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Use of Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] as an Analytical Reagent for the Extractive Spectrophotometric Determination of U(VI)

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Author's contribution

This whole work was carried out by the author RPS.

Original Research Article

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ABSTRACT

Extraction and spectrophotometric determination of Uranium (VI) was carried out using Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] as an analytical reagent. A reddish brown coloured complex is formed at pH 9.2 between U(VI):HCHNM which is extracted in n-butanol. An intense peak for the complex was observed at 385nm, well separated from that of ligand. Beer's law is obeyed over the range of 2 to 20 ppm. Composition of M:L in the complex was ascertained by Job's method, mole ratio method and slope ratio method and found to be 1:2. Extraction and spectrophotometric determination of U(VI) was carried out using Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] as an analytical reagent. A reddish brown coloured complex is formed at pH 9.2 between U(VI):HCHNM which is extracted in n-butanol. An intense peak for the complex was observed at 385nm, well separated from that of ligand. Beer's law is obeyed over the range of 2 to 20 ppm. Composition of M:L in the complex was ascertained by Job's method, mole ratio method and slope ratio method and found to be 1:2. Diverse ion effect was studied for various ions and the proposed method was found to be highly selective for the trace concentration of U(VI). Molar absorptivity and Sandell sensitivity values calculated are $0.1566 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0585 \mu\text{g/cm}^2$ respectively. Proposed method has been successfully applied to analyse synthetic samples and the results were found to be in good agreement with standard gravimetric methods.

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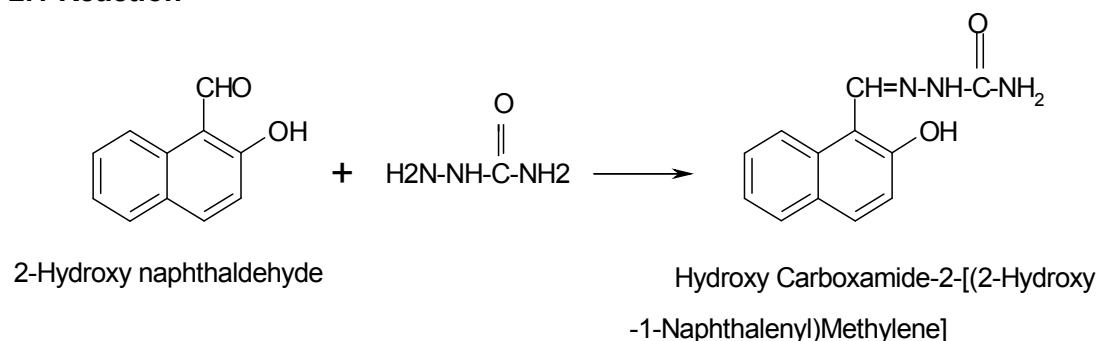
1. INTRODUCTION

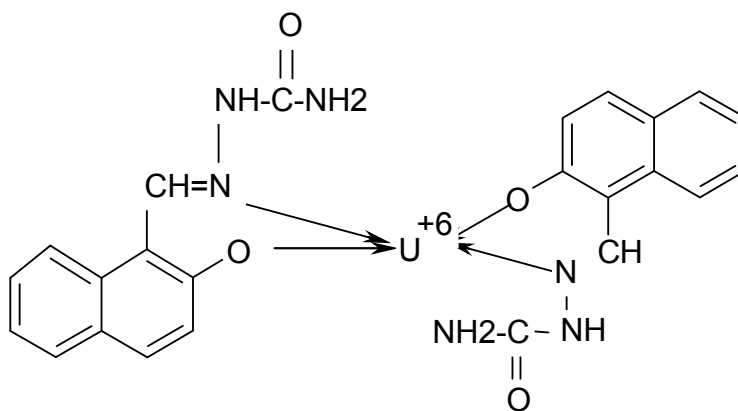
Uranium as an actinide metal has wide spectrum of applications in many frontier areas of study particularly in nuclear power industry, military sector. Many contemporary uses of uranium exploit its unique nuclear properties. Large intake of uranium is can cause damage to the kidneys because in addition to being radioactive, uranium is a toxic metal. Hence owing to the significance of uranium, its determination from associated elements by exactive spectrophotometry has been considerable importance. A wide variety of reagents has been reported for the spectrophotometric determination of uranium. A number of reagents such as oxime [1-2], hydrazone [3], calyx [4-8] etc have been used for the determination of uranium. However these methods suffer from limitations such as requirement of masking agents [3,7,9], interference of some ions [10-13],equilibrium time [1,14] in sensitivity and selectivity. A close literature survey indicates that HCHNM has far not been employed for analytical studies [15-23]. The proposed new method is simple, selective and sensitive.

