly associated elements and was employed to separate thallium(III) in synthetic mixtures and alloy samples.

EXPERIMENTAL

Apparatus

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

Reagents

A standard stock solution of thallium(I) was prepared by dissolving 1.303 g of thallium(I) nitrate (Across) in 25 ml 1.0 M nitric acid and diluting to 1000 ml with distilled water. It was then standardized complexometrically[34] after oxidation to the thallium(III) state with saturated bromine water. The solution contained 1.0 mg ml^{-1} of thallium(I).

A standard solution of thorium nitrate (0.01 M) was prepared by dissolving 5.881 g thorium nitrate (AR) and diluting to 1.0 l with distilled water. This solution was standardized against standard zinc(II) solution.[35]

A standard solution of EDTA (disodium salt) (0.01 M) was prepared by dissolving 3.722 g of the disodium salt of EDTA in 1.0 l of distilled water.

An acetate buffer solution (pH 4.63) was prepared by mixing equal volumes of 0.2 M sodium acetate trihydrate and 0.2 M of glacial acetic acid.[35]

A 0.025 M solution of 2-octylaminopyridine (2-OAP) was prepared by dissolving in chloroform.[36]

Other standard solutions of the different metals used to study the effect of diverse ions were prepared by dissolving weighed quantities of their salts in distilled water or dilute hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in water. All the employed chemicals were of A. R. grade and double distilled water was used through out.

General extraction and determination procedure for thallium(III)

To an aliquot of solution containing 1.0 mg of thallium(I), few drops of bromine water were added to oxidize the thallium(I) to thallium(III). The solution was then evaporated carefully to remove the excess bromine water. To this, a sufficient quantity of sodium succinate was added to give a final concentration 0.0075 M in a total volume of 25 ml of solution. The pH of the solution was adjusted to 3.0 using dilute hydrochloric acid and sodium hydroxide solutions. The aqueous solution was shaken with 10 ml of 0.025 M 2-OAP in chloroform for 2 min. After phase separation, the organic phase was stripped with three 15 ml portions of acetate buffer. The extracts were evaporated to moist dryness and the residue was dissolved in distilled water. To this, an excess of EDTA solution (10 ml 0.001 M EDTA) was added and the pH of the solution was adjusted to 3.5. The solution was titrated with a standard solution of 0.001 M thorium nitrate using xylenol orange as the indicator. The end point was yellow to red to red violet.[34]

RESULTS AND DISCUSSION

Extraction as a function of pH

The effect of pH on the percent thallium(III) extracted with 2-OAP in chloroform was studied in the pH range 1.0–10.0 in the presence of sodium succinate (0.0075 M). It was observed that the extraction of thallium(III) was quantitative in the pH range 2.0 to 6.0 (Fig. 1). In the proposed method, all the extractions were performed at a fixed pH of 3.0. At pH values, above 6.0, there exists the possibility of hydrolysis, which results in a lowering of the distribution ratio. This indirectly promotes an equilibrium competing with the formation of the ion pair complex, resulting in a decrease in extraction with increasing pH.

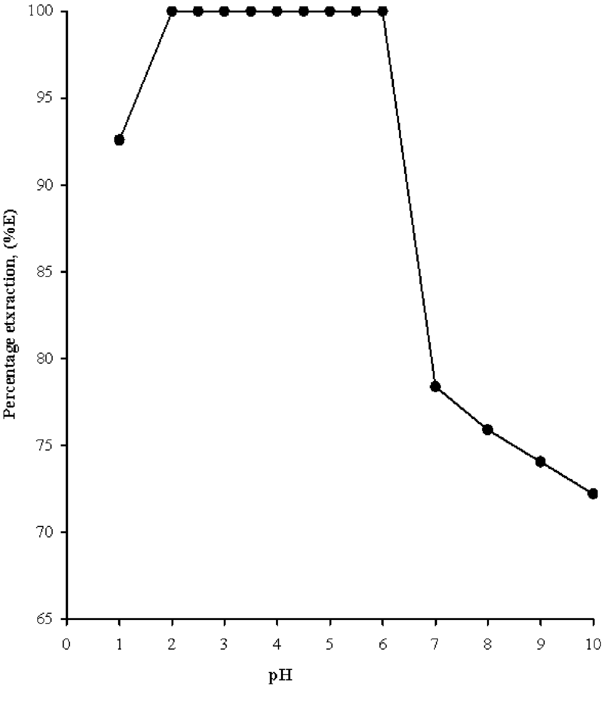

Fig. 1. Extraction behaviour of thallium(III) as a function of pH.

