

***N-n*-OCTYLANILINE AS A NEW REAGENT FOR ANALYTICAL LIQUID-LIQUID EXTRACTION OF YTTRIUM(III) FROM MATRICES OF VARIOUS METAL IONS**

**Balasaheb N. Kokare, Aniruddha M. Mandhare, Sanjay S. Kolekar,
Mansing A. Anuse***

*Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University,
Kolhapur, 416 004 India*

*mansinganuse@yahoo.co.in

A systematic study of solvent extraction behavior of yttrium(III) with *N-n*-octylaniline from salicylate media was carried out. Yttrium(III) was quantitatively extracted from 0.02–0.05 mol dm⁻³ NaSal at pH 9.7 – 10.5 with 0.17 mol dm⁻³ *N-n*-octylaniline in xylene. The extraction was found to proceed by an anion exchange mechanism with the extraction species being [CH₃(CH₂)₇(C₆H₅)NH₂+Y(C₇H₄O₃)₂⁻] ascertained on the basis of slope analysis. The extracted metal ion was separated by selective stripping with hydrochloric acid or perchloric acid from the metal loading organic phase and estimated spectrophotometrically following a complexation with Alizarin Red S. A binary separation of yttrium(III) from Th(IV), U(VI), Zr(IV), Nb(V), La(III), Nd(III), Ce(IV) and Gd(III) is discussed.

Keywords: yttrium(III); *N-n*-octylaniline; solvent extraction; salicylate

***N-n*-ОКТИЛАНИЛИН КАКО НОВ РЕАГЕНС ЗА АНАЛИТИЧКА ТЕЧНО-ТЕЧНА ЕКСТРАКЦИЈА НА ИТРИУМ(III) ОД МАТРИЦИ НА РАЗНИ МЕТАЛНИ ЈОНИ**

Направена е систематска студија на однесување на итриум(III) при екстракција со *N-n*-октиланилин од салицилатен медиум. Итриум(III) беше квантитативно екстрахиран од 0,02–0,05 mol dm⁻³ NaSal при pH = 9,7 до 10,5 со 0,17 mol dm⁻³ *N-n*-октиланилин во ксилен. Најдено е дека екстракцијата се одвива преку механизам на анјонска измена со екстракционите единки [CH₃(CH₂)₇(C₆H₅)NH₂+Y(C₇H₄O₃)₂⁻] што беше утврден преку анализа на наклонот. Екстрахираниот метален јон беше одделен со метод на селективно слекување со помош на хлороводородна или перхлорна киселина од метало-органската фаза и пресметан спектрофотометриски преку комплексирање со ализарин црвено S. Дискутирано е бинарното раздвојување на итриум(III) од Th(IV), U(VI), Zr(IV), Nb(V), La(III), Nd(III), Ce(IV) и Gd(III).

Клучни зборови: итриум(III); *N-n*-октиланилин; екстракција со растоворувач; салицилат

1. INTRODUCTION

Solvent extraction is one of the most efficient methods for separation technology because of its simplicity, speed and applicability to both trace and macro amount of metal ions. Though there are various solvent extraction systems being used for metal ion separation, the ion-pair extraction systems have received much attention for a long time. Yttrium is an important element used in atomic reactors for the control rods. The separation of yttrium(III) from lanthanides remains a challenging problem because of their close similarities, i.e. similar ionic radii and coordination behaviour. Because of the importance of this element in nuclear energy programme, the separation and purification of yttrium is demanded. The pre-concentration and purification of yttrium can be achieved by solvent extraction. Yttrium-90 is used for the production of labelled monoclonal antibodies for the tumour therapy studies.

A literature survey revealed that, over the years, various organophosphorus compounds have been effectively used for the extraction and separation of yttrium, these are, tributyl phosphine oxide (TBPO) [1], tris(2-ethylhexyl) phosphate (TEHP) [2], Cyanex 302 [3, 4], Cyanex 923 [5, 6], di(2-ethylhexyl) phosphoric acid [7–9], (2-ethylhexyl) phosphonic acid mono(2-ethylhexyl) ester (EHPNA) [10], sec-octyl- phenoxy acetic acid (CA-12) and bis (2, 4, 4-trimethylpentyl) phosphinic acid (Cyanex 272, HL) [11]. Oxygen containing compounds also plays an important role for the liquid-liquid extraction of yttrium(III) such as CA-100 [12–14], dibenzo-18-crown-6 [15], (CA-12) [16], 2-bromoalkanoic acids [17], alkyl salicylic acids [18], 5,7-dichloro-8-hydroxyquinoline [19], carboxylic acid [20], *N,N'*-dimethyl-*N,N'*-diphenylpyridine-2,6-dicarboxamide (DMDPhPDA) [21], dialkyl sulphoxides [22], 5,11,17,23-tetra-tert-butyl-25,27-bis (diethyl-carbamoyl methoxy)-26,28-dihydroxycalix[4]arene [23], calyx[4]arene [24]. There are very few studies published dealing with the extraction process of yttrium(III) with high molecular

weight amines [25–30]. However, the existing methods suffers from limitations such as stringent control of pH [2, 4, 12, 13, 14, 28], high reagent concentration [8, 17, 25], long extraction time [4, 7, 10, 11, 12, 15, 21, 23, 24], interference and co-extraction of other rare earths and associated metal ions [1, 2, 4, 9, 14, 16], need of masking agent to enhance the selectivity [10, 13]. In a few methods, there is requirement of synergism and salting out agents [11, 18, 19, 22, 26, 27, 29, 30] for quantitative extraction of yttrium(III).

