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Direct, derivative and simultaneous spectrophotometric methods of determination of Iron(II) and Uranium(VI) in various environmental, biological and ore samples

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ABSTRACT

Simple, sensitive and reproducible direct and derivative spectrophotometric methods for the determination of iron(II) and uranium(VI) are reported. The method is based on the formation of orange coloured complex of a stoichiometric ratio 2:3 between iron(II) and 2-hydroxy-3-methoxybenzaldehyde- isonicotinoylhydrazone (HMBAINH) and the formation of yellow coloured complex of stoichiometric ratio 1:1 between uranium(VI) and HMBAINH at pH 4.0. The maximum absorbance of [Fe(II)-HMBAINH] complex was measured at 385nm. Under the optical conditions, Beer's law is obeyed over the range 0.139-1.396 $\mu g\ mL^{-1}$. The molar absorptivity and detection limits are calculated as $2.0x10^4$ L mol^{-1} cm^{-1} and 0.013 $\mu g\ mL^{-1}$ respectively. [U(VI)-HMBAINH] complex shows maximum absorbance at 395nm, Beer's law range, molar absorptivity and detection limits are 1.19 -11.9 $\mu g\ mL^{-1}$, 0.9 x 10^4 L mol^{-1} cm^{-1}, and 0.224 $\mu g\ mL^{-1}$ respectively. A simultaneous third order derivative spectrophotometric method of determination of iron(II) and uranium(VI) is also reported. The proposed methods were successfully employed in the determination of iron and uranium in various environmental, biological and ore sample.

Key words: Iron (II), Uranium (VI), HMBAINH, Simultaneous determination.

INTRODUCTION

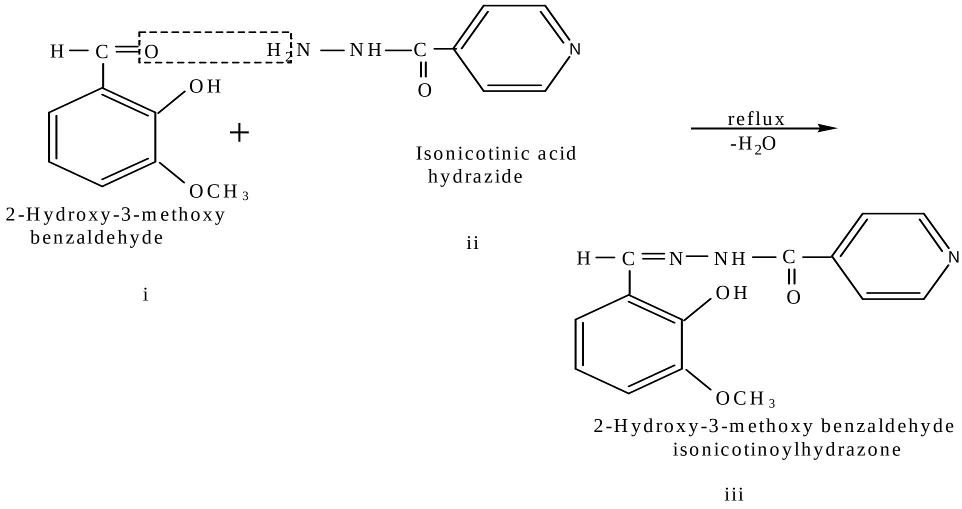
Iron plays an important role in biochemical and environmental systems. Iron and its compounds got several industrial uses. Uranium finds extensive applications as nuclear fuel in power plants. The main sources of uranium are rocks, plants, sand and water. Iron is present in small amounts in uranium minerals like davidite and brannerite. Iron and uranium coexist in phosphate rocks. Iron is present in thoranite a mineral of thorium and uranium. Though there are many advanced methods developed for the determination of metals, spectrophotometry is widely used due to its simplicity, low cost and adaptability. Several reagents have been reported for the direct and derivative spectrophotometric determination of iron and uranium. Very few methods[25] have been reported for the simultaneous determination of iron and uranium. We are now reporting a rapid, reasonably sensitive and selective method of determination of iron and uranium using HMBAINH by direct, derivative and simultaneous methods.

MATERIALS AND METHODS

Reagents

0.01M iron (II) and uranium(VI) solutions were prepared by dissolving appropriate amounts of Mohr's salt (Sd.Fine) and uranyl nitrate(Loba) in 100ml distilled water. The stock solutions were diluted appropriately as required. Other metal ion solutions were prepared from their nitrates or chlorides. Buffer solutions of pH 1-10 are prepared using appropriate mixtures of CH_3COOH and HCl, CH_3COOH and CH_3COONa, NH_4OH and NH_4Cl.

Preparation of HMBAINH: Equimolar solutions of 2-hydroxy-3-methoxy benzaldehyde in methanol and isonicotinic acid hydrazide in water were refluxed for two hours on water bath and cooled. The light brownish yellow coloured solid obtained was then separated by filtration, washed and dried. The product was recrystallized from aqueous alcohol in the presence of norit. The product showed melting point of 224°C



The structure (III) of the synthesized 2-hydroxy-3-methoxybenzaldehydeisonicotinoylhydrazone (HMBAINH) was determined from infrared and NMR spectral analysis. $1x10^{-2}$M solution of the reagent was prepared by dissolving 0.271g in 100 ml of dimethylformamide (DMF). Working solutions were prepared by diluting the stock solution with DMF.

