



ORIGINAL ARTICLE

Determination of thorium(IV) with rifampicin in synthetic mixture and soil samples by spectrophotometry



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Received 5 July 2011; accepted 10 December 2011

Available online 21 December 2011

KEYWORDS

Spectrophotometry;
Thorium nitrate
pentahydrate;
Rifampicin;
Validation

Abstract A validated spectrophotometric method has been described for the determination of thorium(IV) in synthetic mixture and soil samples. The method is based on the complexation of thorium(IV) with rifampicin at room temperature which absorbs maximally at 525 nm. Beer's law is obeyed in the concentration range 1.16–23.2 $\mu\text{g mL}^{-1}$ with apparent molar absorptivity and Sandell's sensitivity of $8.23 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.0232 $\mu\text{g/cm}^2/0.001$ absorbance unit, respectively. The influence of variables was investigated and optimized. Interference due to other metal ions was studied and the tolerance limit was achieved. The proposed method was applied to the analysis of thorium(IV) in a synthetic mixture containing various other metal ions and in soil samples. The results of analyses of the proposed method were statistically compared with the reference method showing acceptable recovery and precision.

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1. Introduction

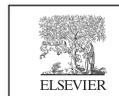
Thorium is a naturally occurring actinide element found in the environment or associated with other metal ions in different complex matrices, nuclear fission products, monazite sands and geological materials. Thorium is known to have acute tox-

icological effects on human and progressive and irreversible renal injury (Sahoo et al., 2004). The determination of thorium(IV) in the presence of various metal ions found in soil and rivers is of special interest. Various analytical techniques such as thin layer chromatography (Soran et al., 2005), gravimetry (Arora and Rao, 1981), titrimetry (Maiwal and Srinivasula, 1982), reversed phase liquid chromatography (Hao et al., 1996), fluorimetry (Pavon et al., 1989), potentiometry (Baumann, 1982; Chandra et al., 2005), X-ray fluorescence (Golson et al., 1983) and inductively coupled plasma mass spectrometry (Aydin and Soylak, 2007) have been reported for Th(IV) determination. These reported methods such as liquid chromatography, X-ray fluorescence, and inductively coupled plasma mass spectrometry are sensitive but expensive due to high cost

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and laborious cleanup procedure (Hao et al., 1996) required prior to the analysis of thorium(IV). Thorium(IV) has been determined spectrophotometrically based on the reaction with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol in the presence of sodium acetate-acetic acid buffer solution of pH 4.86 at 580 nm (Abu-Zuhri, 1984), sodium 4,8-diamino-1,5-dihydroxyanthraquinone-2,6-disulphonate in acidic pH at 685 nm (Navas and Garcia-Sanchez, 1979), sodium 5-(4-diethyl-amino-2-hydroxyl phenyl azo) 1,2,4-triazole-3-carboxylate in acidic pH at 535 nm (Thimmaiah et al., 1984) and bromocresol orange at 560 nm (Khalifa and Hafez, 1998). Two extractive spectrophotometric methods have been utilized for the estimation of thorium(IV) based on isoamyl alcohol extractable ion pair complex of thorium(IV) with 2-hydroxy-1-naphthaldehyde isonicotinoyl hydrazone at pH 3 with λ_{\max} 420 nm (Kavlentis, 1988) and chloroform extractable ion pair complex with 8-quinolinol in the presence of acidic buffer at 390 nm (Goto et al., 1966). The present communication describes a simple and sensitive spectrophotometric method for the determination of Th(IV). The method is based on the reaction of Th(IV) with rifampicin resulting in the formation of a colored complex which absorbs maximally at 525 nm.

2. Experimental

2.1. Materials and reagents

All absorbance measurements were made on a spectronic 20D⁺ spectrophotometer (Milton Roy Company, USA) with 1 cm matched glass cells. An Elico model LI-10 pH meter (Hyderabad, India) was used to measure pH of the solutions.

All chemicals and solvents used were of analytical reagent grade. Glass distilled deionized water was used throughout the experiment.

- 1.0×10^{-2} M thorium nitrate pentahydrate (CAS: 16065-92-2, M.W. = 570.13, Fluka Chemie AG, Darmstadt, Germany) was prepared in distilled water.
- 1.125×10^{-3} M (0.1%) rifampicin (CAS: 13292-46-1, M.W. = 822.94, Merck, USA) was prepared in methanol.