Most of the work reported so far deals with the extraction of metals from mineral acid solutions. Relatively less information exists on the extraction of metals in these extractants from organic acid media. One of the distinct advantages of the organic acid media is the facility of controlling the concentration of complexing ligand, the ease of adjustment of pH and wide difference in pH at which various metal from anionic complexes. The comparative ease of stripping of the complexes from the organic phase can be achieved by fully exploiting the differences in reactivity of various metals to backwash in the aqueous phase by mineral acid. It is known that organic acid media offers better separation of metals possibly due to high stability of metal organic acids complexes. *N-n*-octylaniline is a secondary amine; the presence of an octyl group attached to an amino group in aniline renders this amine less soluble in water. It has explored as an extractant for yttrium(III) in salicylate media, *N-n*-octylaniline has its potential advantages with respect to lower cost, completely miscible with diluents and high purity. There is no emulsion formation and it has the potential of being prepared on large scale. Recently solvent extraction of palladium(II), antimony(III) with *N-n*-octylaniline from mineral acid [31, 32], platinum(IV), rhodium(III), zirconium(IV) from weak organic acid [33–35] and tellurium(IV) in halide [36] media has been reported, from the laboratory. The present work deals with a study of extraction of yttrium(III) and separation from some commonly associated metal ions such as,

Th(IV), U(VI), Zr(IV), Nb(V), La(III), Nd(III), Ce(IV) and Gd(III) from salicylate media with *N-n-octylaniline* in xylene.

2. EXPERIMENTAL

2.1. Reagents and apparatus

A standard stock solution of yttrium(III) was prepared by dissolving 0.3175 g of yttrium oxide (dehydrated by ignition) in 5 cm³ of hot HCl (1:1) and diluted to 250 cm³ with water. The solution was standardized [37] by known method and further diluted as required for the working solution. Alizarin red S (S.D. Fine chemicals) was prepared as a 0.1 % aqueous solution for the spectrophotometric determination of yttrium(III). The extractant *N-n-octylaniline* was prepared by the method of Gardlund's [38]. A solution of distilled aniline and *n*-octylbromide (3:1 molar ratio) was refluxed overnight. After cooling to room temperature, the reaction mixture was made basic with diluted aqueous ammonia. The aqueous layer was repeatedly washed with pentane. The pentane washings were combined with organic layer and treated with 50 % aqueous ZnCl₂ solution. Extraction of resulting solid with pentane, followed by drying with anhydrous potassium carbonate and flash evaporation of pentane yield crude *N-n-octylaniline*. Pure compound was obtained by fractional distillation on a spinning band column. The yield and boiling range was as follows: 98.5 %, 177–178 °C at 25 mm pressure. (Found C, 82.1; H, 11.4; C₁₄H₂₃N requires C, 81.9; H, 11.3 %). The density of *N-n-octylaniline* was found to be 0.89 g/cm³. The *p*-toluenesulphonyl derivative crystallized from alcohol in fan shaped cluster of needles, m.p. 42–43 °C (found: N, 4.1; C₂₁H₂₉O₂NS requires N, 3.8 %).

0.17 mol dm⁻³ solution of *N-n-octylaniline* in xylene was used for the proposed extraction procedure for yttrium(III).

All other chemicals (S.D. Fine) used in this work were of AR grade. Double distilled water was used throughout the procedure.

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

2.2. Procedure of extraction and determination of yttrium(III)

An aliquot of 2 ml yttrium(III) solution (75 µg/cm³) was mixed with sodium salicylate (0.120 g) to make its concentration 0.03 mol dm⁻³ in a total volume of 25 ml of the solution. The pH of the aqueous solution was adjusted to 10.3 with diluted HCl and NaOH solution. The solution was then transferred to a 125 cm³ separating funnel and shaken with 10 cm³ of 0.17 mol dm⁻³ *N-n-octylaniline* in xylene for 5 min. After separating the phases, the aqueous phase was discarded and the organic phase was stripped with two 10 cm³ portions of 0.05 mol dm⁻³ HCl. The combined aqueous phase was equilibrated with 5 cm³ of xylene to remove the traces of dissolved amine and evaporated to moist dryness and determined spectrophotometrically with alizarin red S [39].

The slightly acidic solution was transferred to a 25 cm³ volumetric flask followed by 2 cm³ of acetate buffer solution (pH 4.7) and 5 cm³ of 0.1 % alizarin red S and diluted to the mark. The absorbance was measured at 535 nm against the reagent blank in the reference cell.

3. RESULTS AND DISCUSSION

3.1. Effect of extraction condition

The effect of pH on yttrium(III) extraction recovery, R (%), was studied within the pH range of 1 to 11 in the presence of weak organic acid as a NaSal (0.03 mol dm⁻³). The extraction started at pH 3.0 and after that extraction of yttrium(III) increased with the increases of pH and became quantitative within pH range 9.7 – 10.5 (Figure 1). Therefore, the value of pH 10.3 was selected for the recommended procedure.

