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### Solvent extraction of lanthanum(III) by N-n-octylaniline from salicylate media

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#### ABSTRACT

In this paper, solvent extraction of lanthanum(III) using N-*n*-octylaniline in salicylate media has been systematically investigated. The effect of various parameters, such as equilibrium time, aqueous pH, extractant concentration, weak acid concentration, aqueous to organic volume ratio, back strippant and organic solvent, on the extraction have been discussed. Lanthanum(III) is quantitatively extracted at pH 5.3–6.5 from 0.04 M sodium salicylate with 0.065 M N-*n*-octylaniline dissolved in xylene. Experimental data have been analysed graphically to determine the stoichiometry of extracted species  $[RR'NH_2^+La(sal)_2^-]_{(org)}$ . The extracted metal ion was separated by using selective strippant and estimated spectrophotometrically with arsenazo I. The method is applicable for binary separation of lanthanum(III) from yttrium(III) and associated metal ions.

Keywords: Solvent extraction; Lanthanum(III); N-n-octylaniline; Salicylate media

#### 1. Introduction

Although the rare earth metals are in great demand as excellent functional materials, it is widely recognized that their mutual separation is very difficult. They find their applications in superconductors, optoelectronic materials, special alloys, catalysts and radio therapeutic reagents. Rare earth compounds containing lanthanum are extensively used in carbon lighting application, especially by the motion picture industry for studio lighting and projection. This application consumes about 25% of the rare earth compounds produced. La<sub>2</sub>O<sub>3</sub> improves the alkali resistance of glass. Small amounts of lanthanum, as an additive, can be used to produce nodular cast iron. There is current interest in hydrogen sponge alloys containing lanthanum. These alloys take up to 400 times their own volume of hydrogen and the process is reversible. Every time they take up the gas heat energy is released,

therefore these alloys have possibilities in an energy conservation system.

For variety of uses in these specialized areas, a high purity of the metals is often required. Being intricately similar in their physical and chemical properties, lanthanoids pose an exigent problem in their separations. Amongst the different methods used for the purpose, liquid–liquid extraction is one of the most popular and versatile techniques, because of its simplicity, speed and applicability to both tracer and macro amount of metal ions. As there are different solvent extraction systems that could be used for metal ions separation, ion-pair extraction systems have received attention for a long time. The chemistry and the methods of the lanthanoid separation have been thoroughly reviewed by Nash and Jensen [1].

Over the years a number of extractants have been employed for the extraction and separation of lanthanum(III) and more prominent among these are high molecular weight amines, such as quaternary ammonium salt aliquat 336 [2–5], decylamine [6], primary high molecular

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weight amines [7], tri-*n*-octylamine [8,9], trioctylamine [10].

A literature survey revealed that variety of organophosphorus compounds such as octyl(phenyl)-N,Ndiisobutylcarbamoylmethyl phosphine oxide [11], cyanex 923 [12], 1,3-benzenedimethylbis(phenylphosphinic acid) [13], bis(2-ethylhexyl)-phosphinic acid [14], tributyl phosphine oxide [15], di-(2-ethylhexyl)-phosphoric acid [16], tri-n-octylphosphine oxide [17] are reported. However, these methods yield incomplete separation and not free from interferences of associated metal ions.

Several reagents are reported for the solvent extraction of lanthanum(III), these are 5,11,17,23-tetra-tert-butyl-25,27-bis(diethylcarbamoylmethoxyl)-26,28-dihydroxycalix-[4]arene [18], 1,3-calix [4] arene-bis-crown-6 and 1,3-calix [4] arene-bis-crown-5 [19], N,N'-dimethyl-N,N'diphenylpyridine-2,6-dicarboxyamide (DMDPhPDA) [20], N-m-trifluoromethylcinnamoyl-N-phenylhydroxylamine [21], o-vanillinsemicarbazone [22], substituted malonamides [23,24], sec-nonylphenoxy acetic acid [25], diaza-18-crown-6-di-isopropionic acid [26], 1,4,10,13-tetrathia-7,16-diazacyclooctadecane and lauric acid [27], 18-crown-6 and EDTA [28], 3-phenyl-4-benzoyl-5-isoxazolone [29],1-phenyl-3-methyl-4-benzoyl-5-pyrazolones [30], 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane [31], have been used for the extraction of lanthanum(III). However, these methods have limitations such as interferences of different ions, co-extraction, use of high reagent concentration and incomplete extraction.