2.2. Procedure for the determination of thorium(IV)

Into a series of 10 mL volumetric flasks, aliquots of 0.05–1.0 mL of 1.0×10^{-2} M standard thorium nitrate solution were pipetted. To each flask 1.7 mL of 1.125×10^{-3} M rifampicin was added and diluted up to the mark with distilled water (pH 3.5). The contents of each flask were mixed well at room temperature (25 ± 1 °C) and the absorbance was measured at 525 nm against the reagent blank prepared similarly except thorium(IV) within the stability time period of 24 h. The concentration of thorium (IV) was calculated either from a calibration curve or regression equation.

2.3. Determination of thorium(IV) in synthetic mixture sample

The synthetic sample of thorium was prepared by taking 570.13 mg of thorium nitrate pentahydrate with 596 mg Pb(NO₃)₂, 580 mg ZrOCl₂·8H₂O, 523 mg Ba(NO₃)₂, 480 mg CrCl₃·6H₂O, 222 mg CaCl₂·2H₂O, 119 mg NiCl₂·6H₂O, 65 mg FeCl₃ and 341 mg CuCl₂·2H₂O, in 100 mL standard vol-

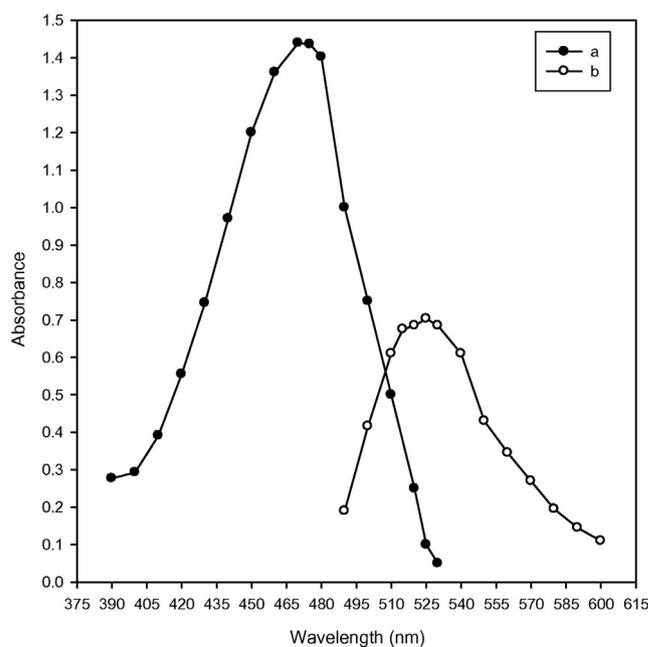


Figure 1 Absorption spectra: (a) 9.721×10^{-5} M rifampicin in methanol, (b) 2.066×10^{-4} M rifampicin in methanol + 7.0×10^{-3} M thorium(IV) in distilled water.

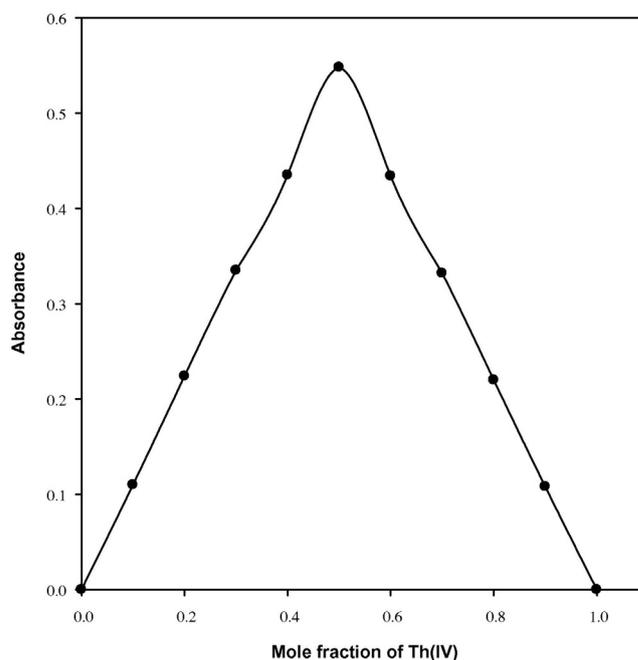


Figure 2 Job's plot for thorium-rifampicin complex.

umetric flask and diluted up to the mark with distilled water. The amount of thorium(IV) was determined by the proposed procedure.

