

# Non-Extractive Spectrophotometric Determination of U(VI) Using 5-Bromo Salicylaldehyde Isonicotinoyl Hydrazone in Environmental, Phosphate Rocks and Fertilizer Samples

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**Abstract-** A highly sensitive and selective spectrophotometric method was developed for the determination of trace amount of uranium (VI) in water samples in aqueous DMF medium. The uranyl ion forms a pale yellow colored complex with 5-Bromo salicylaldehyde isonicotinoyl hydrazone (5-BrSAINH) in an acidic buffer of pH 5.0. The complex has an absorbance maximum at 395nm, was stable for more than 72 hours. The complex shows maximum absorbance at 395nm. Beer's law is obeyed in the range 0.119-1.071  $\mu\text{gml}^{-1}$ . The molar absorptivity and sandell's sensitivity of the proposed method were found as  $1.17 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$  and  $0.02\mu\text{gcm}^{-2}$ , respectively. The pale yellow colored complex has 1:1 (Uranium (VI)- 5BrSAINH) Stoichiometry. The stability constant of the complex was determined as  $1.80 \times 10^5$  by Job's method. A sensitive and selective second order derivative spectrophotometry has also been proposed for the determination of U (VI). The interference of various cations and anions were studied. The developed methods were successfully employed in the determination of U (VI) in environmental, phosphate rocks and fertilizer samples.

**Index Terms-** Spectrophotometry, 5-BrSAINH, Determination of Uranium (VI), environmental samples, phosphate rocks and fertilizer samples.

## I. INTRODUCTION

Uranium finds extensive applications as nuclear fuel in atomic power plants and in the preparation of filaments of electric lamps, as an additive in special steels and in ceramic and glass, products as coloring agent. Uranium is a mobile element in surface, or near surface environments. Its geochemical exploration methods demand the measurement of the trace quantities of the metal ion in water samples collected for prospecting purposes. Uranium compounds are carcinogenic and hence there is a need for the development of low cost rapid methods for its determination in soil and water samples.

## II. DIFFICULTIES RAISED IN PREVIOUS METHODS

It is difficult to determine directly by uranium colorimetry due to its low concentrations in natural samples of minerals and water. The anions such as oxalate, fluoride, tartate and citrate interfere in many colorimetric methods. Many colorimetric

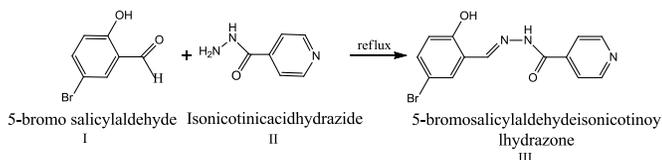
methods reported earlier for the determination of uranium with organic reagents. Many organic compounds react uranyl ion give colored complexes or precipitates. Sandell procedures using thiocyanate, peroxide, ferrocyanide and diethyl dithiocarbamate, as reagents in colorimetric determination of uranium. However colorimetric methods are not sensitive and not well suited for the determination of many of these small amounts of the element. Several methods for colorimetric determination of uranium (VI), arsenazo<sup>1</sup>, thiocyanate<sup>2</sup>, dibenzoyl methane<sup>3</sup>, perchloric acid<sup>4</sup> solutions have been reported as reagents for quantitative determination but lack selectivity. Uranium forms strong complexes with organic reagents, resultant effect on precipitation and interference, a direct spectrophotometric analysis in the presence of anions would be possible.

A wide variety of techniques are available for the spectrophotometric determination of uranium. Its solid phase extraction in surface water<sup>5</sup>, determination in some synthetic matrices<sup>6</sup>, river and saline water samples<sup>7</sup>, spectrophotometric measurements of uranium in sea water by means of arsenazo (III)<sup>8-11</sup>, simple spectrophotometry in aqueous solution<sup>12-13</sup>, spectrophotometric determination of uranium (VI) in tap water, well water, waste water samples<sup>14</sup> and spectrophotometric determination of uranium (VI) with dyes in surfactant media<sup>15-16</sup>. In the present paper, a simple and sensitive method is developed for the spectrophotometric determination of trace amounts of uranium (VI) by complexing with 5-bromo salicylaldehyde isonicotinoyl hydrazone (5-BrSAINH). The reagent forms pale yellow colored complex with uranium (VI) in acid medium in the pH range 4.5-5.5 is stable for more than 72 hours. Hence, a systematic study has been made to develop a spectrophotometric method for the determination of uranium in environmental, phosphate rocks and fertilizer samples.