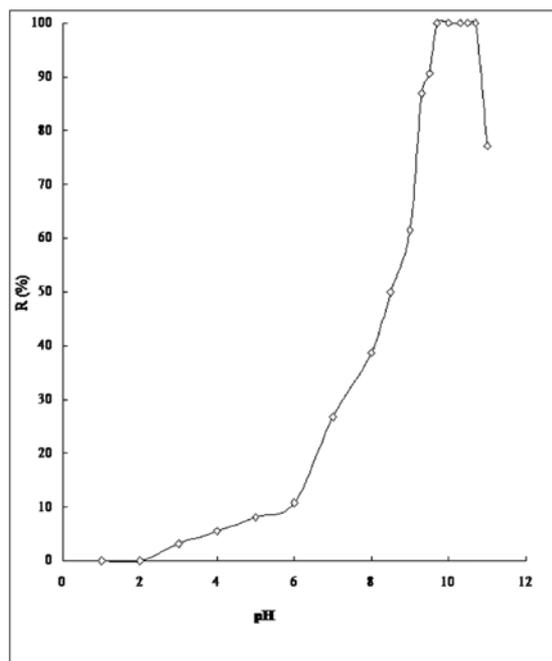


Fig. 1. Extraction behaviour of yttrium(III) as a function of pH from 0.03 mol dm^{-3} NaSal with 0.17 mol dm^{-3} *N-n*-octylaniline, $\gamma (\text{Y}^{3+}) = 150 \mu\text{g}/25 \text{ cm}^3$

The influence of *N-n*-octylaniline concentration on the extraction recovery of yttrium(III) was investigated by varying with concentration of this reagent dissolved in xylene of 0.0002 to 0.64 mol dm^{-3} . It was found that 10 cm^3 of 0.13 mol dm^{-3} *N-n*-octylaniline was quite needed for the complete extraction of yttrium(III) from 0.03 mol dm^{-3} NaSal, but to ensure the complete extraction of metal ion by the recommended procedure as an optimal concentration of *N-n*-octylaniline in xylene was used 0.17 mol dm^{-3} (Table 1A).

The extraction of yttrium(III) was investigated at pH 10.3 with 0.17 mol dm^{-3} *N-n*-octylaniline in xylene in the presence of varying concentration from 0.005 to 0.1 mol dm^{-3} sodium succinate, sodium salicylate, sodium malonate, sodium citrate and ascorbic acid (S.D. Fine) as a weak acid media. It is evident from data in Table 1B that yttrium(III) was extracted incompletely from

Table 1A

Extraction behaviour of yttrium(III) as a function of N-n-octylaniline concentration

$\gamma (\text{Y}^{3+}) = 150 \mu\text{g}/25 \text{ cm}^3$, pH = 10.3, c (sodium salicylate) = 0.03 mol dm^{-3} ,

Aq : Org = 25 : 10 $\text{cm}^3:\text{cm}^3$, Strippant = 0.05 mol dm^{-3} HCl ($2 \times 10 \text{ cm}^3$), equilibrium time = 5 min

Concentration of <i>N-n</i> -octylaniline / mol dm^{-3}	R (%)	Distribution ratio D
0.0002	25.0	0.83
0.0004	33.3	1.25
0.0022	54.3	2.97
0.0030	59.0	3.60
0.0044	69.7	5.75
0.022	74.7	7.38
0.031	77.1	8.42
0.043	84.8	13.95
0.087	93.1	33.73
0.11	95.2	49.58
0.13	100	∞
0.17	100	∞
0.22	100	∞
0.43	100	∞
0.64	100	∞

Table 1B

Extraction behaviour of yttrium(III) as a function of the concentration of the weak organic acids

γ (Y^{3+}) = 150 $\mu\text{g}/25\text{ cm}^3$, pH = 10.3, extractant = 0.17 mol dm^{-3} N-n-octylaniline in xylene (10 cm^3),
Aq : Org = 25 : 10 $\text{cm}^3:\text{cm}^3$, Strippant = 0.05 mol dm^{-3} HCl (2 x 10 cm^3), equilibrium time = 5 min

c/mol dm^{-3}	Sodium succinate		Sodium salicylate		Sodium malonate		Ascorbic acid		Sodium citrate	
	R (%) ^a	D ^b	R (%)	D	R (%)	D	R (%)	D	R (%)	D
0.00	20.8	0.66	20.8	0.65	20.8	0.65	20.8	0.65	20.8	0.65
0.005	89.0	20.23	53.3	2.84	74.3	7.22	25.0	0.83	21.3	0.70
0.01	77.6	8.66	75.6	7.75	79.3	9.58	32.0	1.17	27.6	0.95
0.02	65.2	4.68	100	∞	75.3	7.62	32.9	1.23	31.2	1.13
0.03	63.3	4.31	100	∞	54.2	2.96	35.9	1.40	32.9	1.23
0.04	60.1	3.77	100	∞	50.0	2.50	38.7	1.58	34.3	1.30
0.05	54.6	3.00	100	∞	46.2	2.15	42.0	1.81	36.9	1.46
0.06	51.7	2.67	86.7	16.33	36.5	1.44	47.3	2.47	46.7	2.19
0.07	47.0	2.21	70.5	5.97	32.9	1.22	46.4	2.16	54.8	3.03
0.08	44.2	1.98	68.3	5.39	29.5	1.05	37.1	1.47	44.8	2.03
0.09	42.0	1.81	62.8	4.21	27.1	0.93	32.1	1.84	38.1	1.54
0.1	40.7	1.71	46.3	2.16	23.5	0.77	29.0	0.98	31.0	1.12

a – percentage of extraction recovery, b – distribution ratio

Table 1C

Extraction behaviour of yttrium(III) as a function of diluents

γ (Y^{3+}) = 150 $\mu\text{g}/25\text{ cm}^3$, pH = 10.3, extractant = 0.17 mol dm^{-3} N-n-octylaniline in xylene (10 cm^3),
c (sodium salicylate) = 0.03 mol dm^{-3} , Aq : Org = 25 : 10 $\text{cm}^3:\text{cm}^3$,
Strippant = 0.05 mol dm^{-3} HCl (2 x 10 cm^3), equilibrium time = 5 min

Diluent	Dielectric constant ϵ	R (%)	Distribution ratio D
Benzene	2.28	95.8	57.02
Toluene	2.38	100	∞
Xylene	2.30	100	∞
Carbon tetrachloride	2.24	83.5	12.65
Chloroform	4.81	92.4	30.57
Kerosene	1.80	73.0	6.75
Methyl isobutyl ketone	13.11	70.0	5.83
n-Butanol	17.80	85.9	15.21
Amyl alcohol	13.90	66.0	4.85
1, 2-Dichloroethane	10.5	85.5	14.71

