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ICP-AES determination of trace metallic constituents in thorium matrix after preferential extraction of thorium using TBP, TOPO and DHOA: a comparative study

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Abstract ICP-AES based methodology was developed for the determination of trace metallic constituents in thorium matrix after preferential extraction of thorium using TBP, TOPO and DHOA. The distribution ratio for thorium followed the trend TOPO > TBP > DHOA with the formation of 1:2 complex. Oxalic acid was found to strip Th effectively. La, Ce, Pr, Gd, Dy, Lu can be determined at 0.1 mg L^{-1} using all the ligands, while common analytes can be determined at 0.1, 0.5 and 1 mg L^{-1} concentrations by using DHOA, TBP and TOPO, respectively.

Keywords Thorium · Trace metal assay · TBP · TOPO · DHOA · Preferential extraction

Introduction

Trace metallic impurity analysis is one of the prime steps for chemical quality control of nuclear fuels and associated materials [1–4]. Presence of these elements beyond the specification limits not only modifies the overall neutron economy and fissile content of the fuel materials, also changes their metallurgical properties. ICP-AES being multielemental technique with good analytical performance is used for trace metal assay in nuclear materials [5–9]. The major problem encountered in this case is the spectral interference of matrix element like U, Pu, Zr, Th etc., having line rich emission spectra [10–15]. Chemical separation of the major matrix followed by the determination of analytes in the raffinate is well accepted protocol in nuclear industry [16–20].

As uranium reserves are depleted, thorium would supplement uranium as a fertile material in a three stage nuclear power programme of India [21]. Tri-n-butyl phosphate (TBP) is known as work-horse for nuclear industries in Plutonium Uranium Reduction Extraction (PUREX) process and its analytical applications [22–25]. Cyanex 923 has also been utilized for preferential extraction of thorium for the determination of trace analytes [26]. Since both of them are phosphorous based ligands, they are not completely incinerable. Hence, there is always a hunt for environmentally benign ligand which can serve the purpose of selective separation of emission rich matrix element thorium without loss of the analytes even at the trace level. In view of this, di-n-hexyl octanamide (DHOA) was employed for the determination of trace metallic constituents in plutonium and uranium matrices [27–29].

In the present case, a comparative study was carried out on thorium extraction by TBP, TOPO and DHOA. It includes understanding the nature of the complex, evaluation of different thermodynamic constants during extraction and stripping of metal ion. Finally, to apply the solvent system for the trace level determination of analytes (Ag, Al, B, Ba, Bi, Ca, Cr, Cu, Cd, Co, Fe, Ga, In, K, Mn, Mg, Na, Ni, Pb, Sr, Zn, La, Ce, Pr, Gd, Dy and Lu) in thorium matrix.

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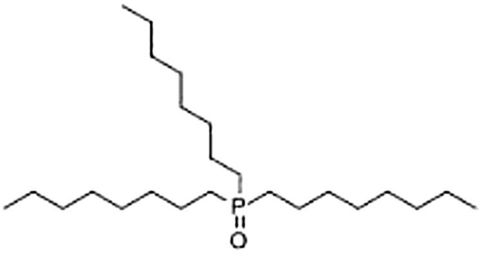
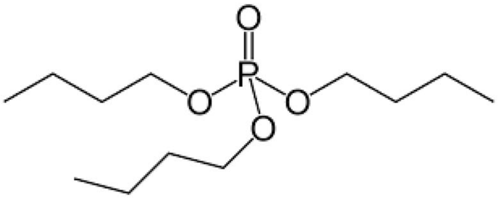
Experimental

Reagents and standard solutions

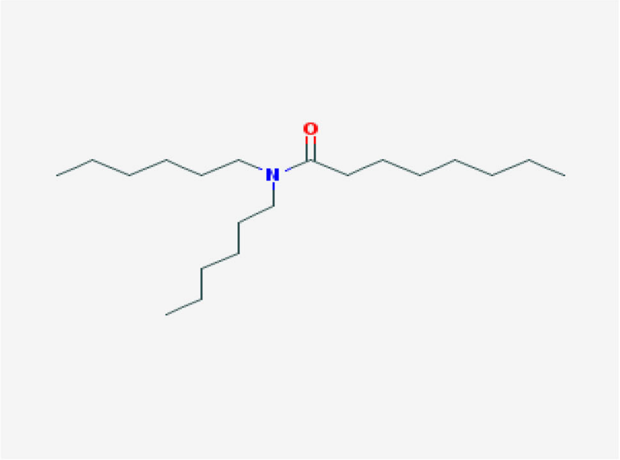
Standard solutions for the analytes were prepared from CertiPUR® ICP multi standard solutions (E-Merck, Darmstadt, Germany). Supra- pure HNO_3 (E-Merck, Darmstadt, Germany) and quartz double distilled water were used throughout the study. Th stock solution was prepared by dissolving high purity ThO_2 powder using HF-HNO_3. After repeated evaporation to dryness (for removal of fluoride ion) the feed was adjusted to 3 M HNO_3. Xylene was procured from Prabhat Chemicals, Gujrat Mumbai, whereas oxalic acid and Na_2CO_3 were procured from Thomas Baker Chemical Limited and Qualigens fine Chemicals, Mumbai, India, respectively. TBP was procured from Koch-Light Laboratories, USA. DHOA was synthesized by previously reported method [29]. The structures of the ligands i.e. TBP, TOPO and DHOA were shown in Fig. 1.



