



Spectrophotometric Determination of Trace Amounts of Uranium with 5,10,15,20 – Tetra (4- Sulfophenyl) Porphyrin (TPPS₄)

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ABSTRACT

In this paper, the complex reaction of water – soluble tetra (4-sulfophenyl) porphine with uranium ion was studied spectrophotometrically and kinetics as well as photodecomposition of complex was determined. The porphyrin was found to be a highly sensitive and highly selective reagent for direct spectrophotometric determination of uranium ion at $2 \times 10^{-9} \text{M}$ (0.47ngl^{-1}) level. The sorbet band of the complex lies at 420 nm in the presence of hydroxyl amine, the reaction can be formed within 2 minutes in a boiling water bath at pH 3.0. Beer's law is obeyed for uranium in the rang of 0.01 - 120 μgl^{-1} . The molar ratio of complex is 1:2(U: TPPS₄) and the apparent molar absorptivity of the method is ($\epsilon = 2.2 \times 10^5$) $\text{L.M}^{-1} \cdot \text{CM}^{-1}$. This method has been applied to determine uranium in a tap water samples and can be used for rare earth samples with satisfactory results.

Keywords: Porphyrin, uranium spectrophotometry.

1. INTRODUCTION

The porphyrins are a class of naturally occurring macrocyclic compounds, which play a very important role in the metabolism of living organisms. These have been extensively studied due to their biological importance as well as analytical applications [1]. The porphyrin molecule contains four pyrrole rings linked via methane bridges and the porphyrin nucleus is a tetradentated ligand in which the space available for a coordinated metal has a maximum diameter of approximately 3.7Å [2].

When coordination occurs, two protons are removed from the pyrrole nitrogen atoms, leaving two negative charges.

Because the porphyrins is a highly sensitive chromogetic reagents for spectrophotometric determination of several metal ions based on the use of the so- called sorbet band at 400 – 500 nm [3-8]. Porphyrin metal complexes play an important role in biological activities as for instance iron complex in the haemoproteins, magnesium complexes in the chlorophylls, an a cobalt complex in vitamin B₁₂. Complexes of many metals with various porphyrins have been extensively studied in order to understand the biosynthetic formation and biological activity of natural compounds. Such complexes have been used in a variety of applications as models for biological electron transport, oxygen transport and metalloenzymes. TPPS₄ was applied previously as a complexing reagent of many metal ions such as Hg(II) , Pb(II) , Cd (II) and Zn ions [1,5,9,11] and many workers have been used water soluble porphyrins to determined

trace amounts of many transition metals such as Cu, Ni, Pb, Zn, Fe, Cd, Mn and other elements [14-20] based on color complexation. Because the uranium ion is one of the important inorganic cations which have made a great effect on both environment and human body. Uranium ion settles in to water and food as a result of wars it represents a major toxicity to macroorganisms and environment even in low concentrations. Uranium can damage the heart, kidney, stomach, skin addition to that the delayed effect of its raditions in human is that hemoglobin cannot bind oxygen molecule and therefore it is necessary to use a method that determines concentration of very small amounts of uranium [27].

2. EXPERIMENTAL

2.1 Chemicals

Tetra (4- sulfophenyl) porphyrin sodium salt Na₄ (H₂ TPPS₄) was synthesized by the method described before [12].U (CH₃ COO)₄ was obtained from Fluka (Germany) and was used without further purification , acetic acid and sodium acetate were from Merck at high purity grad NaOH, NH₂OH. HCl and ascorbic acid from Fluka company and were used as supplied. All dilute solutions were prepared from double – distilled water with a conductivity equal to (1.33±0.1) $\mu\text{s.cm}^{-1}$. Stock solution (10⁻³M) of TPPS₄ was prepared by dissolving of 0.3098 g in 250 ml of water. The structure of the porphyrin used in this paper is shown in **fig1**.

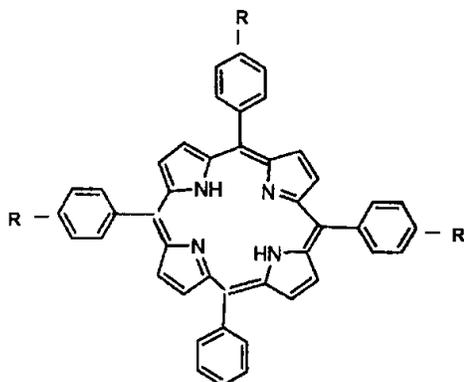


Fig. 1. Structure of the porphyrin

$R = \text{SO}_3\text{H}$ 5, 10, 15, 20- tetrakis (4-sulfonatophenyl) porphyrin, TSP

$\text{U}(\text{acac})_4$ standard stock solution of 0.011M was prepared by dissolving 90 mg of $\text{U}(\text{acac})_4$ in 25 ml buffer solution PH= 2.5 , farther dilutions were done with deionized water.

To determine the purity of the synthesized porphyrin, the absorption coefficient of H_2TPPS_4 was measured at different pH values. The absorption coefficient was calculated and compared with the value in the literature [12].

2.2 Apparatus

Spectrophotometric measurements were performed on a UV-Vis Jenway 6800 spectrophotometer with hp type computer and using 10 mm quartz cells for spectra recording. Spectra were recorded in the range from 380 to 600 nm with 0.2 resolutions. A Hi 9812 & Hi 9812-5 portable HANNA pH-meter with orion electrode was used for pH measurement and adjustment.