Extraction of thallium(III) as a function of the 2-OAP concentration

The effect of varying the 2-OAP concentration (0.0005–0.5 M) on the distribution of thallium(III) (1.0 mg) was investigated at pH 3.0 in an aqueous solution of ionic strength 0.0075 M sodium succinate. The optimum concentration of 2-OAP required for the quantitative extraction of thallium(III) was found to be 0.005 M. In the recommended procedure 10 ml of 0.025 M 2-OAP was used in order to ensure the complete extraction of thallium(III). However, at higher reagent concentration (> 0.1 M), there was decrease in the extraction of thallium(III). This was probably due to an increase in the concentration of the dimer with increasing concentration of 2-OAP and hence the distribution coefficient decreased due to reduced concentration of monomer.[37]

Extraction as a function of weak organic acid concentration

The extraction of thallium(III) was performed at pH 3.0 with 0.025 M 2-OAP in chloroform in the presence of varying concentrations (0–0.2 M) of sodium succinate, sodium salicylate, sodium malonate and sodium oxalate, as weak acid media (Table I). The extraction of the ion pair complex of thallium(III) was found to be quantitative in the range 0.004 to 0.08 M sodium succinate and at 0.006 M sodium salicylate. With increasing concentration of sodium succinate above this value, the extraction of thallium(III) decreased. The decrease in the extraction at high acid concentration was presumably due to the preferential formation of the succinate of 2-OAP. Therefore, 0.0075 M sodium succinate was used throughout this work. Sodium salicylate was not employed because of its narrow concentration range for extraction and high cost as compared to sodium succinate. The extraction of thallium(III) was found to be incomplete in sodium malonate and sodium oxalate media.

TABLE I. Extraction behaviour of thallium(III) as a function of the concentration of the weak organic acids; *m*(Tl(III)) = 1.0 mg, pH 3.0, 10 ml of 0.025 M solution of 2-OAP in chloroform, aqueous:organic ratio = 2.5:1, equilibrium time = 2 min, strippant = acetate buffer pH 4.63 (3×15 ml)

Acid concentration mol dm^{-3}	Sodium succinate[a]		Sodium malonate		Sodium salicylate		Sodium oxalate	
	% E	D	% E	D	% E	D	% E	D
0	35.85	1.39	35.85	1.39	35.85	1.39	35.85	1.39
0.0020	88.68	19.58	94.34	41.66	84.91	14.06	39.62	1.64
0.0040	100	∞	98.11	130.0	96.23	63.75	43.39	1.91
0.0060	100	∞	98.11	130.0	100.0	∞	18.86	0.58
0.0075	100[a]	∞	81.13	10.75	98.11	130.0	7.54	0.20
0.0080	100	∞	64.15	4.47	98.11	130.0	7.54	0.20
0.0100	100	∞	58.49	3.52	88.68	19.58	0.0	0.0
0.0200	100	∞	54.72	3.02	86.79	16.42	0.0	0.0
0.0400	100	∞	54.72	3.02	83.01	12.22	0.0	0.0
0.0600	100	∞	33.96	1.28	71.42	6.24	0.0	0.0
0.0800	100	∞	11.32	0.31	67.92	5.29	0.0	0.0
0.1000	92.45	30.61	5.62	0.15	49.05	2.40	0.0	0.0
0.2000	75.45	7.68	0.0	0.0	37.73	1.51	0.0	0.0

[a] Recommended for the general extraction procedure

Extraction with various diluents

Ten systems containing identical amounts (1.0 mg) of thallium(III) were prepared and extracted with 10 ml of 0.025 M 2-OAP in each of various solvents (Table II). The following percentage extractions were obtained. 1,2-dichloroethane (55.10) < kerosene (59.18) < *n*-butanol (63.26) < pentanol = pentyl acetate

(67.34) < toluene (73.46) < carbon tetrachloride (93.87) < benzene = xylene = = chloroform (100). No correlation between dielectric constant and percent extraction was observed. 2-Butanone did not extract thallium(III) into the organic phase. In the case of chloroform, a quicker phase separation was observed and this was used as the diluent for all subsequent studies.

TABLE II. Extraction behaviour of thallium(III) as a function of the diluent; m(Tl(III)) = 1.0 mg, pH 3.0, 10 ml of 0.025 M solution of 2-OAP in chloroform, aqueous:organic ratio = 2.5:1, equilibrium time = 2 min, strippant = acetate buffer pH 4.63 (3×15 ml)

Diluent	Dielectric constant, ε	Percentage extraction, % E	Distribution ratio, D
1,2-Dichloroethane	10.50	55.10	3.06
Kerosene	1.80	59.18	3.62
n-Butanol	17.80	63.26	4.30
Pentanol	13.90	67.34	5.15
Pentyl acetate	4.80	67.34	5.15
Toluene	2.38	73.46	6.91
Carbon tetrachloride	2.24	93.87	38.28
Benzene	2.28	100	∞
Xylene	2.30	100	∞
Chloroform[a]	4.40	100	∞

[a] Recommended for the general extraction procedure

Nature of extracted species

The stoichiometry of the extracted species was determined from the experimental studies using the slope analysis method. The plots of log $D_{[\mathrm{Tl(III)}]}$ *vs.* log $c_{[\text{2-OAP}]}$ at a fixed sodium succinate concentration (0.0075 M) were found to be linear with slopes of 1.25 and 0.93 at pH 7.0 and 10.0, respectively (Fig. 2). This indicates that the metal:extractant ratio was 1:1. In addition, plots of log $D_{[\mathrm{Tl(III)}]}$ *vs.* log $c_{[\mathrm{succinate}]}$ at a fixed 2-OAP concentration (0.025 M) were linear with slope values of 1.92 and 1.73 at pH 7.0 and 10.0, respectively (Fig. 3). This indicates two ions of succinate participate in the formation of the anionic species. Thus, the probable composition of the extracted species was 1:2:1 (metal:acid:extractant). The possible mechanism of extracted species appears to involve protonated 2-OAP, which forms cationic species, such as $\mathrm{RR'NH_2^+}$, while the succinate combines with thallium(III) to form anionic species, such as $[\mathrm{Tl(succinate)_2}]^-$, both of which associate to form an ion pair of the type $[\mathrm{RR'NH_2^+Tl(succinate)_2^-}]_{\mathrm{(org)}}$, which, being neutral, constitutes the extractable species.