TOPO (tri-n-octyl phosphine oxide)



TBP (tri-n- butyl phosphate)



DHOA (dihexyl octanamide)

Fig. 1 Structures of the ligands, TOPO, TBP and DHOA

Methods

All the solvent extraction experiments were carried out using 5 mL of the aqueous phase and 5 mL of organic phase containing ligand. After half an hour of shaking at 300 K to achieve complete equilibration, the reaction mixture was allowed to settle for 2 min. Then suitable aliquots were taken for the subsequent studies.

For tracer studies, liquid scintillation counting technique was used while for bulk analysis ICP-AES technique was used.

The distribution ratio values (D_{Th}) were calculated as the ratio of the total analytical concentration of Th in the organic phase to that in the aqueous phase. Higher D_{Th} values indicate higher extraction efficiency of thorium. Since D_{Th} is the ratio of analytical concentration, it is thus unitless.

Instrumentation

A computer controlled, high resolution, atomic emission spectrometer (Spectro Arcos, Germany) with ICP and DC Arc as excitation sources and charged coupled device (CCD) as detector was used for carrying out all the analytical experiments. The instrumental specifications and experimental parameters are summarized in Table 1.

Results and discussion

Extraction profiles of thorium

The main aim of the above investigation is the preferential and quantitative extraction of thorium to such an extent that it does not have spectral interference on the determination of analytes. During this separation, the elements of interest should not be co-extracted into the organic phase along with thorium even in trace amount. Mainly phosphorous based ligands were found to extract uranium from moderately acidic solution. TBP is the ideal choice for the extraction of thorium. The k_H value for TOPO was found to be more than that of TBP, indicating higher electron donating efficiency of TOPO. DHOA was reported to be the potential alternative to TBP and TOPO. In view of these, the comparative study was taken up for development of methodology for the determination of trace metallic constituents at trace and ultra trace level in thorium matrix.

It is desirable to use an efficient ligand to reduce the number of contact of the organic phase. The extraction profiles were established for thorium using TBP, TOPO and DHOA in xylene at various feed acidity to obtain

Table 1 Specifications and operating conditions of ICP-AES

Instrumental specification	
Optical design	Paschen–Runge mounting, Circular design
Focal length	750 mm
Grating	Holographic
Groove density	1800 grooves/mm (1), 3600 grooves/mm (2)
Wave length range	130–800 nm
Entrance slit width	15 microns
Resolution (FWHM)	0.01 nm from 130 to 450 nm 0.02 nm from 450 to 800 nm
Thermal regulation	Controlled to 30 ± 1 °C
Frequency	27.12 MHz
Pump	Dual channel peristaltic pump
Detector	Linear arrays of CCD (3648 pixels/array)
Nebulizer	Concentric nebulizer with cyclonic spray chamber
ICP-torch	Demountable, radial viewing
Operating condition	
Coolant flow	16 L min^{-1}
Auxiliary flow	0.6 L min^{-1}
Total time of measurement	28 s
Pump speed	30 Rpm
RF power out put	1.2 Kw
Input power	230 V AC

almost quantitative separation of thorium. For 1.1 M TBP, the D_{Th} was found to increase gradually with feed acidity up to 2 M HNO_3 followed by a plateau with D_{Th} $\sim$15. At higher feed acidity the distribution ratio was found to decrease. Since TBP is known to extract metal ion by ‘solvation’ mechanism, the initial rise can be due to the law of mass action. At higher acidity, the enhanced H^+ ion competes with thorium resulting the plateau or decrease in D_{Th} value. In case of DHOA the D_{Th} value increases up to 1 M HNO_3 followed by a plateau with D_{Th} $\sim$5. Similar trend was also observed in case of TOPO with D_{Th} $\sim$35. The D_{Th} value was found to follow the order TOPO > TBP > DHOA. The observed trend may be attributed to the basicity of the ligands. The conditional acid uptake constant was found to be $\sim$0.2 for TBP and $\sim$8.9 for TOPO [30, 31]. The variation of D_{Th} using TOPO, TBP and DHOA as a function of feed acidity was shown in Fig. 2. The above study also revealed that 3–4 M HNO_3 should be the ideal feed acid concentration for the effective separation of Th. The overall extraction process can be expressed by the following equation

