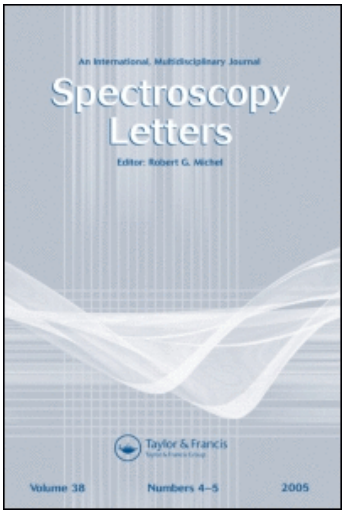

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Spectrophotometric Determination of Uranium in Ores Using Di-2-Pyridyl Ketone Hydrazone Derivatives

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SPECTROPHOTOMETRIC DETERMINATION OF URANIUM IN ORES USING DI-2- PYRIDYL KETONE HYDRAZONE DERIVATIVES

KEY WORDS : Uranium (VI), Di-2-Pyridyl Ketone hydrazone derivatives, spectrophotometric determination, Monazite.

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ABSTRACT

Two methods for the spectrophotometric determination of uranium (VI) are described. The methods are based on the formation of colored complexes for uranium (VI) with (1)di-2-pyridyl ketone nicotinoylhydrazone (DPKNH),

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and (2)di-2-pyridyl ketone thiophenoylhydrazone (DPKTH) in 50% (v/v) ethanolic sclution. The complexes formed a uranium (VI): complexing reagent mole ratio of 1:?. Maximum absorbance is at 373 nm for U(VI)-DPKNH, and at 389 nm for U(VI) - DPKTH. Ranges of linearity, effec of pH, effect of excess reagent, stability of the complexes, and the tolerance limit for many metal ions and common anions have been reported. The two methods have been applied to the determination of uranium in eygeptian monazite sand.

INTRODUCTION

Many methods have been proposed for the spectrophotometric determination of uranium. Most of these methods are based on the formation of colored complexes for uranium (VI) with chromogenic reagents. Among these chromogenic reagents are glyoxal bis (2-hydroxyanil)(GBH) and 1-(2-pyridylazo) naphth -2- ol (PAN) (1), Rhodamine 6G(?), ?-hydroxy-1-naphthaldehyde isonicotinoylhydrazone(3) and 2-(5-bromo-?-pyridylazo)-5-diethylaminophenol (bromo - PADAB) (4).

This paper describes two new methods for the spectrophotometric determination of uranium (VI) on the base of its binary complexes with di-2-pyridyl ketone nicotinoylhydrazone (DPKNH) and di-?-pyridyl-?-thiophenoylhydrazone (DPKTH), in aqueous solution.

EXPERIMENTAL

All reagents and solvents used were of analytical reagent grade.

Reagents :

Di-2-pyridyl ketone nicotinoylhydrazone (DPKNH). The ligand was prepared by interaction of di-?-pyridyl ketone and nicotinic acid hydrazide in stoichiometric amounts and was recrystalized from ethanol to a constant melting point (174 - 175°c).

Di-2-pyridyl ketone-2-thiophenoylhydrazone (DPKTH). The ligand was prepared by interaction of di-2-pyridyl ketone and 2-thiophenecarboxylic hydrazide in stoichiometric amounts and was recrystalized from ethanol to a constant melting point (144 - 145°c).

The purity of the prepared reagents was checked by elemental analysis and the structural forms were also confirmed by the infrared spectrum of the ligands.

Stoch, 10^{-2}M, reagent solutions, were prepared by dissolving the appropriate amounts in known volumes of ethanol.

Standard uranium (VI) solution 10^{-2}M. It was prepared from $UO_2(NO_3)_2 . 6H_2O$. The working solutions were prepared by appropriate dilution.

Buffer solutions. The buffer solutions used were acetic acid - sodium acetate mixtures for pH in the range 3.0 - 6.0, hydrochloric acid-borax mixtures for pH in the range 6.0 - 9.2, and sodium hydroxide-borax for pH above 9.2.

Apparatus :

Perkin - Elmer Lamda 5 uv/visible spectrophotometer with 1x1 cm quartz cells for spectral studies, and digital pH meter PBS 750 for pH measurements were used.

Procedure :

Dissolution of uranium ore (1) :

An amount of 200 - mesh uranium ore in the range 0.1 - 1.0 g is weighed out accurately in a platinum crucible. 5 ml of concentrated nitric acid and 5 ml of 48% hydrofluoric acid are added, and the mixture is evaporated to dryness on a water - bath. A further 5 ml of nitric acid and 5 ml of 48% hydrofluoric acid are added and the mixture is evaporated to dryness on a hot - plate. The residue is cooled and then dissolved in 10 ml of 5M nitric acid, filterred and then transferred into a 25-ml volumetric flask and the volume is completed with distilled water.

Separation of uranium (VI) :

Uranium (VI) is seperated from the interferring ions by extraction with tributyl phosphate (TBP) and stripping it back to the aqueous phase (5).

General Spectrophotometric procedure for the determination of uranium(VI):

A portion of solution containing an amount of uranium (VI) within the range 5 - 350 µg is transferred into a 25 - ml volumetric flask, then 5 ml of 10^{-3}M DPKNH or DPKTH complexing agent is added followed by 7.5 ml of ethanol and the volume is completed with the buffer solution pH 8. The absorbance is measured at 373 nm (with DPKTH as complexing reagent) or at 389 nm (with DPKTH as complexing reagent) after 10 min. against a reagent blank as a reference.

