# SPECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH DI-2-PYRIDYL KETONE BENZOYLHYDRAZONE

Key Words: Uranium (VI), Di-2-Pyridyl Ketone Benzoyl hydrazone (DPKBH), Spectrophotometric Determination, Monazite.

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ملخص

يقدم لنا هذا البحث طريقة جديدة لتعيين اليورانيوم بواسطة التحليل الطيفي. تعتمد هذه الطريقة على قياس الامتصاص للمركب المعقد المتكون بين اليورانيوم والمتصله دايبراديل كيتون بنزول هيدرازون (DPKBH) في محلول يحتوى 50٪ كحول ايثيلي .

النسبة المولية للمركب المعقد المتكون (DPKBH:U) هي 2:1 ويمتص عند طول موجه λ = 377nm. ضمن التعيير أعطى خط مستقيم لتركيز اليورانيوم في المجال 0.2 - 12 ميكروغرام/سم$^2$ و كما تم في هذا البحث دراسة العوامل المؤثرة على تكون المركب المعقد ومنها تأثير الرقم الهيدروجيني، تأثير الزيادة في تركيز المتصلة، النسبة المئوية للكحول الايثيلي . ثبات المركب وتأثير الايونات الأخرى . كما تم تطبيق هذه الطريقة على تعيين اليورانيوم في رمل المونازايت المصري.

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# ABSTRACT

A method for the spectrophotometric determination of uranium (VI) by complexation with di-2-pyridyl ketone benzoylhydrazone (DPKBH) in 50% (v/v) ethanolic solution is described. Uranium (VI) forms a 1:2 complex with DPKBH. The complex has a maximum absorbance at 377 nm. Beer's law is obeyed over the range 0.2 - 12 $\mu g.ml^{-1}$. The effect of pH, excess reagent, percentage of ethanol (v/v), stability of the complex and the tolerance limit of many metal ions and common anions have been reported. The method has been applied to the determination of uranium in egyption monazite sand.

# INTRODUCTION

Di-2- pyridyl ketone benzoylhydrazone (DPKBH) has been proposed as a sensitive and selective analytical reagent for the spectrophotometric determination of certain metal ions including iron (II)[1], iron (III)[2], palladium (II)[3] and cobalt (II)[4].

Many methods have been described for the spectrophotometric determination of uranium (VI)[5-8]. Some of these methods involve liquid extraction of the complex into an organic phase[8].

In the present work a new simple sensitive and selective method has been proposed for the spectrophotometric determination of uranium (VI) as its complex with DPKBH in aqueous solution.

# EXPERIMENTAL

## Reagents:

All reagents and solvents used were of analytical-reagent grade.

Di-2- pyridyl ketone benzoylhydrazone (DPKBH) was prepared by refluxing for two hours equimolar amounts of di-2- pyridyl ketone and benzoylhydrazide in absolute ethanol. The crude compound was recrystallized from ethanol to a constant melting point (130-132 °C)[9]. The purity was checked by elemental analysis and by the infrared spectrum. A $10^{-2}$ M stock solution was prepared by dissolving the appropriate amount in a known volume of ethanol.

Standard uranium (VI) solution ($10^{-2}$M) was prepared from $UO_2(NO_3)_2.6H_20$. The working solutions were prepared by appropriate ditution.

Buffer solution made up of acetic acid-sodium acetate mixtures for pH in the range 3.0 - 6.0, hydrochloric acid - borax mixtures for pH in the range 6.5 - 9.2, and sodium hydroxide - borax mixtures for pH above 9.2, were used.

## Apparatus:

A Perking - Elmer Lamda 5 UV/visible spectrophotometer with 1 cm quartz cells for spectral studies, and a digital pH meter PBS 750 for pH measurements were used.

## PROCEDURE

A portion of uranium (VI) solution containing not more than 300μg is transfered into a 25 ml volumetric flask, 2.5 ml of $10^{-2}$M DPKBH is added followed by 10 ml of ethanol and the volume is completed with the buffer solution pH 8. Absorbance is measured at 377 nm after 5 min. using a reagent blank as a reference.