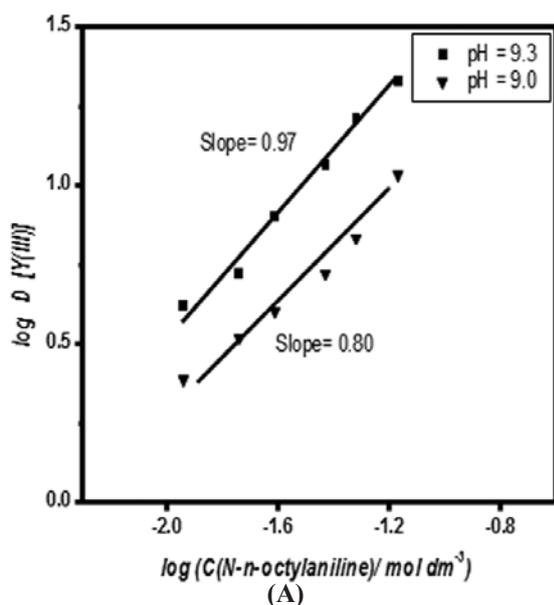
sodium succinate, sodium malonate, L-ascorbic acid and sodium citrate media. The quantitative extraction of yttrium(III) expressed by R (%) was found to be in the range of 0.02 – 0.05 mol dm⁻³ NaSal. Therefore, 0.03 mol dm⁻³ was used for further experimental investigations.

The formation of very stable complexes of yttrium(III) with NaSal prior to solvent extraction is a prerequisite.

The extraction of yttrium(III) was carried out with various solvents (S.D. Fine) (probably NOA was dissolved in various solvents). It was found that xylene is the most adequate solvent for quantitative extraction of yttrium(III) and preferred as a diluent for further extraction procedure (Table 1C).

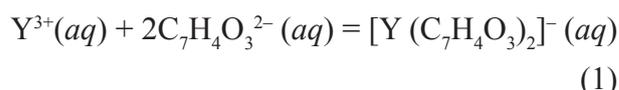
3.2. Nature of extracted species

The nature of extracted species was ascertained by using logD-logC plots. The graphs of log D_[Y(III)] against log C_[N-n-octylaniline] at fixed NaSal concentration (0.03 mol dm⁻³) were found to be linear and having slope values of 0.80 and 0.97 at pH 9.0 and 9.3, respectively (Figure 2A).

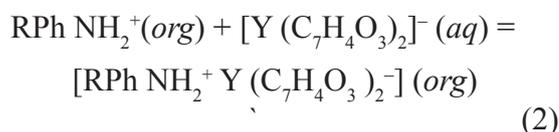


Also plots of log D_[Y(III)] against log C_[salicylate] at fixed N-n-octylaniline concentration (0.17 mol dm⁻³) were linear and slope values were found to be 1.75 and 2.05 at pH 9.0 and 9.3, respectively (Figure 2B). This indicates a mole ratio of yttrium(III) with respect to N-n-octylaniline as 1:1 and that of salicylate is 1:2. The nature of extracted species was found to be, 1 : 2 : 1 (metal : acid : extractant).

The probable mechanism of the formation of ion-pair complex as follows:



Then this complex reacts with N-n-octylanilinium cation, CH₃(CH₂)₇(C₆H₅)NH₂⁺, dissolved in xylene as follows:



The back extraction process would be

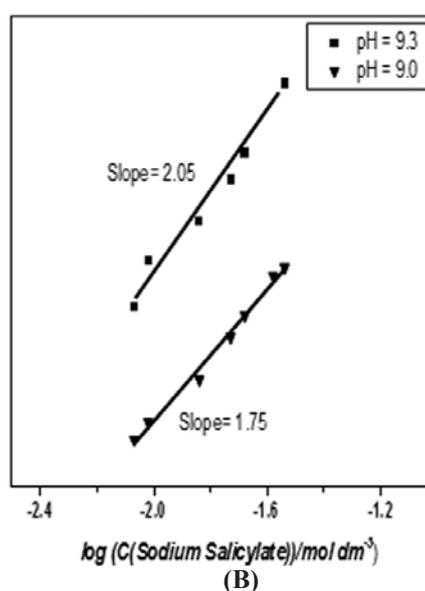
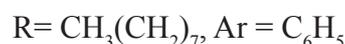
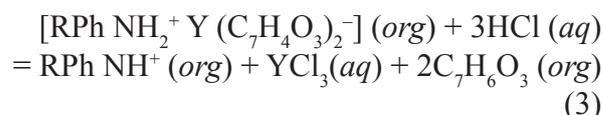


Fig. 2 (A) Log-log plot of log D_[Y(III)] against log (c (N-n-octylaniline) / mol dm⁻³) at fixed NaSal concentration (0.03 mol dm⁻³), γ(Y³⁺) = 150 μg/25 cm³, pH 9.0 and 9.3
(B) Log-log plot of log D_[Y(III)] against log (c (NaSal) / mol dm⁻³) at fixed N-n-octylaniline concentration (0.17 mol dm⁻³), γ(Y³⁺) = 150 μg /25 cm³, pH 9.0 and 9.3

3.3. Effect of stripping agents

It was found that, two 10 cm³ portions of HCl (0.03 – 0.06 mol dm⁻³), and HClO₄ (0.06 – 0.07 mol dm⁻³) were useful for quantitative stripping of yttrium(III) from the organic phase. Acetate buffer (pH 4.27) and water become unsuccessful for the recovery of yttrium(III) from organic solution (Table 1D). In actual practice, two 10 cm³ portion of 0.03 mol dm⁻³ HCl were found to be suitable stripping agent.