$$Th^{4+}_{aq} + 4NO^{-}_{3_{aq}} + mL_{or} = [Th(NO_3)_4 \cdot mL]_{or} \tag{1}$$

$$H^{+}_{aq} + NO^{-}_{3_{aq}} + nL_{or} = [HNO_3 \cdot nL]_{or} \tag{2}$$

where, ‘aq’ and ‘or’ represent the aqueous and organic phase respectively, ‘*m*’ and ‘*n*’ represent the number of ligand molecules associated with Th^{4+} and H^+, respectively ‘L’ represents the ligands (TBP, DHOA, TOPO).

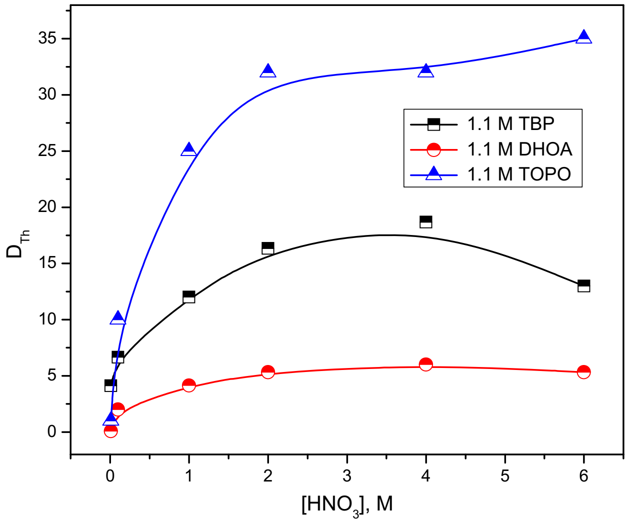


Fig. 2 Variation of distribution ratio of thorium as a function of HNO_3 feed acidity

Effect of thorium concentration on D_{Th}

Though, the approach of reporting *D* values for tracer is very effective in understanding the basic chemistry of the metal ion, the actual scenario is quite different. When we are dealing with the bulk of metal ion, the extraction efficiency is expected to reduce due to the decrease in the effective concentration of the ligand molecules. In view of this, D_{Th} values were determined as a function of Th concentration (Fig. 3). The D_{Th} values were found to be 35, 15 and 5 for TOPO, TBP and DHOA at trace level concentration of Th while they became 12, 7 and 1, respectively at 1000 mg L^{-1} concentration of Th.

Number of contact of organic phase

The D_{Th} values obtained so far revealed that it is not possible to extract the thorium almost quantitatively by using any of these ligands in a single stage of extraction. Muli-stage extraction is therefore necessary. The main objective was to evaluate the number of contact required to bring down the Th concentration from 1000 mg L^{-1} to less than 1 mg L^{-1}. In case of 1.1 M TBP in xylene, after three contacts of equivolume of organic phase the Th concentration in raffinate became ~1 mg L^{-1}. Therefore, fourth contact of TBP-xylene was found to be sufficient to avoid the spectral interference of Th. In case of 1.1 M TOPO in xylene even third contacts of the organic phase with phase ratio 1 was found to be sufficient to bring down the Th level in raffinate at less than 1 mg L^{-1}. After fourth contact of TOPO-Xylene, the raffinate was found to contain only 0.003 mg L^{-1} of Th. In case of 2 M DHOA, after fourth contact of organic phase the Th concentration in the raffinate was found to be more than 1 mg L^{-1}. Therefore, fifth contact was necessary to bring down the Th level in the raffinate below 1 mg L^{-1}. Figure 4 summarizes the above study.

