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Research Article

EXTRACTION CHROMATOGRAPHIC STUDIES OF THALLIUM(III) WITH N-n-OCTYLANILINE

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Abstract

A selective method has been developed for extraction, chromatographic separation of thallium(III) with N-n-octylaniline (a liquid anion exchanger) as a stationary phase on silica gel. Quantitative extraction of thallium(III) has been achieved in 1.0 mol L^{-1} hydrochloric acid media from 0.0315 mol L^{-1} (0.7%) N-n-octylaniline. The extracted metal has been eluted with 25.0 ml distilled water and estimated spectrophotometrically. The effects of acid concentrations, reagent concentration and diverse ions have been studied. Thallium(III) has been separated from its associated elements and synthetic mixtures corresponding. The probable extracted species were ascertained from log C - log D plots.

Keywords: Extraction chromatography, N-n-Octylaniline, Thallium(III)

Introduction

Thallium has low abundance in the earth's crust, but wide uses. A low melting glass of thallium, sulpher, arsenic and selenium is used as an encapsulating material for semiconductors, capacitors and other electrical devices. Due to various applications of thallium it is necessary to develop a selective separation method from associated metals. Liquid anion exchangers have been used for solvent extraction of many metals[1,2] Thallium(III) has been extracted with 2-propanol/water phase using sodium chloride[3]. Extraction separation of thallium(III) from thallium(I) has been reported by using n-Octylaniline from salicylate medium[4]. N-octylaniline has been also used extensively for the solvent extraction, separation of various elements[5-10]. N-n-Octylaniline has been used for reversed phase paper chromatographic separation of zinc, cadmium and mercury[11]. Recently N-n-octylaniline was applied for extraction chromatographic separation of platinum[12], palladium[13], ruthenium[14], iridium[15], gold[16], copper[17], molybdenum[18], manganese[19] and lead(II)[20]. In the present communication, reversed phase extraction behavior of thallium (III) towards N-n-octylaniline as a function of hydrochloric acid has been studied. A simple, rapid method for separation of thallium (III) from its associated elements has been proposed.

Experimental

Instrumentation

Elico make (model SL-191) double beam UV-visible spectrophotometer with matching 10 mm quartz cells was used for absorbance measurements. An electronic balance (Contech make, model CA-123) was used for

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weighing purposes. Calibrated glassware were used and are cleaned by soaking in dilute nitric acid followed by washing with soap and rinsed two times with water.

Reagents

All the reagents used were of analytical reagent grade unless otherwise stated. A standard stock solution of thallium (III) has been prepared by dissolving 2.0 gm of thallous nitrate ($TlNO_3$ dried at 110°c) into distilled water containing 2.0 mL of concentrated nitric acid and diluted this solution to 250 mL with distilled water. Thallium (I) was oxidized to thallium (III) by adding few drops of saturated bromine water and warming to remove excess bromine. The solution was standardized by complexometrically[21]. A working standard solution of thallium (III) 100 µg mL^{-1} was prepared by diluting the standard stock solution with distilled water. Other standard solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving their respective salts in water or dilute hydrochloric acid and diluted suitably. The N-n-octylaniline was prepared using the method reported by Gardlund[22]. Chloroform is used for further dilutions of N-n-octylaniline. Double distilled water was used throughout the work.

Recommended procedure

In a 25 mL volumetric flask, an aliquot of 100 µg Tl (III) was taken and sufficient amount of hydrochloric acid was added to make solution 1.0 mol L^{-1} after dilution with water to the mark. The solution was passed through 0.7% (V/V) N-n-octylaniline coated silica gel (pre-saturated with 1.0 mol L^{-1} hydrochloric acid) column at a rate of 1.0 mL min^{-1}. The Tl(III) found completely extracted on the column. The Tl (III) was eluted by 40 mL of distilled water. Collected fraction was analyzed for Tl(III) spectrophotometrically by iodide-starch method[23].

Results and discussion

Effect of hydrochloric acid concentration on extraction of Tl(III)

Thallium(III) 100 µg in final volume 25 mL of 0.01 to 4.0 mol L^{-1} hydrochloric acid media was studied for effect of acid concentration on extraction of Tl(III) as per the recommended procedure. It was observed that the extraction of thallium(III) increases with increase in concentration of hydrochloric acid. It was found that there is quantitative extraction at 1.0 mol L^{-1} hydrochloric acid. Hence all the extractions were carried out at the concentration 1.0 mol L^{-1} of hydrochloric acid (Figure 1).