3.4. Effect of equilibration time, loading capacity of N-n-octylaniline, and effect of aqueous to organic volume ratio

The results indicate that the extraction is fast and 4 minute equilibrium time is adequate for quantitative extraction of yttrium(III). In general procedure, 5 min. equilibrium time was recommended in order to ensure the complete extraction of metal ion.

The loading capacity of the extractant was determined by the repeated contact of the

organic phase with a fresh feed solution of the metal of various concentrations. For a 10 cm³, 0.17 mol dm⁻³ solution of N-n-octylaniline in xylene at 0.03 mol dm⁻³ NaSal concentration and at *aq/org* phase ratio of 2.5 : 1, the maximum loading capacity for yttrium(III) was found to be 400 µg.

Results of contacting different volume ratios of aqueous (*aq*) to organic phase (*org*) indicate that a preferred *aq/org* phase ratio exists for the system under study, and this was found to be 5:1 or less. This is evident from the sharp increase in the separation factor as well as the distribution ratio of yttrium(III), when phase ratio *aq/org* was changed from 50 : 1 to 6 : 1. However, in the recommended procedure, the phase ratio used is 2.5 : 1 (25 : 10 cm³ : cm³), to avoid the large consumption of the NaSal.

3.5. Effect of diverse ions

The effect of various cations and anions in the separation and determination of yttrium(III) was studied by the recommended procedure

Table 1D

Extraction behaviour of yttrium(III) as a function of stripping agents

γ (Y³⁺) = 150 µg /25 cm³, pH = 10.3, extractant = 0.17 mol dm⁻³ N-n-octylaniline in xylene (10 cm³),
c (sodium salicylate) = 0.03 mol dm⁻³, Aq : Org = 25 : 10 cm³:cm³,
 Strippant = 0.05 mol dm⁻³ HCl (2 x 10 cm³), equilibrium time = 5 min

<i>c</i> /mol dm ⁻³	HCl	HClO ₄	HNO ₃	CH ₃ COOH	H ₂ SO ₄	NH ₄ Cl	KNO ₃
	R (%) ^a	R (%)	R (%)	R (%)	R (%)	R (%)	R (%)
0.01	77.3	73.0	84.7	68.3	92.1	58.6	9.5
0.02	90.6	77.1	53.2	69.1	80.7	60.4	2.8
0.03	100	90.6	57.0	70.1	62.9	61.6	2.4
0.04	100	95.1	74.1	73.0	44.6	62.5	15.4
0.05	100	95.5	68.2	64.1	16.9	63.9	10.5
0.06	100	99.0	64.6	60.8	00.0	66.3	15.6
0.07	96.9	99.4	45.8	57.6	00.0	76.1	18.9
0.08	93.4	98.2	42.6	52.6	00.0	79.1	20.1
0.09	90.6	95.9	36.1	51.4	00.0	92.2	24.5
0.10	85.4	94.3	31.8	47.6	00.0	96.6	25.0

Water = 4.0 %. Acetate buffer (pH 4.27) = 67.1 %. a – Percentage of extraction recovery

(Table 2). The tolerance limit was set by the amount of foreign ions causing a change $\pm 2\%$ error in the recovery of yttrium(III). Interference due to V(V), Zr(IV), Ce(IV) and Ti(IV) were eliminated by masking with 10 mg F⁻, Mn(II) was masked with 5 mg oxalate. EDTA, citrate and tartarate interfere.

4. APPLICATIONS

4.1. Separation and determination of yttrium(III) from binary mixtures

4.1.1 Separation of yttrium(III) from Th(IV), U(VI), Zr(IV), Nb(V), La(III) and Nd(III)

It was found that, metal ions (S.D. Fine) such as Th(IV), U(VI), Zr(IV), Nb(V), La(III)

and Nd(III) remained unextracted under the optimum extraction condition of yttrium(III) using 0.03 mol dm⁻³ NaSal with 10 cm³ 0.17 mol dm⁻³ *N-n*-octylaniline in xylene. The yttrium(III) was stripped with 0.05 mol dm⁻³ HCl (2 × 10 cm³) from organic phase and determined spectrophotometrically with alizarin red S. The aqueous phase was washed with 5 cm³ xylene to remove traces of the reagent. Metal ions from aqueous phase were determined by standard procedure [39–43].

4.1.2. Separation of yttrium(III) from Ce(IV)

The proposed method was also extended for separation of yttrium(III) from Ce(IV) by masking with 10 mg of fluoride. The masked

Table 2

Effect of foreign ions on the extraction of 150 µg yttrium(III) at pH 10.3 in 0.03 mol dm⁻³ sodium salicylate with 0.17 mol dm⁻³ N-n-octylaniline in xylene