Although not as widely used as their organophosphorus counterparts, extractants of the high molecular weight amine type have found some applications in the hydrometallurgical processing of transition and inner transition metals. N-*n*-octylaniline is a secondary amine, which acts as liquid anion exchanger. In this work, N-*n*octylaniline–salicylate system was studied to investigate the extraction of aqueous lanthanum(III) solution as a function of various parameters. From a practical point of view, reagents of the high molecular weight amine type are relatively inexpensive, readily available or easily synthesized in laboratory.

The aim of this study is to develop an efficient extraction process for the sequential separation of lanthanum(III) from Y(III). The present work deals with a study of extraction of lanthanum(III) and its separation from some commonly associated metal ions such as Th(IV), U(VI), Nb(V), Gd(III), Nd(III), Ce(IV) and Zr(IV). The proposed method is simple, precise, rapid and free from the limitations described earlier.

#### 2. Experimental

#### 2.1. Apparatus and reagents

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.

A stock solution of lanthanum(III) was prepared by dissolving 1.173 g of lanthanum oxide in 5 mL of hot hydrochloric acid (1:1) and diluted to 1000 mL with distilled water. The solution was standardized [32] and the working solution containing  $60 \mu g/mL$  of lanthanum(III) was prepared by appropriate dilution of the standard stock solution.

Ammonium chloride buffer solution (0.1 M) was prepared by adding an appropriate amount of ammonia to ammonium chloride solution to results in solution of pH 9.

0.1% aqueous solution of arsenazo I was prepared and used for the spectrophotometric determination of lanthanum(III).

The extractant N-*n*-octylaniline was prepared by the method of Gardlund et al. [33] and its solutions were prepared in xylene.

All other chemicals used in this work were of AR grade. Double distilled water was used throughout the procedure.

### 2.2. General extraction and determination procedure for *lanthanum(III)*

An aliquot of lanthanum(III) solution containing 60 µg was mixed with a sufficient quantity of sodium salicylate (0.160 g) to make its concentration 0.04 M in a total volume of 25 mL of the solution. The pH of the aqueous solution was adjusted to 5.5 with dilute hydrochloric acid and sodium hydroxide solution. The solution was then transferred to a 125 mL separating funnel and shaken with 10 mL of 0.065 M N-n-octylaniline in xylene for 5 min. After separating the two phases, the aqueous phase was discarded and the organic phase was stripped with three 10 mL portions of 0.07 M acetic acid solution. The combined aqueous phase was equilibrated with 5 mL of xylene to remove the traces of dissolved amine and evaporated to moist dryness and lanthanum(III) was determined spectrophotometrically [34] with arsenazo I as follows: transfer slightly acidic solution to a 25 mL volumetric flask followed by 5 mL of buffer solutions (pH 9) and 2 mL 0.1% of arsenazo I, then diluted to the mark and measured the absorbance at 575 nm against the reagent blank in the reference cell. Lanthanum(III) content in the solution was calculated from calibration graph.

#### 3. Results and discussion

#### 3.1. Extraction as a function of pH

The effect of pH on the percentage extraction of lanthanum(III) was studied with varying pH range of 1–12 in the presence of weak organic acid as a 0.04 M sodium salicylate. The quantitative extraction of lanthanum(III) was observed in the pH range of 5.3–6.5 (Fig. 1, curve a),

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Fig. 1. Curve 'a' — extraction behaviour of lanthanum(III) as a function of pH from 0.04 M sodium salicylate with 0.065 M N-*n*-octylaniline.(La(III) 60  $\mu$ g). Curve 'b' — extraction behaviour of yttrium(III) as a function of pH from 0.04 M sodium salicylate with 0.065 M N-*n*-octylaniline.(Y(III) 150  $\mu$ g).

and favourable to formation of ion pair complex from sodium salicylate media. Thus the optimum pH 5.5 was used for efficient extraction of lanthanum(III) for further recommended procedure.

