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Derivative Spectrophotometric Determination of Uranium(VI) using 2-Hydroxy-3-methoxybenzaldehydeisonicotinoyl-hydrazone Reagent

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A 1:1 (M:L) yellow coloured water-soluble complex of U(VI) is formed with 2-hydroxy-3-methoxybenzaldehyde-isonicotinoylhydrazone (HMBIH) in acidic buffer solution. The reaction between U(VI)-HMBIH is instantaneous at pH 4.0 and the absorbance remains constant for more than 2 h. The molar absorptivity and sandell's sensitivity is 1.05×10^4 L mol^{-1} cm^{-1} and 0.0238 μg cm^2, respectively at λ_{max} 374 nm. Beer's law obeyed in the concentration range of 1.19-11.9 μg/mL. The stability constant of U(VI)-HMBIH complex is 2.08×10^6. The first and second order derivative spectrophotometric determination of U(VI) was carried out by measuring peak height technique at 436 and 441 nm, respectively. This method has been satisfactorily applied for the determination of U(VI) in rock and synthetic samples. The effect of various diverse ions also studied.

Key Words: 2-Hydroxy-3-methoxybenzaldehydeisonicotinoylhydrazone, Derivative spectrophotometry, U(VI) determination.

INTRODUCTION

The potential application of hydrazone derivatives for the spectrophotometric determination of metal ions has been reviewed by Singh *et al.*[1]. The spectrophotometric determinations of uranium by using hydrazones are not used much[2,3]. In the light of good analytical characteristic of hydrazones, here in we report the synthesis, characterization and analytical properties of 2-hydroxy-3-methoxybenzaldehydeisonicotinoylhydrazone (HMBIH). In continuation of our previous work, herein we report zero, first and second order derivative spectrophotometric determination of U(VI) in aqueous medium. Derivative spectrophotometric methods for the determination of metal ions[4-7] are not exploited much.

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EXPERIMENTAL

Spectrophotometric measurements were made in an Schimadzu 160A microcomputer based UV-Visible spectrophotometer equipped with 1.0 cm quartz cells, an ELICO LI-120 digital pH meter was used for pH adjustments.

All reagents used were of AR grade unless otherwise stated. All solutions were prepared with distilled water. The standard U(VI) solution (0.01 M) was prepared by dissolving 0.5161 g of uranyl acetate ($UO_2(CH_3COO)_2\cdot 6H_2O$ AR Merk) in minimum amount of dilute acetic acid and diluted up to the mark using distilled water in a 100 mL standard flask.

The reagent, 2-hydroxy-3-methoxybenzaldehydeisonicotinoylhydrazone was prepared by simple condensation of 1 mol of 2-hydroxy-3-methoxybenzaldehyde with 1 mol of isonicotinoylhydrazide. In a 250 mL round bottom flask hot methanolic solution of 2-hydroxy-3-methoxybenzaldehyde (1.5 g, 0.01 mol) and isonicotinoylhydrazide (1.37 g, 0.01 mol) are mixed and refluxed using water condenser for 3 h. On cooling the reaction mixture, a yellow coloured product was separated out, collected by filtration, washed with cold methanol, yield 60 %, m.p. 228 ºC.

The mass spectrum of HMBIH shows a molecular ion (M) peak at 271.1(m/z) corresponding to its molecular weight and (M+I) peak at 271.9.

The Infrared spectrum of HMBIH shows bands at 1690 (s), 3200 (b), 3003 (m), 1566 (s) cm^{-1} for –C=O–NH, intermolecular –O–H, –C–H stretch, imine group (=N–), respectively.

A ^1H NMR spectrum shows the δ value 3.8(s, H), 6.9(m, 1H), 7.1(d, 1H), 7.4(d, 1H), 7.7(m, 2H), 8.7(s, 1H), 8.8(s, 2H), 10.7(s, 0H), 12.2(s, NH, 1H) and the structure is confirmed based upon NMR, IR and Mass spectral data given in Fig. 1.

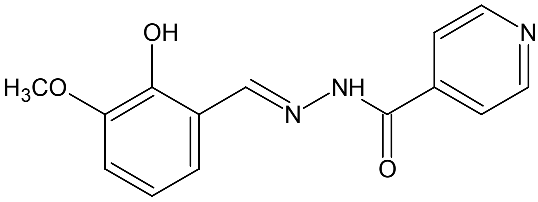

Fig. 1. Structure of 2-hydroxy-3-methoxybenzaldehydeisonicotinoylhydrazone

The reagent solution (0.01 M) was prepared by dissolving 0.271 g of HMBIH in 100 mL of DMF. The reagent is stable for 48 h.