RESULTS AND DISCUSSION

Absorption Spectra :

The absorption spectra of DPKNH, DPKTH and uranium (VI) complexes with each of these ligands prepared as described in the general procedure have been studied at pH 8 in the wavelength range 300 - 500nm. The results obtained are presented in Fig.1. It can be seen from the figure that uranium (VI)-DPKNH has one maxima at 373 nm, while uranium (VI) - DPKTH has one maxima at 389 nm. Spectral interference of the reagents can be eliminated by taking the measurements against reagent blank solutions.

Effect of pH :

The effect of pH on the absorption of uranium (VI) - DPKNH and uranium (VI) - DPKTH complexing systmes prepared as described in the general procedure were studied in the pH range 3.0 - 11.0. Both complexing systems showed maximum absorbance in the pH range 7.3 - 8.5.

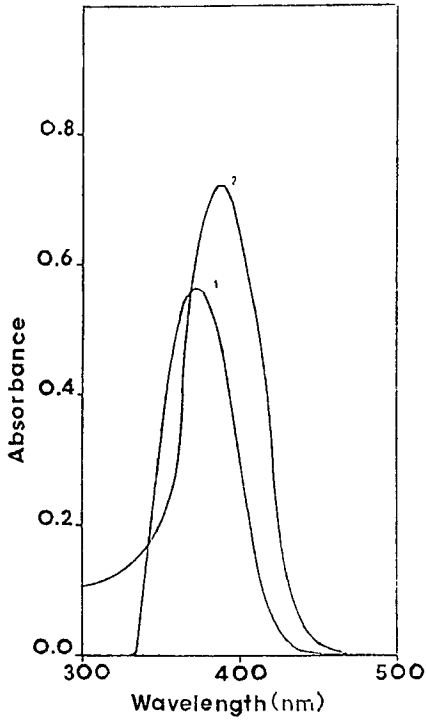

Fig. 1 : Absorption spectra for uranium (VI) complexes with (1) DPKNH (2) DPKTH.
Conditions : 3.0×10^{-5}M uranium (VI), 1.0×10^{-3}M complexing reagent. The reference in each case is a reagent blank.

Composition of the complexes :

The composition of the uranium (VI) - DPKNH complexes were studied by the continous variation and the mole ratio methods. Plots of both methods suggested a uranium (VI): ligand mole ratio of 1:2.

Table (1)

Effect of foreign ions on the determination of 48 μg of uranium (VI)

Ion	Tolerance limit in μg using	
	DPKNH	DPKTH
Pd(II).	85	63
Cu(II).	25	38
Ni(II).	35	24
Fe(II), Fe(III)	22	22
Pt(II)(a).	270	390
Hg(II).	2000	2000
Co(II).	23	60
Na(I), K(I), Ca(II), Th(IV), Al(III), Mg(II), Pb(II), Ce(III), Eu(III), La(III).	10,000	10,000
Cl^-, Br^-, ClO_4^- CH_3COO^-, SO_4^{2-}, NO_3^-, Silicate, Oxalate, Borate,	10,000	10,000

(a) negative interference.

Stability of the complexes :

The color of the uranium (VI) complexes with DPKNH and DPKTH is attained within 5 min. after the addition of uranium (VI) ion. The color intensity remains constant for at least 24 hours. The values of the apparent stability constant (log β) for uranium (VI) - DPKNH and uranium (VI) - DPKTH complexing systems were calculated to be 8.99 and 9.08 respectively. While the free energy change ($-\Delta G°$) for both complexing systems was 12.3 $Kcal.mol^{-1}$.

Table 2

Determination of uranium (VI) in eygeptian monazite sand.

Sample size (g)	Uranium (VI) found (%) using		
	DPKNH	DPKTH	Expected (6)
0.236	0.35	0.35	0.37
0.249	0.35	0.35	0.37
0.257	0.34	0.38	0.37
0.253	0.36	0.37	0.37
0.251	0.37	0.36	0.37

Effect of excess reagent :

The effect of excess reagent on the absorbance of uranium (VI) complexes with DPKNH and with DPKTH has been studied. Similar results were obtained for both complexing systems. It was found that keeping the uranium (VI) concentration fixed and changing the reagent concentration affected an increase in the absorbance up to uranium (VI): reagent mole ratio of 1:2 beyond which any further increase in the reagent concentration did no affect the absorbance up to at least 1:100.

Beer's Law and sensitivity :

When the recommended procedure is followed a rectilinear relationship is obtained between the absorbance and the concentration of uranium (VI) over the range 0.2 - 14 μg ml^{-1} at 373 nm with DPKNH as a complexing reagent, and over the range 0.2 - 10 μg ml^{-1} at 389 with DPKTH as a complexing reagent. The sensitivity of the determination expressed in terms of molar absorptivity is 2.13×10^4 and 2.33×10^4 L $mol^{-1}cm^{-1}$ with DPKNH and DPKTH, respectively.

Interference studies :

The tolerance limit for various foreign ions in the determination of 48 µg of uranium (VI) with DPKNH or DPKTH as a complexing reagent are presented in Table 1. It can be seen from the results that palladium (II) copper (II), nickel (II), iron (II), iron (III) and cobalt (II) interfere seriously and should be absent in both complexing systems. Mercurry (II) showed slight interference and more than 2000 µg can not be tolerated. Platinum (II), however, interfers negatively and more than 270 µg can not be tolerated with DPKNH as complexing reagent, while not more 390 µg can be tolerated with DPKTH as complexing reagent. On the other hand 10,000 µg of other metal ions and common anions did not show any interference.

Applications :

The two methods have been applied to the determination of uranium (VI) in eygeption monazite sand. The results obtained by following the proposed procedure are compared with the expected value (6), as illustrated in Table 2.

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