Sample solutions

Soil samples:

The soil sample (5.0g) was weighed into a 250ml Teflon high pressure microwave acid digestion bomb and 50ml aquaregia were added .The bomb was sealed tightly and then positioned in the carousel of a microwave oven. The system was operated at full power for 30 minutes. The digested material was evaporated to incipient dryness. Then, 50ml of 5% hydrochloric acid was added and heated close to boiling to leach the residue. After cooling, it was filtered and the undissolved residue was washed two times with 5% hydrochloric acid. The filtrates were quantitatively collected in a 250ml volumetric flask and diluted to the mark with distilled water.

Alloy steel sample solution

0.5 g of the alloy sample was dissolved in a mixture of 2ml HCl and 10ml HNO_3. The resulting solution was evaporated to a small volume. To this 5ml of 1:1 H_2O and H_2SO_4 mixture was added and evaporated to dryness. The residue was dissolved in 15ml of distilled water and filtered through Whatman filter paper No 40. The filtrate was collected in a 100ml volumetric flask and made up to the mark with distilled water. The solution was further diluted as required.

Preparation of food and biological samples:

A wet ash method was employed in the preparation of the sample solution. 5 g of food or fruit or tissue sample dried for about 24 hours is dissolved in a 1:1 mixture of nitric acid and perchloric acid. The solution was evaporated to dryness and the residue was ashed at 300^oC. The ash was dissolved in 2ml of 1M sulphuric acid and made up to the volume in a 25ml standard flask with distilled water.

Phosphate rock and fertilizer sample:

The phosphate rock which is the raw material for manufacturing of phosphate fertilizers, NPK and DAP fertilizers were collected from a fertilizer industry, Anantapur. The collected samples were finely grounded. 10g of each sample was transferred separately into Erlenmeyer flask containing 100 ml of 0.1M citric acid. All these flasks were incubated in the orbital shaker at 30^0C at 100 rev min^{-1}. These samples were removed and centrifuged to remove solid suspension.

Apparatus

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

RESULTS AND DISCUSSION

HMBAINH forms orange and yellow colored complexes with Fe(II)) and U(VI) respectively, The colour of the complexes is stable for more than 72 hours.

Direct method

pH effect: The study of effect of pH 1.0-10.0 on the colour intensities of both the reaction mixtures [Fe(II)-HMBAINH] and [U(VI)-HMBAINH], showed that maximum colour was obtained in the pH region of 3.5-5.5. Therefore further studies were carried out at pH 4.0

Effect of reagent concentration: A 15 fold excess reagent is required to develop maximum and stable colour for Fe(II) where as 10 fold excess reagent is sufficient for U(VI).

Absorption spectra: The absorption spectra of [Fe(II)-HMBAINH] and [U(VI)-HMBAINH] solutions with suitable buffer and reagents were recorded between 350 nm - 600 nm. The spectra show that [Fe(II)-HMBAINH] complex has maximum absorbance at 385nm and that of [U(VI)-HMBAINH] complex at 395nm. Reagent blank showed least absorbance at these wave lengths.

Calibration curves: The calibration curves were constructed for both the complexes at their respective absorption maxima and these were linear over wide concentration range, which are shown in table.10 and 11 along with the slope, intercept, standard deviation detection and determination limits.

Composition of the complex: The stoichiometry of the complexes were determined by job's method, mole ratio method and slope ratio methods, which is found to be 2:3 for [Fe(II)-HMBAINH] and 1:1 for [U(VI):HMBAINH]

Table.1 Tolerance limits of foreign ions

Amount of Fe(II) taken = 0.767 μg mL^{-1} pH = 4.0

Foreign ion	Tolerance limit (μg mL^{-1})	Foreign ion	Tolerance limit (μg mL^{-1})	Foreign ion	Tolerance limit (μg mL^{-1})	
Sulphate	960	Ba(II)	1785	Hg(II)	24	
Iodide	959	Na(I)	1609	Zn(II)	21	
Phosphate	940	Ca(II)	1403	Co(II)	18	
Thiosulphate	772	K(I)	1401	Ag(I)	13	
Thiourea	760	Sr(II)	1226	Tl(III)	12	
Citrate	700	Mg(II)	1123	Ni(II)	10	
Bromide	681	La(III)	372	Al(III)	10	45^a
Nitrate	551	Y(III)	338	Zr(IV)	9	70^a
Tartrate	543	Te(IV)	319	Ru(III)	<1	-
Carbonate	440	W(VI)	313	V(V)	<1	-
Thiocyanate	393	Se(IV)	253	Sn(II)	<1	50^a
Chloride	240	Cd(II)	164	Cu(II)	<1	50^a
Oxalate	207	Mn(II)	151	Pd(II)	<1	100^c
Fluoride	80	Ir(III)	39	Mo(VI)	<1	60^a
EDTA	64	Ce(IV)	39	Ga(III)	<1	50^a
		Pb(II)	25	Bi(III)	<1	80^b

Interferences: In order to study the effect of other ions on the determination of iron, the absorbance of different solutions containing 0.764 μg of Fe(II) and variable amounts of a given foreign ion was measured at 385nm. The measured absorbance values were compared with that of a solution containing no foreign ion and the tolerance limits of the interfering ions were calculated. Out of the tested ions, only Sn(II), Bi(III), Mo(VI), Cu(II), Ru(III), Pd(II), V(V) and Al(III) were interfered seriously. Of these, except Ru(III) and V(V), the tolerance limits of other metals were increased up to 50 fold excess by using appropriate masking agents (Table.1).