### 3.2. Extraction of lanthanum(III) as a function of the N-n-octylaniline concentration

The concentration of N-n-octylaniline in xylene was

Table 1

Extraction behaviour of lanthanum(III) as a function of N*n*-octylaniline concentration. Lanthanum(III) 60  $\mu$ g, pH 5.5, sodium salicylate 0.04 M, aq.:org 2.5:1, strippant 0.07 M acetic acid (3×10 mL), equilibrium time 5 min

Reagent concentration (M)	% E <sup>a</sup>	Db
0.0013	26.3	0.91
0.0022	61.0	3.91
0.0044	72.9	6.73
0.022	78.5	9.11
0.030	84.2	13.35
0.043	100	$\infty$
0.065	100	$\infty$
0.087	100	$\infty$
0.11	94.0	39.45
0.13	62.3	4.13
0.17	91.6	3.42
0.22	40.2	1.68
0.30	27.1	0.93
0.43	18.7	0.63

<sup>a</sup> Percentage extraction

<sup>b</sup> Distribution ratio

studied by extracting a fixed amount of lanthanum(III) with varying concentration in the range of 0.0013-0.43 M N-*n*-octylaniline at the pH 5.5. The quantitative extraction of 60µg of lanthanum(III) was found in 0.043-0.087 M N-*n*-octylaniline with 0.04 M sodium salicylate at pH 5.5. However the increase of N-n-octylaniline concentration causes an adverse effect on extraction of lanthanum(III) (Table 1). Further extraction studies of lanthanum(III) were carried out using 0.065 M N-*n*-octylaniline in xylene.

Extraction behavior	of lanthai	num (III) as a	function of w	eak organic <i>a</i>	cid concentra	tion. Lanthar	ոսm(III) 60 µչ	g, pH 5.5, e	xtract
ant 0.065 M N-n-oc	tylaniline i	in xylene (10	mL), aq.:org2	25:10, strippa	nt 0.07 M ace	tic acid (3×10	mL), equilibi	rium time 5	i min
Acid	Sodium	succinate	Sodium	salicylate	Sodium	malonate	Ascorbic	c acid	
concentration (M)	0/ <b>E</b> a	Dh	0/ Ea	Dh	0/ <b>E</b> a	Dh	0/ Ea	Dh	

Acid	Sodium succinate		Sodium s	Sodium salicylate		Sodium malonate		Ascorbic acid	
concentration (M)	% E <sup>a</sup>	D <sup>b</sup>	% E <sup>a</sup>	$D^{b}$	% E <sup>a</sup>	$D^{b}$	% E <sup>a</sup>	D <sup>b</sup>	
0.05	23.6	0.77	39.7	1.29	33.6	1.09	29.5	0.95	
0.01	63.4	4.34	74.8	7.43	49.8	2.48	46.7	2.19	
0.02	73.6	6.98	88.1	18.43	63.5	4.35	48.9	2.39	
0.03	76.2	8.00	96.1	61.93	64.5	4.54	50.2	2.52	
0.04	95.2	49.37	100	$\infty$	77.5	8.62	61.9	4.06	
0.05	92.6	31.28	100	$\infty$	72.3	6.53	70.5	5.97	
0.06	83.9	13.05	94.8	45.95	38.8	1.58	78.1	8.92	
0.07	81.4	10.90	81.9	11.34	37.1	1.48	84.8	13.91	
0.08	76.9	8.30	77.4	8.57	36.8	1.46	88.9	19.98	
0.09	71.1	6.14	73.9	7.07	33.6	1.26	75.6	7.72	
0.1	66.6	4.97	72.9	6.73	30.0	1.07	56.5	3.35	

