

Determination of Uranyl Nitrate with Several Ligands by Spectrophotometry

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Abstract : Trace amount of uranyl (II) has been determined spectrophotometrically by measuring the optical density of the light blue yellowish coloured solutions formed by reaction between the metal ion and nicotino hydroxamic acid (NHx) in presence of different secondary ligands in strong isoamyl alcohol alkaline medium. The absorption maxima for both aqueous and extracted systems measured at their respective optimum pH were found to be 360 and 559 nm (DETA), 375 and 358 nm (EDA), 369 and 362 nm (piperidine), 354 and 341 nm (pyridine) and 363 and 336 nm (3 piperidine), 354 and 341 nm (pyridine) and 363 and 336 nm (3 - picoline), respectively at which Beer's law was obeyed. Effect of pH, reagent concentration, order of addition of reagent, time, temperature and solvent media on the absorption spectra have also been studied. Among the different systems studied, the shortest concentration range of uranyl(II) adhering to Beer's Law was 2.4 - 10.5 ppm observed for UO₂(II) - NHx - DETA system in aqueous medium and also for iso amyl alcohol(IAA) extracted UO₂ - NHx - pyridine system was 2.4 - 7.8

Key words : Uranium ions, Nicotino hydroxamic acid, Several secondary ligands

1. Introduction

Uranium is dissolved in seawater at a concentration of about 3 mg/m³ in the ionic form of uranyl nitrate ions.¹ Atomic power plants continuously require uranium resources, therefore, 5 billion tons of total uranium in seawater can be recovered for atomic power utilization.

A variety of adsorbents used for the recovery of uranium ions in seawater have been reported.²⁻⁴ Especially adsorbents containing amidoxime groups, which make chelate complexes with uranyl ions, are

notable for the recovery of uranium from seawater. Our laboratory also developed adsorbents used for the recovery of uranium ions from seawater, which reported.⁵ In this study, we mentioned UO₂(II) with nicotino hydroxamic acid (NHx) in presence of secondary ligands by spectrophotometric determination.

Nicotino hydroxamic acid has been found to be an excellent chelating agent for forming coloured products with many metal ions⁶⁻¹⁶ Mustafa and Chakraburty¹¹ reported the solvent extraction and spectrophotometric determination of Ti(IV) with NHx in presence of thiocyanate. M . Hassiruzzaman *et. al*¹². reported the estimation of Cu(II) with Salysylic hydroxamic acid (SHx) in presence of secondary ligands like pyridine, piperidine, 3 - picolin, dimethyl sulfoxide(DMSO), ammo-

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nium hydroxide (NH_4OH), ethylenediamine (EDA) and diethylenetriamine (DETA). No attempt seems to have been made for the estimation of $\text{UO}_2(\text{II})$ with NH_x in presence of secondary ligands like DMSO, NH_4OH .

In this paper we report some rapid, selective and suitable methods for the spectrophotometric determination of $\text{UO}_2(\text{II})$ with NH_x in presence of the above mentioned secondary ligands. Light blue yellowish to deep blue yellowish colour were produced in presence of different organic bases at higher pH values of the solution having sharp absorption maxima. Studies were carried out on the effect of pH, reagent concentration, order of addition of reagent, time, temperature and solvent media on the absorption spectra, adherence to Beer's law precision (accuracy) on the system. Detailed results of these investigations are presented in this paper.

2. Experimental

2.1. Apparatus:

Absorbance measurements were carried out with a Shimadzu model 160 A, UV - Visible recording double beam spectrometer employing tungsten filament and a matched pair of 1 sq. cm. fused silica absorption cells. A HANNA digital pH meter with recorder was used for pH measurements. A Gallenkamp Hot Box (Oven) was used for drying purpose of the glass wares and the desiccant (Na_2SO_4).

A Gallenkamp Melting point apparatus with digital thermometer MBF 598 D/OM was used for the determination of melting point of the primary ligand (NH_x). A Mettler PJ 360 Delta ranger^R weighing apparatus was used for the Gravimetric measurements of the reagents and chemicals. All glass wares including burettes and pipettes employed were of standard type Beakers, volumetric and measuring flasks used were of corning brand pear shaped 50 cm^3 separatory funnels with short stem were used for extraction work.