2. EXPERIMENTAL

The absorbance measurements was carried out on a Shimadzu UV visible 2100 Spectrophotometer with 1 cm quartz cells and the digital pH meter Li- 120 model of Elico Pvt. Ltd. was used for pH measurement study. The chemicals used were of analytical reagent grade. Stock solution of Uranium was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ in double distilled water and was standardized by known gravimetric method [11]. The working solutions were prepared by appropriate dilution as required. The reagent was prepared as reported in the literature [15]. Equimolar quantity of 2-hydroxy naphthaldehyde (dissolved in alcohol) and semicarbazide hydrochloride (aqueous solution) mixed together in round bottom flask and aqueous solution of sodium acetate was added. The mixture was reflux for half an hour below $90^\circ C$. The mixture was cooled by keeping it overnight at room temperature, yellowish colour product was obtained. The product was then filtered recrystallised from methanol.

2.1 Reaction





Metal Complex

3. PROCEDURE FOR EXTRACTION

1.0ml of aqueous solution containing 0.2mg of metal and 1 ml of reagent was mixed in a 50ml beaker. The pH of the solution adjusted to 9.2, keeping the volume 10 ml. The solution was transferred to 100ml separatory funnel. The beaker was washed twice with 5 ml n-butanol and transferred to the same funnel. The two phases were shaken for two minutes and allowed to separate. The organic phase was collected in 10ml volumetric flask and made up to the mark with organic solvent if required. The amount of uranium present in the organic phase determined quantitatively by spectrophotometric method by taking absorbance at 385 nm and in aqueous phase was determined by gravimetric method [24].

4. RESULTS AND DISCUSSION

The reagent forms reddish brown coloured complex with U (VI), which was extracted in organic phase and the results obtained are as follows.

4.1 Extraction as a Function of PH

The extraction of uranium with Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] has been studied over the pH range 1-10 and was observed that percentage extraction of U (VI) is maximum at pH 9.2.

4.2 Absorption Spectrum

The absorption spectrum of U(VI): Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] in n-butanol shows the maximum absorption at 385nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 385nm.

4.3 Influence of Diluents

The suitability of solvents was investigated using organic solvents such as chloroform, ethyl acetate, ethyl methyl ketone, diethyl ether, toluene, n-butanol, carbon tetrachloride, MIBK,

nitrobenzene, etc. The extraction of uranium (VI) was quantitative with HCHNM in n-butanol. Hence, n-butanol was used for further extraction studies as it gave better and quicker phase separation and gave maximum absorption.

4.4 Effect of Salting Out Agents

The presence of 0.1M nitrate salts of alkali and alkaline metals do not show any effect over the absorbance value of U (VI): Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] complex extract.

4.4 Effect of Reagent Volume

The studied range of reagent volume was 0.1cm³ to 1.0 cm³. Various volumes of 0.1% reagent solution were added to the sample solution containing 120 µg of uranium at respective pH values. It was found that 1ml of 0.1% reagent is sufficient for the colour development of the uranium in 10 ml of aqueous solution at pH 9.2.