<sup>a</sup> Percentage extraction

<sup>b</sup> Distribution ratio

Table 2

#### 3.3. Extraction as a function of weak organic acid concentration

The extraction of lanthanum(III) was performed at pH 5.5 with 0.065 M N-*n*-octylaniline in xylene in the presence of varying concentration (0.05–0.1 M) of sodium salicylate, sodium succinate, sodium malonate, L-ascorbic acid and sodium citrate as weak acid media (Table 2). The extraction of the ion pair complex of lanthanum(III) was found to be quantitative in the range of 0.04–0.055 M sodium salicylate. Therefore, a 0.04 M concentration of sodium salicylate was used throughout this experimental work. However, the extraction of lanthanum(III) was found to be incomplete in sodium succinate, sodium malonate, L-ascorbic acid and sodium citrate media.

#### 3.4. Effect of solvent on the extraction of lanthanum(III)

That extraction of lanthanum(III) was carried out with various solvents. The extraction was quantitative with xylene, benzene and toluene, while incomplete in methyl isobutyl ketone (MIBK), kerosene, chloroform, 1, 2-dichloroethane, carbon tetrachloride (Table 3). Benzene and toluene are too toxic solvents, xylene is the most adequate and efficient diluent for quantitative extraction of lanthanum(III). Hence in this work extraction studies on lanthanum(III) were carried out with xylene as a diluent.

#### 3.5. Nature of extracted species

The nature of extracted species was ascertained by using log D – log C plots. The graphs of log  $D_{\text{[La(III)]}}$  against log  $C_{\text{[N-$ *n* $-octylaniline]}}$  at fixed sodium salicylate concentration (0.04 M) were found to be linear and having slope values of 1.01 and 0.88 at pH 2.0 and 4.0 respectively (Fig. 2). This indicates that the metal: extractant ratio was 1:1. Also plots of log  $D_{\text{[La(III)]}}$  against log  $C_{\text{[salicylate]}}$  at fixed N-*n*-octylaniline concentration (0.065 M) were linear and slope values found to be 1.98 and 2.12 at pH 2.0 and 4.0 respectively (Fig. 3). This indicates two ions of salicylate participate in the formation of the anionic species. Thus the probable composition of extracted species is calculated to be 1:2:1 (metal:acid:extractant).The possible mechanism of extracted species as

$$RR'NH_{(org)} + H^+_{(aq)} = RR'NH^+_{2(org)}$$
(1)

$$La_{(aq)}^{3+} + 2 sal_{(aq)}^{2-} = [La (sal)_2]_{(aq)}^{-}$$
(2)

$$[La (sal)_{2}]_{(aq)}^{-} + RR'NH_{2(org)}^{+} = [RR'NH_{2}^{+} La(sal)_{2}^{-}]_{(org)}$$
(3)

#### 3.6. Effect of stripping agents

Various stripping agents were examined for back extraction of lanthanum(III) from the organic phase (Table 4). Back extraction of lanthanum(III) was quantitative with 0.05–0.07 M acetic acid and 0.04–0.05 M hydrochloric acid. The stripping was found to be complete

#### Table 3

Extraction behaviour of lanthanum(III) as a function of diluents. Lanthanum(III) 60 µg, pH 5.5, sodium salicylate 0.04 M, aq.:org 25:10, extractant 0.065 M N-*n*-octylaniline (10 mL), equilibrium time 5 min, strippant 0.07 M acetic acid (3×10 mL)

Solvent	Dielectric constant, ε	% E <sup>a</sup>	$D^{b}$
Benzene	2.28	100	∞
Toluene	2.38	100	$\infty$
Xylene	2.30	100	$\infty$
Carbon tetrachloride	2.24	73.3	6.85
Chloroform	4.81	63.1	4.28
Kerosene	1.80	35.8	1.39
Methyl isobutyl ketone	13.11	91.7	27.62
<i>n</i> -butanol	17.80	78.6	9.18
Amyl alcohol	13.90	95.8	47.5
1,2-dichloroethane	10.5	73.0	6.75

