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Spectrophotometric Determination of Lanthanum(III) with *O*-Methoxy Phenylthiourea as a Chromogenic Ligand

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Abstract

A precise method was developed for extraction spectrophotometric determination of lanthanum(III) using *o*-methoxy phenylthiourea (OMePT) as a chromogenic ligand. The basis of the proposed method is lanthanum(III)-OMePT complex formation in 0.1 mol L^{-1} aqueous hydrochloric acid media with 2 mL of 0.01 mol L^{-1} OMePT in ethanol at room temperature. Lanthanum(III)-OMePT complex was extracted in 10 mL chloroform after single extraction it was measured at 320 nm against the reagent blank. Beer's law was obeyed up to 45.0 µg mL^{-1} for lanthanum. The Molar absorptivity and Sandell's sensitivity of the complex were 1.5002×10^3 $Lmol^{-1}$ cm^{-1} and 0.0926 µg cm^{-2} respectively. The stoichiometry of lanthanum(III)-OMePT complex was 1:1. The stability of lanthanum(III)-OMePT complex was >48 h. Proposed method was successfully applied for determination of lanthanum(III) from binary synthetic mixtures and real samples.

1. Introduction

Lanthanum is a silvery white metallic element found together with lanthanide elements in monazite and other minerals [1]. It is used in the motion picture industry for studio lighting and projection. Lanthanum improves the alkali resistance of glass and is highly useful in the manufacturing of expensive lenses for camera and telescope as it imparts high refractive index to the glass. It is highly useful as an electron dense tracer in molecular biology [2]. Mischmetal is an alloy of Lanthanum and it is used in lighter flints. Small amount of lanthanum was added to steel to improve its properties like malleability and ductility. Recently, cerium activated lanthanum bromide is used as scintillator for both high light yield and best energy resolution. The liquid-liquid extraction and ion exchange chromatographic methods are commonly used for the separation of lanthanides [3-5]. As per literature survey very few spectrophotometric methods were reported till now for the determination of lanthanides. The spectrophotometric methods using Eriochrome Black T [6] and Arsenazo-(III) [7] are less sensitive and suffer from interference by diverse ions. The determination of lanthanum is highly critical due to its technological applications in superconductors, super magnets, lasers and alloys [8]. High purity lanthanum is used in nuclear power production and in automobile and nuclear industries as a catalyst. The problems of genesis of ore deposits can be solved by the analysis of environmental samples, like monazite sand [9]. Lanthanum is present in monazite sands, for separation of lanthanides the monazite sand is treated with an alkali followed by acid digestion and extraction with tetra butyl phosphate.

However, the process is time consuming. A large number of reagents have been reported for the separation of lanthanum, however, several closely related ions interfere [10-14]. The techniques like atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) cannot be applied directly for the trace determination of lanthanum as they have high detection limits [15,16] and hence prior separation is mandatory [17, 18]. This leads us to develop a specific method to extract and determine lanthanum from samples of small volume of solution. The comparison of present method with reported methods [19-24] for spectrophotometric determination is reported in Table 1. Negar Rajabi has extracted lanthanum(III) with a solid-phase microextraction performed using Fe_3O_4 nanoparticle coated with the chitosan, with a linear response range of 0.008–0.1 ng L^{-1} with a detection limit of 0.008 ng L^{-1} was obtained [25]. In our laboratory we have developed extraction and spectrophotometric determination of rhodium(III) [26], ruthenium(III) [27], iridium(III) [28], selenium(IV) [29], and osmium(IV) [30], using *o*-methylphenyl thiourea (OMPT). In the extension of our work we have developed extraction spectrophotometric determination methods for cerium(IV), [31] palladium(II) [32], osmium(IV) and ruthenium(III) [33] with *o*-methoxyphenyl thiourea (OMePT). Current study reports the analytical applications of *o*-methoxyphenyl thiourea (OMePT) for spectrophotometric determination of lanthanum(III).

2. Experimental

2.1. Apparatus and Reagents

A double beam UV-visible spectrophotometer (Elico make model SL-191) with matched 10 mm quartz cells was used for absorbance measurements. Contech make electronic balance model CA-123 was used for weighing purpose. Calibrated glassware were used and cleaned by soaking in dilute nitric acid followed by washing with soap water and rinsed two times with distilled water.

