Research Article

2-Hydroxy-1-naphthaldehyde-P-hydroxybenzoichydrazone: A New Chromogenic Reagent for the Determination of Thorium(IV) and Uranium(VI)

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Simple, sensitive, selective, direct, derivative, and simultaneous spectrophotometric methods are developed for the determination of uranium and thorium individually and simultaneously. The methods are based on the reaction of 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNAHBH) with thorium(IV) and uranium(VI). HNAHBH reacts with thorium and uranium at pH 6.0 forming stable yellow and reddish brown coloured complexes, respectively. [Th(IV)-HNAHBH] complex shows maximum absorbance at 415 nm. Beer's law is obeyed over the concentration range 0.464–6.961 $\mu\text{g mL}^{-1}$ with a detection limit of 0.01 $\mu\text{g mL}^{-1}$ and molar absorptivity, ϵ , $3.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Maximum absorbance shown by [U(VI)-HNAHBH] complex is at 410 nm with Beer's law range 0.476–7.140 $\mu\text{g mL}^{-1}$, detection limit 0.139 $\mu\text{g mL}^{-1}$ and molar absorptivity, ϵ , $1.78 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Highly sensitive and selective second-order derivative methods are reported for the direct and simultaneous determination of Th(IV) and U(VI) using HNAHBH. The applicability of the developed methods is tested by analyzing water, ore, fertilizer, and gas mantle samples for thorium and uranium content.

1. Introduction

Among the various actinides, uranium and thorium due to natural abundance are very important, especially in view of energy sources, but seriously hazardous in view of environmental pollution. Powdered thorium metal is often pyrophoric and should be handled carefully. Exposure to thorium can lead to increased risk of cancers of the lung, pancreas, and blood. Exposure to thorium internally leads to increased risk of liver diseases. All isotopes and compounds of uranium are toxic, teratogenic, and radioactive carcinogens. When uranium gets inside the body, it can lead to cancer or kidney damage. Inhaled uranium increases the risk of lung cancer. There is also the possibility of ground-water contamination with the toxic chemicals used in the separation of the uranium ore. On these considerations measurement of these metals under the microgram levels is very important [1]. Many advanced methods have already been developed for the determination of uranium and thorium.

These methods include alpha spectrometry [2], inductively coupled plasma atomic emission spectrometry (ICP-AES) [3], inductively coupled plasma mass spectrometry (ICP-MS) [4], and capillary zone electrophoresis (CZE) [5]. However, these methods are hampered by less sensitivity or by matrix effect. Furthermore, availability of these techniques is limited due to expensive equipment and higher running cost.

Spectrophotometry is a relatively easy alternative method which provides some advantages, like simplicity and moderately low cost. A number of reagents have been used for the spectrophotometric determination of uranium and thorium. Among the various chromogenic agents reported for the determination of thorium (IV), most of them were found to be nonselective involving in serious interference from the diverse ions [6–9]. Majority of the reported methods require prior removal of closely associated metal ions and hence lack selectivity. Some of the early chromogens employed for the spectrophotometric determination of uranium include Arsenazo-III [10], dibenzoyl methane [11],

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and 1-(2-pyridylazo)-2-naphthol [12, 13]. They were highly sensitive reagents with less selectivity involving prior separation of interference. In the present investigation simple, sensitive and nonextractive direct and derivative spectrophotometric methods for the determination of thorium and uranium using HNAHBH are reported. A selective simultaneous second-order derivative spectrophotometric method is also proposed for the determination of Th(IV) and U(VI).

2. Experimental

2.1. Reagents. All chemicals used were of analytical-reagent grade. Doubly distilled water was used for preparing aqueous solutions. 0.01 M solution of U(VI) and Th(IV) solutions were prepared by dissolving appropriate amounts of uranyl nitrate (Loba) and thorium nitrate (Loba) in 100 mL distilled water, solutions of lower concentrations were prepared by successive dilution of the stock solution. 1% cetylpyridiniumchloride (CPC) is used as a cationic surfactant. Buffer solutions of pH 1–10 are prepared using appropriate mixtures of 1 M CH_3COONa + 1 M HCl (pH 1.0–3.0), 0.2 M CH_3COONa + 0.2 M CH_3COOH (pH 3.2–6.0), 0.1 M CH_3COONa + 0.2 M CH_3COOH (pH 7.0), and 2 M NH_4OH + 2 M NH_4Cl (pH 8.0–10.0).

