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Spectrophotometric studies on chelating behavior of oxalohydroxamic acid with uranium in aqueous streams

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Abstract

Study of the complex formation of oxalohydroxamic acid (OHA) with uranium is investigated by spectrophotometry. Oxalohydroxamic acid forms orange-yellow complex with uranium(VI) in aqueous medium and shows maximum absorbance at 381 nm at pH 6.2. The stoichiometry of the coloured species is determined to be 1:5 ratios (uranium-oxalohydroxamic acid). A calibration graph is made for the concentration range of uranium from 10-100 *mg/L*. The molar absorption coefficient at 381nm, detection limit and Sendell's sensitivity are 2230 $LMol^{-1}cm^{-1}$, 11 *mg/L* and 0.11 $\mu g/cm^2$ respectively. Relative standard deviation is less than 2% and correlation coefficient is 0.998. In these studies, oxalohydroxamic acid complex with uranium, effect of reagent-metal ratio, pH and reagent stabilities are investigated. The results obtained by the proposed procedure are in good agreement with those obtained by the standard procedure. The advantage of the present study is that, it does not generate analytical waste because hydroxamic acids are composed of only C, H, N and O atoms they can be decomposed to gases so that their application in industrial processes will not lead to increase in waste volume. The method is also applicable for the determination of concentration of uranium in reprocessing samples.

Keywords: Uranium, Oxalohydroxamic acid, Spectrophotometry, pH, Molar absorptivity

1. Introduction

Hydroxamic acids are colourless, crystalline, weakly acidic compounds which form metal complexes by chelation of metal ion between the two oxygen atoms of the monoanion to give a five membered ring. They are well known to form both soluble and insoluble colored complexes [1]. Heavy metal ions react with hydroxamic acids to form soluble colour complexes or precipitates [2-3]. Hydroxamic acids are characterized by a remarkable versatility as reactants in analytical chemistry. The general formula of hydraoxamic acid is R-C=O-N(OH)-R' where R and R' are hydrogen, alkyl, aryl or acyl group and large number of derivatives are reported with different R and R' group. As O,O donor ligands they have a strong affinity for hard metal ions such as uranium, iron, zirconium and plutonium [4-5]. Complexation of uranyl cations with hydroxamic acids in solutions leads to the formation of 1:1 and 1:2 orange-yellow complexes. Under conditions of low acid concentrations, the solubility of uranyl-hydroxamate complexes drops rapidly and the insoluble orange-brown uranyl $(hydroxamate)_2$ complexes precipitates [6]. In acidic solutions, the hydroxamic group is hydrolyzed to the parent carboxylic acid and hydroxyl-amine [6-7]. Since hydroxamic acids are salt free compounds they decompose to gases and nitrous acid. So hydroxamic acids do not increase the mass of the aqueous waste of the industrial processes [8]. However, the fast complex formation with metal prevents hydrolysis and stabilization of hydroxamic acid chelate. Behavior of hydroxamic acids during nuclear solvent extraction operations was first reported by Grossi et al. [2-3] in late 1960s and recently, number of papers relevant to the purex process have been published. Hydroxamic acids have wide range of applications such as salt-free (thus not adding significantly to the aqueous waste), readily water soluble and in extractable into 30% TBP/nDD, reasonably stable in nitric acid and the extractability of U(VI) into 30% TBP/nDD must remains unaffected [9]. Numerous analytical methods have been reported for determination of uranium in samples of various compositions [10-12]. Many of the more sensitive chromogenic reagents such as PAR, Br-PADAP etc generated analytical waste and required special treatment and storage. The present method is simple, fast accurate and precise. It is applicable for nuclear reprocessing plant samples and does not generate analytical waste.

2. Experimental

2.1 Reagents

All reagents used in this work are analytical reagent grade only. Doubly distilled water is used for solution preparation. Stock solution of uranyl nitrate [UO_2 $(NO_3)_2.6H_2O$] is prepared and standardized by Davies Gray method [13]. From this stock solution, different concentrations of uranium standards are prepared with proper dilution. Oxalohydroxamic acid is prepared by earlier reported method [14]. Buffer solution (pH 6.2) is prepared by mixing 9.5 mL of 2 $mol.L^{-1}$ sodium acetate with 0.5 mL of 2 $mol.L^{-1}$ acetic acid then diluted to 100 mL with doubly distilled water [15].