2.4. Determination of thorium(IV) in synthetic soil sample

Soil samples were taken from Aligarh district of Uttar Pradesh. The digested soil samples were analyzed for thorium (IV) but tested negative. Therefore, an air-dried finely pow-

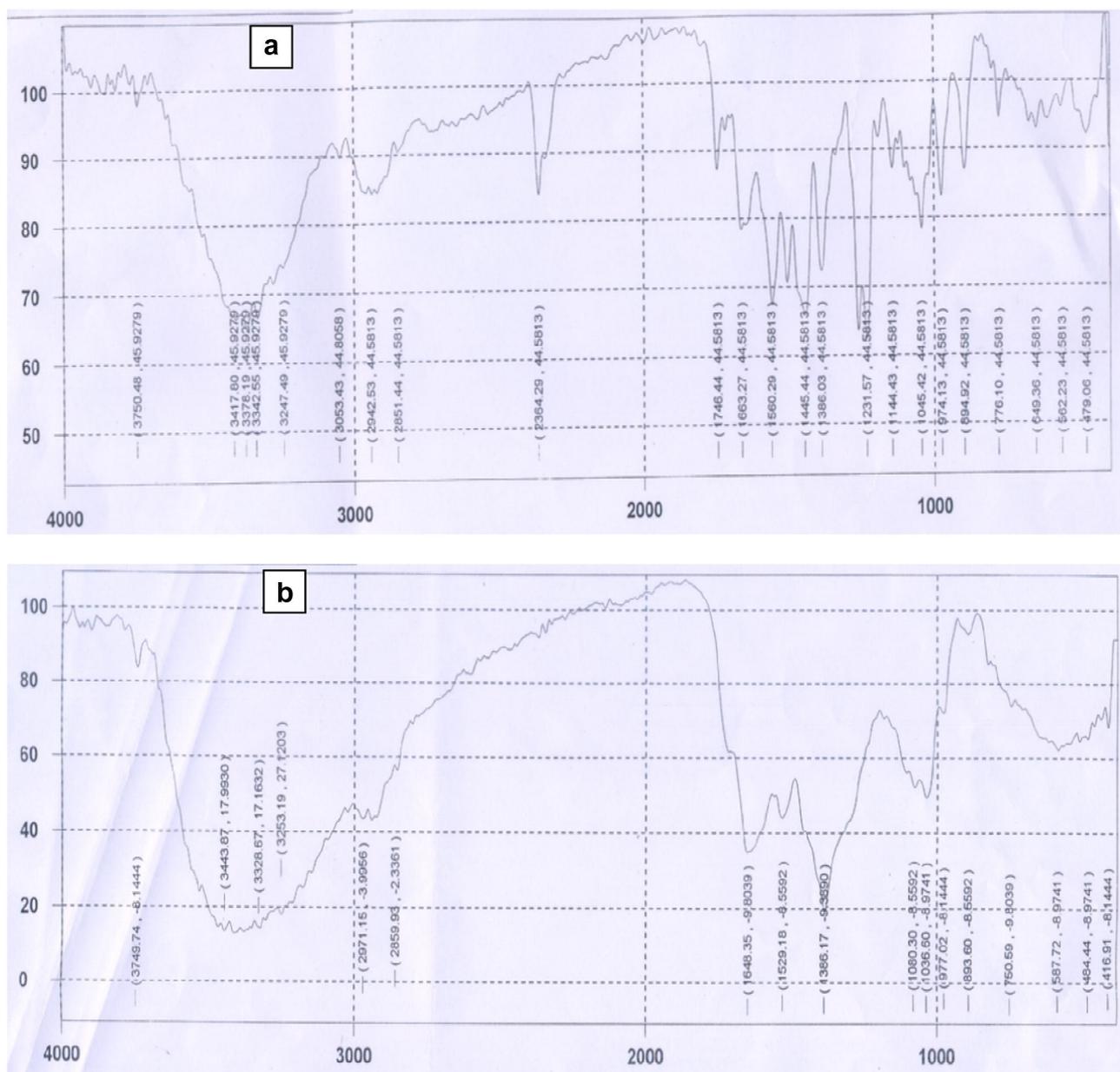


Figure 3 IR spectra of (a) free rifampicin and (b) Th(IV)-rifampicin complex.