Buffer solutions were prepared by 1 M HCl -1 M CH_3COONa (pH 0.5-3.5); 0.2 M CH_3COOH -0.2 M CH_3COONa (pH 4.0-7.0); 2 M NH_4Cl-2 M NH_4OH (pH 7.5-12.0).

Reaction with metal ions: The reactions of some important metal ions were tested at different pH values. The samples were prepared in 10 mL volumetric flasks by adding 4 mL of buffer (pH, 1-11), metal ion (0.5 mL of 1×10^{-3} M) and 0.5 mL of 1×10^{-2} M HMBIH solution. The solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 350-600 nm range against reagent blank. The results are summarized in Table-1.

TABLE-1
ANALYTICAL CHARACTERISTICS OF
2-HYDROXY-3-METHOXYBENZALDEHYDEISONICOTINOYL-HYDRAZONE (HMBIH)

Metal ion	pH	λ_{max} (nm)	Molar absorptivity (L mol^{-1} cm^{-1})
Co^{2+}	5.50	435	2.02×10^4
Ni^{2+}	6.00	372	1.02×10^4
Al^{3+}	6.50	394	3.20×10^4
V^{5+}	4.75	346	8.10×10^4
U^{6+}	4.50	374	1.05×10^4

Recommended procedure

Determination of U(VI) (zero order spectrophotometry): An aliquot of the solution containing 1.19-11.9 µg/mL of U(VI), 4 mL of buffer solution pH 4.0 and 0.5 mL of 0.01 M HMBIH reagent were taken in a 10 mL volumetric flask and the solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at 374 nm in a 1.0 cm cell against reagent blank prepared in the same way but without U(VI) metal solution. The measured absorbance was used to compute the amount of U(VI) from the calibration plot.

Determination of U(VI) by first order derivative spectrophotometry: For the above solution of U(VI)-HMBIH first order derivative spectrum was recorded, with a scan speed having degrees of freedom 9 in a wavelength range 350 to 600 nm. The derivative spectrum was measured by peak height (h) method at 436 nm. The peak height (h) at 436 nm is proportional to the concentration of uranium(VI). Therefore, the peak heights were measured at this wavelength for the construction of calibration plots.

Determination of U(VI) by second order derivative spectrophotometry: The second order derivative spectra of U(VI)-HMBIH system recorded in a wavelength range 350-600 nm shows maximum amplitude at 441 nm. Therefore the amplitude at this wavelength was measured for the construction of calibration plots.

RESULTS AND DISCUSSION

The colour reactions of some important metal ions with HMBIH are summarized in Table-1. The colour reaction are mainly due to the complex formation of HMBIH with divalent, trivalent, pentavalent and hexavalent metal ions such as Ni(II), Co(II), Al(III), V(V) and U(VI) in acidic buffer medium to give intense coloured complexes. In acidic medium, the ligand presumably coordinates the metal ions as di-anion to give a neutral complexes.

Determination of U(VI) Using HMBIH: U(VI) reacts with HMBIH in acidic medium to give yellow water-soluble species. The colour reactions between U(VI) and HMBIH are instantaneous even at room temperature in the pH range 3.0-6.0. The absorbance of the yellow coloured species remains constant for more than 2 h. The maximum colour intensity has been observed at pH 4.0.

A 5-fold molar excess of reagent is adequate for full colour development. The order of addition of metal ion, reagent and buffer solution has no adverse effect on the absorbance. The complex formation reaction between U(VI) and HMBIH has been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Important physico-chemical and analytical characteristics of U(VI) and HMBIH are summarized in Table-2.

TABLE-2
PHYSICO-CHEMICAL AND ANALYTICAL CHARECTERISTICS OF U(VI)-HMBIH COMPLEX

Characteristics	Results
λ_{max} (nm)	374
pH range (optimum)	3.5-4.5
Mole of reagent required per mole of metal ion for full colour development	5 folds
Molar absorptivity (L mol^{-1} cm^{-1})	1.05×10^4
Sandell's sensitivity (μg cm^{-2})	0.0238
Beer's law validity range (μg/mL)	1.19 to 11.9
Composition of complex (M:L) obtained in jobs and mole ratio method	1:1
Stability constant of the complex	2.08×10^6
Standard deviation in the determination of 1.12 μg/mL of U(VI) for ten determinations	0.007
Relative standard deviation (%)	0.05

Derivative spectrophotometry is a very useful technique, in the sense that (1) it decreases the interference *i.e.* increase the tolerance limit value of the foreign ions and (2) it may be advantageously used for the determination of metal ions having overlapping spectra. The recommended procedure has been employed for the determination of U(VI).