<sup>a</sup> Percentage extraction

<sup>b</sup> Distribution ratio



Fig. 2. log–log plot of log  $D_{[La(III)]}$  against log  $C_{[N-n-octylaniline]}$  at fixed sodium salicylate concentration (0.04 M).

with three 10 mL portion of acetic acid (0.05–0.07 M) and hydrochloric acid (0.04–0.05 M). While perchloric acid, nitric acid, acetate buffer pH 3.42, 4.27 and water become unsuccessful for the recovery of lanthanum(III) from the



Fig. 3. log-log plot of log  $D_{[La(III)]}$  against log  $C_{[sodium salicylate]}$  at fixed N-*n*-octylaniline concentration (0.065 M).

organic phase. In actual procedure, three 10 mL portion of 0.07 M acetic acid was used as a suitable stripping agent.

#### 3.7. Equilibration time

The solution of lanthanum(III) was shaken by performing the equilibration for various periods of time 0.16–20.0 min. The extraction of lanthanum(III) was quantitative over a period range of 2–7 min shaking of the solution. In the actual work, a 5 min equilibration time was recommended in order to ensure the complete extraction of lanthanum(III). However, a prolonged shaking above 10 min was found to have an adverse effect on the percentage extraction of lanthanum(III).

# 3.8. Extraction behavior of lanthanum(III) as a function of metal loading capacity

The loading capacity of the extractant was determined by the repeated contact of organic phase with a fresh feed solution of the metal with same concentration. The concentration of lanthanum(III) was varied from 50 to  $1500 \mu g/10 mL$ . The maximum loading capacity of 10 mL 0.065 M N-*n*-octylaniline in xylene was found to be  $600 \mu g$  lanthanum(III).

#### 3.9. Effect of aqueous to organic volume ratio

The extraction of lanthanum(III) was carried out in different aqueous to organic volume ratios in the range 10–500 mL of 0.04 M aqueous sodium salicylate medium with 10 mL 0.065 M N-*n*-octylaniline in xylene have been studied. There was sharp increase in the separation efficiency and distribution ratio of lanthanum(III), when phase ratio A/O varied from 2:1 to 6:1. The recommended procedure the phase ratio is used 2.5:1.

#### 3.10. Effect of diverse ions

The effect of various cations and anions in the separation and determination of lanthanum(III) was studied by the recommended procedure. When the interference was found to be intensive, the tests were repeated with successively smaller amount of foreign ion until a concentration giving an error less than  $\pm 2\%$  in the recovery

#### Table 4

Extraction behavior of lanthanum(III) as a function of stripping agents. Lanthanum(III) 60 µg, pH 5.5, sodium salicylate 0.04 M, aq.:org 25:10, extractant 0.065 M N-*n*-octylaniline in xylene (10 mL), equilibrium time 5 min

Molarity (M)	HCl (%R) <sup>a</sup>	HClO <sub>4</sub> (%R) <sup>a</sup>	HNO <sub>3</sub> (%R) <sup>a</sup>	CH <sub>3</sub> COOH (%R) <sup>a</sup>	H <sub>2</sub> SO <sub>4</sub> (%R) <sup>a</sup>	NH <sub>4</sub> Cl (%R) <sup>a</sup>	
0.01	63.3	50.6	61.0	88.7	93.3	86.7	
0.02	77.0	84.4	61.9	93.0	94.2	68.3	
0.03	98.5	84.1	44.1	96.0	90.5	63.6	
0.04	100	78.7	42.9	98.0	76.8	55.8	
0.05	100	76.0	40.3	100	55.7	52.0	
0.06	95.8	38.3	34.6	100	47.7	43.9	
0.07	88.4	38.3	33.3	100	42.5	32.6	
0.08	83.6	31.4	11.4	95.3	37.0	31.7	
0.09	82.4	29.0	0.0	89.7	35.2	30.4	
0.1	78.5	26.7	0.0	87.0	24.5	30.1	

<sup>a</sup> Percentage recovery.