Determination of metal–ligand stoichiometry

The metal–ligand stoichiometry and the thermodynamics associated with the separation process were investigated. In order to that, the D_{Th} value was varied as a function of ligands concentrations. From Eq. 1, the equilibrium constant for extraction can be represented as

$$K_{\mathrm{ex}} = \frac{[\mathrm{Th(NO_3)_4}.m\mathrm{L}]_{\mathrm{or}}}{[\mathrm{Th}^{4+}]_{\mathrm{aq}}[\mathrm{NO_3^-}]^4_{\mathrm{aq}}[\mathrm{L}]^m_{\mathrm{or}}} \tag{3}$$

$$K_{\mathrm{ex}} = \frac{D_{\mathrm{Th}}}{[\mathrm{NO_3^-}]^4_{\mathrm{aq}}[\mathrm{L}]^m_{\mathrm{or}}} \tag{4}$$

Taking logarithm in both side and rearranging the Eq 4 one can obtain

$$\log D_{\mathrm{Th}} = \log K'_{\mathrm{ex}} + m.\log\,[\mathrm{L}]_{\mathrm{or}} \tag{5}$$

where, K'_{ex} is conditional extraction constant. From Eq. (5), it can be revealed that a plot of log D_{Th} as a function of log ligand concentration can give a straight line. From the slope, the number of ligand molecules per metal ion can be determined while the intercept can give the conditional extraction constant and from it the free energy change of the extraction process can be evaluated by the following equation

$$\Delta G = -2.203\,RT\log K'_{\mathrm{ex}} \tag{6}$$

A variation of D_{Th} values as a function of TBP, TOPO and DHOA concentration was shown in Fig. 5 while Table 2 summarized the slope and intercepts value along with metal ligand stoichiometry, conditional extraction constants and change in Gibb's free energy. The above study revealed that for all the ligands, two ligand molecules

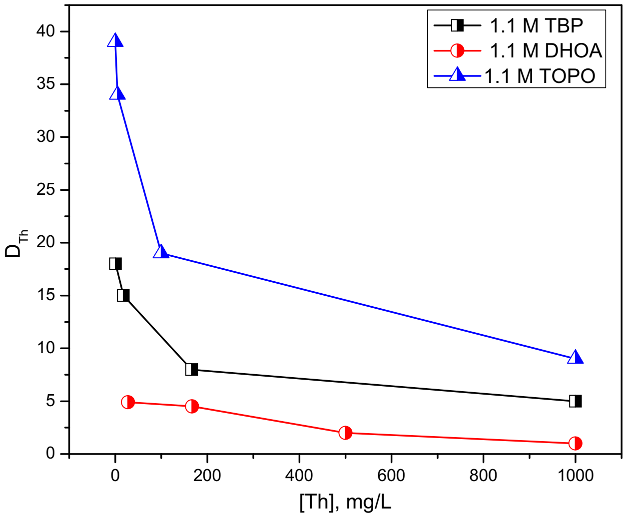


Fig. 3 Variation of distribution ratio of thorium as a function of thorium loading in aqueous phase

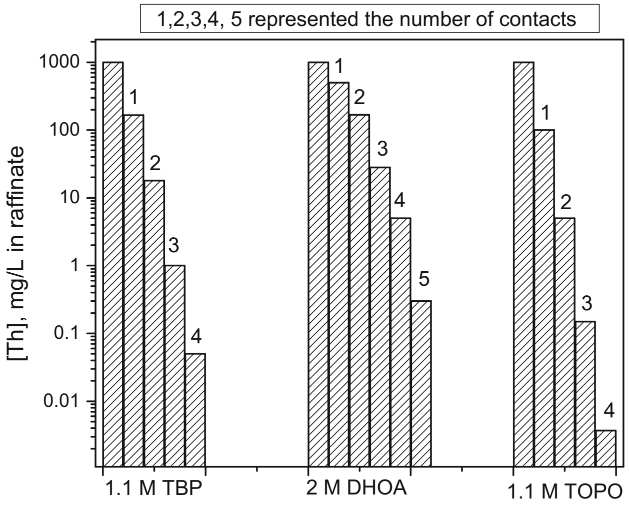


Fig. 4 Variation of distribution ratio of thorium as a function of the number of contacts of organic phase

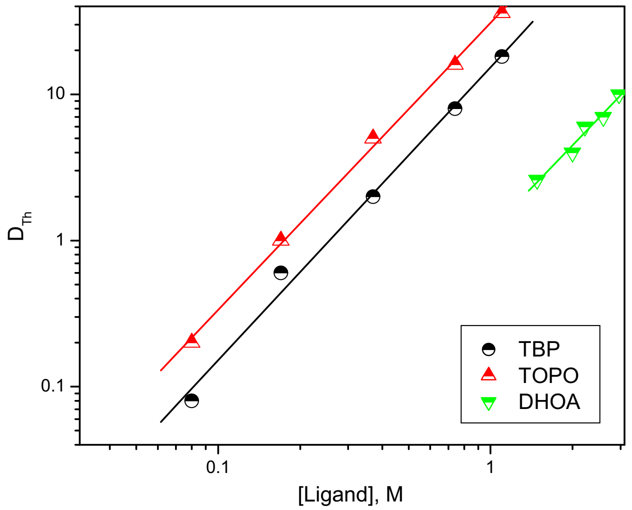


Fig. 5 Variation of distribution ratio of thorium as a function of ligand concentration