The zero order, first and second order derivative spectra of U(VI) complex of HMBIH are given in Figs. 2-4, respectively.

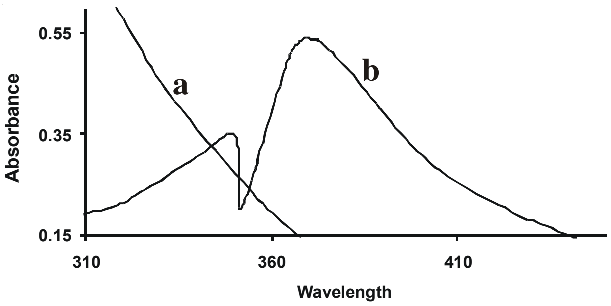

Fig. 2. Zero order Absorption spectra of (a) Reagent HMBIH 5 × 10^{-4} M *vs.* Water blank at pH = 4.0 (b) U(VI)-HMBIH Complex *vs.* Reagent blank at pH = 4.0, U(VI) = 5 ×10^{-5} M, HMBIH = 5 ×10^{-4} M

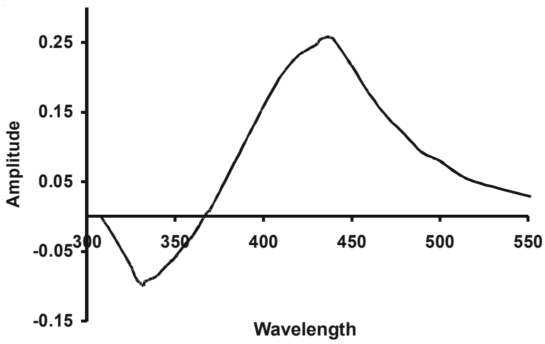

Fig. 3. First order derivative spectra of U(VI)-HMBIH complex *vs.* Reagent as blank, At pH = 4.0, U(VI) = 5 × 10^{-5} M, HMBIH = 5 × 10^{-4} M

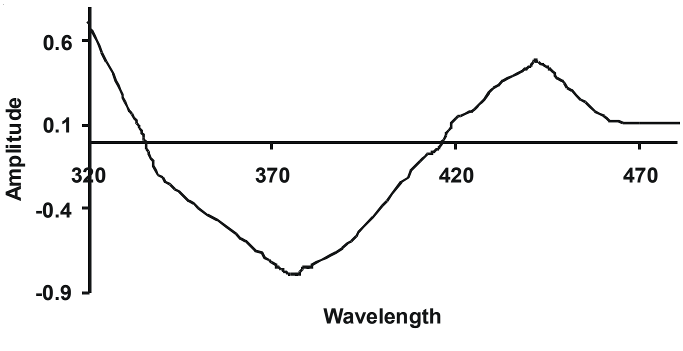

Fig. 4. Second order derivative spectra of U(VI)-HMBIH complex *vs.* reagent blank at pH = 4.0, U(VI) = 5 × 10^{-5} M, HMBIH = 5 × 10^{-4} M

Effect of diverse ions: The effect of various diverse ions in the determination of U(VI) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ± 2 % in the absorbance or amplitude. The results are given in Table-3. The data obtained in the first and second derivative methods is also incorporated. The data suggest that several associated anions and cations do not interfere when they are present in large excess. Such as Br^-, urea, tartarate, CH_3COO^-,

TABLE-3
TOLERENCE LIMIT OF FOREIGN IONS IN THE DETERMINATION OF 5.95 μg/mL URANIUM(VI)

Ion added	Tolerance limit (μg/mL)		
	Zero order	Fist derivative	Second derivative
I^-	6345	6345	5076
Urea	3071	3071	3071
Br^-	1598	1977	1598
Tartarate	1483	2225	2225
Tetraborate	1228	1228	1228
$S_2O_3^{2-}$	1121	1682	1682
SO_4^{2-}	768	961	961
Thiourea	764	1146	764
PO_4^{3-}	760	950	950
NO_3^-	496	620	620
SCN^-	465	465	465
Cl^-	284	284	177
Ascorbic acid	88	88	88
F^-	57	66	66
$C_2O_4^{2-}$	35	35	35
Citrate	19	19	19
W^{6+}	515	515	515
Na^+	496	496	496
Hg^{2+}	301	301	301
Cd^{2+}	281	281	281
Sr^{2+}	175	175	175
Ca^{2+}	80	80	80
Mn^{2+}	55	55	55
La^{3+}	28	28	28
Sn^{2+}	24	59	24
Zn^{2+}	6.0	6.0	13
Fe^{3+}*	6.0	6.0	6.0
Pb^{2+}	4.0	17	4.0
Co^{2+}	1.0	1.0	1.0
Ce^{4+}	0.3	0.3	3.0
Cu^{2+}**	0.1	0.1	0.1

*Masked by fluoride 6 μg/mL; **Masked by thiourea 917 μg/mL.