## III. EXPERIMENTAL

Equimolar solutions of 5-bromo salicylaldehyde (Sd-fine) and isonicotinic acid hydrazide (Sd-fine) in water were mixed and refluxed for one hour on water bath and cooled. The light yellow solid formed was separated by filtration, washed with water at room temperature. The product was recrystallized from aqueous alcohol. The product showed a melting point of 238-240°C.  $1 \times 10^{-2}\text{M}$  solution of the reagent was prepared by dissolving 0.320gm of the reagent in 100ml of

dimethylformamide (DMF). Working solutions were prepared by diluting the stock solution with DMF.



0.01 M uranium (VI) solutions were prepared by dissolving appropriate amount of uranyl acetate (E-Merck) 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 were prepared by mixing appropriate volumes of 1M CH<sub>3</sub>COOH and 1M HCl, (p<sup>H</sup> 1.0-3.5) CH<sub>3</sub>COOH and CH<sub>3</sub>COONa (p<sup>H</sup> 4.0-7.0) NH<sub>4</sub>OH and NH<sub>4</sub>Cl (p<sup>H</sup> 8.0-10).

### Sample solutions

#### Spiked saline water solution

Saline water sample solutions (3M NaCl) were spiked with uranium and the absorbance of each were measured at the appropriate wavelength.

#### Water samples

Filtered environmental water samples (100ml) were analyzed for uranium. To samples, not containing U (VI) known amounts of U (VI) were added and remaining mixtures were analysed by the proposed procedure for uranium.

#### Phosphate rock and fertilizer sample

The phosphate rock which is generally used as the raw material for manufacturing phosphate fertilizers, NPK and DAP were collected from a fertilizer industry, Anantapur. The collected samples were finely grounded and 10g of each sample was transferred separately into Erlenmeyer flasks containing 100 ml of 0.1M citric acid.

## IV. PROCEDURE

Aliquots of solutions containing 0.1-1.0µgml<sup>-1</sup> of uranium (II) were transferred into a series of 10ml volumetric flasks. To these 5-BrSAINH (5X10<sup>-4</sup>) was added and the contents were diluted to the mark with distilled water and mixed well. The absorbance was measured at 395nm against the reagent blank. The calibration graph was constructed by plotting the absorbance against the concentration of U(VI) ions. For the solutions as prepared above, the second derivative spectra were recorded with reference to the reagent blank in the wavelength range 400-480nm. The derivative amplitudes were measured at wavelength 423nm and 463nm and were plotted against the amount of uranium (VI) to obtain the calibration plot. The absorbance and P<sup>H</sup> measurements were made on a Perkin Elmer (LAMDA 25) UV-Visible spectrophotometer (Model UV-160A) controlled by a computer fitted with 1cm path length quartz cell and an ELICO digital p<sup>H</sup> meter of (Model LI 613), respectively.