2.1.1. Preparation of HNAHBH. 2-hydroxy-1-naphthaldehyde in methanol was mixed with p-benzoichydrazide in hot aqueous ethanol in equal amounts and refluxed for three hours on water bath. A reddish brown coloured solid was obtained on cooling. The product was filtered and dried. It was recrystallized from aqueous ethanol in the presence of norit. The product showed melting point 272–274°C. The structure of the synthesized 2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNAHBH) was determined from infrared and NMR spectral analysis. 1×10^{-2} M solution of the reagent was prepared by dissolving 0.306 g in 100 mL of dimethylformamide (DMF). Working solutions were prepared by diluting the stock solution with DMF (Scheme 1).

2.2. Sample Solutions

2.2.1. Preparation of Monazite Sand Sample [26]. The monazite sand was collected from the Arabian Sea coast at Mangalore, India. 1.0 g of the monazite sand was mixed with 5 mL of concentrated sulphuric acid and heated at 250°C for about 4 hours to digest the monazite sand. The resultant viscous paste was dissolved in distilled water by heating at 45°C for half an hour. The resultant solution was filtered

and thorium from the filtrate is precipitated as hydroxide by adding ammonia solution. The precipitate was filtered off and dissolved in minimum quantity of dil HCl and then diluted to 25 mL.

2.2.2. Preparation of Gas Mantle Sample [27]. 0.5 g of gas mantle sample was accurately weighed and placed in a 100 mL beaker. 10 mL of con HNO_3 was added and gently boiled for 20 minutes. The residue was diluted with 10 mL of distilled water and filtered. The resultant solution was diluted to 250 mL in a volumetric flask with distilled water.

2.2.3. Preparation of Phosphate Rock and Fertilizer Sample [28, 29]. The phosphate rock which is the raw material for manufacturing of phosphate fertilizers, NPK and DAP fertilizers, was collected from a fertilizer industry, Anantapur, India. The collected samples were finely grounded. 10 g of each sample was transferred separately into Ernermeyers flask containing 100 mL of 0.1 M citric acid. All these flasks were incubated in the orbital shaker at 30°C at 100 rev min^{-1} . These samples were removed and centrifuged to remove solid suspension.

2.2.4. Preparation of Ore Solution [30]. 0.25 g of 20283 MALINIM-G (Granite) or 20383 MALINIM-L (Lujavrite) ore samples was weighed and dissolved in a mixture of 15 mL of con H_2SO_4 , 5 mL of con. HNO_3 , and 45 mL of HF by boiling in a teflon beaker. The solution was evaporated to dryness, and the residue was dissolved in 10 mL of distilled water.

2.2.5. Preparation of Water Samples. Natural water samples from different sources of Anantapur town were collected and filtered through Whatman filter paper no. 41 to remove the suspended particulate matter. The filtered water was then treated with 5 mL of con. HNO_3 to prevent the possible hydrolytic precipitation of some mineral salts. Different known amounts of U(VI) and Th(IV) were then spiked into 100 mL of these treated water samples.

2.3. Apparatus. A Perkin Elmer (LAMBDA25) spectrophotometer controlled by a computer and equipped with a 1 cm path length quartz cell was used for UV-Vis spectra acquisition. Spectra were acquired between 350–600 nm (1 nm resolution). An ELICO model LI-120 pH-meter furnished with a combined glass electrode was used to measure pH of buffer solutions.

TABLE 1: Tolerance limits of foreign ions. Amount of Th(IV) taken = $0.928 \mu\text{g mL}^{-1}$ pH = 6.0.

Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)	Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)	Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)
Iodide	1904	Ba(II)	1650	Hg(II)	20
EDTA	1861	Na(I)	1500	Ru(III)	20
Thiosulphate	1680	K(I)	1400	Mn(II)	11
Sulphate	1440	Ca(II)	1140	Zr(IV)	10
Bromide	1215	Mg(II)	1000	Sn(II)	10
Citrate	945	W(VI)	55	Sr(II)	9
Nitrate	930	Hf(IV)	54	Cr(VI)	6
Tartrate	740	Pb(II)	42	Cu(II)	5
Thiocyanate	870	Ti(IV)	40	Ni(II)	<1, 55 ^a
Carbonate	600	Au(III)	40	Co(II)	<1, 100 ^a
Chloride	533	Te(IV)	40	Zn(II)	<1, 60 ^a
Phosphate	475	Cd(II)	34	Bi(III)	<1, 150 ^a
Thiourea	380	Se(IV)	31	Fe(II)	<1, 60 ^a
Oxalate	280	Mo(VI)	29	Al(III)	<1, 120 ^b
Fluoride	95	La(III)	28	U(VI)	<1, 70 ^b
		Pd(II)	22	In(III)	<1, 50 ^b
		Ag(I)	22	Ga(III)	<1, 60 ^b

Masking agents, ^ain the presence of 800 ppm of EDTA; ^b500 ppm of tartrate.

3. Results and Discussions

3.1. Direct Spectrophotometric Determination of Thorium(IV) and Uranium(VI). HNAHBH forms yellow and reddish brown coloured complexes with Th(IV) and U(VI), respectively. The colour of complexes is stable for more than 72 hours. Influence of pH, reagent, and surfactants on the absorbance of the complexes was investigated as follows.

3.1.1. pH Effect. The study of effect of pH 1.0–10.0 on the absorbance of both the reaction mixtures [U(VI)-HNAHBH] and [Th(IV)-HNAHBH] showed that maximum absorbance was obtained in the pH region of 5.5–6.5. Therefore further studies were carried out at pH 6.0.

3.1.2. Effect of Reagent (HNAHBH) Concentration. A 15-fold excess reagent (HNAHBH) is sufficient to develop maximum and stable colour for Th(IV) whereas 20-fold excess reagent (HNAHBH) is required for U(VI).

3.1.3. Surfactant Effect. 0.15% of CPC enhances the colour and stability of [U(VI)-HNAHBH] complex. [Th(IV)-HNAHBH] complex has no surfactant influence.

3.1.4. Absorption Spectra. The absorption spectra of [Th(IV)-HNAHBH] and [U(VI)-HNAHBH] complexes in presence of suitable buffer, surfactant, and reagent were recorded. [Th(IV)-HNAHBH] complex shows maximum absorbance at 415 nm and that of [U(VI)-HNAHBH] complex is at 410 nm. Reagent blank shows the least absorbance at these wave lengths.

3.1.5. Calibration Curves. The calibration curves were constructed for both the complexes taking variable amounts of metal ions at their respective absorption maxima. The calibration plots were linear over wide concentration ranges which are shown in Table 10 along with the slope, intercept, standard deviation, detection, and determination limits.

3.1.6. Composition of the Complex. The stoichiometry of the complex [metal:reagent] was determined by job's method, mole ratio method, and slope ratio methods and is found to be 1:1 for [U(VI):HNAHBH] and 2:3 for [Th(IV):HNAHBH].

3.1.7. Interferences. The effect of diverse ions in the determination of Th(IV) and U(VI) was studied in detail, and the tolerance limits were calculated and presented in Tables 1 and 2. Most of the anions and good number of cations did not interfere in the present methods even when present in more than 50-fold excess. Some cations, which interfere seriously, could be masked up to 50-fold excess with suitable masking agents as shown in the Tables 1 and 2.

3.1.8. Application of Proposed Direct Methods. The proposed direct spectrophotometric methods were employed for the determination of thorium in monazite sand and environmental water samples and for the determination of uranium in phosphate rock and fertilizer samples.

Suitable aliquots of prepared sample solutions are treated with required amount of reagent and suitable buffer media, and the absorbances of resultant solutions were measured at appropriate wave lengths; the amounts of metal ions present

TABLE 2: Tolerance limits of foreign ions. Amount of U(VI) taken = $4.760 \mu\text{g mL}^{-1}$ pH = 6.0.

Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)	Foreign ion	Tolerance limit	Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)
Tartrate	1480	K(I)	1760	Hg(II)	20
Sulphate	1440	Ca(II)	1560	Ru(III)	20
Phosphate	1430	Mg(II)	1510	Mn(II)	11
Thiosulphate	1200	Na(I)	1450	Zr(IV)	10
Bromide	1200	Ba(II)	1170	Sn(II)	10
Thiourea	1140	Hf(IV)	72	Sr(II)	9
Nitrate	960	W(VI)	55	Cr(VI)	7
Thiocyanate	870	Pb(II)	42	Ni(II)	3, 55 ^b
Iodide	734	Ti(IV)	40	Cu(II)	2, 65 ^a
Oxalate	440	Au(III)	40	Co(II)	2, 100 ^a
Chloride	360	Te(IV)	40	Zn(II)	2, 60 ^c
Carbonate	300	Cd(II)	34	Bi(III)	0.6, 75 ^a
Fluoride	290	Se(IV)	31	Fe(II)	0.6, 60 ^a
EDTA	236	Mo(VI)	29	Al(III)	0.3, 60 ^a
Ascorbate	190	La(III)	28	Th(IV)	0.3, 70 ^a
Citrate	136	Pd(II)	22	In(III)	0.4, 50 ^a
		Ag(I)	22	Ga(III)	0.3, 60 ^a

Masking agents, ^ain presence of 600 ppm of Tartrate, ^b300 ppm of oxalate, ^c500 ppm of thiocyanate.

TABLE 3: Determination of thorium in monazite sand samples.

Sample	Amount of thorium ($\mu\text{g mL}^{-1}$) $\pm$ SD*		
	Present method	AAS method	Relative error (%)
S1	2.29 ± 2.20	2.20 ± 0.56	4.10
S2	5.08 ± 1.68	4.90 ± 2.14	3.67
S3	3.22 ± 1.68	3.26 ± 0.56	-1.25

*Average of three determinations.

TABLE 4: Determination of thorium in environmental water samples.

Sample	Amount of thorium ($\mu\text{g mL}^{-1}$) $\pm$ SD ($n = 4$)		
	Added	Found	Recovery %
Tap water	1.5	1.55 ± 0.84	103.30
Bore-well water	2.0	2.19 ± 1.56	109.50
Stream water	4.5	4.44 ± 1.16	98.60
Domestic sewage water	3.5	3.62 ± 1.88	103.42

in samples are computed from the measured absorbance values and predetermined calibration plots. The results are presented in Tables 3, 4, and 5. The results are further compared with those obtained by AAS method, and relative errors are calculated and presented.

3.2. Derivative Spectrophotometric Determination of Th(IV) and U(VI). Second-order derivative spectra at pH 6.0 in the wavelength region of 350–600 nm is recorded for

TABLE 5: Analysis of phosphate rock and fertilizers for their uranium content.

Sample	Uranium content (mg kg^{-1})	
	Proposed method $\pm$ SD ($n = 4$)	AAS method $\pm$ SD ($n = 2$)
Phosphate rock (India)	33.96 ± 0.032	35.26 ± 0.018
NPK fertilizer	19.25 ± 0.010	17.95 ± 0.012
DAP fertilizer	49.95 ± 0.024	50.06 ± 0.022

TABLE 6: Tolerance limits of foreign ions. [Th(IV)-HNAHBH] system.

Foreign ion	Tolerance limit (in folds)	
	Zero order	Second derivative
Cu(II)	5	25
Ni(II)	<1	20
Co(II)	<1	18
Zn(II)	<1	22
Bi(III)	<1	12
Fe(II)	<1	45
Al(III)	<1	60
U(VI)	<1	35
In(III)	<1	30
Ga(III)	<1	40

both [Th(IV):HNAHBH] and [U(VI)-HNAHBH] complexes (Figures 1 and 2). The second-order derivative spectra

TABLE 7: Tolerance limits of foreign ions. [U(VI)-HNAHBH] system.

Foreign ion	Tolerance limit (in folds)	
	Zero order	Second derivative
Ni(II)	3	10
Cu(II)	2	15
Co(II)	2	15
Zn(II)	2	8
Bi(III)	<1	20
Fe(II)	<1	30
Al(III)	<1	25
Th(IV)	<1	35
In(III)	<1	30
Ga(III)	<1	50

TABLE 8: Determination of thorium in gas mantle.