Foreign ion	Added as	Tolerance limit/mg	Foreign ion	Added as	Tolerance limit/mg
Ca(II)	CaCl ₂	5.0	Nd(III)	Nd ₂ O ₃	0.3
Mg(II)	MgCl ₂ · 6H ₂ O	5.0	Sm(III)	Sm(NO ₃) ₃ · 6H ₂ O	0.3
Sr(II)	Sr(NO ₃) ₂	3.0	Rh(III)	RhCl ₃	0.2
Cr(VI)	K ₂ Cr ₂ O ₇	3.0	Ce(IV) ^a	Ce(SO ₄) ₂	0.2
Ni(II)	NiCl ₂ · 6H ₂ O	1.0	La(III)	La ₂ O ₃	0.2
W(VI)	Na ₂ WO ₄ · 2H ₂ O	1.0	Ti(IV) ^a	K ₂ · TiF ₆ · H ₂ O	0.2
U(VI)	UO ₂ (NO ₃) ₂ · 6H ₂ O	1.0	Nb(V)	Nb ₂ O ₅	0.2
Ba(II)	BaCl ₂ · 2H ₂ O	0.5	Thiourea	Thiourea	50
Co(II)	CoCl ₂ · 6H ₂ O	0.5	Bromide	Potassium bromide	50
Mn(II) ^b	MnCl ₂ · 6H ₂ O	0.5	Nitrate	Sodium nitrate	50
Cd(II)	CdCl ₂ · 2 1/2 H ₂ O	0.5	Thiosulphate	Sodium thiosulphate	25
Zn(II)	ZnSO ₄ · 7H ₂ O	0.5	Malonate	Sodium malonate	25
Pd(II)	PdCl ₂	0.5	Acetate	Sodium acetate	25
Fe(II)	FeSO ₄ · 7H ₂ O	0.5	Iodide	Potassium iodide	25
V(V) ^a	NH ₄ · VO ₃ · H ₂ O	0.5	Nitrite	Sodium nitrite	25
Mo(VI)	(NH ₄) ₆ Mo ₇ O ₂₄ · 2H ₂ O	0.5	Fluoride	Sodium fluoride	15
Zr(VI)	Zr(NO ₃) ₄	0.3	Ascorbate	Ascorbic acid	1.0
Ta(V)	Ta ₂ O ₅	0.3	Phosphate	Disodium hydrogen orthophosphate	0.5

^amasked with 10 mg F⁻, ^bMasked with 5 mg oxalate

Ce(IV) remained in the aqueous phase quantitatively. After demasking of Ce(IV) with 5 cm³ concentrated perchloric acid and evaporated to moist dryness, it was estimated spectrophotometrically with 0.1% arsenazo III at 535 nm [40]. Yttrium(III) was stripped from organic phase and determined.

4.1.3. Separation of yttrium(III) from Gd(III)

Under the optimum extraction procedure of yttrium(III), Gd(III) was coextracted in the organic phase. However, yttrium(III) from the organic phase was back stripped with 0.05 mol dm⁻³ HCl (2 × 10 cm³) while there is no back extraction of Gd(III). Yttrium(III) was determined via general procedure. Gadolinium(III) was stripped by 0.1 mol dm⁻³ HClO₄ (2 × 5 cm³)

and was determined spectrophotometrically [44] (Table 3).

4.2. Separation of yttrium(III) from synthetic mixtures

A solution containing 150 µg yttrium(III) was taken and known amount of other metals were added. Amount of yttrium(III) was extracted under the optimum extraction conditions. The results obtained were in good agreement with the amount added (Table 4).

5. CONCLUSION

The developed method is simple, rapid, selective, reproducible and suitable for separa-

Table 3

Separation of yttrium(III) from binary mixtures

γ (Y³⁺) = 150 µg / 25 cm³, pH = 10.3, extractant = 0.17 mol dm⁻³ N-n-octylaniline in xylene (10 cm³),
c (sodium salicylate) = 0.03 mol dm⁻³, Aq : Org = 25 : 10 cm³: cm³, strippant = 0.05 mol dm⁻³ HCl (2 × 10 cm³),
equilibrium time = 5 min

Metal ion	Mass of metal ion/µg	R (%) ^b	Chromogenic ligand	Reference number
Y(III)	150	98.3		
Th(IV)	50	98.8	Arsenazo III	40
Y(III)	150	99.4		
U(VI)	50	98.4	PAR	41
Y(III)	150	99.7		
Zr(IV)	150	98.5	Alizarin red S	39
Y(III)	150	99.5		
Nb(V)	50	98.9	PAR	41
Y(III)	150	99.6		
La(III)	60	99.7	Arsenazo I	43
Y(III)	150	99.3		
Nd(III)	60	100	PAR	42
Y(III)	150	98.8		
Ce(IV) ^a	50	99.0	Arsenazo III	40
Y(III)	150	99.4		
Gd(III)	75	99.28	Arsenazo I	44

^amasked with 10 mg F⁻, ^bAverage of six determinations.

tion and determination of yttrium(III) from binary and synthetic mixture of associated metal ions. The extraction mechanism corresponds to an anion exchange, in which a complex of stoichiometric formula $[RPh NH_2^+ Y (C_7H_4O_3)_2^-]$ (*org*) is formed in the organic phase. The used solvent, xylene, is less toxic and quite suitable for applied method. The extraction reagent, *N*-*n*-octylaniline, can be synthesized at low cost, with high yield and purity.

Acknowledgements: Mr. B. N. Kokare is grateful to University Grants Commission, New Delhi, for providing financial assistance. The authors thank to UGC-SAP and DST-FIST for financial support for this research work.