The tolerance limits of different diverse ions in the determination of 5.95 μg mL^{-1} of U(VI) were calculated and presented in table.2.Large number of anions and cations do not interfere in the present method even present in large excess. Some of the cations are tolerable in moderate amounts. The interference of some metal ions can be reduced by masking them with appropriate masking agents as shown in the table.2

Masking agent: In the presence of 300 µg of 500 µg of tartrate (a), 200 µg of oxalate(b), and 600 µg of thiourea (c)

Table.2 Tolerance limits of foreign ions

Amount of U (VI) taken = 5.95 µg mL^{-1} pH = 4.0

Foreign ion	Tolerance limit (µg mL^{-1})	Foreign ion	Tolerance limit (µg mL^{-1})	Foreign ion	Tolerance limit (µg mL^{-1})	
Iodide	1270	Ca(II)	1603	Zn(II)	29	
Thiosulphate	1120	Ba(II)	1373	Ce(IV)	20	
Sulphate	960	Mg(II)	1215	Co(II)	15	60^{a}
Bromide	800	K(I)	1173	Zr(IV)	10	70^{b}
Thio urea	760	Na(I)	1149	Ni(II)	3	65^{b}
Nitrate	620	Sr(II)	876	Sn(II)	3	40^{b}
Thiocyanate	580	Te(IV)	370	Mo(VI)	2	50^{e}
Tartrate	481	Se(IV)	292	Cu(II)	<1	50^{c}
EDTA	471	La(III)	278	V(V)	<1	-
Phosphate	384	Y(III)	222	Pd(II)	<1	80^{c}
Chloride	346	Mn(II)	109	Al(III)	<1	100^{d}
Carbonate	212	Cd(II)	108	Fe(II)	<1	100^{a}
citrate	211	W(VI)	82			
Oxalate	55	Hg(II)	60			
Fluoride	23	Pb(II)	59			
		Ir(III)	39			

Masking agent : In the presence of 500 µg of thiocyanate (a), 350µg of phosphate (b), 500 µg of thiourea (c), 400 µg of EDTA (d) and 150 µg Citrate (e)

Applications

The proposed direct spectrophotometric methods were employed in the determination of iron in some surface soil and alloy steel samples and for the determination of uranium in phosphate rock and fertilizer samples.

Suitable aliquots of prepared sample solutions were treated with required amount of reagent and suitable buffer media and the absorbances of resultant solutions were measured at appropriate wave lengths, the amount of metal ions present in samples are computed from the measured absorbance values and predetermined calibration plots. The results are shown in table.3, 4 and 5, which are in good agreement with the certified values and with the AAS method.

Table.3 Determination of iron in surface soil samples

Sample	Source of the sample	Amount of iron (mg Kg^{-1}) ±SD*
S1	Ground nut cultivation soil, Akuthotapalli, Anantapur	38.46 ± 0.34
S2	Cottoncultivation soil, Singanamala,Anantapur district,	27.48 ± 0.36
S3	Sweet lemon cultivation soil, Garladinne, Anantapur distrcct	26.28 ± 0.28
S4	Paddy cultivation soil, Garladinne, Anantapur district	46.86 ± 0.43

** Average of five determinations*

Table.4 Determination of iron in alloy steels.

Alloy steel composition %	Amount of iron(%)		
	Certified Value	Present method± SD*	Relative error(%)
High tensile steel			
BY0110-1 (42.98Zn,19.89Si, 0.04Cd,0.024As, 0.14Cu and 4.13 Fe)	4.13	4.06± 0.014	0.41
YSBC19716 (34.26Zn,0.38Si, 1.2Cd,48.57Sb, 0.95S,and 0.32F)	34.26	34.7± 0.018	0.04
GSBD33001-94 (9.29Al,1.04Ca,9.53Fe, 14.64Si, 49Mg,32.79Cr)	9.53	9.28±0.035	0.27

* *Average of five determinations*

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

Sample	Uranium content(mg kg-1)	
	proposed method ±SD (n=4)	AAS method ±SD(n=2)
Phosphate rock(India)	34.68 ±0.02	35.26 ±0.018
NPK fertilizer	18.36 ± 0.014	17.95 ± 0.012
DAP fertilizer	48.35 ± 0.032	50.06 ± 0.022

Fig.1 First order derivative spectra of [Fe(II)-HMBAINH]
Amount of Fe(II) (µg mL^{-1}) : a. 0.279; b.0.558; c. 0.837; d. 1.116; e. 1.396