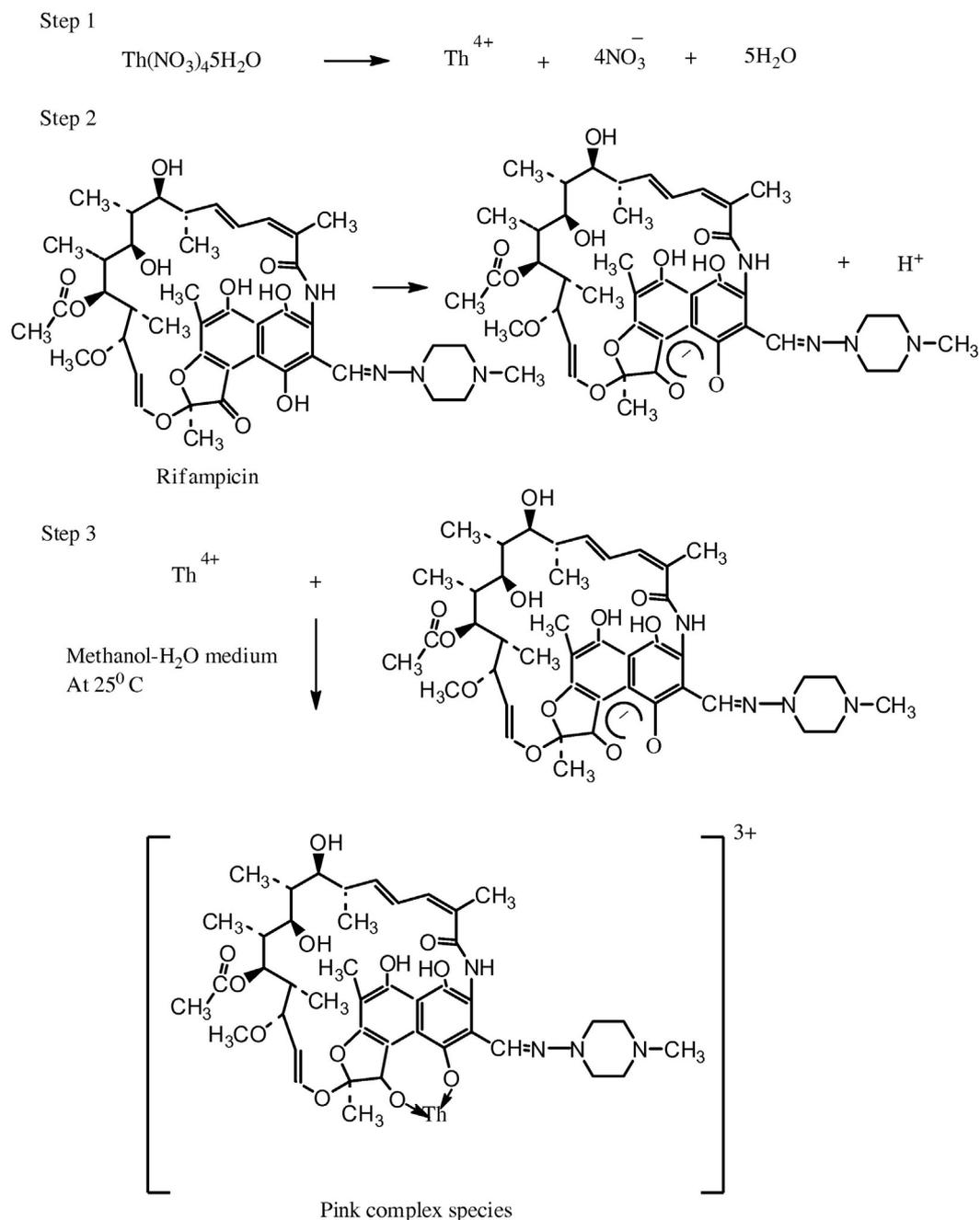
dered soil sample (500 mg) with 570.13 mg of thorium nitrate pentahydrate was digested with 2 mL of concentrated H_2SO_4 in a closed platinum crucible following the method reported by Hughes and Carswell (1970). After digestion, the content of the crucible was cooled and transferred to ice-cold water. The mixture was stirred until all the soluble matters had dissolved and then filtered through Whatmann No. 42 filter paper (Whatmann International Limited, Kent, UK) in 100 mL standard volumetric flask. The filtrate was diluted up to the mark with distilled water. A 20 mL portion of this solution was percolated through the column packed with Amberlite IR 400. The column was washed with 150 ml of 0.1 M H_2SO_4 to remove unadsorbed species. Thorium (IV) was eluted with 0.5 M H_2SO_4 at a flow rate of 2 mL per minute. The effluent was evaporated to dryness. After evaporation, 10 mL of distilled water was added and the pH of the solution was adjusted

to 3.5 by the addition of ammonia. The final volume of the solution was maintained at 20 mL. The concentration of thorium (IV) was determined by the proposed procedure.