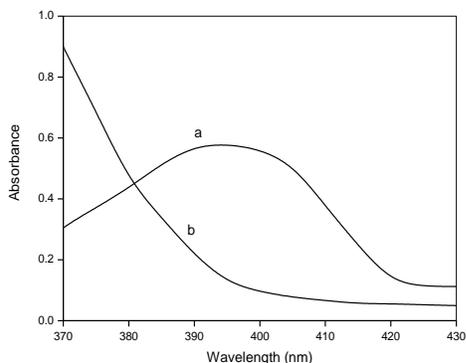
## V. RESULTS AND DISCUSSION

The reaction of 5-BrSAINH with U(VI) at room temperature gives a Pale yellow colored soluble complex. The U(VI) - 5-BrSAINH complex shows maximum absorbance at 395nm where the reagent blank does not absorb appreciably, shown in fig 1. Therefore, subsequent analytical studies were carried out at 395nm using the reagent blank. The plot between absorbance and p<sup>H</sup> reveal that the metal complex shows maximum p<sup>H</sup> of the experimental solution and stable constant absorbance in the p<sup>H</sup> range 4.5-5.5. Therefore, p<sup>H</sup> 5.0 was selected for further studies. The minimum amount of reagent acquired maximum color intensity with a given amount of U (VI) was evaluated from the absorbance measurements of the experimental solutions containing different amount of reagents. The results showed that a 25-fold molar excess of the reagent was required for the development of maximum color intensity with a given amount of Uranium (VI). The composition of the complex was determined using Job's continuous variation method and molar ratio method, the results indicate a 1:1 stoichiometry between the U(VI) and the reagent, was shown in fig 2. The stability constant of the complex was determined as 1.80x10<sup>4</sup> by Job's method. From the calibration plot, it was observed that Beer's law was obeyed in the concentration range 0.119-1.071 µgml<sup>-1</sup> of U (VI). The straight line obeys the equation A<sub>395</sub>=0.0645C+0.0078. The molar absorptivity and sandell's sensitivity of the method were found as 1.17 x 10<sup>4</sup> L.mol<sup>-1</sup>cm<sup>-1</sup> and 0.02 µgcm<sup>2</sup>, respectively. The effect of various anions and cations normally associated with U (VI) on the absorbance of the experimental solution was studied. The tolerance limits of the tested foreign ions which bring about a change in the absorbance by +2% were calculated. Almost all the tested anions possess high tolerance levels (>100 fold excess). The metal ions Ce (IV), V (III) and Fe (III), were tolerable up to 15-40 fold excess, and Ti (III) and Bi (III) interferes seriously presented in **Table 1**. The second derivative curves recorded(fig.3) for experimental solutions showed the derivative amplitudes were measured at 423nm and 463nm for different concentrations of U(VI) and plots were made between the amount of U(VI) and the derivative amplitude. The plots were linear and obeyed beer's law in the range 0.1297-9.52µg ml<sup>-1</sup> at 423 nm and 0.2975-7.14 µg ml<sup>-1</sup> at 463nm respectively. The effect of various cations and anions on the derivative amplitude was studied and it was noticed that all the ions that did not interfere in the zero order determinations of U (VI) also did not interfere in second order derivative method. The metal ion with V(III) were interfered in 20 fold excess, Ti (IV) and Bi (III) were interfered in 5-fold excess in zero order method, but second order derivative method V (III) were tolerable up to 35 folds. Further Ti (IV) and Bi (III) were interfere 5-fold excess in second order derivative method. The analytical results of both direct and derivative methods were summarized and are presented in **Table 2**.

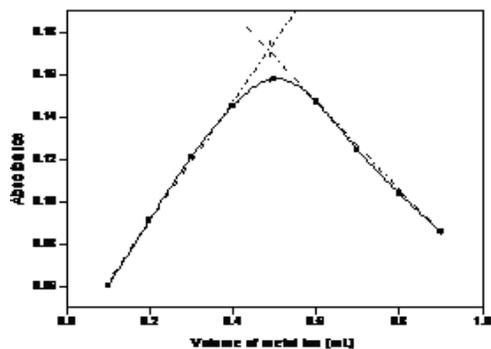
#### Applications

The direct spectrophotometric method was developed which were suitable for the determination of uranium in some environmental water samples and in phosphate rock and fertilizer samples. Suitable aliquots of the sample solutions were treated with required amount of the reagent and suitable buffer media

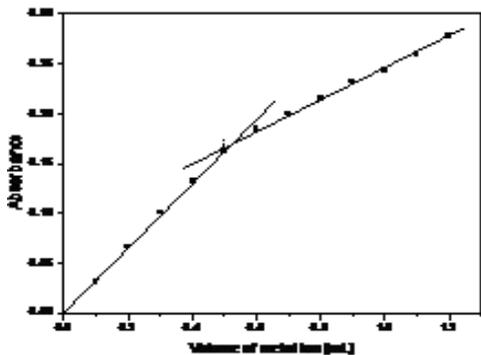
and the absorbances of resultant solutions were measured at appropriate wavelengths. The amount of metal ions present in samples were computed from the measured absorbance values. The results are shown in table 3,4 and 5, which are in good agreement with the certified values and with the AAS method.



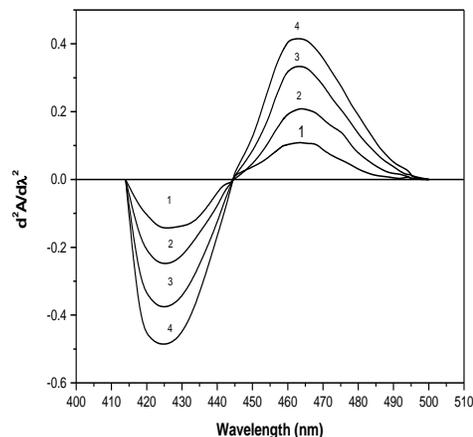
**Fig. 1. Absorption spectra of**  
(a) [U(VI)-5-Br-SAINH] Vs Reagent blank  
(b) 5-Br-SAINH Vs Buffer blank  
[U(VI)] =  $5 \times 10^{-5}$  M; [Br-SAINH] =  $5 \times 10^{-4}$  M  
pH = 5.0