REFERENCES

- [1] M.H. Chhatre, V.M. Shinde, Analytical separation of scandium(III) from yttrium(III) and lanthanum(III) by tributyl phosphine oxide (TBPO), *Sep. Purif. Technol.* **17**, 117–124 (1999).
- [2] M.H. Chhatre, V.M. Shinde, Separation of scandium(III) and yttrium(III) by tris(2-ethylhexyl)phosphate (TEHP), *Talanta* **47**, 413–419 (1998).
- [3] D. Wu, C. Niu, D. Li, Y. Bai, Solvent extraction of scandium(III), yttrium(III), lanthanum(III) and gadolinium(III) using cyanex 302 in heptane from hydrochloric acid solution, *J. Alloys Compd.* **374**, 442–446 (2004).
- [4] M. Karve, B. Vaidya, Selective separation of scandium(III) and yttrium(III) from other rare earth elements using cyanex 302 as an extractant, *Sep. Sci. Technol.* **43**, 1111–1123 (2008).
- [5] B. Gupta, P. Malik, A. Deep, Solvent extraction and separation of trivalent lanthanides and yttrium using Cyanex 923, *Solvent Extr. Ion Exch.* **21**, 239–258 (2003).
- [6] M.L. P. Reddy, R.L. Varma, T.R. Ramamohan, K.S. Sahu, V. Chakravorty, Cyanex 923 as an extractant for trivalent lanthanides and yttrium, *Solvent Extr. Ion Exch.* **16**, 795–812 (1998).
- [7] E. Antico, A. Masana, M. Hidalgo, V. Salvado, M. Iglesias, M. Valiente, Solvent extraction of yttrium from chloride media by di(2-ethylhexyl)phosphoric acid in kerosene. Speciation studies and gel for-

Table 4

Separation of yttrium(III) from synthetic mixtures corresponding to commonly associated metal ions

Composition of mixture		Yttrium(III) mass found µg	R (%) ^a	RSD (%)
Ion	metal mass/ µg			
Y(III)	150			
Fe(III)	60	148.8	99.2	0.33
U(VI)	50			
Y(III)	150			
Ce(IV) ^b	50	149.4	99.6	0.10
La(III)	60			
Y(III)	150			
Fe(III)	60	148.8	99.2	0.20
Zr(IV)	150			
Y(III)	150			
U(VI)	50	149.1	99.4	0.20
Th(IV)	50			
Y(III)	150			
Ca(II)	40	149.0	99.3	0.31
Fe(III)	60			
Y(III)	150			
Fe(III)	60	148.8	99.2	0.27
Th(IV)	50			

^aAverage of triplicate analysis, ^bmasked by 10 mg fluoride

- mation, *Anal. Chim. Acta* **327**, 267–276 (1996).
- [8] F. Bunu, R. Dumitrescu, Simultaneous extraction of rare earth elements and uranium from phosphoric acid, *Hydrometallurgy* **28**, 331–338 (1992).
- [9] M. Iglesias, E. Antico, V. Salvado, A. Masana, M. Valiente, Effect of Y(III) distribution between aqueous nitrate and organic D2EHPA solutions on Y(III) precipitation stripping using oxalic acid, *Solvent Extr. Ion Exch.* **17**, 277–300 (1999).
- [10] S. Nishihama, T. Hirai, I. Komasa, Selective extraction of yttrium from a Ho/Y/Er mixture by liquid-liquid extraction in the presence of a water-soluble complexing agent, *Ind. Eng. Chem. Res.* **39**, 3907–3911 (2000).
- [11] X. Sun, J. Zhao, S. Meng, D. Li, Synergistic extraction and separation of yttrium from heavy rare earths using mixture of sec-octylphenoxy acetic acid and bis(2,4,4-trimethylpentyl) phosphinic acid, *Anal. Chim. Acta* **533**, 83–88 (2005).
- [12] Y.G. Wang, S.T. Yue, D.Q. Li, M.J. Jin, C.Z. Li, Solvent extraction of scandium(III), yttrium(III), lanthanides(III), and divalent metal ions with sec-nonylphenoxy acetic acid, *Solvent extr. Ion Exch.* **20**, 701–716 (2002).
- [13] X. Sun, Y. Wang, D. Li, Selective separation of yttrium by CA-100 in the presence of a complexing agent, Proceedings of Rare Earths'04 in Nara, Japan, *J. Alloys Compd.* **408–412**, 999–1002 (2006).
- [14] Y.G. Wang, Y. Xiong, S.L. Meng, D.Q. Li, Separation of yttrium from heavy lanthanides by CA-100 using the complexing agent, *Talanta* **63**, 239–143 (2004).
- [15] Y.K. Agrawal, S.K. Menon, S. Sudhakar, Solvent extraction and separation of yttrium with dibenzo-18-crown-6, *Sep. Purif. Technol.* **24**, 197–203 (2001).
- [16] W. Li, X. Wang, S. Meng, D. Li, Y. Xiong, Extraction and separation of yttrium from the rare earths with sec-octylphenoxy acetic acid in chloride media, *Sep. Purif. Technol.* **54**, 164–169 (2007).
- [17] J.S. Preston, Solvent extraction of the trivalent lanthanides and yttrium by some 2-bromoalkanoic acids, *Solvent Extr. Ion Exch.* **12**, 29–54 (1994).
- [18] J.S. Preston, A.C. Du Preez, Synergistic effect in solvent extraction system based on alkyl salicylic acids III. Extraction of the trivalent lanthanides and yttrium from chloride media in the presence of dialkyl and diaryl sulphoxides, *Extr. Ion Exch.* **14**, 755–772 (1996).
- [19] D. Czakis-Sulikowska, N. Pustelnik, A. Malinowska, B. Kuznik, Solvent extraction of yttrium(III), gadolinium(III), terbium(III), thulium(III) and ytterbium(III) with 5,7-dichloro-8-hydroxyquinoline from water and water-methanol solutions, *Chem. Anal.* **42**, 23–25 (1997).
- [20] D.K. Singh, H. Singh, J.N. Mathur, Extraction of rare earths and yttrium with high molecular weight carboxylic acids, *Hydrometallurgy* **81**, 174–181 (2006).
- [21] A. Shimada, T. Yaita, H. Narita, S. Tachimori, K. Okuno, Extraction of lanthanide(III) ions with N,N'-dimethyl-N,N'-diphenylpyridine-2,6-dicarboxamide (DMDPhPDA) from nitric acid solution, *Solvent Extr. on Exch.* **22**, 147–161 (2004).
- [22] J.S. Preston, A.C. Du Preez, Solvent extraction of the trivalent lanthanides and yttrium from nitrate media by dialkyl sulphoxides, *Solvent Extr. Ion Exch.* **19**, 581–595 (2001).
- [23] M.R. Yaftian, M. Vahedpoor, M. Burgard, D. Matt, Solvent extraction and transport of rare earth metal ions using 5,11,17,23-tetra-tert-butyl-25,27-bis(diethylcarbamoyl methoxy)-26,28-dihydroxycalix[4] arene, *Iran. J. Chem. & Chem. Eng.* **19**, 60–64 (2000).
- [24] F. Kubota, K. Shinohara, K. Shimojo, T. Oshima, M. Goto, S. Furusaki, T. Hano, Extraction of rare earth metals by calyx[4]arene solubilised in AOT reversed micellar solution, *Sep. Puri. Technol.* **24**, 93–100 (2001).
- [25] D.D. Desai, V.M. Shinde, Liquid anion-exchange extraction and separation of yttrium, neodymium and samarium, *Anal. Chim. Acta* **167**, 413–417 (1985).
- [26] A.G.I. Dalvi, C.S. Deodhar, B.D. Joshi, Chemical separation and spectrographic estimation of rare earths and yttrium in PuO₂ and (U, Pu)O₂, *Talanta* **24** (1977), 143–145.
- [27] S. A. Sayed, T. A. Sami, A. A. Abd El Tawab, Synergistic extraction of some rare earths(III) from nitrate media by thenoyltrifluoroacetone and tri-n-octylamine, *Sep. Sci. Technol.* **31**, 2579–2587 (1996).
- [28] O.A. Desouky, A.M. Daher, Y.K. Abdel-Monem, A.A. Galhoum, Liquid-liquid extraction of yttrium using Primene-JMT from acidic sulfate solutions, *Hydrometallurgy* **96**, 313–317 (2009).
- [29] A.K. Pyartman, V.V. Lishchuk, V.A. Keskinov, Extraction of thorium(IV), lanthanum(III) and yttrium(III) nitrates with a composite solid extract-