Sample	Amount of thorium ($\mu\text{g mL}^{-1}$) $\pm$ SD ($n = 4$)		
	Added	Found	Recovery %
Sample 1	—	1.54 ± 0.83	—
	0.5	2.15 ± 1.84	98.62
	1.5	3.14 ± 2.24	98.70
	2.5	3.94 ± 1.10	94.20
Sample 2	—	2.42 ± 1.15	—
	0.5	3.14 ± 1.68	118.49
	1.5	3.78 ± 2.64	103.56
	2.5	4.82 ± 1.48	103.65

TABLE 9: Analysis of environmental water samples.

Sample	Uranium added ($\mu\text{g mL}^{-1}$)	Uranium found ($\mu\text{g mL}^{-1}$) $\pm$ SD* Found	Recovery (%)
Tap water	0.5	0.51 ± 0.010	102.0
	2.5	2.48 ± 0.016	99.2
	5.0	4.96 ± 0.018	99.2
Well water	0.5	0.49 ± 0.013	98.0
	2.5	2.47 ± 0.018	98.8
	5.0	4.97 ± 0.011	99.4
Waste water	0.5	0.48 ± 0.018	96.0
	2.5	2.52 ± 0.022	100.8
	5.0	4.98 ± 0.013	99.6

* Average of four determinations.

of [Th(IV):HNAHBH] complex show maximum amplitude at 434 nm and 453 nm with zero crossing at 443 nm (Figure 1). The second derivative spectra of yellowish brown coloured [U(VI)-HNAHBH] solution show a small crust at 448 nm, a small trough at 459 nm, and an intensified crust at 477 nm with zero cross at 453 nm and 466 nm (Figure 2). The measured derivative amplitudes at appropriate wavelengths as mentioned above for second derivative spectra were plotted against the amount of Th(IV) and U(VI). Linear

FIGURE 1: Second-order derivative spectra of [Th(IV)-HNAHBH]. Amount of Th(IV) $\mu\text{g mL}^{-1}$: a = 0.234, b = 0.464, c = 0.696, d = 0.928, e = 0.139, and f = 1.856. FIGURE 2: Second-order derivative spectra of [U(VI)-HNAHBH]. Amount of U(VI) $\mu\text{g mL}^{-1}$: a = 0.238; b = 0.476; c = 0.952; d = 1.428; e = 1.904.

plots were obtained in the range of 0.232–6.961 $\mu\text{g mL}^{-1}$ for Th(IV) and 0.238–2.38 $\mu\text{g mL}^{-1}$ for U(VI). Other analytical properties are listed in Table 10.

3.2.1. Effect of Foreign Ions in Derivative Methods. Interference of various metal and anions were studied on the derivative amplitudes. It was noticed that all metal ions and anions which did not interfere in direct methods also did not interfere in derivative methods. The metal ions which interfere seriously in zero order method are tolerable up to 20–25 fold excess (Tables 6 and 7). The above studies reveal that the derivative methods are more sensitive and selective than proposed direct methods.

TABLE 10: Analytical properties of [Th(IV)-HNAHBH] and [U(VI)-HNAHBH].

Parameter	Direct method		Second derivative			
	Thorium	Uranium	Thorium		Uranium	
	415 nm	410 nm	434 nm	453 nm	459 nm	477 nm
Beer's law range ($\mu\text{g mL}^{-1}$)	0.464–6.961	0.476–7.140	0.232–6.961	0.232–6.961	0.238–2.38	0.238–2.38
Molar absorptivity, ($\text{L mol}^{-1} \text{cm}^{-1}$)	3.5×10^4	1.78×10^4	—	—	—	—
Sandell's sensitivity, $\mu\text{g cm}^{-2}$	0.007	0.0134	—	—	—	—
Angular coefficient (m)	0.365	0.0827	0.0007	0.0006	0.0001	0.0001
Y-intercept (b)	0.0013	0.0081	-0.9×10^{-3}	-0.9×10^{-3}	-0.6×10^{-4}	0.5×10^{-4}
Correlation coefficient (r)	0.9999	0.9994	0.9998	0.9998	0.9999	0.9999
RSD	0.335	1.65%	1.46	0.17	0.98%	2.25
Detection limit ($\mu\text{g mL}^{-1}$)	0.01	0.139	0.014	0.044	0.03	0.067
Determination limit, $\mu\text{g mL}^{-1}$	0.03	0.417	0.043	0.132	0.09	0.2
Composition (M:L)	2:3	1:1	—	—	—	—
Stability constant	2.72×10^{19}	3.3×10^5	—	—	—	—

3.3. Application of Proposed Derivative Methods

3.3.1. Determination of Thorium in Gas Mantle. A known aliquot of the prepared sample solution was treated according to the recommended procedure, and the amount of thorium was evaluated from the predetermined calibration plot. The results are shown in Table 8 along with recovery percentages.