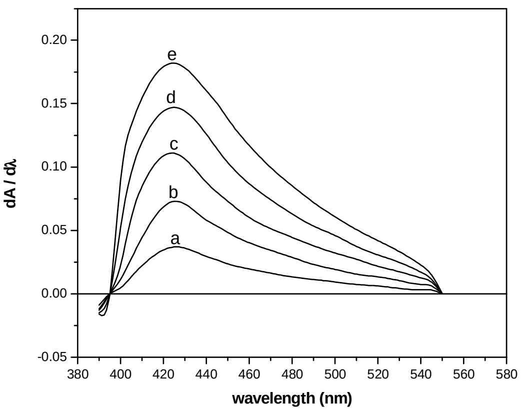
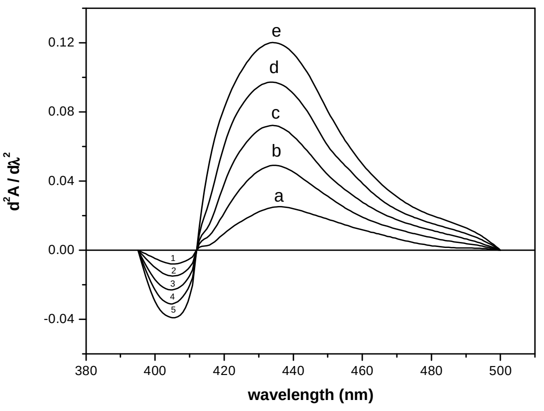


Fig.2 Second order derivative spectra of [Fe (II) – HMBAINH]
Amount of Fe (II) (µg mL^{-1}): a. 0.279; b.0.558; c. 0.837; d. 1.116; e. 1.396



Derivative Method
[Fe(II)-HMBAINH] System:

The derivative spectra of different orders, recorded in the wavelength region 350-600 nm for the orange coloured [Fe(II)-HMBAINH] complex solution at pH 4.0, showed that the 1st, 2nd and 3rd order derivative spectra (fig.1, 2 and 3) permit the determination of the metal ion in much lower concentrations than the zero order method (Table.10) The first derivative spectrum showed maximum derivative amplitude at 425 nm with no zero cross (fig.1) The second order derivative spectrum gave one small trough at 405 nm and a large crust at 435 nm with zero cross at 412 nm (fig.2). A large trough at 413 nm, a small crust at 450 nm and a negligible trough at 485nm with zero cross at 430nm and 473 nm were observed for the third derivative spectrum (fig.3). Hence Fe(II) was determined by measuring the derivative amplitudes at 425nm for 1st order, at 405nm and 435nm for 2nd order and at 413 nm and 450 nm for 3rd order spectra.

Fig.3 Third order derivative spectra of [Fe (II) – HMBAINH]
Amount of Fe (II) (µg mL^{-1}): a. 0.279; b.0.558; c. 0.837; d. 1.116; e. 1.396

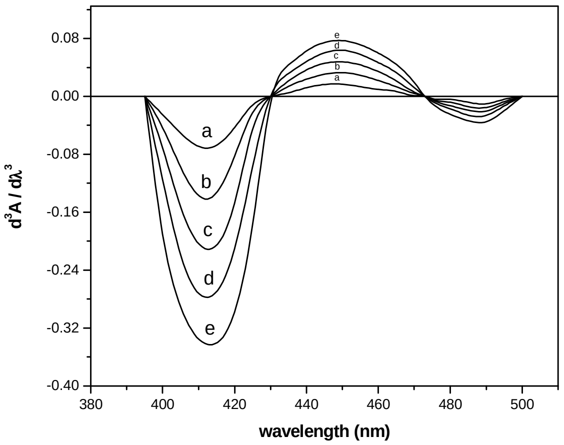
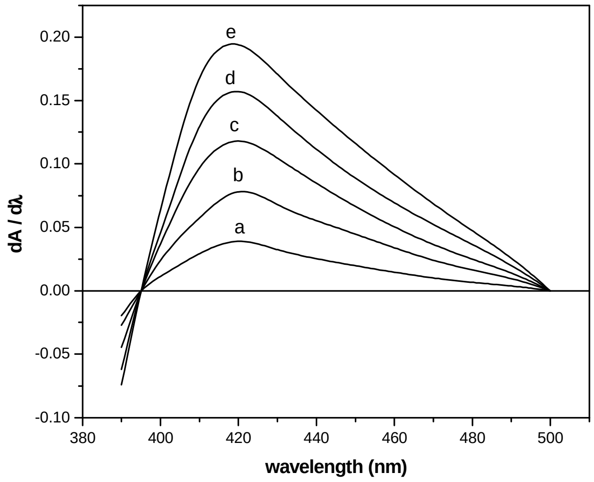


Fig.4. First order derivative spectra of [U(VI) – HMBAINH]
Amount of U(VI) µg mL^{-1} : a. 2.38; b. 4.76; c. 7.14
d. 9.52; e. 11.90



[U(VI)-HMBAINH] System:
The 1st, 3rd and 4th derivative order spectra of the yellow coloured [U(VI)- HMBAINH] solution at pH 4.0 were recorded in the wavelength region 360-600 nm for various solutions containing different amounts of U(VI) and presented in figures 4,5 and 6. The first derivative spectra

showed maximum amplitude at 420 nm which was proportional to the amount of uranium taken. The third derivative spectra showed a trough at 470 nm and a crust at 510 nm whose amplitudes were proportional to the amount of the metal ion with a zero crossing at 495 nm. The fourth derivative spectra again showed a crust at 445 nm and a trough at 495 nm with zero crossing at 470 nm. The analytical studies were carried out by measuring the derivative amplitudes at 420 nm for the first order, at 470 nm and 510 nm for the third order and at 445 nm and 495 nm for the fourth derivative spectra.