O-Methoxy phenylthiourea (OMePT) was synthesized as per method reported by frank and smith [34]. The stock solution of OMePT, 0.1 mol L^{-1}, was prepared after dissolving 0.911 g OMePT in 20 mL ethanol and diluted to 50 mL in volumetric flask with ethanol. The working OMePT solution was prepared from the stock solution using ethanol as a solvent.

2.2. Metal Solutions

A standard stock solution of lanthanum(III) was prepared after dissolving 1.336 g Lanthanum chloride heptahydrate ($LaCl_3.7H_2O$) in double distilled water and was made up to mark in a 500 mL volumetric flask with distilled water. This stock solution was standardized using gravimetric method [35]. The working standard solution, 200 µg mL^{-1}, was prepared from standard stock solution. Standard solutions of different metal ions used for interference study were prepared after dissolving exactly weighed quantities of their respective salts in distilled water or dilute hydrochloric acid. Standard solutions of anions were prepared after dissolving their respective alkaline metal salts in distilled water. Different synthetic mixtures were prepared by combining their definite compositions.

2.3. Recommended procedure

In a 25 mL volumetric flask, an aliquot of solution containing 200 µg lanthanum(III) and 2 mL, 0.01 mol L^{-1} OMePT in ethanol was added. This solution was made 0.1 mol L^{-1} with respect to hydrochloric acid after dilution up to mark with distilled water. The lanthanum(III)-OMePT complex formed atroom temperature was extracted in 10 mL chloroform and was measured at 320 nm against the reagent blank.

Table 1: *Comparison of present method with other extraction spectrophotometric determination methods of Lanthanum(III)*

Reagents	λ_{max} (nm)	Condition	Beer's Law validity range (μg mL^{-1})	Solvent	Molar Absorptivity, (L mol^{-1} cm^{-1})	M : L	Remark	Ref
2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoichydrazone	390	pH 8.0	0.14 – 9.72	Aqueous	1.929×10^4	2 : 3	low beer's range, longer equilibration time	19.
N-phenylbenzo-18-crown-6 hydroxamic acid	385	pH 8.8	0.77 - 18	Dichloromethane	9.0×10^3	1 : 3	low beer's range	20.
Arsenazo-III	660	pH 3.3	NM	Aqueous	0.762×10^3	NM	Low stability of complex	21.
2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone	415	pH 3.5	0.277 – 8.334	Aqueous DMF	2.38×10^4	2 : 3	Study of interference is done for very few foreign ions.	22.
Di-(2-ethylhexyl)phosphoric acid		0.6 mol/L lactic acid	NM	P204 extractant	-	NM	Shaking time 30 min.	23.
2-octylaminopyridine	575	0.0075 M sodium salicylate, pH 11.0	NM	Xylene	NM	1 : 1	5 min of equilibration time	24.
O-methoxy phenylthiourea	320	0.1 M HCl	Up to 50	Chloroform	1.5002×10^3	1 : 1	Simple and precise, instant complex formation at room temperature, large beer's range, low reagent concentration, single extraction.	PM

NM: Not Mentioned; PM: Present Method

3. Results and discussion

3.1 Absorption spectra

The absorption spectrum of lanthanum(III)-OMePT complex shows maximum absorbance at 320 nm (Figure 1). The reagent blank has minimum absorbance at the maximum absorbance wavelength.

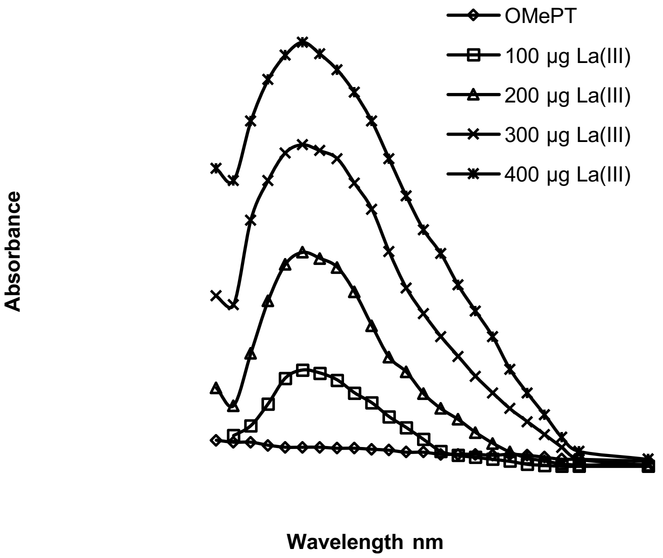


Figure 1: Absorption spectra of lanthanum(III)-OMePT complex.