## RESULTS AND DISCUSSION

### Absorption Spectra:

Uranium (VI) forms a yellow complex with DPKBH in the pH range 4 - 11. The absorption of DPKBH and uranium (VI)-DPKBH complex prepared as described in the recommended procedure were studied over the wavelength range 300 - 500 nm. The results obtained showed that U(VI)-DPKBH complex exhibits one absorption maxima at 377 nm as shown in Fig. 1. Spectral interference of the reagent can be eliminated by taking the measurements against a reagent blank solution.

### Effect of pH:-

The effect of pH on the absorbance of U(VI)-DPKBH complex was studied in the pH range 4.0-11.0 using a solution prepared as described in the recommended procedure. Maximum absorbance was obtained in the pH range 7.5-8.5, whereas no absorbance was detected below pH 3.5.

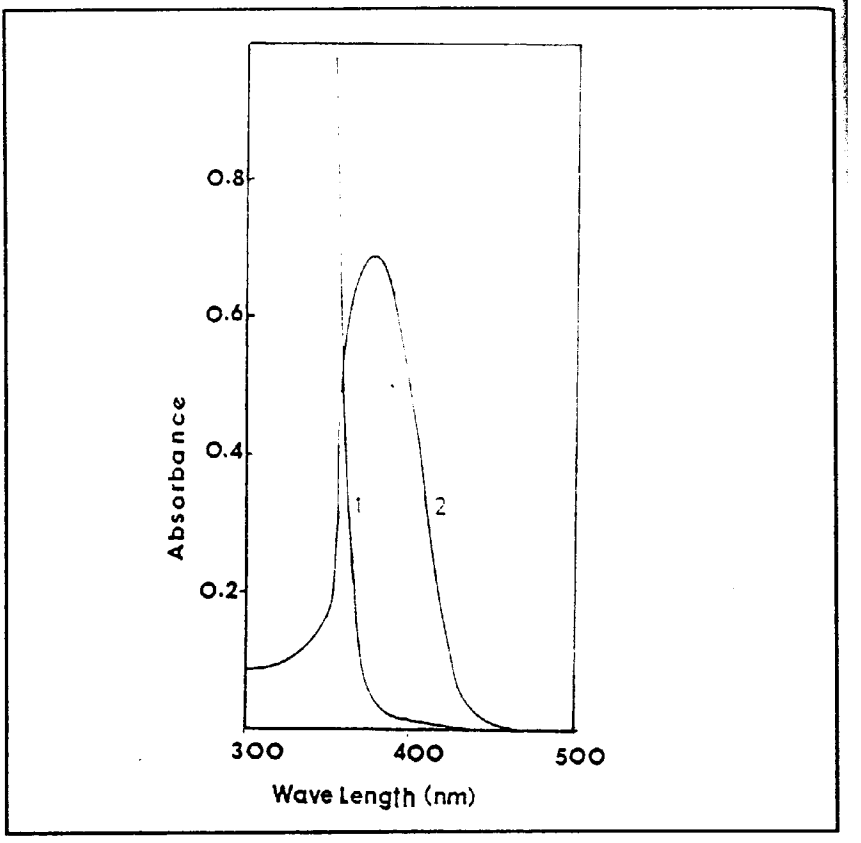


Fig. 1 : Absorption spectra for:

1. 1x $10^{-3}$ M DPKBH solution, with ethanol 50% (v/v) as a reference.
2. U(VI) - DPKBH complex at U(VI) concentration of 3.2 x $10^{-5}$M and DPKBH concentration of 1 x $10^{-3}$M, with reagent blank as a reference .

## Composition of the complex:-

The composition of the U(VI)-DPKBH complex was established by the continuous variation and the mole ratio methods. Plots of both methods suggested a ratio of 1:2 as shown in Fig. 2.