The analytical results of both the derivative methods [Fe(II)-HMBAINH] and [U(VI)-HMBAINH] are shown in table.10 and 11

Fig.5 Third order derivative spectra of [U(VI) – HMBAINH]
Amount of U(VI) µg mL^{-1} : a. 2.38; b. 4.76; c. 7.14;
d. 9.52; e. 11.90

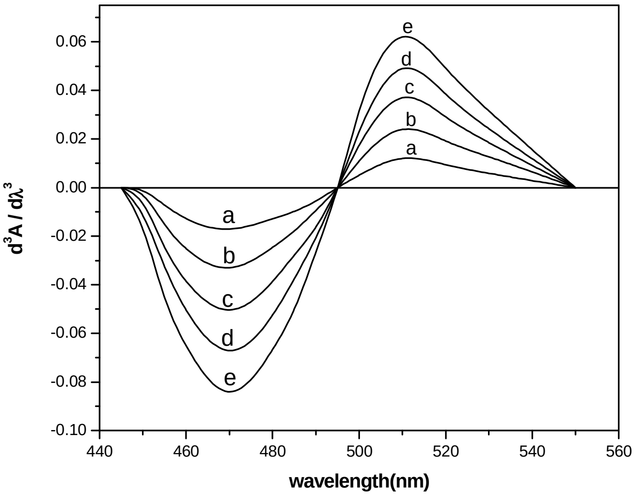
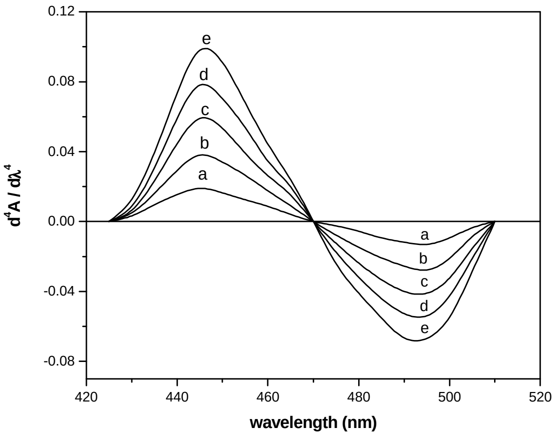


Fig.6 Fourth order derivative spectra of [U(VI) - HMBAINH]
Amount of U(VI) µg mL^{-1} : a. 2.38; b. 4.76; c. 7.14; d. 9.52; e. 11.90



Effect of foreign ions in derivative method

Interference of various metal ions 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 25-50 fold excess (Table. 6 and 7). The above studies reveal that all the derivative methods are more sensitive and selective than proposed direct methods.

Table.6 [Fe(II)-HMBAINH] system

Foreign ion	Tolerance limit (in folds) Zero order	First derivative	Second derivative	Third derivative
In(III)	4	40	100	60
Bi(III)	2	60	55	50
Th(IV)	2	10	25	30
Mo(VI)	2	10	40	25
Ga(III)	<1	65	50	50
Al(III)	<1	15	70	30
Ru(III)	<1	25	30	35
U(VI)	<1	35	55	40
Cu(II)	<1	10	40	25
V(V)	<1	15	50	35
Pd(III)	<1	45	110	65

Table.7 [U(VI)-HMBAINH] system

Foreign ion	Tolerance limit (infolds) Zero order	First derivative	Third derivative	Fourth derivative
Fe(II)	<1	interfere	>50	interfere
Ru(III)	<1	interfere	>50	interfere
Pd(II)	<1	interfere	>50 f	interfere
Ga(III)	<1	interfere	10 (470 nm) >50(510 nm)	interfere
Bi(III)	<1	interfere	20	interfere
Cu(II)	<1	5 fold	15	interfere
V(V)	<1	7 fold	25	interfere

Applications

The third order derivative method using HMBAINH is employed in the analysis of food and biological samples for iron content and some environmental water samples for uranium content.

Analysis of food and biological samples for the iron content

Known aliquots of the prepared food and biological sample solutions were treated with suitable volumes of HMBAINH and buffer solution and diluted to the volume in 10 ml volumetric flask. The derivative spectra were recorded and the derivative amplitudes were measured at analytical wave length. The amounts of Fe(II) in the samples were computed from pre-determined calibration plots and presented in table.8. The food and biological samples were further analyzed by Atomic Absorbance Spectrophotometric method and the results obtained were compared with those of the present method.