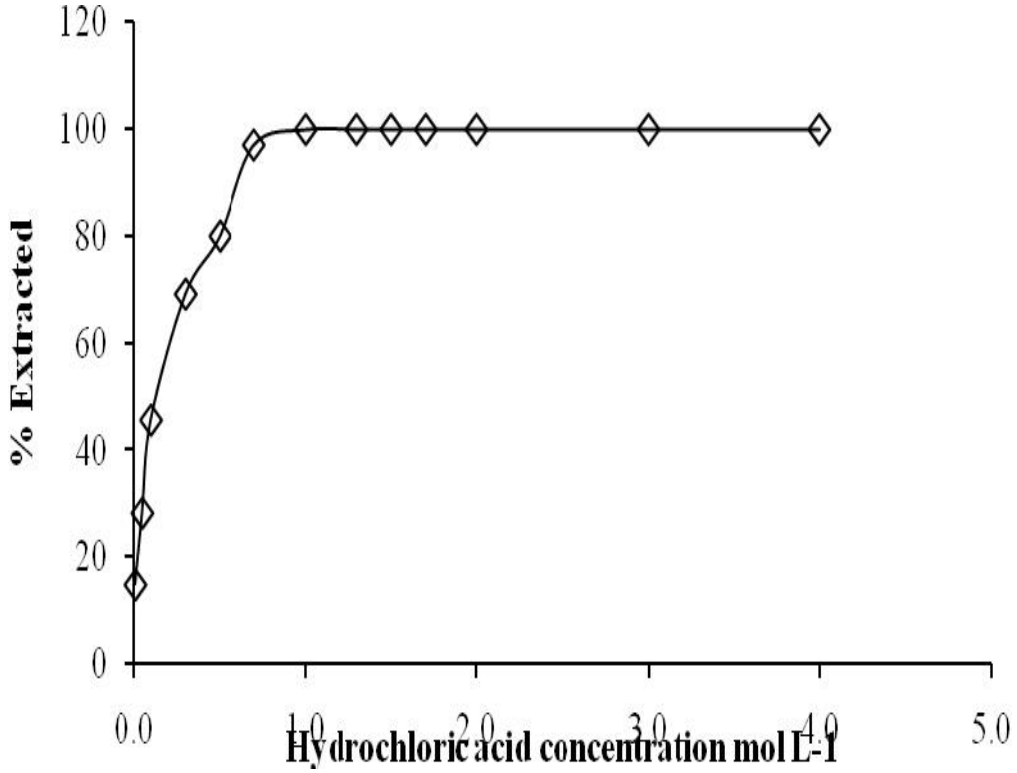

Figure 1. Effect of hydrochloric acid concentration on extraction of Tl(III).

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Effect of N-n-octylaniline concentration

The concentration of N-n-octylaniline on a silica support was varied from 0.1% (v/v) to 1.0% (v/v). It was observed that 0.7% (v/v) N-n-octylaniline was sufficient for quantitative extraction of Tl(III) from 1.0 mol L^{-1} hydrochloric acid media. There is an increase in the extraction of Tl(III) with increasing concentration of N-n-octylaniline. The plot of log D Vs log C for 0.1 and 0.5 mol L^{-1} hydrochloric acid gave a slope of 1.17 and 1.09 respectively (Figure 2). The probable composition of extracting species was calculated as 1:1 (metal to amine ratio).