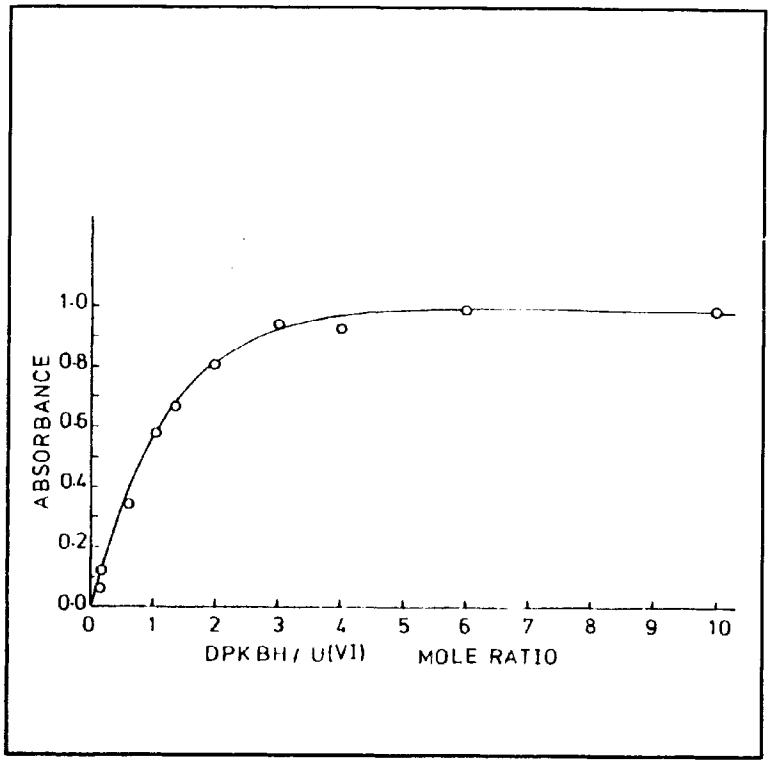


Fig. 2: Effect of changing DPKBP/uranium (VI) mole ratio on the absorbance of U(VI)- DPKBH-complex. Conditions:
5.0 x $10^{-5}$M uranium (VI), pH8 and 50% (v/v) ethanolic solution. The reference is a reagent blank .

## Stability of the complex:-

The color of uranium (VI)-DPKBH complex is attained within 5 min. after addition of uranium (VI) ion. The color intensity remains constant for at least 24 hours. The values of the apparent stability constant (log $\beta$) and the free energy change ($-\Delta G^{\circ}$) were calculated to be 8.02 and 10.89 Kcal. $mol^{-1}$ respectively.

## Effect of percentage ethanol:

The effect of percentage of ethanol (v/v) on the absorbance of the uranium (VI) - DPKBH complex was studied. It was found that increasing the percentage of ethanol from 10% to 50% effected an increase in the absorbance by 8% any further increase in the percentage of ethanol did not effect the absorbance. On the other hand this increase is also accompanied with red shift in the absorption spectra from 371 nm in 10% ethanolic solution to 377 nm in 50% ethanolic solution.

## Beer's law and sensitivity:

From the investigation of the aforementioned variables, the conditions for color development and absorbance measurements were selected. When the recommended procedure is followed, a linear relationship is obtained between the absorbance and the concentration of uranium (VI) within the range 0.2 - 12$\mu$g. $ml^{-1}$ as shown in Fig. 3. From the calibration curve the molar absorbitivity is calculated to be $2.02 \times 10^{4}$ 1.$mol^{-1}$. $cm^{-1}$ and the relative standard deviation for 150 $\mu$g of uranium (VI) was 3.3% for 5 measurements.