Analysis of environmental water samples for the uranium content

100 ml of each of the water sample was filtered using Whatman filter paper and spiked with known amounts of uranium. Suitable aliquots were taken and analyzed for uranium amount. The results obtained along with the recovery percentages are shown in table.9

Table.8 Determination of iron in food and biological samples

Samples	Amount of iron(µg ml^{-1}) ± SD (n=4) Found present	 Found AAS	 Added	 Recovered present	 Recovered AAS	 % recovery
Wheat	6.52±0.22	6.40±0.09	5	12.46± 0.68	11.28±0.10	97.6
Rice	14.36 ± 0.20	16.46±0.18	5	18.85±0.96	21.04±0.48	102.0
Tomato	12.66 ± 0.34	12.68±0.14	5	17.98±0.35	17.44±0.95	104.0
Orange	17.54 ± 0.89	16.94±0.66	5	21.86±1.15	22.26±0.68	96.0
Banana	9.39 ±1.11	11.4±0.12	5	15.75±1.18	15.86±1.46	98.3
Prostrate gland	2.84 ± 0.16	2.98±0.08	6.5	9.19 ±1.25	9.54±0.94	103.0
Benign(enlarged prostrate gland	11.46 ± 2.12	13.15±1.1	6.5	18.85±2.12	20.18±1.66	95.12

Table.9 Analysis of environmental water samples

Sample	Uranium added (µg ml^{-1})	Uranium found (µg ml^{-1}) ±SD Found	 Recovery(%)
Tap water	0.5	ND	-
	2.5	2.46 ± 0.013	98.4
	5.0	5.08 ± 0.014	101.6
Well water	0.5	ND	-
	2.5	2.52 ± 0.015	100.8
	5.0	5.12 ± 0.020	102.4
Waste water	0.5	ND	-
	2.5	2.44 ± 0.025	100.8
	5.0	4.92 ± 0.014	99.6

* *Average of four determinations*

Table.10 Analytical characteristics of [Fe(II) – HMBAINH

Parameter	Direct method 385 nm	First derivative 425 nm	Second derivative 405 nm	Second derivative 435 nm	Third derivative 413 nm	Third derivative 450 nm
Beer's law range (µgmL^{-1})	0.139-1.396	0.035-1.536	0.279-1.536	0.070-1.535	0.035-1.536	0.070-1.536
Molar absorptivity,ε (L mol^{-1} cm^{-1})	2.0 x10^{4}	-	-	-	-	-
Sandell's sensitivity, (µg cm^{-2})	0.003	-	-	-	-	-
Angular coefficient (m)	0.365	0.145	0.028	0.093	0.262	0.053
Y- intercept (b)	0.0013	-0.0014	-0.0009	0.00006	-0.0011	0.003
Correlation coefficient (r)	0.9999	0.9997	0.9999	0.9999	0.9998	0.9984
Relative standard deviation(%)	0.57%	0.52%	1.59%	0.56%	0.59%	3.60%
Detection limit (µgmL^{-1})	0.013	0.011	0.033	0.013	0.013	0.091
Determination limit (µgmL^{-1})	0.039	0.034	0.098	0.039	0.040	0.272
Composition (Metal: Ligand)	2 : 3	-	-	-	-	-
Stability constant	1.25 x 10^{19}	-	-	-	-	-

Table. 11 Analytical characteristics of [U(VI) – HMBAINH]

Parameter	Direct method 395 nm	First derivative 420 nm	Third derivative		Fourth derivative	
			470 nm	510 nm	445 nm	495 nm
Beer's law range (µg mL^{-1})	1.19 –11.9	0.29 –13.09	0.59 – 13.09	1.19 –13.09	0.59 – 13.09	1.19 – 13.09
Molar absorptivity,ε (L mol^{-1} cm^{-1})	0.9 x 10^4	-	-	-	-	-
Sandell's sensitivity, (µg cm^{-2})	0.0256	-	-	-	-	-
Angular coefficient (m)	0.0362	0.0184	0.0071	0.0052	0.0087	0.0061
Y- intercept (b)	-0.0024	-0.0009	-0.00004	-0.00035	-0.0001	-0.00012
Correlation coefficient(r)	0.9998	0.9999	0.9997	0.9998	0.9999	0.9995
Relative standard deviation	1.15%	0.44%	0.43%	0.82%	0.87%	0.69%
Detection limit (µg mL^{-1})	0.224	0.082	0.084	0.173	0.172	0.148
Determination limit(µg mL^{-1})	0.672	0.245	0.253	0.519	0.517	0.443
Composition (Metal: ligand)	1: 1	-	-	-	-	-
Stability constant	1.65 x 10^5	-	-	-	-	-

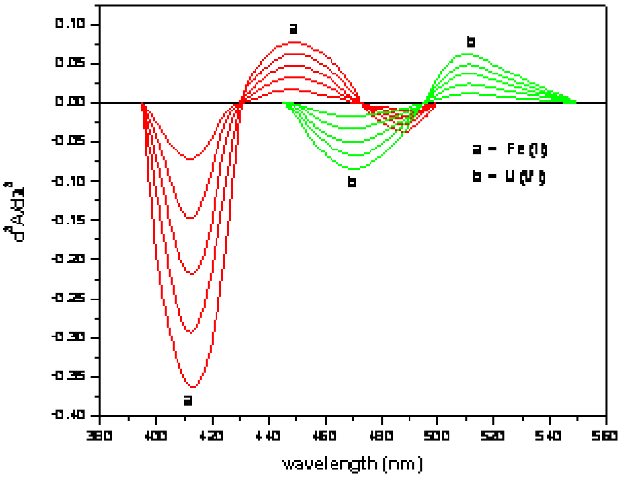
Simultaneous third order derivative spectrophotometric determination of uranium and thorium

Present method provides a simple and selective derivative spectrophotometric procedure for the simultaneous determination of iron and uranium without separation and without solving simultaneous equations.