3.3.2. Analysis of Environmental Water Samples for the Uranium Content. 100 mL of each of the sample was filtered using Whatman filter paper and spiked with known amounts of uranium. Suitable aliquots were taken and analysed for uranium amount (Table 9).

3.4. Simultaneous Second-Order Derivative Spectrophotometric Determination of Uranium and Thorium. A good number of spectrophotometric methods have already been developed for the simultaneous determination of uranium and thorium [31–33]. The present method provides a simple and selective derivative spectrophotometric procedure for the simultaneous determination of uranium and thorium without prior separation and without solving simultaneous equations.

3.4.1. Derivative Spectra. The 2nd-order derivative spectra recorded for [U(VI)-HNAHBH] and [Th(IV)-HNAHBH] at pH 6.0 showed sufficiently large derivative amplitude for thorium at 448 nm, while the U(VI) species exhibits zero amplitude, at 477 nm maximum derivative amplitude was noticed for U(VI) where there is no amplitude for Th(IV) (Figure 3). This facilitates the determination of U(VI) and Th(IV) simultaneously by measuring the second derivative amplitudes of binary mixtures containing U(VI) and Th(IV) at 477 nm and 448 nm, respectively.

3.4.2. Determination of U(VI) and Th(IV). Aliquots of solutions containing $0.238\text{--}2.380 \mu\text{g mL}^{-1}$ of U(VI) or $0.232\text{--}4.640 \mu\text{g mL}^{-1}$ of Th(IV) were transferred into a series of 10 mL calibrated volumetric flasks. HNAHBH (1×10^{-2} M, 0.6 mL), CPC (1%, 0.5 mL), and buffer solution

FIGURE 3: Second order derivative spectra of (a) [Th(IV)-HNAHBH] and (b) [U(VI)-HNAHBH]. Th(IV) ($\mu\text{g mL}^{-1}$): 0.464; 0.928; 1.392; U(VI) ($\mu\text{g mL}^{-1}$): 0.952; 1.428; 1.904.

(pH 6.0, 4 mL) were added to each of these flasks and diluted to the mark with distilled water. The zero crossing points of [U(VI)-HNAHBH] and [Th(IV)-HNAHBH] species were determined by recording the second-order derivative spectra of both the systems with reference to the reagent blank. Calibration plots for the determination of U(VI) and Th(IV) were constructed by measuring the second derivative amplitudes at zero crossing points of [Th(IV)-HNAHBH] (448 nm) and [U(VI)-HNAHBH] (477 nm), respectively and plotting against the respective analyte concentrations. [U(VI)-HNAHBH] and [Th(IV)-HNAHBH] coloured solutions obeyed Beer's law in the range $0.238\text{--}2.380 \mu\text{g mL}^{-1}$ and $0.232\text{--}4.640 \mu\text{g mL}^{-1}$ at 477 nm and 448 nm, respectively. To test the mutual independency of the analytical signals of U(VI) and Th(IV) in the presence of each other, the calibration plots were drawn for each metal ion alone and in the presence of a known amount of the other metal ion. The slopes, intercepts, and correlation

TABLE 11: Linear regression analysis of the determination of U(VI) and Th(IV) in mixture by second derivative spectrophotometry.

Metal ion determined	Wave length (nm)	Other metals present ($\mu\text{g mL}^{-1}$)		Slope	Intercept	Correlation coefficient
		U(VI)	Th(IV)			
Uranium(VI)	477			1.0×10^{-4}	5×10^{-5}	0.9998
			1.856	0.9×10^{-4}	4×10^{-5}	0.9996
Thorium(IV)	448			6.9×10^{-4}	-1.0×10^{-6}	0.9999
		1.908		5.8×10^{-4}	-0.8×10^{-6}	0.9998

TABLE 12: Simultaneous determination of U(VI) and Th(IV) in binary mixtures.