The mechanism of formation of the ion pair complex is:

$$\mathrm{RR'NH_{(org)} + H^+_{(aq)} \rightleftharpoons RR'NH_2{}^+_{(org)}}$$

$$\mathrm{Tl^{3+}_{(aq)} + 2\ Succinate^{2-}_{(aq)} \rightleftharpoons [Tl(Succinate)_2]^-_{(aq)}}$$

$$\mathrm{RR'NH_2{}^+_{(org)} + [Tl(Succinate)_2]^-_{(aq)} \rightleftharpoons [RR'NH_2{}^+Tl(Succinate)_2{}^-]_{(org)}}$$

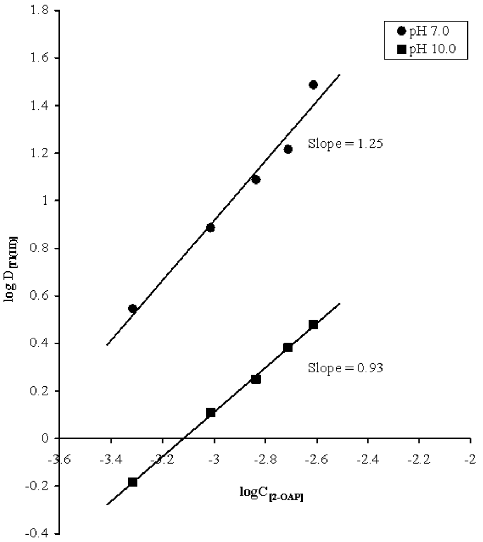

Fig. 2. Log–log plot of log $D_{[Tl(III)]}$ *vs.* log $c_{[2\text{-}OAP]}$ at a fixed succinate concentration (0.0075 M).

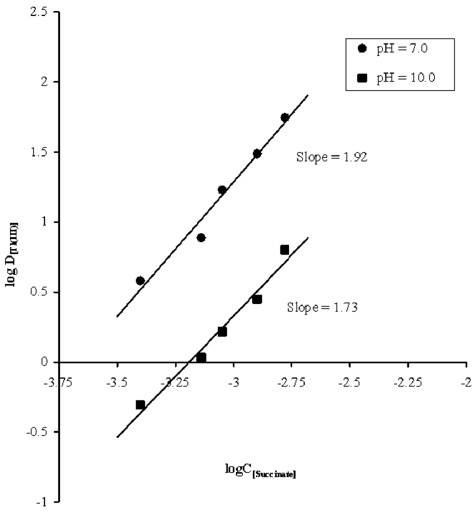

Fig. 3. Log–log plot of log $D_{[Tl(III)]}$ *vs.* log $c_{[Succinate]}$ at a fixed 2-OAP concentration (0.025 M).

Effect of equilibrium time

The experiments to investigate the influence of contact time on the extraction of thallium(III) were carried out by shaking an aqueous solution of 1.0 mg thallium(III) containing 0.0075 M succinate with an organic solution of 0.025 M 2-OAP in chloroform at an A/O ratio of 2.5 for various lengths of time at 25±3 °C. The obtained results showed that equilibrium was achieved within 30 s of contact. In the actual work, a two-minute equilibrium time was recommended in order to ensure the complete extraction of thallium(III). However, prolonged shaking above 20 min decreased the percentage extraction of thallium(III).

Extraction behaviour of thallium(III) as a function of metal loading capacity

The amount of thallium(III) was varied to determine the loading capacity of 2-OAP. The loading capacity of 10 ml 0.025 M 2-OAP was found to be 3 mg of thallium(III).

Effect of aqueous to organic volume ratio

Thallium(III) was extracted from 10 to 250 ml of 0.0075 M aqueous sodium succinate medium with 10 ml 0.025 M 2-OAP in chloroform. Thallium(III) was stripped with acetate buffer and estimated as in the recommended procedure. It was found that the extraction of thallium(III) was quantitative when the aqueous to organic volume ratio was 2 to 15, while it decreased when the ratio was in the range 20–25. Hence, the recommended aqueous to organic volume ratio in the procedure is 2.5, in order to minimize the consumption of sodium succinate.