2.2. Standard Uranyl Nitrate [$\text{UO}_2(\text{II})$] solution:

A stock solution of uranyl 200 ppm or 0.2 mg/cm^3

was prepared by dissolving analytical grade uranyl (II) nitrate hexahydrate in 0.01 M nicotino hydroxamic acid and standardized. The desired solutions of particular strength were prepared by proper dilution of the stock solution with deionized water.

2.3. Reagent solutions:

Nicotino hydroxamic acid was synthesized according to the method outlined by Gardener et al.¹⁷ A 0.1 M solution of nicotino hydroxamic acid was prepared in 99% methanol. This solution was found to remain stable for several days. 10% (v/v) aqueous solution of EDA, pyridine, piperidine, 3 - picolin, DETA and 10% (v/v) alcoholic solution of all secondary ligands were used. Buffer solutions of Titrisol (*E. Merck*) of different pH values were used. Isoamylalcohol (*Merck*) was used for extraction as a solvents. Solutions of diverse foreign ions were prepared from reagent grade salts using the procedure of West.¹² All other chemicals used were of analytical grade (*E. Merck*, BDH or *SIGMA*).

2.3. Procedure for direct spectrophotometry:

An aliquots containing 200 μg to 240 μg uranyl(II) was taken in a 10.0 mL volumetric flask followed by addition of 2 mL of buffer solution (of a definite pH) and 1 mL of NH_x and an appropriate volume (0.5 mL) of secondary ligand, respectively. The mixture was then transferred into a 10.0 mL volumetric flask and made up to the mark with deionized water and the final pH measured. The absorbance was then recorded at the respective absorption maxima against reagent blank.

2.4. Procedure for extraction spectrophotometry:

The procedure for extraction spectrophotometry was almost identical as elsewhere¹⁰ except that the aliquot of the test solution contained 20 to 240 μg of uranyl(II) and that 3.0 mL of 0.1 M nicotino hydroxamic acid solution was added instead of cinnamoyl hydroxamic acid.

3. Results and discussion

Uranyl ion(II) gives a light blue yellowish colour with nicotino hydroxamic acid in alkaline medium. This colour is gradually changed to brown, yellow and deep blue yellowish in presence of different organic bases at higher pH values of the solution having sharp absorption maxima.

3.1. Absorption spectra:

The absorption spectra of uranyl(II) - NHx - pyridine, uranyl(II) - NHx - piperidine, uranyl(II) - NHx - 3 - picoline, uranyl(II) - NHx - EDA, uranyl(II) - NHx - DETA systems for both direct and Iso amyl alcohol(IAA) extraction spectrophotometry recorded at their respective reagent blank are shown in (Fig. 1 and 2) respectively. The absorption maxima of the system were found to be 360 and 359 nm (DETA), 375 and 358 nm (EDA), 369 and 362 nm (piperidine), 354 and 341 nm (pyridine) and 363 and 336 nm (3 - picoline) for direct and extracted systems, respectively. Therefore, all subsequent absorption measurements were carried out at their respective absorption maxima.

3.2. Effect of pH, reagents, order of addition of reagents, time and temperature on the development of color and extraction :

There was no appreciable colour development below pH 8.0 and the intensity of the colour increased with the increasing pH values of the solutions up to 9.4. The effect of pH was studied with 5 ppm uranyl (II) for both direct and extraction spectrophotometry. The optimum pH of the systems (direct and extracted) for maximum colour development is given in the parentheses of the secondary ligands. DETA (9 and 9.75), piperidine (9.4 and 10.2), pyridine (8 and 7.2), 3 - picoline (9 and 8.5). All the subsequents with these systems were therefore carried out at their optimum pH values.