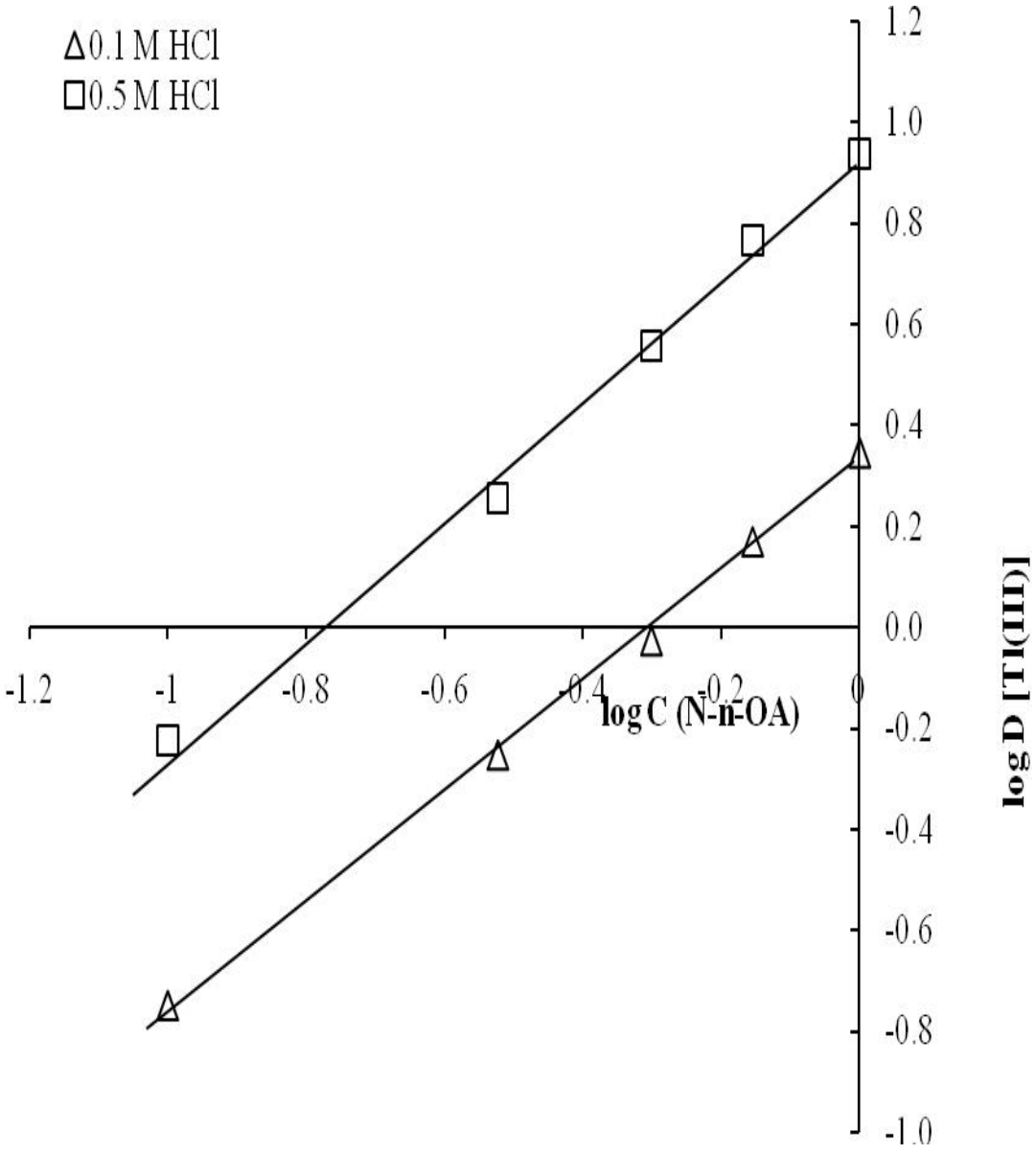

Figure 2. Plot of log $C_{(N\text{-}n\text{-}OA)}$ vs. log $D_{[Tl(III)]}$: Tl(III): 100.0 µg; N-n-OA: 0.1% to 1%; HCl concentration: 0.1 mol L^{-1}, 0.5 mol L^{-1}, λ_{max}: 590 nm.

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Extraction mechanism

$[RR'NH]_{org.} + [H^+]_{aq.} \rightleftharpoons [RR'NH_2^+]_{org.}$

$[Tl^{3+}]_{aq} + [Cl^-]_{aq.} \rightleftharpoons [TlCl_4^-]_{aq}$

$[RR'NH_2^+]_{org} + [TlCl_4^-]_{aq} \rightleftharpoons [RR'NH_2^+ .TlCl_4^-]_{org}$

Where R= $-C_6H_5$ R'= $-CH_2(CH_2)_6CH_3$

Effect of foreign ions

Various amounts of foreign ions were added to a fixed amount of thallium(III) to investigate the interference of these ions and to find their tolerance limit in the extraction of Tl(III). Thallium(III), 100 µg, was extracted in the presence of a large number of foreign ions. An error of ± 2% in the absorbance values was considered to be tolerable. It was observed that the proposed method is free from interference of the large number of alkaline earth metals, toxic metals, transition metals and anions (Table 1).