Effect of stripping agents

Stripping of the metal loaded organic phase containing thallium(III) was attempted with hydrochloric acid, nitric acid, sulphuric acid, perchloric acid, acetic acid, ammonia, acetate buffer, ammonia buffer and water as various stripping agents (3×15 ml). The results are shown in Table III. It is clear that of all the examined solutions, only perchloric acid (7–10 M) and acetate buffer (pH 4.63) were effective in stripping thallium(III) from the organic layer. However, acetate buffer (pH 4.63) is recommended because removal of the acetate buffer by evaporation is easier than the removal of perchloric acid and causes less pollution.

TABLE III. Extraction behaviour of thallium(III) as a function of the employed strippant; *m*(Tl(III)) = 1.0 mg, pH 3.0, 10 ml of 0.025 M solution of 2-OAP in chloroform, aqueous:organic ratio = 2.5:1, equilibrium time = 2 min

c mol dm^{-3}	HCl recovery, %	HNO_3 recovery, %	H_2SO_4 recovery, %	$HClO_4$ recovery, %	CH_3COOH recovery, %	NH_3 recovery, %
0.1	18.0	0.0	20.0	18.0	10.63	0.0
0.5	18.0	0.0	34.0	24.0	10.63	0.0
1.0	18.0	24.0	10.0	54.0	10.63	2.12
2.0	22.0	24.0	40.0	54.0	12.76	10.63
3.0	42.0	28.0	42.0	54.0	19.14	10.63
4.0	66.0	42.0	42.0	62.0	19.14	10.63
5.0	84.0	68.0	42.0	70.0	21.27	10.63
6.0	90.0	70.0	52.0	76.0	21.27	10.63
7.0	46.0	70.0	60.0	100.0	21.27	0.0
8.0	42.0	74.0	64.0	100.0	23.40	0.0
9.0	36.0	74.0	68.0	100.0	23.40	0.0
10.0	24.0	74.0	74.0	100.0	27.65	0.0

TABLE IIIA. Recoveries for various stripping agents

Strippant	Recovery, %
Acetate buffer (pH 4.63)	100.0[a]
Ammonia buffer (pH 10.0)	69.79
Water	0.0

[a] Recommended for the general extraction procedure

Effect of temperature on the extraction of thallium(III)

The results of the extraction of thallium(III) from a pH 7.0 succinate solution by 0.025 M 2-OAP in chloroform at temperatures varying from 298 to 310 K are given in Table IV. It was found that the distribution ratio increased with increasing temperature in the extraction of thallium(III) by 2-OAP in chloroform.

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

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

TABLE IV. Effect of temperature on the extraction of thallium(III) with 2-OAP in chloroform; *m*(Tl(III)) = 1.0 mg, pH 3.0, 10 ml of 0.025 M solution of 2-OAP in chloroform, aqueous:organic ratio = 2.5:1, equilibrium time = 2 min, strippant = acetate buffer pH 4.63 (3×15 ml)

T / K	Log D	Log K_{ex}	ΔG / kJ mol^{-1}	ΔS / J K mol^{-1}	ΔH / kJ mol^{-1}
298	0.77	4.64	–26.51	329.28	–
301	0.86	4.73	–27.04	327.75	–
304	1.02	4.9	–27.96	327.53	71.61
307	1.15	5.03	–28.71	326.77	–
310	1.23	5.10	–29.15	325.04	–

The plot of log K_{ex} *vs.* 1000/T is linear with a slope of –3.74 (Fig. 4) and the enthalpy change of the extraction performed at constant pH 7.0 was evaluated as ΔH = 71.61 kJ mol^{-1}, which means it is an endothermic process. The free energy ΔG and entropy ΔS were calculated from Eqs. (2) and (3):

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

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

The negative values of free energies imply that the reaction is spontaneous. The positive enthalpy value indicates that the extraction of thallium(III) with 2-OAP in chloroform is favoured by increasing temperature.

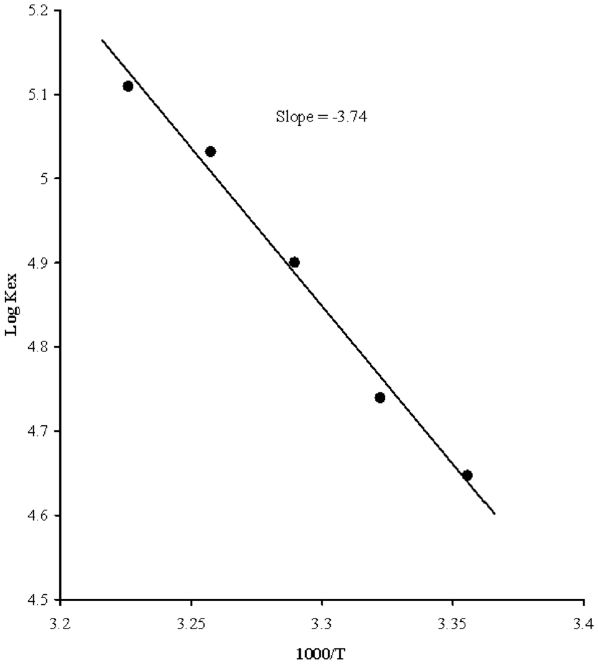

Fig. 4. Extraction behaviour of thallium(III) as a function of temperature.