2.2. Instrumentation

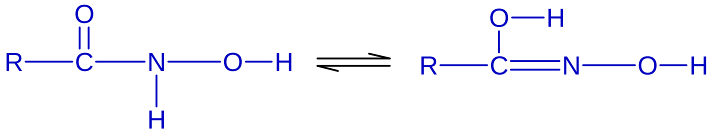
ECIL-make UV-VIS Spectrophotometer model UV5704SS equipped with 1 cm quartz cuvettes is used for absorbance measurements. The wavelength range of this spectrophotometer is 180-1100 nm. Chemlabs, Banagalore make Micro pH/mv meter coupled with glass electrode is used for pH measurements. Shimatzu made FTIR Serial No.A21374700647 is used for FTIR scanning of the Oxalohydroxamic acid. The wavelength range of this spectrophotometer is 450-4000 nm.

2.3. Developed Procedure

In each of a set of different 25 ml volumetric flask numbered 1-10, 7.5 ml of buffer solution (pH 6.2), various concentration of uranium and fix concentration of oxalohydroxamic acid are added in 1:5 ratios. The contents are made up to the mark with distilled water. The absorbance is measured at 381 nm against reagent blank.

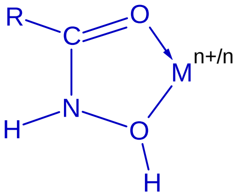
3. Results and Discussion

The structure of oxalohydroxamic acid is shown in figure.1. The oxalohydroxamic acid is characterized by Fourier Transform Infra Red Spectroscopy (FTIR). FTIR spectrum of OHA is represented in figure. 2. The absorption band observed at ν_{max} 3263 cm^{-1} arises due to N-H stretching vibration. The OH bonds in crystalline oxalohydroxamic acid are strongly hydrogen bonded, and thus the associated vibrational bands are observed at ν_{max} 3184-3074 cm^{-1} and ν_{max} 2862 cm^{-1}. The bands at ν_{max} 1651 cm^{-1} arise due to C=O stretching vibration. The absorption bands at 1531 cm^{-1}, 1444 cm^{-1}, 1226 cm^{-1}, 1099 cm^{-1} and 846 cm^{-1} arises from the vibrations of N-H bending, OH bending, OCN stretching, N-O stretching, and C-NO bending respectively. There are two possible structures of the hydroxamic acids, RCONHOH and RC(OH)NOH.



(I) (II)

Such keto-enol tautomerism provides a number of sites for chelation. On the basis of an ultra-violet study of several hydroxamic acids, Plapinger *et al* concluded that hydroxamic acids exists predominately in Keto form (I) [16]. Because the keto form predominates in an acidic medium [17], which is required for most precipitates or colours to form, it is probable that the structure of the majority of hydroxamic acid-metal ion complexes is:



Oxalo-hydroxamic acids forms orange-yellow complex with uranium(VI) in aqueous medium and shows maximum absorbance at 381 nm. The stoichiometry of the coloured species is determined to be 1: 5 ratio (U-OHA) at pH 6.2.

$$UO_2^{2+} + HO \leftrightarrow UO_2O^+ + H^+$$

A linear plot passing through the origin is obtained when absorbance is plotted against the concentration of uranium. The calibration graph follows the equation, $y = mx + c$, where x is concentration of the solution, y is measured absorbance and m and c are constants. The absorption spectrum of the reagent and the complex are recorded in the wavelength range 340-600 nm at pH 6.2 against the buffer solution and reagent blank respectively. A calibration graph is made at 381nm for the concentration range of uranium from 10-100 *mg/L* Figure.3. The molar absorption coefficient at 381nm, detection limit and Sendell's sensitivity are 2230 $LMol^{-1}cm^{-1}$, 11 *mg/L* and 0.11 $\mu g/cm^2$ respectively. Relative standard deviation is less than 2% and correlation coefficient is 0.998. The results obtained by this developed procedure are in good agreement with those obtained by the standard procedure [11] and represented in table 1.

3.1 Effect of pH

Complex formation was studied in the pH range 1-10 with same concentration of uranium and oxalohydroxamic acid. It was observed that the complexation of U-OHA and colour intensity of the complex vary with pH. The absorbances of U-OHA complex are measured at different pH values were recorded and presented in figure.4. U-OHA complex shows the maximum absorbance and stability of the complex is for more than 24 hours at pH 6.2. It should be noted that at pH 8.0 an unstable complex forms initially but rapidly decomposes and intensity of the complex is also very less. The pH 6.2 is optimum. Same is maintained in all studies.