3. Results and discussion

A pink colored complex was obtained with λ_{max} at 525 nm due to the interaction of thorium (IV) with rifampicin while the rifampicin in methanol-water medium showed an absorbance peak at 470 nm (Fig. 1). The reaction was carried out at room temperature. The absorbance measurement at 525 nm as a function of initial concentration of thorium (IV) was utilized to develop a rapid and selective spectrophotometric method for the determination of thorium (IV).

The stoichiometry of the reaction between thorium(IV) and rifampicin was studied by Job's method of continuous varia-



Scheme 1 Reaction sequence of the proposed spectrophotometric method.

tions (Likussar and Boltz, 1971) using equimolar concentrations of 3.037×10^{-3} M. As can be seen from Job's plot (Fig. 2) that one mole of thorium(IV) reacted with one mole of rifampicin. Thus, the combining molar ratio between thorium(IV) and rifampicin is 1:1.

The I.R. spectra of free rifampicin and Th(IV)-rifampicin complex are shown in Fig. 3(a) and (b), respectively. Rifampicin has $-\text{OH}$ and $-\text{C}=\text{O}$ potential sites for coordination with metal ions. Comparison of IR spectrum of the complex with those of free rifampicin indicates that a phenolic $\nu(\text{C}-\text{OH})$ band appears at 2364 cm^{-1} in the free rifampicin while the complex does not show this band suggesting that there is coordination

that occurs with Th(IV) at this potential site. The carbonyl band, $\nu(\text{C}=\text{O})$ in the free rifampicin appears at 1746 cm^{-1} with a weak shoulder at 1663 cm^{-1} , while the Th(IV)-rifampicin complex shows this band at 1648 cm^{-1} indicating that the complexation occurs through the coordination of oxygen atom. The phenolic $\text{O}-\text{H}$ at carbon 9 in rifampicin is most deshielded (Sadeghi and Karimi, 2006). So, it is deprotonated followed by chelate formation through oxygen atoms of keto and phenolic $\text{C}-\text{O}$ groups. The Th-O stretching vibration occurs at 416 cm^{-1} (Nakamoto, 1963). A tentative mechanism for the complexation between Th(IV) and rifampicin is given in Scheme 1.

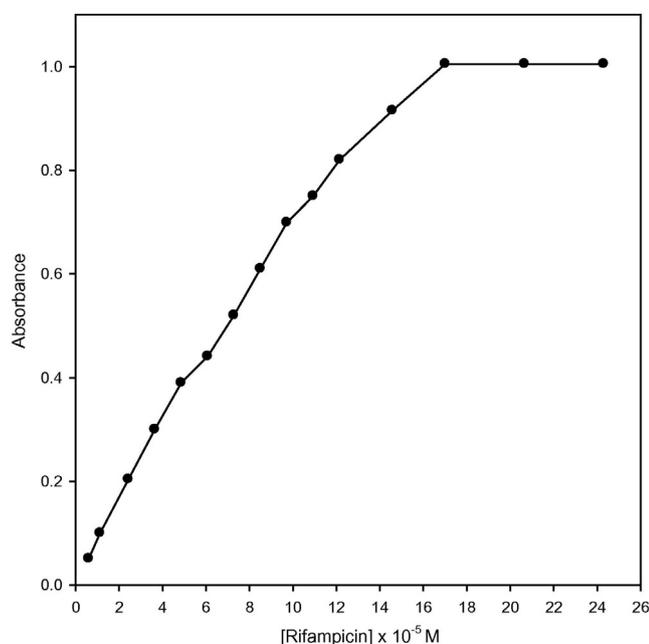


Figure 4 Effect of the concentration of rifampicin on the absorbance of the product.

3.1. Optimization of variables

The optimization of variables was assessed by testing several parameters such as reaction time, concentration of rifampicin, and solvents.

The effect of the reaction time on the absorbance of the pink colored complex and its stability was investigated. The complex got stabilized immediately at 25 ± 1 °C after mixing the analyte and reagent. The complex remained stable for about 24 h.