Effect of diverse ions

The effect of various foreign ions commonly associated with thallium(III) was studied by the recommended procedure. The tolerance limits for the test ions are given in Table V. When the interference was found to be intensive, the tests were repeated with successively smaller amounts of foreign ion until a concentration giving an error less than ±2 % in the recovery of thallium(III) was attained. It was observed that the method is free from interference from a large number of transition and non-transition metal ions and anions. The interference due to Al(III) and Te(IV), Ga(III) and Fe(III) was eliminated by masking each metal ion with 1.0 mg citrate, 1.0 mg fluoride and 1.0 mg oxalate, respectively. Vanadium(V) and Sn(IV) interfered in the extraction procedure of thallium(III).

TABLE V. Effect of foreign ions on extraction behaviour of thallium(III); *m*(Tl(III)) = 1.0 mg, pH 3.0, 10 ml of 0.025 M solution of 2-OAP in chloroform, aqueous:organic ratio = 2.5:1, equilibrium time = 2 min

Ions	Added as	Tolerance limit, mg	Ions	Added as	Tolerance limit, mg
Acetate	Sodium acetate	100.0	Mn(VII)	$KMnO_4$	5.0
Nitrate	Sodium nitrate	100.0	Mo(VI)	$(NH_4)_6Mo_7O_{24}\cdot 6H_2O$	2.0
Nitrite	Sodium nitrite	100.0	Sr(II)[a]	$Sr(NO_3)_2$	2.0
Salicylate	Sodium salicylate	100.0	Ni(II)	$NiCl_2\cdot 6H_2O$	1.0
Bromide	Potassium bromide	25.0	Cr(VI)	$K_2Cr_2O_7$	1.0
Phosphate	Disodium hydrogen orthophosphate	25.0	Sn(II)	$SnCl_2$	1.0
			Tl(I)	$TlNO_3$	1.0
			Co(II)	$CoCl_2\cdot 2H_2O$	1.0
Malonate	Sodium malonate	2.0	Ba(II)	$BaCl_2\cdot 2H_2O$	1.0
Tartarate	Tartaric acid	2.0	Se(IV)	SeO_2	1.0
Fluoride	Sodium fluoride	2.0	Mg(II)	$MgCl_2\cdot 6H_2O$	1.0
Citrate	Citric acid	2.0	Bi(III)	$Bi(NO_3)_3\cdot 5H_2O$	1.0
Oxalate	Oxalic acid	2.0	Te(IV)[b]	Tellurium metal	1.0
Iodide	Potassium iodide	2.0	Cr(III)	$CrCl_3$	1.0
Cd(II)	$Cd(NO_3)_2\cdot 4H_2O$	25.0	W(VI)	$Na_2WO_4\cdot 2H_2O$	1.0
Mn(II)	$MnCl_2\cdot 6H_2O$	25.0	Fe(II)	$FeSO_4\cdot 7H_2O$	1.0
Zn(II)	$ZnSO_4\cdot 7H_2O$	25.0	In(III)	$InCl_3\cdot 4H_2O$	1.0
Hg(II)	$HgCl_2$	10.0	Ga(III)[a]	$GaCl_3$	1.0
Pb(II)	$Pb(NO_3)_2$	10.0	Al(III)[b]	$AlCl_3\cdot 6H_2O$	1.0
Ca(II)	$CaCl_2$	5.0	Fe(III)[c]	$NH_4\ Fe(SO_4)_2\cdot 12H_2O$	1.0
Cu(II)	$CuSO_4\cdot 5H_2O$	5.0	Sb(III)	Sb_2O_3	0.5
			V(V)	V_2O_5	0.0
			Sn(IV)	$SnCl_4$	0.0

[a]Masked by 1 mg fluoride; [b]masked by 1 mg citrate; [c]masked by 1 mg oxalate

APPLICATIONS

Separation and determination of thallium(III) from binary mixture

The suitability of the developed method was examined by applying it to the separation and determination of thallium(III) in a variety of binary mixtures containing commonly associated elements (Table VI).