4.5 Effect of Equilibration Time

The studied range of time to study the effect of equilibrium time is 20sec to 5 minutes. The change in absorbance with variation in equilibrium time for extraction of U (VI) shows that equilibrium time of 30 sec. are sufficient for quantitative extraction of uranium.

4.6 Stability of the Complex with Time

The stability of colour of the U (VI): Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] complex with respect to time shows that the absorbance due to extracted species is stable up to 72.0 hours, after which slight decrease in absorbance is observed.

4.7 Calibration Plot

A calibration plot of absorbance against concentration of U (VI) gives linear and reproducible graph. A Beer's law is obeyed from 2 to 20 ppm of uranium (Fig. 1). The molar absorptivity and sandell sensitivity were calculated to be is 0.1566X10⁴ L mol⁻¹cm⁻¹ and 0.3019 µg cm⁻².

4.8 Nature of Extracted Species

The composition of extracted species has been determined by Job's continuous variation method (Fig. 2), Slope ratio method (Fig. 3), and Mole ratio method. It shows that the composition of U (VI): HCHNM complex is 1:4.

4.9 Effect of Divalent Ions and Foreign Ions

No interference was shown by other ions in various amount in the spectrophotometric determination of 120µg of uranium. The ions which show interference in the spectrophotometric determination of uranium were overcome by using appropriate masking agents. Ag(I) and Cd(II) by Potassium iodide, Pb(II) by Sodium thiosulphate, Mn(II) and Ce(IV) by Sodium fluoride, Cr(II) by Ammonium acetate (Table 1).

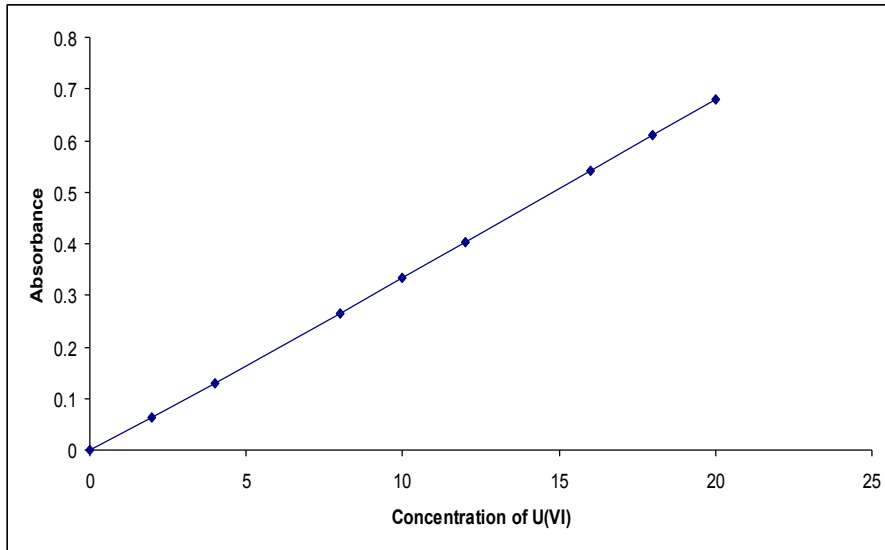


Fig. 1. Calibration plot of U (VI) with HCHNM
X axis-1 cm=1 ppm, Y axis 1cm=0.050