Table 2 Determination of metal–ligand stoichiometry, conditional extraction constant and change in Gibb's free energy

Ligand	Slope	Intercept	Metal: ligand	K'_{ex}	ΔG (kJ/mol)
TBP	2.00	1.19	1:2	15.48	−6.84
TOPO	1.96	1.48	1:2	30.19	−8.50
DHOA	1.93	0.06	1:2	1.14	−0.34

are associated with each thorium ion while the conditional extraction constants for thorium were found to follow the trend TOPO > TBP > DHOA. In case of of TOPO, three n-octyl groups were attached to the phosphoryl oxygen. The +I effect (inductive effect) of these three alkyl group enhances the electron density on the phosphorous hence on the oxygen. As a result of this, the phosphoryl O of TOPO showed maximum electron donating capabilities compared to the other two ligands. In case of TBP, three butoxy groups were attached to the P atom. The −I effect of butoxy group reduces the electron density over phosphoryl P and hence the electron donating ability of TBP was found to be poorer than TOPO. Due to similar size of C and O atom, the back bonding of carbonyl O to carbonyl C is more effective than the similar type of backbonding in case of phosphoryl moieties (P=O). As a consequence, the electron density on ligating oxygen will be less in case of DHOA compared to TOPO or TBP.

The negative change in Gibb's free energy revealed that the separation processes were energetically favourable. Though all the extraction processes were found to be thermodynamically favorable, the most favorable process was Th extraction by TOPO. Since for all the extraction systems, the metal–ligand stoichiometry was found to be 1:2. The ligand which posses stronger electron donating ability to the metal ion is expected to release more energy on complexation. As a matter of fact, the process will be spontaneous (negative ΔG value). As it was observed that the strength of the ligands followed the trend: TOPO > TBP > DHOA, same trend was seen in the spontaneity of the separation process.

Stripping of Th from the organic phase

It is required to recover thorium from the loaded organic phase to evaluate the reusability of the solvent systems. In view of these, 0.01 M HNO_3, 0.05 M oxalic acid and 0.05 M Na_2CO_3 were used for the stripping of thorium from loaded organic phase. 0.01 M HNO_3 was found to be effective in stripping only 70, 83 and 66 % of the loaded Th from TBP, DHOA and TOPO extracts, respectively while using 0.05 M Na_2CO_3, 95, 98 and 70 % of the loaded Th were recovered. 0.05 M oxalic acid being a stronger complexing agent was found to recover more than 90 % of Th from TBP and DHOA extracts while only 84 % Th was found to be back extracted from the TOPO extracts. Figure 6 shows pictorially the stripping studies. Based on the above study, 0.05 M oxalic acid and 0.05 M Na_2CO_3 were found to be fruitful. The back extraction from TOPO extract was not very due to the formation of stronger Th-TOPO complex.

Analysis of synthetic samples

The above study demonstrated the efficacy of TBP, TOPO and DHOA for the extraction of Th. For its real analytical application, a series of synthetic samples were prepared

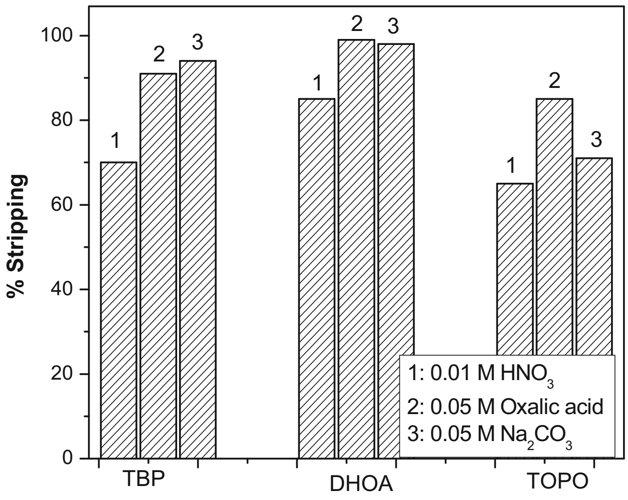


Fig. 6 Stripping of thorium from the extracted organic phase

Table 3 Analysis of thorium blank solution (process blank) after processing with TBP, TOPO and DHOA