Derivative spectra

The 3^{rd} order derivative spectra recorded for[Fe(II)-HMBAINH] and [U(VI)-HMBAINH] at pH 4.0 showed large derivative amplitude for iron at 413nm while the U(VI) species exhibits zero amplitude at this wave length. At 470 nm, maximum derivative amplitude was noticed for the U(VI) species and zero amplitude for Fe(II) species (Fig.7).This allows the determination of Fe(II) and U(VI) simultaneously by measuring the third derivative amplitudes of the binary mixtures containing Fe(II) and U(VI) at 413 nm and 470 nm respectively.

Fig.7 Third order derivative spectra of (a) [Fe(II)-HMBAINH] and (b)[U(VI)-HMBAINH]
Fe(II) (µg mL^{-1}) : 0.28; 0.56; 0.84; 1.12; 1.40
U(VI) (µg mL^{-1}) : 2.40; 4.76; 7.14; 9.52; 11.90



Determination of Fe(II) and U(VI)

Aliquots of solutions containing 0.03-1.53 µgmL^{-1} of Fe (II) or 0.56 – 13.08 µgmL^{-1} of U(VI) were transferred into a series of 10 ml calibrated volumetric flasks. HMBAINH (1x10^{-2} M, 0.3 ml) and buffer solution (pH 4.0, 4 ml) were added to each of these flasks and diluted to the mark with distilled water. The zero crossing points of [Fe(II))-HMBAINH] and [U(VI)-HMBAINH] species were determined by recording the third order derivative spectra of both the systems with reference to the reagent blank. Calibration plots for the determination of Fe(II) and U(VI)were constructed by measuring the third derivative amplitudes at zero crossing points of [U(VI)-HMBAINH] (413 nm) and at the zero cross wave length of [Fe(II)-HMBAINH] (470nm) (Fig.7) respectively and plotting against the respective analyte concentrations, which show that Fe(II) species obeys Beer's law in 0.03-1.53 µg mL^{-1} range and U(VI) species in the range 0.56 - 13.08 µg mL^{-1}. For the same concentration range of Fe(II) solutions 2.380µg mL^{-1} of U(VI) were added and for U(VI) solutions a 0.279 µg mL^{-1} of Fe(II) were added and calibration plots were constructed by measuring the derivative amplitudes at appropriate wave lengths. The slope, intercept and correlation coefficient values of the calibration plots are presented in table.12, shows that the presence of Fe(II) is not influencing the derivative amplitude of [U(VI)-HMBAINH] species and vice versa. This enables the simultaneous determination of Fe(II) and U(VI) by third order derivative method.

Table.12 Linear regression analysis of the determination of Fe(II) and U(VI) in mixture by third derivative spectrophotometry.

Metal ion determined	Wave length (nm)	Other metal present (µg mL^{-1})		slope	Intercept	Correlation coefficient
		Fe(II)	U(VI)			
Fe(II)	413			0.2620	-1.1x10^{-3}	0.9999
			2.380	0.2560	-0.9x10^{-3}	0.9997
U(VI)	470			0.0070	4.0x10^{-5}	0.9996
		0.279		0.0068	5.0x10^{-5}	0.9994

Table.13 Simultaneous third order derivative spectrophotometric determination of Fe(II) and U(VI)

Amount taken (µg mL^{-1})		Amount found* (µg mL^{-1}) (Recovery %)		Relative error (%)	
Fe(II)	**U(VI)**	**Fe(II)**	**U(VI)**	**Fe(II)**	**U(VI)**
0.139	2.380	0.141 (101.8)	2.387 (100.3)	+1.43	+0.29
0.279	2.380	0.275 (98.8)	2.363 (99.3)	-1.43	-0.71
0.558	2.380	0.550(98.6)	2.403 (101)	-1.43	+0.96
0.837	2.380	0.831(99.3)	2.346 (98.6)	-0.71	-1.43
1.116	2.380	1.126 (100.9)	2.370 (99.6)	+0.89	-0.42
1.396	2.380	1.389 (99.5)	2.396 (100.7)	-0.50	+0.49
0.279	1.190	0.277 (99.4)	1.198 (100.7)	-0.71	+0.67
0.279	2.380	0.282 (101.2)	2.353 (98.9)	+1.07	-1.07
0.279	4.759	0.279(100)	4.816 (101.2)	0.00	+1.13
0.279	7.140	0.273 (98.1)	7.097 (99.4)	-2.15	-0.60
0.279	9.519	0.275(98.8)	9.461 (99.4)	-1.43	-0.60
0.279	11.90	0.280 (100.6)	11.959(100.5)	+0.35	+0.49

**Average of four determinations*

Simultaneous determination of Fe(II) and U(VI) in binary mixtures.

Fe(II) and U(VI) were mixed in different proportions and then treated with required amount of HMBAINH and buffer solution (pH 4.0) and diluted to the volume in 10ml volumetric flasks. The third order derivative spectra for these solutions were recorded (350-600nm) and the derivative amplitudes were measured at 413nm and 470nm. 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.13, which indicate the usefulness of the proposed method for the simultaneous determination of U(VI) and Th(IV).