3.2 Effect of acid concentration

Lanthanum(III)-OMePT complex formation takes place in hydrochloric acid media and it depends upon the hydrochloric acid concentration. The hydrochloric acid concentration was varied from 0.02 to 5.0 mol L^{-1} it shows complete complexation and maximum absorbance at the concentration of 0.1 mol L^{-1} hydrochloric acid and further the absorbance decreases (Figure 2).

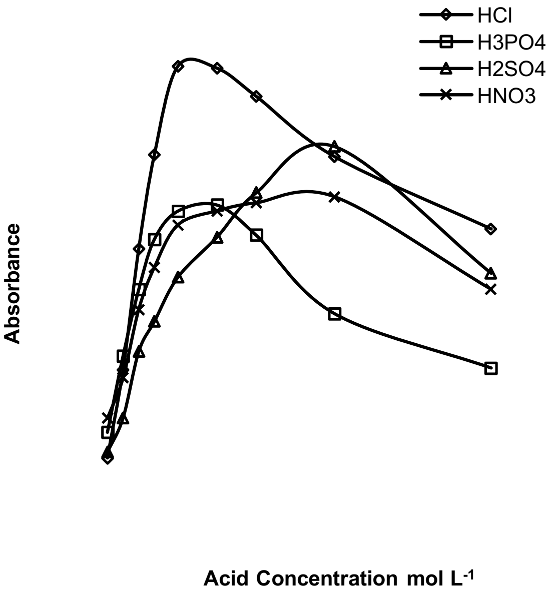


Figure 2: Effect of acid concentration on lanthanum(III)-OMePT complex.

3.3 Effect of ethyl alcohol, N,N-DMF and dimethylsulfoxide medium

The reagent medium in aqueous phase was studied. Different reagent medium as ethyl alcohol, N,N-dimethylformamide (N,N-DMF) and dimethylsulphoxide (DMSO) were varied (from 1.0 % to 50.0 %

(V/V)) keeping other parameters constant. Compared to other solvents maximum absorbance was obtained in presence of ethyl alcohol. For lanthanum(III)-OMePT complex maximum absorbance was obtained in the range of 4.0 % to 36.0 % (V/V) ethyl alcohol. Thus substantially in order to ensure complete complex formation excess reagent medium as 20% (V/V) ethanol in aqueous phase was fixed.

3.4 Effect of Effect of reagent concentration

Different molar concentrations of OMePT in ethanol (2.0 mL) in the range of 0.0002 - 0.2 mol L^{-1} was added to a fixed lanthanum(III), 200 µg, and absorbance measurement was performed as per recommended procedure. A 2.0 mL, 0.01 mol L^{-1} reagent was sufficient for complete complex formation. No adverse effect on excess of reagent.

3.5 Choice of extraction solvent

Various extraction solvents were studied for quantitative extraction of lanthanum(III)-OMePT complex, Viz. chloroform, isoamyl alcohol, methylisobutyl ketone (MIBK), n-butyl acetate, toluene, xylene and benzene. Amongst the extraction solvents studied quantitative extraction with maximum absorbance values ware obtained in chloroform (Table 2).

Table 2: *Effect of solvent on extraction of lanthanum(III)-OMePT complex*

Solvent	**Dielectric constant**	**Percent Extraction**^{a}	**Distribution ratio**
MIBK	13.1	39.81	1.65
Isoamyl alcohol	13.9	60.64	3.85
n-Butanol	17.1	49.07	2.41
1,2Dichloroethane	10.4	56.01	3.18
Chloroform	4.4	99.9	2499.75

a: Average of six determinations

3.6 Effect of equilibration time

The study of change in absorbance with variation in equilibration time was carried out over 5 s to 30 min with 10 mL chloroform. Quantitative extraction of the lanthanum(III)- OMePT complex takes place with 10 mL chloroform by shaking two phases for one minute. There was no adverse effect on prolonged extraction time.