The effect of the concentration of rifampicin on the absorbance of the colored complex was investigated in the range of 6.08×10^{-6} – 2.43×10^{-4} M rifampicin. The results (Fig. 4) showed that the highest absorbance was obtained with 1.70×10^{-4} M rifampicin and remained constant up to 2.43×10^{-4} M. Therefore, 2.07×10^{-4} M rifampicin was taken as the optimum concentration for the determination of thorium(IV).

The effect of solvents such as acetone, acetonitrile, ethanol, dimethylsulfoxide, 1,4-dioxan, methanol and water were investigated on the absorbance of the colored complex. The results

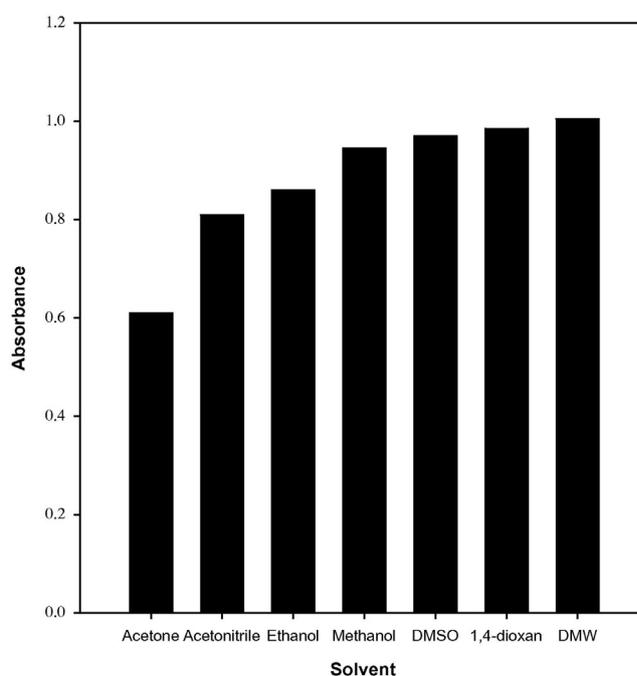


Figure 5 Effect of solvent on the absorbance of the colored complex.

Table 1 Effect of various metal ions on the determination of $23.2 \mu\text{g mL}^{-1}$ thorium(IV).

Metal ions	Added as	Tolerance limit (mg mL^{-1})
Pb^{2+}	$\text{Pb}(\text{NO}_3)_2$	0.596
Zr^{4+}	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	0.580
Ba^{2+}	$\text{Ba}(\text{NO}_3)_2$	0.523
Cr^{3+}	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	0.480
Cu^{2+}	CuCl_2	0.341
Ca^{2+}	CaCl_2	0.222
Ni^{2+}	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.119
Fe^{3+}	FeCl_3	0.065

are shown in the bar graph (Fig. 5). As can be seen from the figure that the complex showed maximum absorbance in demineralized water and the pH of the complex in this medium is found to be 3.5. Therefore, all measurements were done in demineralized water (DMW) at pH 3.5.

Table 2 Test of precision of the proposed method at three concentration levels of thorium(IV).

Parameters	Intra day assay			Inter day assay		
	2.3200	11.600	23.200	2.3200	11.600	23.200
Concentration taken ($\mu\text{g mL}^{-1}$)	2.3200	11.596	23.229	2.3250	11.596	23.234
Concentration found ($\mu\text{g mL}^{-1}$)	0.065	0.051	0.079	0.070	0.056	0.100
Standard deviation ^a ($\mu\text{g mL}^{-1}$)	100.015	99.97	100.20	100.216	99.97	100.15
Recovery (%)	2.79	0.438	0.341	3.028	0.482	0.429
Relative standard deviation (%)	0.029	0.023	0.035	0.029	0.025	0.045
Standard analytical error (%)	0.080	0.063	0.098	0.080	0.069	0.124
Confidence limit ^b						

^a Mean for five independent determinations.

^b Confidence limit at 95% confidence level and four degrees of freedom ($t = 2.776$).

Table 3 Recovery data of Th(IV) in the synthetic mixture sample by the standard addition technique.

Concentration ($\mu\text{g ml}^{-1}$)			Coefficients of linear regression equation of standard addition			Recovery (%)
Synthetic	Standard	Nominal	Intercept	Slope	r^a	
6.96	0, 1.16, 2.32, 4.64, 6.96	6.962	0.30031	0.04313	0.99996	100.04
13.92	0, 1.16, 2.32, 4.64, 6.96	13.94	0.60022	0.04303	0.99998	100.20

^a Mean for five independent analyses.