TABLE VI. Binary separation of thallium(III) from associated elements

Metal ions	Amount taken, mg	Recovery[a] of Tl(III), %	Metal ion remained[a] in the aqueous phase or stripped from the organic phase, %	Separation factor (α)	Estimation procedure for the metal ion in the aqueous phase
Tl(III)	1.0	99.95 Tl(III)	–	∞	–
Zn(II)	1.0	–	100.0 Zn(II)	–	EDTA[35]
Tl(III)	1.0	99.97 Tl(III)	–	3.14×10^5	–
Cd(II)	1.0	–	98.95 Cd(II)	–	EDTA[35]
Tl(III)	1.0	99.61 Tl(III)	–	0.31×10^5	–
Hg(II)	1.0	–	99.2 Hg(II)	–	EDTA[35]
Tl(III)	1.0	98.97 Tl(III)	–	0.10×10^5	–
Pb(II)	1.0	–	99.1 Pb(II)	–	EDTA[35]
Tl(III)	1.0	99.95 Tl(III)	–	3.20×10^5	–
Bi(III)[b]	1.0	–	99.38 Bi(III)	–	EDTA[35]
Tl(III)	1.0	99.0 Tl(III)	–	1.09×10^5	–
Ga(III)[c]	0.5	–	99.91 Ga(III)	–	EDTA[34]
Tl(III)	1.0	98.97 Tl(III)	–	0.10×10^5	–
Al(III)[d]	1.0	–	99.05 Al(III)	–	EDTA[35]
Tl(III)	1.0	99.95 Tl(III)	–	3.36×10^5	–
In(III)[e]	1.0	–	99.41 In(III)	–	EDTA[34]
Tl(III)	1.0	99.47 Tl(III)	–	1.87×10^5	–
Tl(I)[f]	1.0	–	99.9 Tl(I)	–	EDTA[34]
Tl(III)	1.0	99.07 Tl(III)	–	0.10×10^5	–
Se(IV)	1.0	–	99.0 Se(IV)	–	Selenium sol[38]
Tl(III)	1.0	99.43 Tl(III)	–	0.30×10^5	–
Sb(III)	1.0	–	99.43 Sb(III)	–	Potassium iodide[38]
Tl(III)	1.0	99.66 Tl(III)	–	0.85×10^5	–
Te(IV)[d]	0.5	–	99.66 Te(IV)	–	Tellurium sol[38]
Tl(III)	1.0	99.13 Tl(III)	–	0.12×10^5	–
Fe(III)[g]	0.5	–	99.13 Fe(III)	–	Thiocyanate[38]

[a]Average of five determinations; [b]stripped from organic phase with 3×10 ml 0.5 M nitric acid; [c]masked by 1 mg fluoride; [d]masked by 1 mg citrate; [e]Separation at pH 2.0, [f]separation at pH 6.0; [g]masked by 1 mg oxalate

Separation of thallium(III) from Zn(II), Pb(II), Cd(II), Hg(II), Se(IV), Sb(III)

It was found that Zn(II), Pb(II), Cd(II), Hg(II), Se(IV) and Sb(III) remained unextracted under the acidic conditions employed for the extraction of thallium(III) from a 0.0075 M sodium succinate solution by 0.025 M 2-OAP in chloroform. The pregnant organic phase was stripped with acetate buffer (3×15 ml) and thallium(III) was determined by the recommended procedure. The raffinate containing added metal ions was estimated by the standard procedure.[35,38]

Separation of thallium(III) from Ga(III), Al(III), Te(IV) and Fe(III)

The proposed method was extended for the separation of thallium(III) from Ga(III) by masking with 1 mg fluoride, from Al(III) and Te(IV) by masking with 1 mg citrate and from iron(III) by masking with 1 mg oxalate. The masked metal ions remained in the aqueous phase while thallium(III) was selectively extracted from a 0.0075 M sodium succinate solution into the organic phase with 0.025 M 2-OAP in chloroform at pH 3.0. Thallium was stripped from the organic phase with acetate buffer and estimated as per the recommended procedure. The aqueous phases containing the added metal ions was demasked with 2 ml concentrated hydrochloric acid and, after reducing the volume of the aqueous phase, estimated by standard procedures.[34,38]

Separation of thallium(III) from Bi(III)

The separation of thallium(III) from Bi(III) was based on the use of different stripping agents. Bismuth(III) was co-extracted with 0.025 M 2-OAP in chloroform from a 0.0075 M sodium succinate media at pH 3.0. It was found that there was a quantitative recovery of bismuth(III) with 0.5 M nitric acid while thallium(III) remained quantitatively in the organic phase. The thallium(III) was stripped from organic phase by contacting the organic phase with 3×15 ml acetate buffer (pH 4.63). The stripped phases containing thallium(III) and Bi(III) were evaporated to moist dryness and the residues were dissolved in distilled water with heating. Thallium(III) and Bi(III) were estimated by the standard procedure.[34]

Separation of thallium(III) from In(III) and Tl(I)

The separation of thallium(III) from In(III) was based on the use of different pH values. Thallium(III) was extracted quantitatively with 2-OAP (0.025 M) in chloroform at pH 2.0 from 0.0075 M sodium succinate media. It was found that there was zero extraction of In(III) at pH 2.0. Hence, thallium(III) can be extracted quantitatively with In(III) remaining quantitatively in the aqueous phase. Thallium(III) was then estimated after its re-extraction in the aqueous phase, while In(III) was estimated by a complexometric method.[34]

Separation of Tl(I) from Tl(III)

It was found that 10 ml 0.025 M 2-OAP in chloroform transferred about 15 % of Tl(I) into the organic phase from an aqueous 0.0075 M sodium succinate of pH 3.0. However, there was no extraction of Tl(I) at pH 6.0. Hence the extraction of thallium(III) was performed at pH 6.0, at which pH value only thallium(III) is extracted into organic phase, whereas Tl(I) remains in the aqueous phase. The extracted thallium(III) was stripped from the organic phase with acetate buffer and estimated by the recommended method, while Tl(I) from the aqueous phase was estimated by the EDTA method[34] after converting of Tl(I) to Tl(III) with a dilute solution of bromine water.