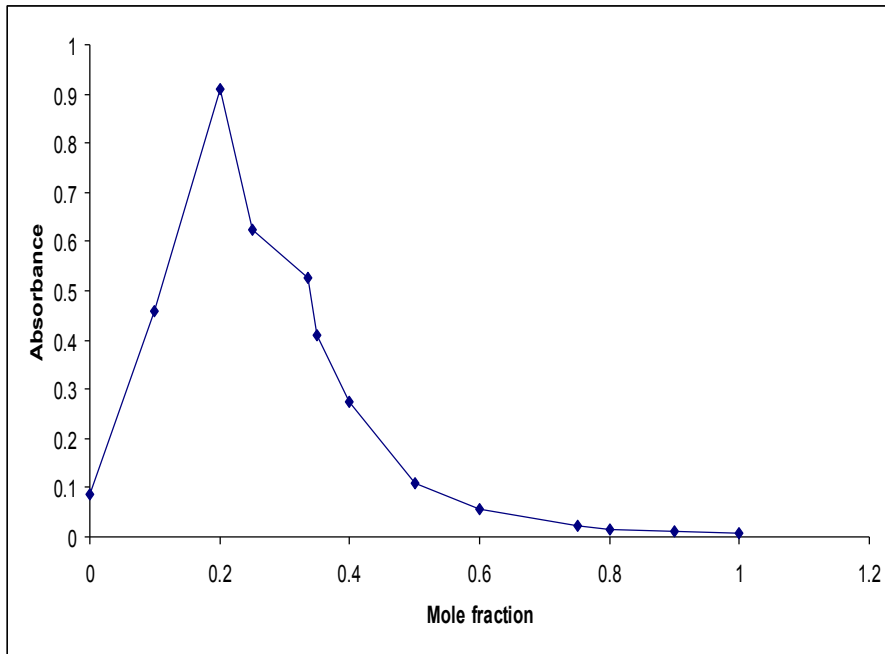


Fig. 2. Job's Continuous variation method
X axis 1 cm=0.10, Y axis 1 cm=0.100

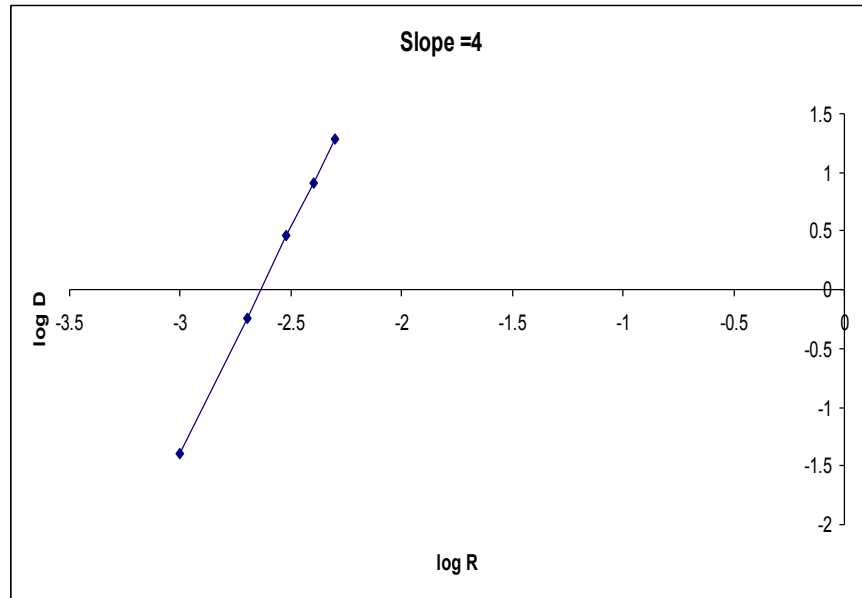


Fig. 3. Slope ratio method for U (VI): HCHNM complex

Table 1. Effect of the interference of cations on Absorbance of U (VI): HCHNM complex in n.butanol

Sr. no.	Salt	Amount added in mg	Absorbance at 385nm
1		--	0.403
2	NaCl	14	0.403
3	KCl	12	0.403
4	CaCl ₂	7	0.403
5	SrCl ₂	8	0.403
6	(NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O	9	0.403
7	MnSO ₄ .7H ₂ O	5	0.403
8	MgSO ₄ .7H ₂ O	9	0.403
9	NH ₄ VO ₃	7	0.403
10	RhCl ₃	8	0.403
11	TiNO ₃	6	0.403
12	Th(NO ₃) ₄ .4H ₂ O	7	0.403
13	LiCl	9	0.403
14	BeCl ₂	6	0.403
15	ZrO(NO ₃) ₂ .H ₂ O	8	0.403
16	BiCl ₂	10	0.403
17	Al ₂ (SO ₄) ₃ .7H ₂ O	8	0.403
18	Hg(NO ₃) ₂	7	0.403
19	(NH ₄) ₄ Ce(SO ₄) ₄ .2H ₂ O	15 µg	0.403
20	CdCl ₂	15 µg	0.403
21	ZnSO ₄ .7H ₂ O	15 µg	0.403