**Fig. 2. Job's method**  
[U(VI)] = [Br-SAINH] =  $1 \times 10^{-3}$  M  
 $\lambda_{max} = 395$  nm  
pH = 5.0



**Fig. 3. Molar Ratio method**  
[U(VI)] = [Br-SAINH] =  $1 \times 10^{-3}$  M  
 $\lambda_{max} = 395$  nm  
pH = 5.0



**Fig.4. Second Order derivative spectra of U(VI)-5Br-SAINH Vs Reagent blank**  
U(VI) ( $\mu\text{g mL}^{-1}$ ) = 1)0.119., (2)0.238; (3)0.317; 4) 0.476

**Table.1** Tolerance limits of foreign ions

Foreign ion	Tolerance Limit ( $\mu\text{g mL}^{-1}$ )	Foreign ion	Tolerance Limit ( $\mu\text{g mL}^{-1}$ )
Iodide	1,280	Ca(II)	1,120
Sulfate	960	Mg(II)	1070
Bromide	780	Na(I)	940
Thiocyanate	660	K(I)	780
Nitrate	570	Zr(IV)	660
Thiosulphate	480	Ba(II)	550
Phosphate	460	La(III)	420
Chloride	450	W(VI)	350
Acetate	310	Se(IV)	290
Carbonate	220	Cu(II)	250
Urea	180	Mo(VI)	230
Oxalate	100	Al(III)	130
		Fe(III)	100
		Th(IV)	80

V(III)	50
Ti(IV)	20
Bi (III)	10

\*Amount of U(VI) taken =  $5.95 \mu\text{g mL}^{-1}$ , pH = 5.0

**Table 2:** Different Analytical parameters concerned into the determination

Parameter	Zero Order	Second derivative	
Analytical Wavelength (nm)	395	423	463
Beer's law range	1.19-19.04	0.11297-9.52	0.2975-7.14
Y-intercept(b)	0.0645	0.22876	0.24771
Correlation coefficient (r)	0.9997	0.9995	0.9996
Standard deviation (s)	0.0998	0.10022	0.0923

**Table 3:** Determination of U (VI) in Spiked Saline Water sample:

Sample No	Amount of U (VI) ( $\mu\text{g mL}^{-1}$ )		Recovery (%)
	Added	Found	
1	2.0	1.80	90.0
2	1.0	0.887	88.7
3	4.0	3.12	78.0
4	2.0	1.82	91.0
5	3.0	2.78	92.6

**Table 4:** Determination of U (VI) in environmental water samples

Sample	Amount of Uranium ( $\mu\text{g mL}^{-1}$ ) $\pm$ SD		Recovery (%)
	Added	Found	
Tap water	0.5	0.505 $\pm$ 0.05	101.0
		2.39 $\pm$ 0.08	
	5.0	4.90 $\pm$ 0.01	98.00
		0.5	0.502 $\pm$ 0.02
Drinking water	2.5		105.2
	5.0	2.63 $\pm$	
		0.012	102.4

	$5.12 \pm 0.03$		
	0.5	$0.503 \pm 0.02$	100.6
Surface water	2.5	$2.53 \pm 0.014$	101.2
	5.0	$4.89 \pm 0.06$	97.8

**Table 5:** Analysis of phosphate rock solutions and fertilizer solutions for uranium content

Sample	Uranium content(mg kg-1)	
	proposed method $\pm$ SD (n=4)	AAS method $\pm$ SD(n=2)
Phosphate rock(India)	$30.25 \pm 0.02$	$32.26 \pm 0.013$
NPK fertilizer	$13.36 \pm 0.014$	$15.65 \pm 0.06$
DAP fertilizer	$46.52 \pm 0.032$	$48.09 \pm 0.017$

## VI. CONCLUSION

The reagent (5-BrSAINH) allows a simple method for the spectrophotometric determination of Uranium (VI). The developed spectrophotometric method does not involve any extraction or heating process and hence the use of the solvents was avoided. A second order derivative spectrophotometric method for determination of U (VI) also developed and was more sensitive than zero order method. The developed method was successfully employed for the determination of Uranium (VI) in the spiked saline, environmental water samples and phosphate rocks and fertilizers.

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