Table 5

Effect of foreign ions on the extraction of 60  $\mu$ g lanthanum (III) at pH 5.5 in 0.04 M sodium salicylate with 0.065 M N-*n*-octylaniline in xylene

Tolerance limit, mg	Foreign ion added
100	Thiosulphate, ascorbate
50	Malonate, acetate, bromide, nitrate, thiourea
25	Tartrate
10	Nitrite
5	Thiocynate
3	Oxalate, fluoride
1	Iodide, phosphate
5	Mn(II), <sup>b</sup> Sr(II), Cd(II), Fe(II), V(V) <sup>b</sup>
3	Ba(II), Zn(II), Ru(III), Fe(III)
1	Ca(II), Mg(II), W(VI), Mo(VI)
0.7	Zr(IV), Y(III)
0.5	U(VI), Pd(II), Ni(II), Ti(IV) <sup>b</sup> , Th(IV)
0.4	Nb(V), Cr(VI), Sm(III) <sup>a</sup>
0.3	Ta(V)
0.2	Nd(III) <sup>a</sup> , Ce(IV) <sup>b</sup>
0.1	Cu(II), Co(II)

<sup>a</sup> masked with 50 mg thiosulphate

<sup>b</sup> masked with 3 mg fluoride

of lanthanum(III) was attained. Initially the foreign ion was added to the lanthanum(III) solution in large excess, 100 mg for anions and 25 mg for cations (Table 5). However, interference due to Sm(III), V(V) and Nd(III) was eliminated by masking with 50 mg  $S_2O_3^{2-}$  Ce(IV), Ti(IV), and Mn(II) was eliminated by masking with 3 mg F<sup>-</sup>. The ion such as EDTA, citrate, tartarate interferes severely.

#### 4. Applications

### 4.1. Separation and determination of lanthanum(III) from binary mixture

The suitability of the above developed method was examined by applying it to the separation and determination of lanthanum(III) in a variety of a binary mixtures which are commonly associated with it by taking the advantages of difference in the extraction conditions of metal such as pH of the aqueous phase, reagent concentration and use of masking agent (Table 6).

### 4.1.1. Sequential separation scheme for lanthanum(III) and yttrium(III)

Lanthanum(III) and Y(III) found together with the lanthanoid elements in bastnaesite, monazite and other minerals. It is extremely difficult to separate the individuals elements because of nearly similar ionic radii of

Table 6 Separation of lanthanum(III) from binary mixtures

Amount of metal ion (µg)	Average (%) recovery*	Chromogenic ligand
La(III), 60	99.6	
Y(III), 150	99.5	Alizarin Red S
La(III), 60	98.8	
U(VI), 50	99.5	PAR
La(III), 60	99.1	
Nb(V), 50	98.8	PAR
La(III), 60	98.8	
Gd(III), 75	99.1	Arsenazo I
La(III), 60	98.5	
Zr(IV), 150	98.5	Alizarin Red S
La(III), 60	99.1	
Th(IV), 50	98.4	Arsenazo III
La(III), 60	99.6	
Ce <sup>a</sup> (IV), 50	99.4	Arsenazo III
La(III), 60	98.2	
Nd <sup>b</sup> (III), 60	98.9	PAR

<sup>a</sup> masked with 5 mg fluoride

<sup>b</sup>masked with 50 mg thiosulphate

\*Average of six determinations.

lanthanum (1.032 Å) and yttrium (0.900 Å) [35]. Hence, we have proposed to separate lanthanum(III) from Y(III).

To an aliquot containing 60 µg of lanthanum(III) and 150 µg of yttrium(III) in 25 mL volumetric flask, enough sodium salicylate and water were added to give a final concentration of 0.04 M with respect to sodium salicylate in a total volume of 25 mL. The pH of the solution was adjusted to 5.5 and the aqueous solution was transferred to 125 ml separating funnel. It was then equilibrated with 10 mL 0.065 M N-n-octylaniline in xylene. Under this condition lanthanum(III) was quantitatively extracted into organic phase as ion-pair complex, leaving behind yttrium(III) in aqueous phase. At low N-n-octylaniline concentration (0.065 M), there was no extraction of Y(III) up to pH 6.0 (Fig. 1, curve b). However, at higher concentration of N-n-octylaniline (0.17 M) the extraction of Y(III) starts at pH 2.0 and becomes quantitative at pH 9.7–10.5. The two phases were separated. The organic phase was back stripped with three 10 mL 0.07 M acetic acid and lanthanum(III) was determined spectrophotometrically as recommended in the procedure.