^b Confidence limit at 95% confidence level and four degrees of freedom (2.776).

^a Coefficient of correlation.

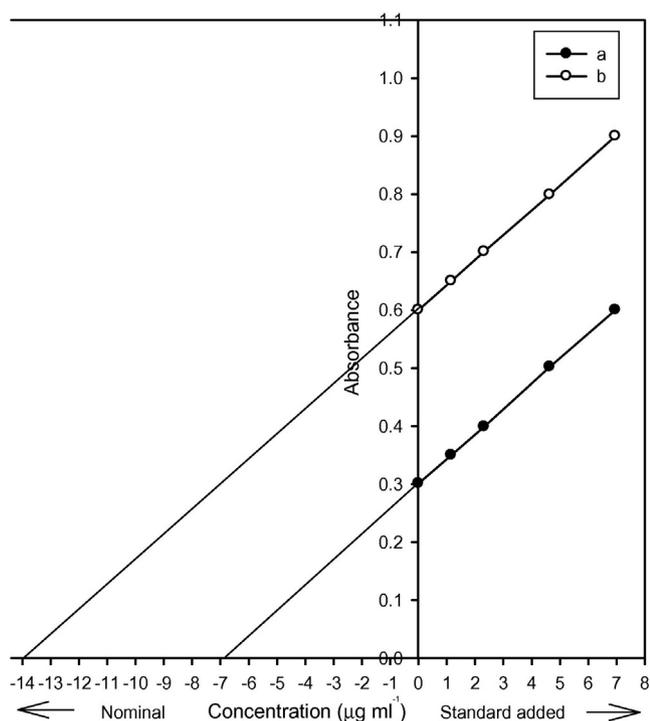


Figure 6 Recovery of thorium(IV) from the synthetic mixture sample by the standard addition technique: (a) 6.963 and (b) 13.949 $\mu\text{g mL}^{-1}$.

3.2. Effect of foreign ions

A study of the effect of competing metal ions showed that the determination of Th(IV) was not subsequently affected by a range of metal ions, i.e. Pb^{2+} (25-fold excess), Zr^{4+} (25-fold excess), Ba^{2+} (22-fold excess), Cr^{3+} (20-fold excess), Cu^{2+} (14-fold excess), Ca^{2+} (9-fold excess), Ni^{2+} (5-fold excess) and Fe^{3+} (2.8-fold excess). The results are summarized in Table 1. However, metal ions such as Mn^{2+} , Zn^{2+} , Hg^{2+} , Cd^{2+} , Mg^{2+} and Sr^{2+} interfere in the determination of Th(IV). The interference caused by metal ions can be removed through a column packed with Amberlite IR 400 resin. Most of the metal ions except Th^{4+} and UO_2^{2+} are washed out on passing 0.1 M H_2SO_4 , whereas Th(IV) was eluted with 0.5 M H_2SO_4 .

3.3. Validation

The intra- and inter day precisions were evaluated within the same day and on five consecutive days. The results are summarized in Table 2. It can be seen from the table that the values of RSD (%) were in the range of 0.341–3.028%.

The accuracy of the proposed method was evaluated by performing recovery experiments through the standard addition technique. The recovery of thorium(IV) in the synthetic sample at two concentration levels was investigated and the results are summarized in Table 3. It is evident from the table and the graph (Fig. 6) that the linearity of the regression line of the standard addition method was good. This indicated that the proposed method is precise and accurate.

The ruggedness of the proposed method was established by deliberately changing the concentration of the reagent as:

Table 4 Optical and regression characteristics of the proposed and reference methods.

Parameters	Proposed method	Reference method
Wavelength (nm)	525	390
Beer's law limit ($\mu\text{g mL}^{-1}$)	1.16–23.2	1.0–20
Molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	8.23×10^3	9.70×10^3
Sandell's sensitivity	$0.0232 \mu\text{g/cm}^2/0.001$ absorbance unit	$0.0239 \mu\text{g/cm}^2/0.001$ absorbance unit
Linear regression equation	$A = 5.917 \times 10^{-4} + 4.31 \times 10^{-2} C$	$A = 4.685 \times 10^{-4} + 4.18 \times 10^{-2} C$
$\pm tS_a$	1.88×10^{-5}	1.722×10^{-3}
$\pm tS_b$	1.32×10^{-5}	1.440×10^{-4}
Correlation coefficient (r)	0.99999	0.99999
Variance (S_0^2) of calibration line	1.69×10^{-6}	1.369×10^{-6}
Detection limit ($\mu\text{g mL}^{-1}$)	0.099	0.092
Quantitation limit ($\mu\text{g mL}^{-1}$)	0.301	0.280

$\pm tS_a$ and $\pm tS_b$ are confidence limits for intercept and slope, respectively.