Amount taken ($\mu\text{g mL}^{-1}$)		Amount found* ($\mu\text{g mL}^{-1}$) (recovery %)		Relative error (%)	
U(VI)	Th(IV)	U(VI)	Th(IV)	U(VI)	Th(IV)
1.908	0.464	1.896 (99.4)	0.460 (99.0)	-0.62	-0.86
1.908	0.928	1.900 (99.6)	0.930 (100.2)	-0.42	0.21
1.908	1.392	1.901 (99.6)	1.395 (100.2)	-0.36	0.26
1.908	1.856	1.898 (99.4)	1.855 (99.9)	-0.52	-0.05
1.908	2.320	1.910 (100.1)	2.340 (100.8)	0.10	0.86
1.908	4.640	1.898 (99.4)	4.650 (100.2)	-0.52	0.21
0.238	1.856	0.234 (98.3)	1.854 (99.8)	-1.60	-0.1
0.476	1.856	0.468 (98.3)	1.849 (99.6)	-1.60	-0.37
0.952	1.856	0.960 (100.8)	1.858 (100.1)	0.84	0.10
1.428	1.856	1.432 (100.3)	1.848 (99.5)	-0.28	-0.43
1.908	1.856	1.860 (97.7)	1.857 (100.0)	-2.50	0.05
2.380	1.856	2.400 (100.8)	1.846 (99.4)	0.84	-0.53

* Average of four determinations.

TABLE 13: Simultaneous determination of uranium and thorium in ore samples.

Ore sample (composition)	Amount of metal ion (ppm)				Relative error	
	Certified		Found		U(VI)	Th(IV)
	U(VI)	Th(IV)	U(VI)	Th(IV)		
20283 MALINIM-G (Granite), (ppm) [Eu(0.35), F(4200), Ga(27), Gd(14), Hf(12), Li(12), Lu(2), Mo(3), Nb(53), d(22), Tb(3), U(15), V(2), Yb(14.2), Zn(50), Zr(300)]	15	51	14.85	52.68	-0.01	0.032
20283 MALINIM-L (Lujavrite), (ppm) [Eu(1.2), F(4400), Ga(54), f(190), Li(48), Lu(0.4), Mo(4), Nb(960), Nd(22), Tb(0.7), U(14), V(81), Yb(3), Zn(400)]	14	66	14.46	64.68	0.03	-0.02

TABLE 14: Determination of uranium and thorium in spiked water samples.

Water sample	Amount ($\mu\text{g mL}^{-1}$)				Recovery (%)	
	Spiked	Found ($n = 4$) $\pm$ SD			U(VI)	Th(IV)
		U(VI)	Th(IV)	U(VI)		
Tap water	0.50	1.45	0.48 $\pm$ 0.02	1.48 $\pm$ 0.03	96.0	102
	1.40	2.60	1.45 $\pm$ 0.01	2.52 $\pm$ 0.01	103.6	96.9
	2.00	3.50	2.04 $\pm$ 0.22	3.38 $\pm$ 0.04	102.0	96.6
Bore well water	0.80	3.80	0.83 $\pm$ 0.004	3.90 $\pm$ 0.03	103.7	102.6
	2.40	2.50	2.48 $\pm$ 0.05	2.44 $\pm$ 0.06	103.3	97.6
River water	0.45	0.60	0.44 $\pm$ 0.01	0.63 $\pm$ 0.03	97.7	105.0
	0.80	1.40	0.84 $\pm$ 0.03	1.45 $\pm$ 0.02	105.0	103.6
	1.50	2.90	1.48 $\pm$ 0.02	2.83 $\pm$ 0.06	98.6	97.6
	2.20	3.80	2.14 $\pm$ 0.03	3.85 $\pm$ 0.04	97.3	101.3

TABLE 15: Comparison of the results.