3.7 Stability of complex

The stability of complex was studied with the absorbance value measurement at regular time intervals of 1.0 h each. The lanthanum(III)-OMePT complex was stable for more than 48 h.

3.8 Analytical figures of merit

The lanthanum(III)-OMePT complex obeys Beer's law over the concentration range up to 45.0 µg mL^{-1} of lanthanum(III) (Figure 3). Ringbom's plot has the range of linearity in the absorbance and concentration 7.5 to 45.0 µg mL^{-1} with a slope value of 0.691 (Figure 4). The Molar absorptivity and Sandell's sensitivity of the complex are 1.5002×10^{3} L mol^{-1} cm^{-1} and 0.0926 µg cm^{-2} respectively.
Ratio between the relative error in concentration and photometric error was 3.3324. The correlation coefficient values of lanthanum(III)-OMePT complex with an independent variable as concentration in µg mL^{-1} and dependent variable as absorbance was 0.99. The stoichiometry of complex was ascertained using slope ratio method and also confirmed by job's continuous variation method. For lanthanum(III)-OMePT complex, the graph of log D[La(III)] against log C(OMePT) at 0.07 mol L^{-1} and 0.09 mol L^{-1}

hydrochloric acid concentration (Figure 5), gave the slope values as 1.19 and 1.02 respectively. The composition of complex was also confirmed as 1:1 by job's continuous variation method (Figure 6).

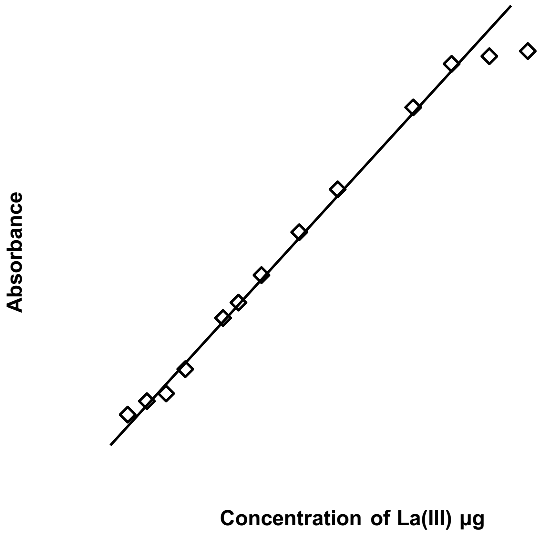


Figure 3: Beer's law range for lanthanum(III)-OMePT

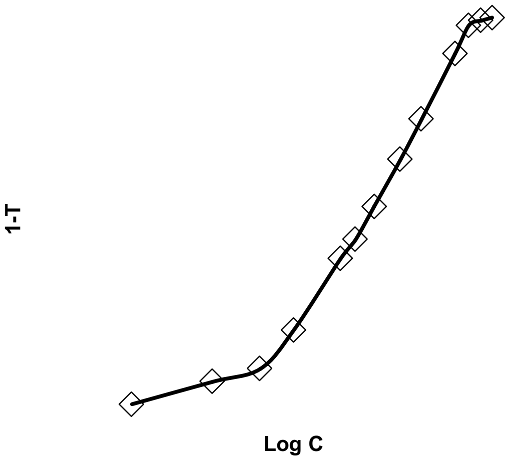


Figure 4: Ringbom's plot for lanthanum(III)-OMePT

OMePT: 2 mL,0.01 mol L^{-1} in ethanol, HCl: 0.1 mol L^{-1}, λ_{max}: 320 nm.