Table.14. Determination of iron and uranium in complex materials

Sample	Amount (μg mL^{-1})					
	Iron content			Uranium content		
	Found±SD(n=4)	Added	Recovery amount±SD(n=4)	Found±SD(n=4)	Added	Recovery amount±SD(n=4)
Phosphate ore	86.58± 1.20	12	11.38± 0.03	24.32±0.04	12	12.30±0.06
Thorium nitrate	28.40±0.98	12	11.92±0.06	66.86±0.09	12	11.84±0.05
Scandium oxide	32.28±1.12	12	12.08±0.03	46.47±0.08	12	12.22±0.08

Table. 15 Comparison of the results with the reported methods

Metal ion	Reagent	λ_{max} (nm)	pH/ medium	Aqueous/ Extraction	Beer's law (μgmL^{-1})	ε x10^4 L mol^{-1} m^{-1}	Interference	Reference
Fe(II)	2-[2-(3,5-ibromopyridyl)azo]-5-dimethylaminobenzoic acid	615	2.0-7.0	Extraction	0-5.5	9.36	Tl(I),Zn(II),Cr(III, W(VI),Co(II), Cu(II),Ni(II),Pd(II)	1
Fe(II)	1,10-Phenanthroline and picrate	510	2.0-9.0	Extraction	0.1-3.6	13	EDTA,CN$^-$	2
Fe(II)	4-(2-Pyridylazo)resorcinol	505	6.0-7.5	Extraction	0-2.0	6.0	Ni(II),Co(II),Pb(II),EDTA	3
Fe(II)	1,10-Phenanthroline-tetraphenylborate	515	4.25	Aqueous	2.24-37.29	1.2	-	4
Fe(II)	1,3-Diphenyl-4-carboethoxy pyrazole-5-one	525	3.5-4.0	Aqueous	0.5-10	1.156	Cu(II),Co(II),Zn(II), Mo(VI),EDTA	5
Fe(II)	Dyformylhydrazine	470	7.3-9.3	Aqueous	0.25-13	0.3258	-	6
Fe(II)	4,7-Diphenyl-1,10-phenanthroline and tetraphenylborate	534	-	Extraction	0-20.0	2.0	-	7
Fe(II)	Thiocyanate-phenanthroline	520	-	Aqueous	0-24	1.87	-	8
Fe(II)	Thiocyanate-acetone	480	$HClO_4$	Aqueous	-	2.1	Cu(II),NO_2^-,$S_2O_3^{-2}$, $H_2PO_4^{-2}$,$C_2O_4^{-2}$	9
Fe(II)	2-hydroxy-3-methoxy benzaldehydeisonicotinoylhydrazone	385	4.0	Aqueous	0.139-1.396	2.0	Ru(III),V(V),Sn(II), Cu(II),Pd(II), Mo(VI) Ga(III), Bi(III)	Present method
U(VI)	N-phenyl-3-styrylacrylohydrox -amic acid	410	6-6.8	Extraction	1.22-22	1.2	-	17
U(VI)	5-(2′-carboxyphenyl)azo-8-quinolinol	524	5.2-6.1	Extraction	1.4-7.1	1.035		18
U(VI)	N-phenylcinnamohydroxamic acid	400	5.5-8.5	Extraction	2-40	0.65		19
U(VI)	5-(2′-carboxyphenyl)azo-8-quinolinol in Triton X-100	568	5.2-6.1	Micellar	0.2-3.3	1.5		20
U(VI)	2-hydroxy-3-methoxybenzaldehyde-isonicotinoylhydrazone	395	4.0	Aqueous	1.19 – 11.9	0.9	Fe(II),Ru(III), Pd(II),Ga(III), Bi(III),Cu(II) V(V)	Present method

Applications

Determination of iron and uranium in complex materials

1 g of phosphate ore or 0.5 g of scandium oxide or 0.5 g of thorium nitrate was dissolved in minimum volume of con.HCl. The solution was diluted with 10 ml of distilled water and boiled for few minutes. It was then cooled and filtered to remove insoluble material. The filtrate was

then neutralized with ammonia solution and then diluted to the volume in a 50ml volumetric flask with distilled water.

Different aliquots of the sample solutions were treated with suitable volumes of buffer solution (pH 4.0), HMBAINH reagent and made up to the volume in 10ml volumetric flasks with distilled water. The third order derivative spectra of the resultant solutions were recorded and derivative amplitudes were measured at 413 and 470 nm. The amounts of iron and uranium in the sample solutions were evaluated from the predetermined calibrated plots and presented in table.14. Known amounts of Fe (II) and U (VI) were added to the sample aliquots and the recovery percentages were also evaluated, which indicate the suitability of the proposed simultaneous method for the determination of iron and uranium in complex materials.

CONCLUSION

The analytical results of present methods of direct and derivative spectrophotometric determination of iron and uranium were compared with some of the recently reported methods and presented in table.15 ,which reveal that the present method of determination of iron is more sensitive and selective than number of methods. Although the present method of determination of uranium is less sensitive than many methods, it is simple, no extraction is required. So, usage of spurious organic solvents has been avoided in both the methods

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