Metal	Reagent	$\lambda_{\max}$ (nm)	pH/medium	Aqueous/extraction	Beer's law ($\mu\text{g mL}^{-1}$)	$\epsilon \times 10^4$ $\text{L mol}^{-1} \text{cm}^{-1}$	Interference	Reference
U	N-phenyl-3-styrylacryloylhydroxamic acid	410	6-6.8	Extraction	1.22-22	1.2	—	[14]
U	5-(2'-carboxyphenyl)azo-8-quinolinol	524	5.2-6.1	Extraction	1.4-7.1	1.035	—	[15]
U	N-phenylcinnamo-hydroxamic acid	400	5.5-8.5	Extraction	—	0.65	—	[16]
U	5-(2'-carboxyphenyl)azo-8-quinolinol in Triton X-100	568	5.2-6.1	Micellar	0.2-3.3	1.5	—	[17]
U	Pyridin-2-carboxaldehyde 2-hydroxybenzoyl hydrazone	375	3.5-6.1	Extraction	1-5.6	—	—	[18]
U	Arsenazo-III (in CTAB)	681	3M HClO ₄	—	1-20 $\mu\text{g g}^{-1}$	39	Cr(III), Co(II)	[19]
U	2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic-hydrazone	410	5.5-6.5	Aqueous	0.476-7.140	1.78	—	Present method
Th	Arsenazo-III	555	2M HClO ₄	Aqueous	1-60 $\mu\text{g g}^{-1}$	30	Ce(III), CN ⁻ , PO ₄ ³⁻ , SCN ⁻ , CH ₃ COO ⁻	[20]
Th	2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid (Thorin)	578	3M HClO ₄	Aqueous	0-25 $\mu\text{g g}^{-1}$	1.6	—	[21]
Th	1-(2'-thiazolylazo)-2-naphthol	681	2.4-2.8	36% methanol	0.32-6.56	3.14	—	[22]
Th	2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic-hydrazone	415	5.5-6.5	Aqueous	0.464-6.961	3.5	—	Present method
U&Th	Arsenazo-III (PLS method)	635 & 713	HCl	Aqueous	0.10-1.20	—	—	[23]
U&Th	Carminic acid (bivariate calibration)	590 & 635	6.25	Aqueous	2.50 (U) 1-40 (Th)	—	—	[24]
U&Th	Arsenazo III	679.5 & 684.4	HCl	Aqueous	0.1-0.7 (U & Th)	—	Lanthanides	[25]
U&Th	2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone	448 & 477	6	Aqueous	0.238-2.38 (U) 0.232-4.640 (Th)	—	—	Present method

coefficients of the prepared calibration plots were calculated and presented in Table 11. The data in table indicate that the presence of Th(IV)/U(VI) is not influencing the calibration plot of U(VI)/Th(IV) to any significant extent. This allows the determination of U(VI) and Th(IV) in their mixtures without any significant error and without the need for their prior separation.

U(VI) and Th(IV) were mixed in different proportions and then treated with required amount of HNAHBH in the presence of buffer solution (pH 6.0) and 0.05% of CTAB and diluted to the volume in 10 mL volumetric flasks. The second-order derivative spectra for these solutions were recorded (350–600 nm), and the derivative amplitudes were measured at 477 nm and 448 nm. The amounts of U(VI) and Th(IV) taken in the mixtures were calculated from the measured derivative amplitudes using the respective predetermined calibration plots. The results obtained along with the recovery percentage and relative errors are presented in Table 12, which indicate the usefulness of the proposed method for the simultaneous determination of U(VI) and Th(IV).

3.4.3. Application of Proposed Simultaneous Method. 0.5 mL of the prepared ore samples and suitable volumes of water samples was analyzed by the proposed second-order derivative spectrophotometric method using HNAHBH and the results obtained and relative errors are tabulated in Tables 13 and 14.

4. Conclusions

The analytical results evaluated in the present paper in direct, derivative, and simultaneous methods were compared with those reported in some of the recently reported methods and presented in the Table 15. The comparison of the results indicate that the proposed method for the determination of uranium is more sensitive than number of reported methods [14–18] and more selective than the method reported by Khan et al. [20]. Regarding the determination of thorium the present method is more sensitive than those reported by Khan et al. [21], Sharma and Eshwar [22]. The results obtained in the simultaneous determination of U(VI) and Th(IV) are well comparable with the reported methods [23–25]. Above all most of the reported methods involve extraction in spurious organic solvents, whereas the present reported methods are simple, nonextractive, and reasonably accurate methods.

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