The aqueous phase was reduced and adjusted to its concentration 0.03 M with sodium salicylate, in a total volume of 25 mL solution .The pH of solution was adjusted to 10.3, then the solution was transferred to 125 mL separating funnel and shaken with 10 mL 0.17 M N-*n*-octylaniline in xylene for 5 min. After separating the two phases, the organic phase was stripped with two



Adjust the pH 5.5 with 0.04 M sodium salicylate in a total volume of 25 mL and extract with 10 mL 0.065 M N-*n*-octylaniline in xylene for 5 min.



Fig. 4. Sequential separation scheme (Flow sheet).

10 mL 0.5 M hydrochloric acid. Y(III) was determined spectrophotometrically with Alizarin Red S [36] (Fig. 4)...

# 4.1.2. Separation of lanthanum(III) from U(VI), Nb(V), Gd(III), and Zr(IV)

Lanthanum(III) was separated from binary mixture of U(VI), Nb(V), Gd(III) and Zr(IV) by its extraction with 10 mL of 0.065 M N-*n*-octylaniline in xylene from 0.04 M sodium salicylate. Under this condition the added metal ions remained quantitatively in aqueous phase. The aqueous phase is washed with 5 mL xylene to remove traces of the reagent. Metal ions from aqueous phase were determined by standard methods [36–38]. The lanthanum(III) from the organic phase was stripped with 0.07 M acetic acid (3×10 mL) and determined spectrophotometrically as recommended in the procedure.

#### 4.1.3. Separation of lanthanum(III) from Th(IV)

Lanthanum(III) was separated from Th(IV) under the optimum condition of lanthanum(III) by adjusting pH 5.5 with 0.065 M N-*n*-octylaniline and 0.04 M sodium salicy-late. Th(IV) was coextracted with lanthanum(III) in the organic phase. Lanthanum(III) from the organic phase was firstly stripped with 0.07 M acetic acid (3×10 mL), while there is no back extraction of Th(IV). Lanthanum(III) was

determined as per the general procedure. Organic phase containing Th(IV) was back stripped with 0.5 M nitric acid [39] and determined by spectrophotometrically [40] with Arsenazo III at 645 nm.

#### 4.1.4. Separation of lanthanum(III) from Ce(IV) and Nd(III)

The proposed method was also extended for separation of lanthanum(III) from Ce(IV) and Nd(III) by masking with 3 mg F<sup>-</sup> and 50 mg of thiosulphate respectively. The masked Ce(IV) and Nd(III) remained in the aqueous phase quantitatively under the optimum extraction condition of lanthanum(III). After demasking of Ce(IV) and Nd(III) with 5 mL concentrated perchloric acid and evaporated to moist dryness, they were estimated spectrophotometrically with 0.05 % Arsenazo III at 660 nm and 0.05 % PAR at 515 nm [40,41] respectively. Lanthanum(III) was stripped with 0.07 M acetic acid (3×10 mL) from organic phase and determined spectrophotometrically as per the general procedure.

#### 5. Conclusion

The proposed extractive separation method is simple, rapid, selective and reproducible. The method facilitates complete sequential separation of lanthanum(III)– yttrium(III) and suitable for separation and determination of other rare earths. The extraction mechanism corresponds to an anion exchange, in which a complex of stoichiometric formula  $[RR'NH_2^+La~(sal)_2^-]_{(org)}$  is formed in the organic phase. It is free from interference of a large number of foreign ions. The solvent like xylene was nontoxic and suitable for proposed method. N-*n*-octylaniline can be synthesized at low cost, with high yield and best purity.

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