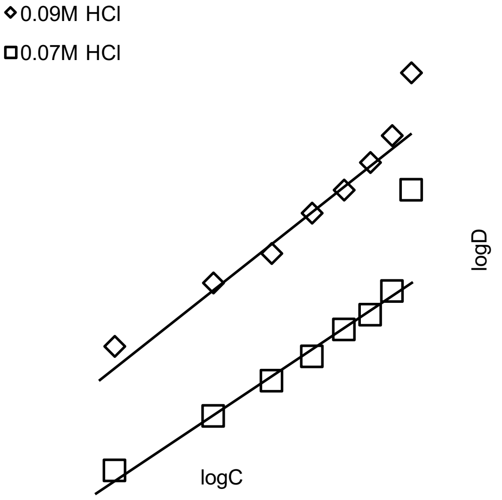


Figure 5: Plot of log $C_{(OMePT)}$ vs. log $D_{[La(III)]}$

Lanthanum(III): 200 µg; OMePT: 2.0 mL, 0.001 mol L^{-1} to 0.008 mol L^{-1}; HCl: 007 mol L^{-1}, 0.09 mol L^{-1}, λmax: 320 nm

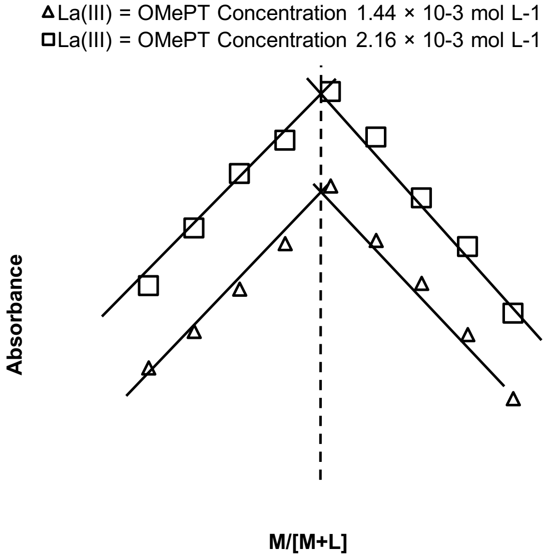


Figure 6: Job's variation method for lanthanum(III)-OMePT complex

Lanthanum(III) = OMePT: 1.44 × 10^{-3} and 2.16 × 10^{-3}mol L^{-1}, HCl: 0.1 mol L^{-1}, λ_{max}: 320 nm.

Hence the probable composition of extracted species was calculated to be 1:1 (lanthanum(III) : OMePT) (Figure 7). To access reproducibility of the results and the accuracy of the method, absorbance measurements of ten identical solutions containing 200 µg lanthanum(III) was carried out as per recommended method, average of these ten determinations and the relative standard deviation was determined which was 0.47 %. Limit of detection of the investigated method was 0.64 µg mL^{-1} as the amount determined corresponding to thrice the standard deviation of blank value.

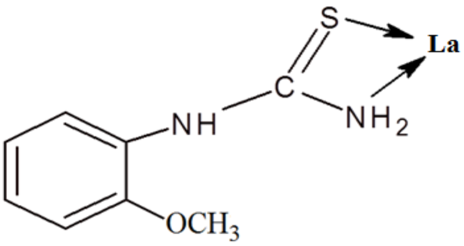


Figure 7: Recommended structure of Lanthanum(III)-OMePT complex

3.9 Interference study

By testing different foreign ions the selectivity of method was checked. The tolerance limit was fixed for the ions which do not cause deviation more than + 2 % in the absorbance value for lanthanum(III)-OMePT complex. The suitable masking agents are used to remove interference due to cations. Maximum limit of cations added was 50 mg and the maximum limit of anions added was 100 mg. Determination of lanthanum(III) was precise and highly selective with the tolerance limit in the range of milligrams in presence of many added cations and anions. The interference due to Mn(II), Fe(III), Ni(II), Cu(II) and Co(II) cations was removed by masking with EDTA (Table 3).