$S_2O_3^{2-}$, W^{6+}, Hg^{2+}, Cd^{2+}, Sr^{2+} and Ca^{2+}. The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ions such as Fe^{3+} and Cu^{2+} is decreased with masking agents fluoride and thiouera, respectively.

Applications

The proposed method was applied for uranium(VI) determination in rock sample and synthetic sample of pitch blend ore.

Preparation and analysis of rock sample: 2.0 g of rock sample (IAEA SY-3) was digested in HF and KNO_3 for several hours; Uranium in the sample was separated as the soluble carbonate[8] and the solution was made up to the mark in a 100 mL standard flask. Uranium in this solution is determined by the recommended procedure from a pre determined calibration plot. The results obtained are compared with Arsenazo(III) method[9] and presented in Table-4.

TABLE-4
ESTIMATION OF URANIUM(VI) mg/g IN ROCK SAMPLES

Sample	Amount of U(VI) mg/g		Error (%)
	Arsenazo(III) method	Amount found by present method*	
IAEA SY-3	5.70	5.58	+2.10
	11.35	11.18	+2.20
	19.25	19.39	-0.73

*Average of best three determinations among five determinations.

Preparation and analysis of synthetic sample of pitch blend ore: A synthetic mixture of pitch blend ore was prepared by mixing in the same ratio, as the components would be present in pitch blend ore. The resultant mixture was dissolved in conc. HCl and evaporated to dryness. The residue was redissolved in distilled water and made up to the mark in a 50 mL volumetric flask. Uranium(VI) present in this mixture was determined by the recommended procedure from a pre determined calibration plot and presented in Table-5.

TABLE-5
ESTIMATION OF U(VI) IN SYNTHETIC SAMPLE OF PITCHBLEND ORE

Composition (%)	Amount of uranium (ppm)		Error (%)
	Taken	Found*	
UO_3-81.63; PbO-6.39	19.00	18.85	+0.8
AS_2O_3-2.34; CaO-1.0	15.20	15.36	-1.0
H_2O-3.17	27.40	27.13	+1.0

*Average of best three determinations among five determinations.

Conclusion

The present method using HMBIH as spectrophotometric reagent for the determination of uranium(VI) in aqueous medium is sensitive and simple. This method was favourably compared with previously reported spectrophotometric methods[2,10-15] presented in Table-6. Most of the spectrophotometric methods involve either heating[10] of the reaction mixture or extraction[11-15]. However heating at a specific temperature and for a long time is laborious and time consuming. The determination of uranium(VI) using HMBIH is not laborious and there is no need of heating the components or extraction. Further, the reagent is easy to synthesize using available chemicals. Moreover, the present method is simple, rapid, reasonably sensitive and selective for the determination of uranium(VI).

TABLE-6
COMPARISON OF SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF U(VI)

Reagent	λ_{max} (nm)	pH	Molar absorptivity (ε) (L mol^{-1} cm^{-1})	Extraction / heating	Beers law range	Ref.
o-Chlorophenyl fluorone	560	7.5	1.42×10^4	Heated at 95 ºC	0-10 mg/ 5 mL	10
4,5-Dibromo-2-nitrophenylfluorone	600	9.0	0.00077	Extracted by TBP	0-15 mg/ 25 mL	11
N-Phenyl cinnamohydroximic acid	400	5.5-8.5	6500	EtOAc extrction	2-40 mg/mL	12
5-(*p*-Carboxyphenylazo)-8-hydroxyquinoline	470	4-6	4.39×10^4	TBP extraction	0-55 mg/ 25 mL	13
5-(2-Carboxyphenylazo)-8-quinolinol	524	5.2-6.1	1.035×10^4	Isobutyl methylketone extraction	1.4-7.1 g/mL	14
NHDTAHA	390	-	1.0×10^4	Extraction chloroform	2-3 mg/ 25 mL	15
2-Hydroxy-1-naphthaldehyde isonicotinoylhydrazone (OHPINH)	430	3.0	9.6×10^3	–	0.2-33 mg/ 25 mL	2
2-Hydroxy-3-benzaldehyde isonicotinoylhydrazone	374	4.0	1.0×10^4	–	1.19-11.9 (μg/mL)	Present method

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