3.2 Stability of colour formation

The minimum time required for complete colour development of U-OHA complex at pH 6.2 is found to be 5 min and the developed colour retained for more than 24 hours.

3.3 Composition of complex

The nature of the complex is investigated by the continuous variation and molar ratio methods with a fixed concentration of uranium, and varying concentration of oxalohydroxamic acid. Complexation of uranyl cations with oxalohydroxamic acid solutions leads to the formation of 1:5orange-yellow U-OHA complex which is represented in figure.5

4. Conclusions

In the present paper a simple, accurate, sensitive and fast spectrophotometric method for the determination of uranium (VI) concentration relevant to purex process used for nuclear fuel reprocessing is discussed. In aqueous medium oxalohydroxamic acid complexes with U(VI) to give an orange-yellow colour complex. This behaviour is affected by pH of solution. The coloured complex shows maximum absorption at 381 nm at pH 6.2. Results obtained by the developed procedure for uranium in samples are compared with those obtained from U-PAR spectrophotometry [11]. The results are found to be in good agreement. The overall recovery of uranium is 98% with 2% relative standard deviation. The method described here for the determination of U (VI) concentrations in processing solutions does not generate corrosive analytical waste.

5. References

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Table 1. Comparison study of two different spectrophotometric methods for determination of uranium

Standard Reference solution of uranium	Determination of uranium (ppm)	
	Present method	PAR [11] method
1	24.121	23.856
2	7.680	7.529
3	69.213	68.997
4	52.164	51.892
5	10.368	10.893

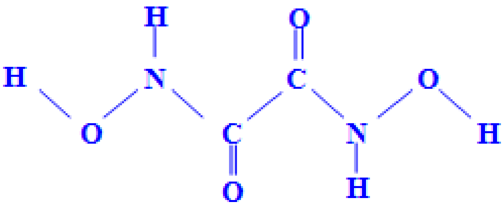

Figure.1 Structure of oxalohydroxamic acid [mol.wt.120.064]