Table 1. Effect of foreign ions

Foreign Ions	Added as	Tolerance limit µg	Foreign Ions	Added as	Tolerance limit µg
Mn(II)	$MnCl_2.6H_2O$	100	W(VI)	$Na_2WO_4.2H_2O$	50
Cd(II)	$CdCl_2.2H_2O$	150	Pb(II)	$PbCl_2$	150
Fe(III)	$(NH_4)Fe(SO_4)_2.12H_2O$	50	Zn(II)	$ZnSO_4.7H_2O$	50
Hg(II)	$HgCl_2$	75	Ti(IV)	TiO_2	200
Bi(III)	$BiCl_3$	75	Mg(II)	$MgCl_2.6H_2O$	100
Ni(II)	$NiCl_2.6H_2O$	50	Fluoride	NaF	500
Al(III)	$AlCl_3.6H_2O$	50	Sulphate	K_2SO_4	500
Fe(II)	$FeSO_4.7H_2O$	25	Citrate	$C_6H_8O_7.H_2O$	500
Sn(II)	$SnCl_2.2H_2O$	50	Malonate	$CH_2(COONa)_2$	500
Mo(VI)	$(NH_4)_6MO_7O_{24}.2H_2O$	100	Acetate	$CH_3COONa.3H_2O$	500
V(V)	V_2O_5	100	Oxalate	$Na_2C_2O_4.2H_2O$	200
U(VI)	$UO_2(CH_3COO)_2.2H_2O$	50	E.D.T.A	Na_2EDTA	500
Co(II)	$CoCl_2.6H_2O$	200	H_2O_2	H_2O_2	0.3 mL

Applications

Separation of thallium(III) from multi-component mixtures

The proposed method was successfully applied for extraction of thallium(III) from multi-component mixtures. The study shows that the separation of thallium (III) is possible in the presence of mercury(II), manganese(II), zinc(II), tin(II), cadmium(II) and aluminum(III) using the proposed method (Table 2).

Table 2. Separation of thallium(III) from multi-component mixtures

Composition µg	Thallium(III) found µg	% RSD
Tl(III) 100; Mn(II) 50; Cd(II) 100; Hg(II) 50	98.36	0.53
Tl(III) 100; Mn(II) 50; Cd(II) 100; Hg(II) 50; Al(III) 25	97.95	0.31
Tl(III) 100; Al(III) 25; Sn(II) 50	99.59	0.58
Tl(III) 100; Cd(II) 100; Hg(II) 50; Zn(II) 50	99.18	0.76
Tl(III) 100; Cd(II) 100; Sn(II) 50; Al(III) 25	98.36	0.93
Tl(III) 100; Cd(II) 100; Sn(II) 50; Al(III) 25; Mn(II) 50	98.77	0.89

Conclusion

The proposed method is simple, selective, reproducible and rapid. It is free from interferences from a large number of foreign ions which are associated with thallium(III). Low N-n-octylaniline and hydrochloric acid concentrations required for quantitative extraction of thallium(III) using the proposed method. It is successfully applied for separation of thallium(III) from multi-component mixtures.