Table 5 Evaluation of bias: Applicability of the proposed method in the synthetic mixture and soil samples and its comparison with the reference method at 95% confidence level.

Thorium samples	Proposed method		Reference method		Paired <i>t</i> - and <i>F</i> values ^b	θ_L^c	θ_U^c
	Recovery (%)	RSD ^a (%)	Recovery (%)	RSD ^a (%)			
Synthetic mixture sample*	99.97	0.438	100.18	0.492	<i>t</i> = 0.699, <i>F</i> = 1.123	0.989	1.006
Soil sample	100.05	0.498	100.18	0.492	<i>t</i> = 0.403, <i>F</i> = 1.024	0.990	1.007

* Synthetic mixture of thorium(IV) contains: 1 mg thorium nitrate pentahydrate + 596 mg Pb²⁺, 580 mg Zr⁴⁺, 523 mg Ba²⁺, 480 mg Cr³⁺, 222 mg Ca²⁺, 119 mg Ni²⁺, 65 mg Fe³⁺ and 341 mg Cu²⁺ in 100 mL distilled water.

^a Mean for five independent analyses.

^b Theoretical *t* (*v* = 8) and *F*-values (*v* = 4, 4) at 95% confidence levels are 2.306 and 6.39, respectively.

^c A bias, based on the recovery experiments, of $\pm 2\%$ is acceptable.

- volume of 1.215×10^{-3} M rifampicin, 1.7 mL (± 0.3 mL).

Under the optimal conditions, the thorium (IV) solution containing 23.2 $\mu\text{g mL}^{-1}$ thorium(IV) (synthetic sample) was analyzed by the proposed method. The results showed the mean percent recovery and RSD (%) of 100.13% and 0.341%, respectively. The results of the analysis indicated the ruggedness of the proposed method.

The calibration curve was constructed by plotting absorbance against the concentration of thorium(IV) in $\mu\text{g mL}^{-1}$. Beer's law was obeyed over the concentration range 1.16–23.2 $\mu\text{g mL}^{-1}$ with molar absorptivity and Sandell's sensitivity of $8.23 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.023 \mu\text{g/cm}^2/0.001$ absorbance unit, respectively. The calibration data (*n* = 9) were treated statistically and the results are summarized in Table 4.

The applicability of the proposed method for the determination of thorium (IV) in the synthetic mixture and soil samples has been tested. The results of the proposed method were statistically compared with those of the reference spectrophotometric method (Goto et al., 1966) using point and interval hypothesis tests. The *t*- (paired) and the *F*-values at 95% confidence level were calculated and found to be less than the tabulated *t*- (2.036 at *v* = 8) and the *F*-values (6.39 at *v* = 4.4) at 95% confidence level (Mendham et al., 2002), thus confirming no significant difference between the performance of the proposed method and the reference method (Table 5). It is also clear from the table that the bias evaluated by the interval hypothesis test (Hartmann et al., 1995) by means of lower limit (θ_L) and upper limit (θ_U) was in the range of 0.98–1.02. Thus, the proposed method is suitable for routine analysis of thorium(IV) in nuclear process laboratories where time and economy are essential.

4. Conclusions

The proposed method is simple and accurate for the determination of Th(IV). The proposed method has the advantages of having low limit of detection ($0.099 \mu\text{g mL}^{-1}$) and low cost of analysis. In addition, the proposed method is based on the complexation of Th(IV) with rifampicin at room temperature showing the involvement of one reagent only and there is no use of buffer solution. Hence, the proposed method can be used for the routine analysis of Th(IV) in real samples as the

interferences caused by some metal ions can be easily removed by anion exchange resin.

Acknowledgements

The authors are grateful to Aligarh Muslim University, Aligarh, India and Higher College of Technology (Ministry of ManPower), Muscat, Sultanate of Oman for facilities.

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