The effect of reagent (NHx) was also studied with 5 ppm UO_2 (II) solution for both direct and extraction spectrophotometer: The optimum volume of 0.1 M (NHx)

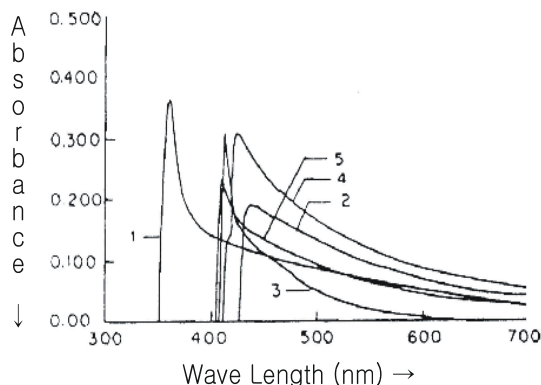


Fig. 1. Absorption spectra of IAA extracted UO_2 (II) - NHx complexes in presence of 1. DETA 2. EDA 3. Piperidine 4. Pyridine 5. 3 - picolin (without any secondary ligand) at pH 9.0, 8.0, 9.4, 8.0 and 9.0 respectively. UO_2 (II) concentration = 5 ppm.

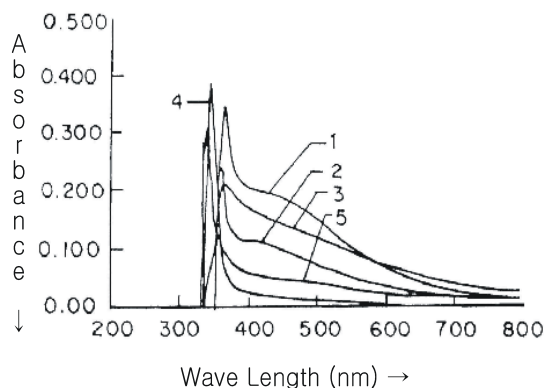


Fig. 2. Absorption spectra of IAA extracted UO_2 (II) - NHx complexes in presence of 1. Pyridine 2. Piperidine 3. 3 - picolin 4. DETA 5. EDA (without any secondary ligand) at pH 7.2, 10.2, 8.5, 9.75, 9.5. UO_2 (II) concentration = 5 ppm.

solution in presence of different bases were found to be 0.5 and 1.5 mL (DETA), 1.5 and 1.0 mL (EDA), 1.5 and 0.5 mL (piperidine), 1.5 and 1.0 mL (pyridine), 1.0 and 1.0 mL (3 - picoline) for both and extraction spectrophotometry, respectively. In practice 0.5 mL and 1.5 mL for both direct and IAA extracted of 0.1 M (NHx) solution was used for colour development in direct and IAA extracted although a larger excess of the reagent had no adverse effect on the estimation of uranyl(II). It was observed that smaller amount of the

secondary ligands could not produce intense colouration of the solutions while higher amounts of these actually decreased the intensity of the coloration due to change in pH. However, the optimum secondary ligands concentration [for 5 ppm $\text{UO}_2(\text{II})$] were found to be 0.2 mL and 0.75 mL (DETA), 0.7 mL (EDA), 0.75 mL and 0.2 mL (piperidine), 1.0 mL (pyridine) and 1.5 mL (3-picoline) for direct and extraction spectrophotometry, respectively.

It was observed that in case of direct spectrophotometry, there was no change in colour intensity or in the absorbance, if the order of addition of the reagents was altered. But in case of extraction spectrophotometry, the secondary ligands must be added to the system just after preliminary extraction of the uranyl(II)-NHx complex in the organic phase to active the best result. Changes in order of the addition of other reagents had no influence on the absorbance. The temperature range 20-40 °C was found to be most favourable and had no effect on the colour intensity of the systems studied.

Full development of colour of the different uranyl(II)-NHx secondary ligand systems took place within five minutes. The uranyl(II)-NHx complexes incorporating different bases were completely extractable in Iso amyl alcohol (IAA). The colour of all these systems were stable for 3 hours. Therefore, the time for measurements of absorbances of all these systems were not critical.