Metal ion	Initial conc. (mgL^{-1})	TBP (mgL^{-1})	TOPO (mgL^{-1})	DHOA (mgL^{-1})
La	0.011	0.01	0.008	0.01
Ce	0.008	0.007	0.005	0.008
Pr	0.007	0.005	0.004	0.006
Gd	0.01	0.01	0.008	0.009
Dy	0.009	0.008	0.006	0.009
Lu	0.009	0.009	0.005	0.009
Ag	0.008	0.006	0.005	0.008
Al	0.007	0.007	0.005	0.006
B	0.01	0.009	0.007	0.009
Ba	0.008	0.007	0.006	0.008
Bi	0.006	0.004	0.004	0.006
Pb	0.011	0.01	0.007	0.01
Zn	0.009	0.008	0.007	0.009
Ca	0.008	0.008	0.006	0.008
Cr	0.009	0.008	0.006	0.009
Cu	0.007	0.006	0.005	0.007
Cd	0.011	0.011	0.01	0.01
Co	0.01	0.01	0.009	0.01
Fe	0.006	0.006	0.005	0.006
Ga	0.005	0.005	0.003	0.005
In	0.007	0.005	0.005	0.006
K	0.008	0.005	0.005	0.008
Mn	0.008	0.005	0.005	0.008
Mg	0.01	0.008	0.007	0.01
Na	0.011	0.009	0.007	0.01
Ni	0.01	0.009	0.007	0.01

with varying concentration of common metallic constituents and rare earth elements. These synthetic samples were subjected to chemical separation followed by the analysis of raffinate. The Th stock solution was characterized by intra laboratory comparison experiments involving different laboratories experiments involving different laboratories of Department of Atomic Energy, India. The analytical results were shown in Table 3. The blank samples after chemical separation were also analyzed to investigate whether there is any process pick up of the analytes. The values reported in Table 3 are having a RSD within 5 %.

The synthetic samples were prepared by the following procedure

1. S1: 0.1 mg L^{-1} of La, Ce, Pr, Gd, Dy, Lu in 1000 mg L^{-1} of Th matrix
2. S2: 1 mg L^{-1} of La, Ce, Pr, Gd, Dy, Lu in 1000 mg L^{-1} of Th matrix
3. S3: 5 mg L^{-1} of La, Ce, Pr, Gd, Dy, Lu in 1000 mg L^{-1} of Th matrix

Table 4 Determination of rare earth elements in presence of Th matrix in synthetic samples after chemical separation

Metal ion	Amount added (mg L^{-1})	Amount estimated (mg L^{-1})			Amount added (mg L^{-1})	Amount estimated (mg L^{-1})			Amount added (mg L^{-1})	Amount estimated (mg L^{-1})		
		1.1 M TBP	1.1 M TOPO	2 M DHOA		1.1 M TBP	1.1 M TOPO	2 M DHOA		1.1 M TBP	1.1 M TOPO	2 M DHOA
La	0.1	0.096 ± 0.002	0.090 ± 0.004	0.102 ± 0.003	1	1.05 ± 0.07	0.93 ± 0.08	1.02 ± 0.05	5	4.7 ± 0.3	5.2 ± 0.3	5.1 ± 0.2
Ce	0.1	0.106 ± 0.004	0.091 ± 0.004	0.097 ± 0.004	1	0.95 ± 0.08	0.99 ± 0.06	1.04 ± 0.05	5	5.3 ± 0.4	4.9 ± 0.2	4.8 ± 0.2
Pr	0.1	0.095 ± 0.006	0.098 ± 0.005	0.099 ± 0.005	1	0.98 ± 0.07	1.02 ± 0.05	0.95 ± 0.08	5	4.9 ± 0.2	5.1 ± 0.2	5.0 ± 0.2
Gd	0.1	0.101 ± 0.005	0.103 ± 0.005	0.104 ± 0.005	1	1.03 ± 0.05	1.05 ± 0.05	0.99 ± 0.06	5	4.9 ± 0.2	4.7 ± 0.3	5.1 ± 0.3
Dy	0.1	0.096 ± 0.002	0.099 ± 0.004	0.098 ± 0.006	1	1.06 ± 0.05	0.99 ± 0.06	1.02 ± 0.04	5	5.0 ± 0.3	5.2 ± 0.3	5.1 ± 0.3
Lu	0.1	0.096 ± 0.002	0.099 ± 0.004	0.105 ± 0.003	1	0.97 ± 0.03	1.06 ± 0.06	0.99 ± 0.04	5	4.7 ± 0.3	4.8 ± 0.3	5.0 ± 0.4

Table 5 Determination of common analytes in presence of Th matrix in synthetic samples after chemical separation