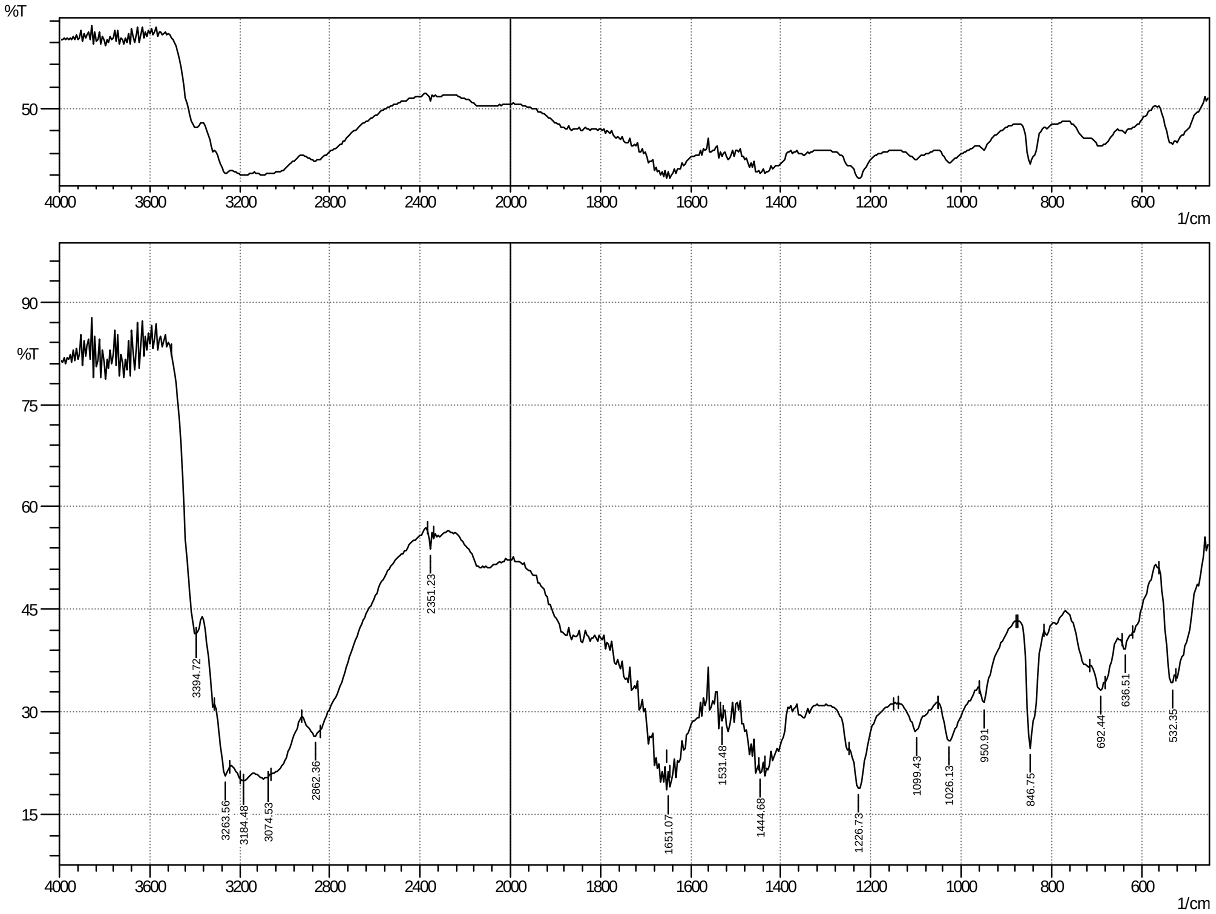

Figure.2 FTIR spectrum of oxalohydroxamic acid

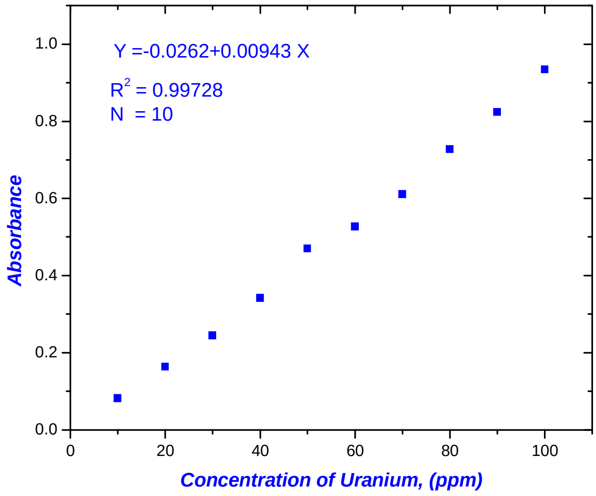

Figure.3 Calibration graph for U-OHA complexes at 381 nm

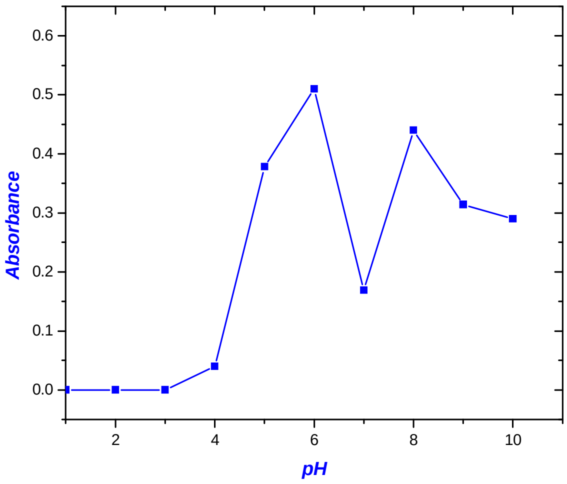

Fig.4 Effect of pH

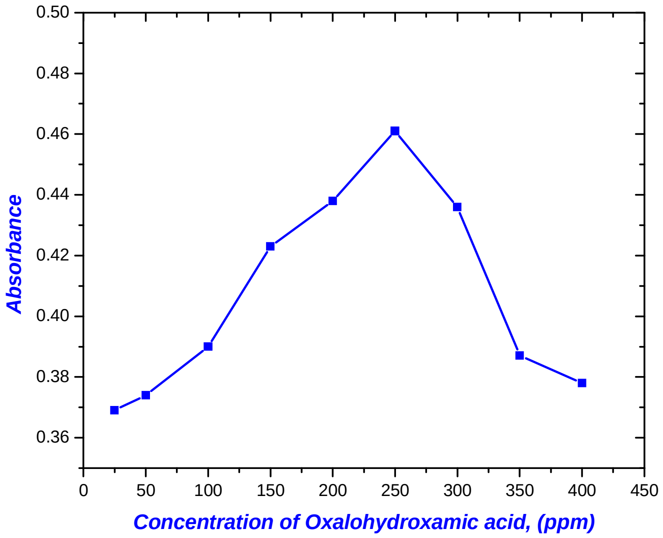

Fig.5 Effect of concentration of OHA at 381 nm

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