Table 3. *Influence of foreign ions*

Foreign Ions	Added as	Tolerance limit mg	Foreign Ions	Added as	Tolerance limit mg
Mn(II)[b]	$MnCl_2.6H_2O$	10.0	Ba(II)	$BaCl_2.6H_2O$	50.0
Cd(II)	$CdCl_2.2H_2O$	7.00	Ca(II)	$CaCl_2.2H_2O$	50.0
Fe(III)[b]	$(NH_4)Fe(SO_4)_2.12H_2O$	4.00	Tl(III)	Tl_2O_3	1.40
Hg(II)	$HgCl_2$	1.50	In(III)	$InCl_3.4H_2O$	2.00
Bi(III)	$BiCl_3$	12.0	Th(IV)	$Th(NO_3)_4\cdot xH_2O$	1.00
Ni(II)[b]	$NiCl_2.6H_2O$	15.0	Pt(IV)	H_2PtCl_6	2.00
Cu(II)[b]	$CuSO_4.5H_2O$	3.00	Ru(III)	$RuCl_3.3H_2O$	1.00
Al(III)	$AlCl_3.6H_2O$	2.00	Zn (II)	$ZnSO_4.7H_2O$	19.5
Li(I)	LiCl	22.0	W(VI)	$Na_2WO_4.2H_2O$	6.5
Mg(II)	$MgCl_2.6H_2O$	21.0	Fluoride	NaF	100
Sn(II)	$SnCl_2.2H_2O$	0.50	Phosphate	Na_3PO_4	100
Ga(III)	$GaCl_3$	0.20	Sulphate	K_2SO_4	100
Au(III)	$HAuClO_4.H_2O$	0.50	Succinate	$CH_3(COONa)_2.6H_2O$	100
Mo(VI)	$(NH_4)_6MO_7O_{24}.2H_2O$	16.0	Citrate	$C_6H_8O_7.H_2O$	100
V(V)	V_2O_5	4.00	Malonate	$CH_2(COONa)_2$	100
Ce(IV)	$Ce(SO_4)_2.4H_2O$	0.90	Tartrate	$(CHOH:COOH)_2$	100
Pb(II)	$PbCl_2$	3.00	Acetate	$CH_3COONa.3H_2O$	100
U(VI)	$UO_2(CH_3COO)_2.2H_2O$	5.00	Oxalate	$Na_2C_2O_4.2H_2O$	100
Co(II)[b]	$CoCl_2.6H_2O$	2.00	E.D.T.A	Na_2EDTA	100

b:masked with 100 mg EDTA

4. Applications

4.1 Separation and determination of lanthanum(III) from binary synthetic mixtures

The proposed method permits separation and determination of lanthanum(III) from associated metal ions containing Ni(II), Co(II), Mo(VI), W(IV), Mn(II), Mg(II) and Al(III). Lanthanum(III) were separated from Mo(VI), W(IV), Mg(II) and Al(III) as per recommended procedure. After quantitative extraction of lanthanum(III) from synthetic binary mixture, aqueous phase was evaporated to moist dryness followed by 3 mL conc. hydrochloric acid. The residue obtained was cooled, dissolved in water and then added metal ions were determined by reported methods [36] (Table 4).

To increase the selectivity of extraction of lanthanum(III) in presence of Ni(II), Co(II) and Mn(II), these metal ions were masked with EDTA and recommended procedure was followed for quantitative extraction of La(III) in 10 mL chloroform. Aqueous phase contains masked metal ions and were de-masked by treatment with 3.0 mL nitric acid then evaporated to moist dryness followed by 3.0 mL conc. hydrochloric acid. The residue was cooled, dissolved in water and the added metal ions were determined by spectrophotometrically as per the reported method [36].

Table 4. Separation of lanthanum(III) from binary synthetic mixtures

Metal ions	Amount taken (µg)	Recovery * (%)	R.S.D. (%)	Chromogenic ligand	Reference
La(III)	200	98.96	0.45	OMePT	-----
Zn(II)	20	99.42	0.82	dithizone	36
La(III)	200	99.31	0.27	OMePT	-----
Mn(II)^{b}	300	99.54	073	permanganate	36
La(III)	200	99.42	0.45	OMePT	-----
W(VI)	300	98.31	1.48	thiocynate	36
La(III)	200	99.54	0.38	OMePT	-----
Cu(II)^{b}	40	99.26	0.86	dithizone	36
La(III)	200	99.07	0.66	OMePT	-----
Co(II)^{b}	500	99.20	0.97	thiocynate	36
La(III)	200	98.96	0.70	OMePT	-----
Fe(III)^{b}	75	99.48	0.43	1,10-phenanthroline	36
La(III)	200	99.31	0.60	OMePT	-----
Hg(II)	50	99.20	1.03	dithizone	36
La(III)	200	98.50	0.45	OMePT	-----
Ni(II)^{b}	50	99.67	1.03	Dimethyl glyoxime	36
La(III)	200	99.65	0.44	OMePT	-----
Au(III)	80	98.86	0.94	Stannous chloride	36

*a: Masked with 100 mg EDTA; *average of four determinations; R.S.D.: Relative Standard Deviation.*

4.2 Separation and determination of lanthanum(III) from multicomponent synthetic mixtures

An aliquot of solution containing 200 µg lanthanum(III) was taken and known amount of different compositions of associated metal ions were added followed by suitable masking agent and lanthanum(III) was separated and determined as per recommended method (Table 5).