5. PRECISION AND ACCURACY

The precision and accuracy of the spectrophotometric method have been studied by analyzing five solutions each containing 100 µg of uranium. Aliquot used is 100 µg/ml. Standard deviation is 0.0435. Confidence limit at 99% is 99.96±0.08.

6. APPLICATIONS

The newly developed method has been successfully applied for the determination of uranium from pharmaceutical samples and real sample. The results indicate that the developed method is compatible with the standard known method (Table 2).

7. COMPARATIVE STUDY OF THE REAGENT WITH PREVIOUS REAGENTS USED IN DETERMINATION OF URANYL

Comparative study of the reagent HCHNM with various previous reagents used in determination of Uranyl was done (Table 3).

Table 2. Determination of U (VI) using HCHNM from different samples

Sr. no.	Sample	Amount of U(VI)	
		Standard method	Present method
1.	Synthetic mixtures		
	1) 1)U(VI) 10ppm +Cd(II)15ppm +Mg(II)10ppm	9.99 ppm	9.97 ppm
	2) U(VI)10 ppm +Ce(IV)10 ppm +V(V)10 ppm	9.98 ppm	9.97 ppm
	3) U(VI)10 ppm +Zr(II)10 ppm+Se(IV)10 ppm	9.99 ppm	9.98 ppm
	4) 4)U(VI)10 ppm +La(III)15 ppm + Al(III)10 ppm	10.0ppm	9..99ppm
2.	Real samples		
	Monazite sand	0.640%	0.630%

Every result is an average of three independent determinations

Table 3. Comparative study of the reagent with previous reagents used in determination of Uranyl

Sr/Ref no	Reagent	pH	max	Molar absorptivity	Beers range ppm	Remarks
1	Hydrazine carboxamide-2-[(2-hydroxy-1-naphthalenyl) methylene]	9.2	385	1561	2-20	Stable upto 72 hrs, equilibrium time is less than 30 sec
2	N-phenyl benzohydroxamic acid+8-hydroxyquinoline [25]	6.0	400	3600	5-40	V(V) and Mo(VI)interfere
3.	1-(Ethoxy caroxylpentadecyl) Triethyl ammonium bromide [26]	1.2	300	--	0.2-5.0	Interference due to Hg(II), Mo(V), W(VI), Co(II), Fe(III), Bi(III), Pd(II), Ru(III), Pt(IV), Au(III)

Table 3 continued in next page

Sr/Ref no	Reagent	pH	max	Molar absorptivity	Beers range ppm	Remarks
4.	3-oxo-N-tolylbutyramide [27]	6.5-6.9	384	3200	16.28-51.80	Equilibrium time of 5minutes
5.	2,6-dichloro 4-dibromo arsenazo [28]	3 M H ₂ SO ₄	640	110000	0.88-5.0	Th(IV)interference
6.	2-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol [29]	7.5	565	10200	2.46-5.0	Heated at 95°C for 1hr.

8. CONCLUSION

The results obtained show that Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] in n-butanol can be effectively used for quantitative extraction of U (VI) from pharmaceutical samples. The proposed method is quick and requires less amount of organic solution. The equilibrium time required is very less and the complex is stable for 72 hours. The results found to be in good agreement with those obtained by the standard method. The method is very fast, accurate and precise. The Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] was used for the first time for extraction of U (VI) from various binary mixtures.

CONSENT

Not applicable.

ETHICAL APPROVAL

Not applicable.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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