3.3. Beer's law:

The calibration curve for all the complex systems was constructed from the absorbance measurements of the different amount of $\text{UO}_2(\text{II})$ ion at the wave length of maximum absorption. The coloured systems obeyed Beer's Law over varying concentration range of uranyl(II) both in direct and in extraction spectrophotometry. Results are given in (Tables 1 and 2). In direct spectrophotometry, the shortest concentration range of $\text{UO}_2(\text{II})$ adhering to Beer's Law was 2.4 - 10.5 ppm for $\text{UO}_2(\text{II})$ -NHx-DETA system while the widest concentration range was 6.0-25.0 ppm observed for the $\text{UO}_2(\text{II})$ -NHx-pyridine system. In case of extraction spectrophotometry the shortest rang of $\text{UO}_2(\text{II})$ 2.4 - 7.8 ppm was found for the IAA extracted uranyl(II)-NHx-pyridine system and the widest range of uranyl (II) 5.0-20.0 ppm found for the IAA extracted uranyl(II)-NHx system.

3.4. Optimum concentration ranges:

The optimum concentration range of uranyl(II) in different systems was evaluated from Ringbom's curve.¹⁴ The results are shown in (Tables 1 and 2) for both direct and IAA extracted systems, respectively. In case of direct spectrophotometry, the shortest range (3.4 - 10.2 ppm) of uranyl(II) was observed for the uranyl(II)-NHx-DETA system while that for the extracted systems was 3.4 - 7.0 ppm $\text{UO}_2(\text{II})$ observed for the IAA extracted uranyl(II)-NHx pyridine system.

Table 1. Spectral characteristics of $\text{UO}_2(\text{II})$ -NHx-complexs in presence of different secondary ligands [$\text{UO}_2(\text{II})$ conc.=5 ppm]

Secondary ligand	Optimum pH	Absorption maxima (nm)	Molar absorptivity $\text{L mol}^{-1} \text{cm}^{-1}$	Sensitivity $\mu\text{g}/\text{cm}^2$	Beer's law [$\text{UO}_2(\text{II})$ con.range]	Photometric error (%)	Standard deviation (and r. s. d)
DETA	9.0	360	19550.23	0.01381	2.4-10.5 (3.4-10.2)	2.74	$\pm 0.527 \times 10^{-3}$ (0.1453)
EDA	8.0	375.0	10855.24	0.024875	5.0-19.5 (7.0-18.5)	2.74	$\pm 0.667 \times 10^{-3}$ (0.3318)
Piperidine	9.4	369.0	13393.53	0.02016	4.0-15.5 (4.8-14.8)	2.74	$\pm 0.4216 \times 10^{-3}$ (0.1601)
Pyridine	8.0	354.0	8424.96	0.03205	6.0-25.0 (6.2-22.8)	2.74	$\pm 0.6666 \times 10^{-3}$ (0.4273)
3-Picolin	9.0	363.0	12367.41	0.02183	3.5-17.5 (4.2-16.3)	2.74	$\pm 0.5270 \times 10^{-3}$ (0.2306)

Table 2. Spectral characteristics of IAA extracted $\text{UO}_2(\text{II})$ - NHx -complexes in presence of different secondary ligands. [$\text{UO}_2(\text{II})$ conc.=5 ppm]

Secondary ligand	Optimum pH	Absorption maxima (nm)	Molar absorptivity $\text{L mol}^{-1}\text{cm}^{-1}$	Sensitivity mg/cm^2	Beer's law	Photometric error (%)	Standard deviation (and r. s. d)
DETA	9.7	359.0	13123.50	0.02057	4.0-17.6 (5.0-15.3)	2.74	$\pm 0.483 \times 10^{-3}$ (0.1990)
EDA	9.5	358.0	14265.64	0.01879	4.0-14.5 (4.5-13.2)	2.74	$\pm 0.6324 \times 10^{-3}$ (0.238)
Piperidine	10.2	362.0	11557.32	0.023364	4.5-18.2 (5.5-16.4)	2.72	$\pm 0.5676 \times 10^{-3}$ (0.2653)
Pyridine	7.2	341.0	21116.41	0.01278	2.4-7.8 (3.4-70)	2.74	$\pm 0.4216 \times 10^{-3}$ (0.1078)
3-Picolin	8.5	336.0	10693.22	0.02525	5.0-20.0 (5.5-19.0)	2.73	$\pm 0.5270 \times 10^{-3}$ (0.2668)