Mteal ion	Amount added (mg/L)	Amount estimated (mg L^{-1})			Amount added (mg L^{-1})	Amount estimated (mg L^{-1})			Amount added (mg L^{-1})	Amount estimated (mg L^{-1})		
		1.1 M TBP	1.1 M TOPO	2 M DHOA		1.1 M TBP	1.1 M TOPO	2 M DHOA		1.1 M TBP	1.1 M TOPO	2 M DHOA
Ag	0.1	0.099 ± 0.005	0.096 ± 0.002	0.097 ± 0.005	0.5	0.51 ± 0.02	0.51 ± 0.02	0.49 ± 0.02	1	1.02 ± 0.05	0.97 ± 0.05	1.00 ± 0.06
Al	0.1	0.101 ± 0.007	0.090 ± 0.005	0.104 ± 0.004	0.5	0.47 ± 0.03	0.47 ± 0.02	0.49 ± 0.03	1	0.99 ± 0.04	1.02 ± 0.06	0.98 ± 0.04
B	0.1	0.106 ± 0.006	0.083 ± 0.006	0.101 ± 0.005	0.5	0.49 ± 0.02	0.45 ± 0.01	0.48 ± 0.03	1	1.05 ± 0.05	1.01 ± 0.05	0.97 ± 0.04
Ba	0.1	0.097 ± 0.005	0.092 ± 0.005	0.098 ± 0.004	0.5	0.52 ± 0.03	0.51 ± 0.02	0.48 ± 0.03	1	1.03 ± 0.05	0.99 ± 0.06	0.98 ± 0.05
Bi	0.1	0.093 ± 0.007	0.087 ± 0.004	0.098 ± 0.005	0.5	0.50 ± 0.03	0.41 ± 0.03	0.49 ± 0.01	1	0.97 ± 0.05	0.97 ± 0.05	1.06 ± 0.05
Ca	0.1	0.104 ± 0.006	0.099 ± 0.005	0.106 ± 0.006	0.5	0.50 ± 0.01	0.50 ± 0.02	0.51 ± 0.01	1	0.98 ± 0.07	0.99 ± 0.04	1.05 ± 0.06
Cr	0.1	0.083 ± 0.005	0.074 ± 0.006	0.102 ± 0.004	0.5	0.48 ± 0.03	0.42 ± 0.03	0.51 ± 0.01	1	0.98 ± 0.05	1.00 ± 0.08	1.04 ± 0.06
Cu	0.1	0.105 ± 0.006	0.081 ± 0.007	0.103 ± 0.004	0.5	0.51 ± 0.01	0.52 ± 0.01	0.50 ± 0.03	1	1.01 ± 0.07	1.02 ± 0.08	1.03 ± 0.08
Cd	0.1	0.102 ± 0.005	0.104 ± 0.003	0.103 ± 0.005	0.5	0.48 ± 0.03	0.48 ± 0.02	0.50 ± 0.03	1	1.03 ± 0.05	1.01 ± 0.05	1.00 ± 0.05
Co	0.1	0.084 ± 0.006	0.074 ± 0.006	0.098 ± 0.006	0.5	0.49 ± 0.01	0.43 ± 0.03	0.47 ± 0.03	1	0.99 ± 0.06	1.03 ± 0.08	0.99 ± 0.08
Fe	0.1	0.089 ± 0.005	0.079 ± 0.007	0.099 ± 0.005	0.5	0.49 ± 0.02	0.39 ± 0.02	0.50 ± 0.01	1	0.98 ± 0.06	1.05 ± 0.05	0.96 ± 0.05
Ga	0.1	0.097 ± 0.004	0.084 ± 0.006	0.094 ± 0.006	0.5	0.50 ± 0.02	0.49 ± 0.03	0.50 ± 0.02	1	0.97 ± 0.06	1.06 ± 0.05	0.97 ± 0.08
In	0.1	0.096 ± 0.004	0.086 ± 0.004	0.101 ± 0.002	0.5	0.51 ± 0.01	0.52 ± 0.01	0.51 ± 0.02	1	1.02 ± 0.05	0.94 ± 0.04	0.97 ± 0.07
K	0.1	0.103 ± 0.003	0.096 ± 0.005	0.097 ± 0.002	0.5	0.49 ± 0.02	0.50 ± 0.01	0.51 ± 0.01	1	1.02 ± 0.05	0.95 ± 0.04	1.02 ± 0.07
Mn	0.1	0.086 ± 0.006	0.075 ± 0.002	0.103 ± 0.005	0.5	0.47 ± 0.03	0.38 ± 0.02	0.52 ± 0.01	1	1.00 ± 0.06	0.95 ± 0.05	1.04 ± 0.05
Mg	0.1	0.097 ± 0.005	0.106 ± 0.006	0.103 ± 0.006	0.5	0.50 ± 0.01	0.47 ± 0.03	0.48 ± 0.03	1	1.00 ± 0.05	0.96 ± 0.06	1.04 ± 0.06
Na	0.1	0.099 ± 0.005	0.103 ± 0.003	0.097 ± 0.003	0.5	0.52 ± 0.01	0.50 ± 0.03	0.48 ± 0.02	1	1.03 ± 0.05	0.97 ± 0.06	1.05 ± 0.06
Ni	0.1	0.087 ± 0.007	0.077 ± 0.002	0.097 ± 0.003	0.5	0.49 ± 0.03	0.40 ± 0.02	0.50 ± 0.02	1	1.03 ± 0.08	0.98 ± 0.05	1.05 ± 0.05
Pb	0.1	0.096 ± 0.005	0.098 ± 0.007	0.098 ± 0.002	0.5	0.47 ± 0.02	0.48 ± 0.01	0.50 ± 0.02	1	0.97 ± 0.05	0.99 ± 0.06	1.06 ± 0.06
Sr	0.1	0.099 ± 0.002	0.091 ± 0.004	0.104 ± 0.003	0.5	0.49 ± 0.02	0.50 ± 0.03	0.49 ± 0.01	1	0.99 ± 0.08	0.99 ± 0.07	1.04 ± 0.04
Zn	0.1	0.090 ± 0.002	0.093 ± 0.005	0.104 ± 0.002	0.5	0.50 ± 0.02	0.40 ± 0.02	0.50 ± 0.01	1	1.01 ± 0.08	0.97 ± 0.07	1.03 ± 0.04