Analysis of synthetic mixtures

The proposed method was applied to the extraction and determination of thallium(III) from 0.0075 M sodium succinate from various synthetic mixtures. The results are given in Table VII.

TABLE VII. Analysis of synthetic mixtures

Composition of synthetic mixture, mg	Amount of thallium(III) found, mg	Recovery[a], %	R. S. D., %
Tl(III), 1.0 Zn(II), 1.0 Cd(II), 1.0	0.995 0.995 0.994 0.997 0.992	99.4	0.6
Tl(III), 1.0 Ga(III)[b], 1.0 In(III), 1.0	1.0 0.993 0.991 1.0 1.0	99.6	0.4
Tl(III), 1.0 Zn(II), 1.0 Fe(III)[c], 1.0	1.0 0.995 0.990 0.980 0.997	99.2	0.8
Tl(III), 1.0 Pb(II), 1.0 In(III), 1.0	0.994 0.989 0.996 0.998 0.997	99.4	0.6
Tl(III), 1.0 Pb(II), 1.0 Hg(II), 1.0 Sb(III), 1.0	1.0 0.996 0.995 1.0 1.0	99.8	0.2

[a]Average of five determinations; [b]masked by 1 mg fluoride; [c]masked by 1 mg oxalate

Analysis of alloys

Since standard alloy samples containing thallium(III) were not available at this working place, a non-ferrous alloy (brass) and a type metal alloy (the Bureau of Analyzed Samples Ltd., UK) to which a known amount of thallium(III) was added. Thallium(III) was recorded from the succinate media by the proposed method (Table VIII). The procedure is given below.

A known weight (0.100 g) of alloy was dissolved in a mixture of 10 ml concentrated nitric acid and 50 ml of distilled water. After the initial reaction was over, the solution was heated with 5 ml portion of 1:1 nitric acid, boiled to dissolve the soluble matter and filtered to remove the silica or metastannic acid. The filtrate was diluted to 100 ml with distilled water. An aliquot of 1.0 ml of filtrate was taken; to this solution 1.0 ml of 1.0 mg ml^{-1} thallium(III) was added and the general procedure for the extraction and determination of thallium(III) was followed.

TABLE VIII. Analysis of alloys

Alloy sample	Composition, %	Thallium(III) taken, mg	Recovery[a], %	R.S.D., %
Non ferrous alloy (Brass)	Pb 2.0 Cu 65.0 Zn 30.0 Sn 1.0	1.0	99.5	0.5
Type metal alloy	Pb 80.0 Sn 17.0 Sb 3.0	1.0	99.2	0.8

[a]Average of five determinations

CONCLUSIONS

The method described herein brings forth the potential of 2-OAP for the separation and recovery of thallium(III). The quantitative extraction of the metal ion can be achieved at pH 3.0 from 0.0075 M sodium succinate using 0.025 M 2-OAP. The extraction proceeds *via* ion pair formation. The partition of thallium(III) in the organic phase is selective in the presence of a number of commonly associated elements. The selectivity of the method can be increased by the use of suitable masking agents and different pH values. The extractant possess a reasonable loading capacity. A very low reagent concentration (0.025 M) is required for the quantitative recovery of thallium(III). The time required for the extraction separation is very short (30 s). It is very simple, selective, reproducible and rapid and can be applied for the analysis of thallium(III) from synthetic mixtures and alloy samples.

Acknowledgements. The financial support to the work by the University Grants Commission (UGC), New Delhi, is gratefully acknowledged. One of the author (SVM) is thankful to the UGC for the award of a fellowship.

ИЗВОД

БРЗА ЕКСТРАКЦИЈА ТЕЧНО–ТЕЧНО ТАЛИЈУМА(III) ИЗ СУКЦИНАТНИХ РАСТВОРА ПОМОЋУ ЕКСТРАКТАНТА 2-ОКТИЛАМИНОПИРИДИНА У ХЛРОФОРМУ

SANDIP V. MAHAMUNI, PRAKASH P. WADGAONKAR[1] и MANSING A. ANUSE

Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur – 416 004 и
[1]Polymer Science and Engineering Division, National Chemical Laboratory,
Dr. Homi Bhabha Road, Pune – 411 008, India

Изведено је једноставно испитивање екстракције из раствора талијума(III). Селективна и квантитативна екстракција талијума(III) изведена је помоћу 2-октиламинопиридина (2-OAP) у хлороформу из воденог раствора натријум-сукцината (0,0075 M) при pH 3,0. Талијум(III) је повратно екстрахован помоћу ацетатног пуфера (pH 4,63). Испитивани су ефекат концентрације сукцината и 2-OAP, улога разних разблаживача, стрипинг агенаса, ефикасност 2-OAP, равнотежно време и однос запремина водене и органске фазе на екстракцију талијума(III). Стехиометрија екстрахованих врста, одређена на основу методе анализе нагиба, износила је

1:2:1 (метал:киселина:екстрактант). Такође је испитивана и температурна зависност константе равноже екстракције да би се процениле термодинамичке функције ΔH, ΔG и ΔS за процес екстракције. Тачност методе не зависи од присуства разних катјона и анјона. Метода је коришћена за селектривну екстракцију талијума(III) из бинарних смеша са Zn(II), Cd(II), Hg(II), Bi(III), Pb(II), Se(IV), Te(IV), Sb(III), Ga(III), In(III), Al(III), Tl(I) и Fe(III). Предложена метода је примењена на синтетичке смеше и легуре. Метода је једноставна, селективна, брза и чиста.