- ant based on a polymeric support impregnated with trialkylamine, *Russian J. Applied Chem.* **79**, 1266–1270 (2006).
- [30] A.K. Pyartman, V.A. Keskinov, V.V. Lishchuk, A.V. Konstantinova, V.V. Belova, Extraction of Th(IV), La(III) and Y(III) nitrates with a composite solid extractant based on a polymeric support impregnated with trialkylmethylammonium nitrate, *Russian J. Applied Chem.* **79**, 1802–1807 (2006).
- [31] T.N. Lokhande, M.A. Anuse, M.B. Chavan, Liquid-liquid extraction of palladium(II) with *N-n*-octylaniline from hydrochloric acid media, *Talanta* **46**, 163–169 (1998).
- [32] B.M. Sargar, M.M. Rajmane, M.A. Anuse, Selective liquid-liquid extraction of antimony(III) from hydrochloric acid media by *N-n*-octylaniline in xylene, *J. Serb. Chem. Soc.* **69**, 283–298 (2004).
- [33] S.S. Kolekar, M.A. Anuse, Selective liquid-liquid extraction of platinum(IV) from ascorbate media by *N-n*-octylaniline: Its separation from associated elements and real samples, *Sep. Sci. Technol.* **38**, 2597–2618 (2003).
- [34] S.S. Kolekar, M.A. Anuse, Solvent extraction separation of rhodium(III) with *N-n*-octylaniline as an extractant, *Talanta* **58**, 761–771 (2002).
- [35] M.M. Rajmane, B.M. Sargar, S.V. Mahamuni, M.A. Anuse, Solvent extraction separation of zirconium(IV) from succinate media with *N-n*-octylaniline, *J. Serb. Chem. Soc.* **71**, 233–234 (2006).
- [36] B.M. Sargar, M.A. Anuse, Liquid-liquid extraction of tellurium(IV) with *N-n*-octylaniline in halide medium and its separation from real samples, *Talanta* **55**, 469–478 (2001).
- [37] F.J. Welcher, *The Analytical Uses of Ethylenediamine tetraacetic Acid*, D. Van Nostrand Company Inc. New York, London, 1958, pp. 50, 185.
- [38] Z.G. Gardlund, R.J. Curtis, G.W. Smith, Influence of molecular structural changes on the mesomorphic behavior of benzylideneanilines, *Liquid Crystals Ordered Fluids Liq., Crystals Ordered Fluids* **2**, 541–545 (1973).
- [39] E.B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience Publishers Inc. New York, London, Third Edition, 1965, pp. 748, 969.
- [40] M. Zygmont, *Spectrophotometric determination of Elements*, John Wiley and Sons. Inc. New York, First Edition, 1976, pp. 442, 443, 540.
- [41] H.A. Flaschka, A.J. Barnard Jr, Chelates in *Analytical Chemistry*, Volume 4, Marcel Dekker Inc., New York, 1972, pp. 148, 162.
- [42] K.N. Munshi, A.K. Dey, Spectrophotometric determination of rare earth metals with 4-(2-pyridylazo) resorcinol, *Anal. Chim.* **36**, 2003–2004 (1964).
- [43] S. Shibata, F. Takerchi, T. Matsumae Spectrophotometric determination of lanthanum(III) with Neothoron, *Anal. Chim Acta*, **21** 177–181 (1959).
- [44] M.R. Shivade, V.M. Shinde, Extraction of gadolinium with liquid ion exchangers, *Fresenius Z. Anal. Chem.* **317**, 792–795 (1984).