4. S4: 0.1 mg L^{-1} of Ag, Al, B, Ba, Bi, Ca, Cr, Cu, Cd, Co, Fe, Ga, In, K, Mn, Mg, Na, Ni, Pb, Sr and Zn in 1000 mg L^{-1} of Th matrix
5. S5: 0.5 mg L^{-1} of Ag, Al, B, Ba, Bi, Ca, Cr, Cu, Cd, Co, Fe, Ga, In, K, Mn, Mg, Na, Ni, Pb, Sr and Zn in 1000 mg L^{-1} of Th matrix
6. S6: 1 mg L^{-1} of Ag, Al, B, Ba, Bi, Ca, Cr, Cu, Cd, Co, Fe, Ga, In, K, Mn, Mg, Na, Ni, Pb, Sr and Zn in 1000 mg L^{-1} of Th matrix

For any measurement, 20 replicate data were collected. The analytical data were presented in the form of $\langle x \rangle \pm 3\sigma$, where, $\langle x \rangle$ = the average of 20 replicate measurements and σ is the standard deviation. Reporting a value of 0.096 ± 0.002 for La, implies that the true value lies in the range of 0.094–0.098 with 99.7 % confidence level. Moreover, up to two digit beyond the decimal point the reported value is certain (0.09) while the third digit (6) is uncertain.

Tables 4 and 5 summarizes the analytical results for rare earth elements and common analytes, respectively. The study revealed that La, Ce, Pr, Gd, Dy, Lu could be determined at 0.1 mg L^{-1} concentration in presence of Th matrix. To determine all the common analytes at 0.1 mg L^{-1} concentration in Th matrix five contacts of DHOA was found to be only successful while if all the analytes are to be determined at 0.5 mg L^{-1} level, both TBP and DHOA can be successfully employed. Moreover, TOPO, TBP and DHOA all can be suitably used if the common analytes are to be determined at the level of 1 mg L^{-1}.

Conclusions

A comparative study was carried out for the determination of Ag, Al, B, Ba, Bi, Ca, Cr, Cu, Cd, Co, Fe, Ga, In, K, Mn, Mg, Na, Ni, Pb, Sr, Zn, La, Ce, Pr, Gd, Dy and Lu at trace level in presence of Th matrix after preferential extraction of Th using TBP, TOPO and DHOA in xylene. The extraction efficiency was found to follow the trend TOPO > TBP > DHOA. The maximum Th extraction was observed in the range of 3–4 M HNO_3. It was observed that for all TBP, TOPO and DHOA, two ligand molecules were associated with one Th molecule and all the extraction processes were found to be thermodynamically favorable. Stripping study revealed that strong complexing agents like oxalic acid could successfully be employed for the quantitative back extraction of Th from DHOA and TBP phases. For TOPO, multi-step stripping was found to be necessary for quantitative back extraction. All the ligands can be used for the determination of La, Ce, Pr, Gd, Dy and Lu at 0.1 mg L^{-1} concentration in presence of Th matrix. For common analytes, DHOA can be successfully used for their determination at 0.1 mg L^{-1} level; TBP can be used for 0.5 mg L^{-1} level while for TOPO they can be determined at 1 mg L^{-1} level.

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