(Примљено 28. маја 2007)

REFERENCES

1. E. Marian, *Metals and Their Compounds in the Environment*, VCH, Wenham, 1991
2. M. J. Sienko, R. A. Plane, *Chemical Principles*, McGraw – Hill, London, 1974
3. P. N. Gabby, *U. S. Geological Survey,* Mineral Commodity summaries, Reston, VA, 2006, p. 172
4. J. E. Fergusson, *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*, Pergamon Press, Oxford, 1990
5. I. C. Smith, B. L. Carson, *Trace Metals in the Environment, Thallium*, Ann Arbor Science Publishers, Michigan, 1977
6. X. Zhang, G. Yin, Z. Hu, *Talanta* **59** (2003) 905
7. B. Y. Mishra, M. D. Rokade, P. M. Dhadke, *Chem. Environ. Res.* **10** (2001) 27
8. S. D. Pawar, P. M. Dhadke, *J. Serb. Chem. Soc.* **68** (2003) 581
9. J. N. Iyer, P. M. Dhadke, *Sep. Sci. Tech.* **36** (2001) 2773
10. T. Sato, K. Sato, Y. Noguchi, I. Ishikawa, *Shigen to Sozai* **113** (1997) 185
11. X.–Z. Liu, D.–W. Fang, J. Li, J.–Z. Yang, S.–L. Zang, *J. Phase Equilib. Diffusion* **26** (2005) 342
12. X.–Z. Liu, D.–W. Fang, Y.–H. Kang, J. Li, S.–L. Zang, *Chin. J. Chem.* **23** (2005) 567
13. S. M. Khopkar, C. Malkhede, *Indian J. Chem.* **42A** (2003) 2945
14. A. R. Ghiasvand, F. Moradi, S. Shadabi, H. Sharghi, A. R. Hasaninejad, *Asian J. Chem.* **18** (2006) 2016
15. P. N. Bongroo, R. C. Saxena, H. C. Arora, *Indian J. Chem.* **38A** (1999) 89
16. Y. S. Kim, Y. S. Choi, W. Loo, *Bull. Korean Chem. Soc.* **23** (2002) 1381
17. S. V. Vartak, V. M. Shinde, *Talanta* **45** (1998) 925
18. K. Watanabe, H. Isomura, M. Itagaki, *Bunseki Kagaku* **49** (2000) 691
19. J. Narbutt, J. Krejzler, *Radiochim. Acta* **9**–**10** (2005) 627
20. D. Zendelovska, T. Stifilov, *Anal. Sci.* **17** (2001) 425
21. J. Gao, Q. Deng, B. Peng, X. Guo, *Rare Metals* **22** (2003) 86
22. T. M. Trtić-Petrović, G. T. Vladisavljević, S. C. Archimandritis, A. Varvarigou, J. J. Comor, *J. Sep. Sci.* **24** (2001) 519
23. T. M. Trtić, G. T. Vladisavljević, J. J. Comor, *Sep. Sci. Technol.* **36** (2001) 295
24. T. M. Trtić, G. T. Vladisavljević, J. J. Comor, *Sep. Sci. Technol.* **35** (2000) 1587
25. T. M. Trtić, G. T. Vladisavljević, M. Tesić, K. Kumrić, J. J. Comor, *Desalination* **148** (2002) 241
26. Y. Nagaosa, K. Horita, *Microchim. Acta* **108** (1992) 151
27. N. H. Chung, J. Nishimoto, O. Kato, M. Tabata, *Anal. Chim. Acta* **477** (2003) 234
28. K. Yamamoto, M. Endo, *Anal. Sci.* **12** (1996) 739
29. I. Nukatsuka, H. Seitoh, K. Ohzeki, *Microchim. Acta* **148** (2004) 177
30. M. A. Taher, *Bull. Kor. Chem. Soc.* **24** (2003) 1177

31. P. K. Saha, U. S. Roy, *J. Indian Chem. Soc*. **75** (1998) 330
32. N. Rajesh, M. S. Subramanian, *J. Hazardous Mater.* **135** (2006) 74
33. T. N. Shilimkar, M. A. Anuse, *Ann. de Chim.* **92** (2004) 717
34. F. J. Welcher, *The Analytical Uses of Ethylenediamine Tetraacetic Acid*, D. Van Nostrand Company Inc., New York, London, 1958, p.p. 176, 178, 182
35. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, ELBS, London, 1961, p.p. 442, 444
36. N. A. Borshch, O. M. Petrukhin, *Zh. Anal. Khim.* **33** (1978) 1805
37. Y. Marcus, A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, New York, 1969
38. Z. Marckzenko, *Spectrophotometric Determination of Elements*, Ellis Horwood Ltd., Chichester, 1976, p.p. 125, 307, 475, 522, 549.