4.3 Determination of Lanthanum in Sea Water

Take 200 mL sea water (collected from Kochi, Kerala, India) in 500 mL beaker and heat it on hot plate to moist dryness. Add 5 mL of concentrated hydrochloric acid and again heat to moist dryness. Dissolve residue in very dilute hydrochloric acid and finally dilute to 50 mL with distilled water. An aliquot (5.0 or 10.0 mL) of this solution is analyzed for determination of lanthanum(III) as per proposed method (Table 6).

4.4 Determination of Lanthanum in Sea Sand

Sea sand sample from Kochi, Kerala, India was analyzed to test the reliability of the present method. The sample was digested in a mixture of perchloric acid and nitric acid and evaporated to dryness. The residue was leached in 0.01 mol L^{-1} hydrochloric acid and diluted to 25.0 mL with distilled water. An aliquot, 2.0 or 5.0 mL, of the solution was taken for the extraction and determination of lanthanum(III) (Table 6).

Table 5. Separation of lanthanum(III) from multicomponent synthetic mixtures

Composition (µg)	Recovery * (%)	R.S.D. (%)
La(III) 200; Ni(II)^{b} 50; Co(II)^{b} 50; Hg(II) 50	99.42	0.45
La(III) 200; Fe(III)^{b} 50; Mn(II)^{b} 50; Zn(II) 10	99.07	0.66
La(III) 200; Cu(II)^{b} 40; W(VI) 50; Co(II)^{b} 50	98.96	0.23
La(III) 200; Au(III) 50; Hg(II) 50; Co(II)^{b} 50	99.54	0.38
La(III) 200; Ni(II)^{b} 50; Mn(II)^{b} 50; Co(II)^{b} 50	99.77	0.27
La(III) 200; Zn(II) 10; Hg(II) 50; W(VI) 50	99.31	0.60
La(III) 200; Hg(II) 50; Co(II)^{b} 50; Fe(III)^{b} 50	99.19	0.45
La(III) 200; Au(III) 50; Cu(II)^{b} 40; Mn(II)^{b} 50	99.42	0.45
La(III) 200; Cu(II)^{b} 40; Zn(II) 10; Co(II)^{b} 50	99.42	0.70

*b:Masked with 100 mg EDTA; *average of four determinations*

Table 6. Determination of lanthanum(III) from sea water and sea sand

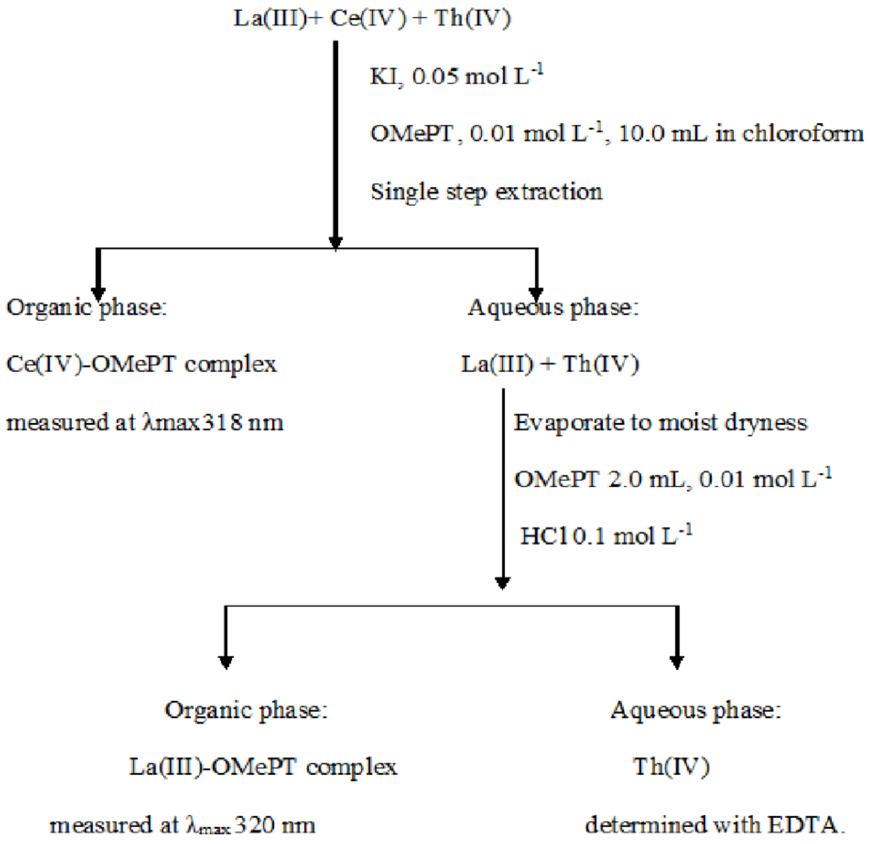
	Pre-concentrated sample mL	La(III) found µg mL^{-1}	RSD*
Sea Water	5	8.50	0.72
	10	8.40	0.65