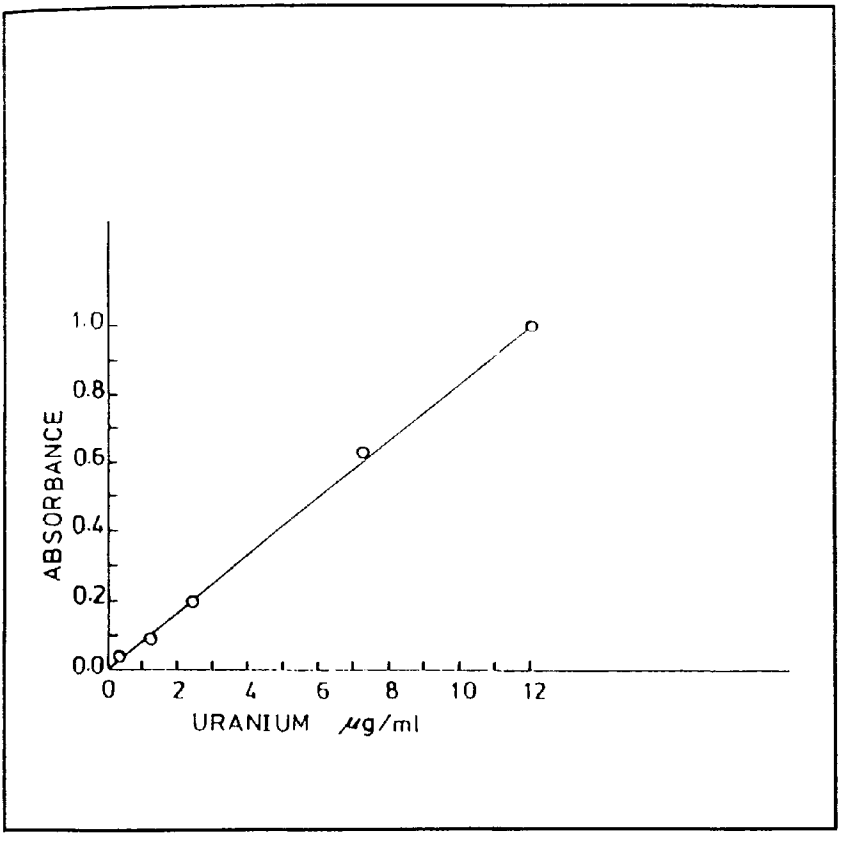


Fig. 3: Calibration curve for absorbance as a function of uranium (VI) concentration. Conditions are those recommended in the procedure.

## Effect of foreign ions:

In order to study the effect of various ions on the determination of uranium (VI) as its complex with DPKBH, a fixed amount of uranium (VI) (48 mg) was taken with different amounts of foreign ions and the recommended procedure was followed. An error of $\bar{+}$ 3% in

the absorbance was considered tolerable. Tolerances for various foreign ions are shown in Table 1. Palladium II), copper (II), Nickel

Table 1 : Effect of divers ions on the determination of 48 μg of uranium (VI)

| Ion | Added as | Ion: U(VI) mole ratio | Error % |
|---|---|---|---|
| Pd (II) | $PdCl_2$ | 0.03 : 1 | 3 |
| Cu (II) | $CuSO_4$ | 0.02 : 1 | 10 |
| Ni (II) | $NiSO_4$ | 0.03 : 1 | 8 |
| Pt (II) | $PtCl_2$ | 0.1 : 1 | 27 |
| Fe (II) | $FeSO_4$ | 0.03 : 1 | 12 |
| Fe (III) | $FeCl_3$ | 0.03 : 1 | 12 |
| Hg (II) | $Hg(No_3)_2$ | 0.5 : 1 | 7 |
| Co (II) | $CoCl_2$ | 0.03 : 1 | 3 |

(II), iron (II), iron (III), cobalt (II), mercury (II) and platinum (II) interfere seriously and should be absent. A 1000 - fold molar excess of sodium (I), potassium (I), calcium (II), thorium (IV), aluminum (III), magnesium (II), lead (II), cerium (III), europium (III), lanthanum (III), terbium (III), chloride, perchlorate, sulfate, nitrate, oxalate, borate, phosphate, and silicate did not interfere.

## Applications :

The method has been applied to the determination of uranium (VI) in egyption monazite sand. The monazite was decomposed by fusion with sodium peroxide[10], and uranium (VI) was separated from interfering ions by liquid extraction with tributyl phosphate method [11]. The general procedure was followed for the determination of uranium (VI) present. The experiment was repeated 5 times and the results obtained are shown in Table 2 .

Table 2 : Determination of uranium (VI) present in Egyption monazite sand

| Sample Size (g) | Amount of uranium Found | (VI)present (%) Expected[12] |
|---|---|---|
| 2.013 | 0.35 | 0.37 |
| 2.139 | 0.37 | 0.37 |
| 2.150 | 0.34 | 0.37 |
| 1.998 | 0.33 | 0.37 |
| 1.958 | 0.34 | 0.37 |

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