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References

[1] Prabhu, A. R. & Khopkar, S. M. (1971). J Sci. Ind. Res. 30: 16.
[2] Starry, J. (1964) The Solvent Extractions of Metal Chelates (Pergamon Press, Oxford).
[3] Chung, N. H., Nishimoto, J., Kato, O. & Tabata, M. (2003) Selective extraction of thallium(III) in presence of gallium(III), indium(III), bismuth(III) and antimony(III) by salting-out of aqueous mixture of 2-propanol. Analytica Chimica Acta, 477(2): 243-249.
[4] Shilimakar, T. N., Anuse, M. A. & Patil, K. J. (2002) Extraction separation of thallium(III) from thallium(I) with n-octylaniline. Ann. Chim., 92(7-8): 717-728.
[5] Kuchekar, S. R. & Chavan, M. B., (1988) Separation of Gallium, Indium and Thallium by extraction with n- Octylaniline in Chloroform Talanta, 35(5): 357-360.
[6] Kuchekar, S. R., Aher, H. R. & Chavan, M. B., (2003) Solvent Extraction of Zinc (II), Cadmium (II), Mercury (II) and Bismuth(III) from n-Octylaniline and their separation, Indian J. Chem. 42A: 1674-1676.
[7] Aher, H. R., Gunjal, P. S., Kuchekar, S. R. & Chavan, M. B. (1998) Solvent Extraction of Lead (II) and its separation from Bismuth (III). Asian J Chem,10(1): 43-45.
[8] Sawant, S. S., Anuse, M. A. & Chavan, M. B. (1996) Spectrophotometric estimation of rhenium with 5-chloro-2-hydroxythiobenzhydrazide after its extraction separation using *n*-octylaniline. Talanta, 43: 2137-2142.
[9] Gedye, R. N., Bozict, J. P., Durbano, P. M. & Wiliamson, B. (1989) The preparation of n-octylaniline and its application in the extraction of noble metals. Talanta, 36(10): 1055-1058.
[10] Haribhau R. Aher & Shashikant R. Kuchekar (2008) Extraction Chromatographic Studies of Gallium (III), Indium (III) and Thallium (III) with n-Octylaniline. Ind. J. Chem. Technol., 15: 403-408.
[11] Aher, H. R. & Kuchekar, S. R. (2004) Reversed Phase Extraction Chromatographic Studies of Zinc (II) Cadmium (II) and Mercury (II). Asian J. Chem. 16 (2): 695-698.
[12] Kokate, S. J. & Kuchekar, S. R. (2009) Extraction chromatographic separation of platinum(IV) from real samples and associated elements. Chin J Chromatogr. 27(6): 809-814.
[13] Kokate, S.J., Aher, H. R. & Kuchekar, S. R. (2009) Reversed phase extraction chromatographic separation of palladium(II) using liquid anion exchanger. Bulg. Chem. Comm. 41(3): 272-276.
[14] Kokate, S. J. & Kuchekar, S. R. (2010) Reversed phase extraction chromatographic separation of ruthenium(III). J. Saudi Chem. Soc.14: 41-45.
[15] Kokate, S. J., Aher, H. R. & Kuchekar, S. R. (2009) Reversed phase extraction chromatographic separation of trivalent iridium using liquid anion exchanger. Anal Chem. An Ind. J. 8(4): 575-579.
[16] Kokate, S. J., Aher, H. R. & Kuchekar, S. R. (2011) Separation of gold(III) from ayurvedic medicines and alloys by extraction chromatography. Bulg. Chem. Comm. 43(3): 406-410.
[17] Phule, S. R., Kokate, S. J. & Kuchekar, S. R. (2011) Reversed phase partion chromatographic separation of divalent copper with N-n-octylaniline on silica gel. J Saudi Chem. Soc. 15(3): 209-213.
[18] Kokate, S. J., Gavande, A. A., Vikhe, V. K., Aher, H. R. & Kuchekar, S. R. (2010) Extraction chromatographic separation of molybdenum(VI) with high molecular weight liquid anion exchanger. Ind. J. Chem. Technol. 17(2): 154-157.
[19] Phule, S. R., Shelar, Y. S. & Kuchekar, S. R. (2010) Extraction separation studies of divalent manganese using N-n-octylaniline as a liquid anion exchanger. Anal Chem. an Indian J. 9(2): 260-264.
[20] Shashikant R Kuchekar , Sachin R Phule, Bhaskar H Zaware & Sung H Han, (2014) Separation of divalent lead from ayurvedic (Herbal) medicine and alloys using extraction chromatography. Ind. J. of Chem. Technol. 21: 205-210.
[21] Welcher, F. J. (1961) The analytical uses of ethylene diamine tetra acetic acid, 1st Edn. Nan. Nostrand, Princeton.
[22] Gardlund, Z. G. Curtis, R. J. and Smith, G. W. (1973) Influence of molecular structural changes on the mesomorphic behavior of benzylideneanilines, Liquid Crystals Ordered Fluids Liq., Crystals Ordered Fluids 2: 541–545.

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[23] Marckzenco, Z. (1976) Spectrophotometric Determination of Trace Elements; Ellis Hardwood Ltd, John Wiley and Sons, Chichester, 533.

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