	Pre-concentrated sample mL	La(III) found µg gm^{-1}	RSD*
Sea Sand	2	21.75	1.10
	5	20.80	0.79

** Average of four determinations*

4.5 Sequential separation of lanthanum(III), cerium(IV) and thorium(IV

Proposed method was applied for sequential separation and determination of lanthanum(III), cerium(IV) and thorium(IV) from synthetic mixtures. The separation of these metal ions was resolved by taking advantage of acid concentrations using the same reagent shown in (Scheme 1). Cerium(IV) was extracted in chloroform from synthetic mixture using 10 mL, 2 × 10^{-4}mol L^{-1} OMePT in chloroform from 0.05 mol L^{-1} in potassium iodide media at room temperature. After extraction of cerium(IV) lanthanum(III) and thorium(IV) remained in the aqueous phase.The aqueous phase was treated with 5.0 mL nitric acid and the mixture was boiled vigorously for 15 to 20 min with addition of water at intervals to maintain the volume. The mixture liberates violet vapours of iodine and after complete evolution of iodides in the form of iodine the raffinate was evaporated to moist dryness followed by treatment with HCl. The residue obtained was cooled dissolved in water and again evaporated to moist dryness. The residue obtained was cooled, dissolved in water and then treated with the solution of 2 mL, 0.01 mol L^{-1} OMePT in ethanol and hydrochloric acid was added to make solution at 0.1 mol L^{-1} with respect to hydrochloric acid and shaken with 10 mL chloroform for 1 min. The La(III)-OMePT complex was extracted chloroform. The aqueous solution containing thorium(IV) was evaporated to moist dryness, cooled and dissolved in hydrochloric acid and distilled water. The pH of solution was adjusted to 2.0 to 3.0 with ammonia solution, seven drops of xylenol orange indicator was added and the solution was titrated with 0.01 mol L^{-1} EDTA to yellow colour.



Scheme 1. *Sequential separation of lanthanum(III), Cerium(IV) and Thorium(IV).*

5. Conclusion

O-Methoxy phenylthiourea (OMePT) has been proved to be sensitive and selective spectrophotometric reagent for extraction and spectrophotometric determination of lanthanum(III). The proposed method was simple, sensitive, selective, reproducible and rapid with low reagent concentration. The quantitative extraction was carried out in a single step. The reported methods were suffer from interferences from cations and anions and were less sensitive. The proposed method is free from interferences from a large number of cations and anions. Reported methods need a laborious lengthy procedure to be adopted; while in the proposed method for spectrophotometric determination of lanthanum(III) is with instant complex formation at 0.1 mol L^{-1} hydrochloric acid. Minimum acidic condition merits the method for its applications. The stability of the complex was greater than 48 h, it confirms the applicability of method for various sample matrices with even lapse in complexation and further its spectrophotometric determination. The proposed method was successfully applied for determination of lanthanum(III) from sea water and sea sand.

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