3.5. Photometric error:

The relative error per 1% absolute photometric error was found from the Ayre's⁷ equation. The results are shown in (Tables 1 and 2) for both direct and IAA extracted systems. The minimum photometric error (2.74%) was observed for the systems containing DETA, EDA, Piperidine, pyridine and 3-picolin in direct medium while 2.72% was the minimum error for IAA extracted systems containing DETA, EDA, piperidine, pyridine, and 3-picolin. The highest photometric error (2.74%) was observed for the IAA extracted uranyl(II)- NHx -EDA system.

3.6 Sensitivity:

Sandell's spectrophotometric sensitivity⁶ for both direct and IAA extracted systems incorporating different bases were studied at their respective adsorption maxima and calculated for $\log I_0/I=0.001$, are shown in (Table 1 and 2) respectively. It was observed that the uranyl(II)- NHx -DETA system is the most sensitive among those studied in aqueous medium while IAA extracted uranyl(II)- NHx pyridine system turned out to be the best in case of extraction spectrophotometry.

3.7. Molar Absorptivity:

The molar absorptivity values of all the complex systems studied are given in (Tables 1 and 2) for both direct and IAA extracted systems respectively. Results

indicate that the highest molar absorptivity value is $19,550.23 \text{ L mol}^{-1} \text{ cm}^{-1}$ $\text{UO}_2(\text{II})$ - NHx -DETA system in direct aqueous medium and that for the extracted system is $21,116.41 \text{ L mol}^{-1} \text{ cm}^{-1}$ IAA extracted $\text{UO}_2(\text{II})$ - NHx pyridine system.

3.8. Precision:

For both direct and extraction spectrophotometry, the precision of the methods have been studied by analyzing ten solutions for each base containing $5 \mu\text{g}$ of uranyl(II)/ cm^2 solution. Standard deviation and relative standard deviation are given in (Tables 1 and 2) for both the systems, respectively. These studies revealed that the methods are precise and give reproducible results.

4. Conclusion

Spectrophotometric studies were carried out on the complexes of $\text{UO}_2(\text{II})$ with nicotino hydroxamic acid (NHx) in presence of different secondary ligands, viz, diethylene triamine (DETA), ethylenediamine (EDA), piperidine, pyridine, 3-picolin etc.. To bring uniformity in the parameters of studies the complexes were produced at a fixed pH using suitable buffer solution. Detailed direct and extraction spectrophotometric studies e.g, investigations on the colour development, absorption spectra, optimum pH range, suitable reagents concentration, effect of time and

temperature, Adherence to Beer's law, determination of sensitivity and molar absorptivity and there tolerance limits etc. were carried out.

A total ten(10) systems were studied in detailed. Reproducibility of each systems was examined and their standard deviation and relative standard deviation were also calculated. Results obtained revealed that all the systems were reproducible.

In moderately strong alkaline medium $\text{UO}_2(\text{II})$ gives light blue yellowish color with NH_x in presence of various secondary ligands. All the five(5) systems studied were completely extractable with Iso amyl alcohol (IAA) giving rise to increase sensitivity in three cases. The following are the two most sensitive $\text{UO}_2(\text{II})$ - NH_x secondary ligand systems:

- I) $\text{UO}_2(\text{II})$ - NH_x - DETA(direct) system having a sensitivity of $0.01381 \mu\text{g}$, $\text{UO}_2(\text{II})/\text{cm}^2$ and a molar absorptivity of $19,550.23 \text{ L mol}^{-1} \text{ cm}^{-1}$ at the absorption maxima (λ_{max}) of 360.0 nm.
- II) IAA extracted $\text{UO}_2(\text{II})$ - NH_x - Pyridine system having a sensitivity of $0.01278 \mu\text{g}$, $\text{UO}_2(\text{II})/\text{cm}^2$ and a molar absorptivity of $21,116.41 \text{ L mol}^{-1} \text{ cm}^{-1}$ at the absorption maxima (λ_{max}) of 341.0 nm.

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