2.3 Applied Procedures

Determination of composition of the forming complex was conducted using mole ratio method .Metal was added to $5 \times 10^{-6}\text{M}$ porphyrin solution in the concentration rang 10^{-6} - $1.5 \times 10^{-5}\text{M}$. After heating in boiling water bath for 2min in darkness, absorbance at wavelengths characteristic for appropriate complex was measured .During photodecomposition experiments, samples were exposed from 10cm distance to UV from D_2 lamp and visible from tungsten lamp. Samples were protected against heating by intensive cooling with fan. Reference samples that were not exposed to light were stored in

dark chamber. All measurements were taken with at least four replications.

2.3.1 Application to Water Sample

The proposed method was applied to determine u ion in tap water (collected from Ramadi city). The pH of water samples were immediately adjusted to 1.0 with nitric acid and filtrated with $0.45 \mu\text{m}$ filter then the pH adjusted to 2.5 with sodium hydroxide. 1ml of water sample was taken in a calibration flask(25ml) and 1 ml of TPPS_4 (10^{-3}M) and 1ml u ion (10 ng ml^{-1}) were added , after dilution with acetate buffer to mark the solution was heated to 100°C in boiling water bath for 2 min , then the absorbance was measured at 420 nm against reagent blank.

2.3.2 Construction of Calibration Curve

Into a series of twelve 25 ml volumetric flasks containing aliquots of standard uranium solution. To each of these were added 1 ml TPPS_4 solution (10^{-3}M) after dilution to the mark , the solutions were heated in darkness for 2 min in boiling water bath adjusted at 100°C , then cooled , and diluted up to the mark with distilled water and Mixed well. The absorbance of complex was measured at 420 nm. Against reagent blank.

3. RESULTS AND DISCUSSION

3.1 Spectrophotometric Study of Porphyrin

Solution of 10^{-5}M TPPS_4 in acetate buffer at pH 2.5 is green and exhibits three absorption maxima one in soret band at 433 nm ($\epsilon = 2 \times 10^5 \text{ L.M}^{-1}\text{cm}^{-1}$) and two in the Q range 500 – 650 nm at 488 530 and 645 with the molar absorption coefficients of $1.4 \times 10^4 \text{ L.M}^{-1}\text{cm}^{-1}$ $7 \times 10^3 \text{ L.M}^{-1}\text{cm}^{-1}$ and $5 \times 10^4 \text{ L.M}^{-1}\text{cm}^{-1}$ respectively. Solution of $5 \times 10^{-5}\text{M}$ TPPS_4 in ethanol solvent is brown and exhibits five absorption , one in soret band at 416nm ($\epsilon = 3.2 \times 10^4 \text{ L.M}^{-1}\text{cm}^{-1}$) and four maxima at 486,512,546 and 588 nm with molar absorption coefficients $1.2 \times 10^4 \text{ L.M}^{-1}\text{cm}^{-1}$, $1.6 \times 10^4 \text{ L.M}^{-1}\text{cm}^{-1}$, $6 \times 10^3 \text{ L.M}^{-1}\text{cm}^{-1}$ and $5 \times 10^3 \text{ L.M}^{-1}\text{cm}^{-1}$ respectively . TPPS_4 solution in pH below 4 showed shift of the maximum from 412 to 433 nm and changes in Q-band, were mentioned before four maxima have changed to three peaks with one dominating at 645 nm.

3.2 Reaction of Porphyrin with Uranium Ion

Addition of U ion to 10^{-5}M of TPPS caused significant changes in ligand spectra , the decrease in the ligand band at 433nm and the

increase in U-TPPS₄ peak at 414nm ($\epsilon = 1.8 \times 10^5 \text{L.M}^{-1}\text{cm}^{-1}$) in the presence of ascorbic acid and at 420 nm ($\epsilon = 2.2 \times 10^5 \text{L.M}^{-1}\text{cm}^{-1}$) in the presence of hydroxyl amine were observed. The relation between changes in absorbance at these wavelengths was linear ($R^2 = 0.997$). Changes in Q-band were observed as well where three- model band was changed to one – model. Complexation reaction of TPPS₄ with uranium ion showed 2:1 molar ratio. It is in good agreement with earlier papers [7, 13]. Precise analysis of titration curve showed changes in absorbance gradient at metal concentrations where complex was expected for 2:1 U-TPPS₄ complex. When solution exposed to room light containing uranium ions ($2 \times 10^{-5} \text{M}$) and TPPS₄ at concentration of $5 \times 10^{-5} \text{M}$ the color of U-TPPS complex changes gradually from yellow to green clear solution and the soret band of U-TPPS₄ complex move from 420nm to 433nm and the later assigned to the TPPS₄ ligand peak at low PH 2.5, that due to photochemical decomposition of complex, such behavior was reported by smith and langry [21], and the rate of decomposition reaction increase strongly when the solution exposed to the sun light. However the same behavior was noticed when the complex U-TPPS was exposed to uv-vis lamp (tungsten and D₂ light) in side the chamber of spectrophotometer see **fig 2** and **3**. Robinson and Hambright [22] also noted decomposition of Hg- TPPS₄ complex into unknown species and explained this fact by the substitution of the ligand β -pyrrole protons by metal atoms

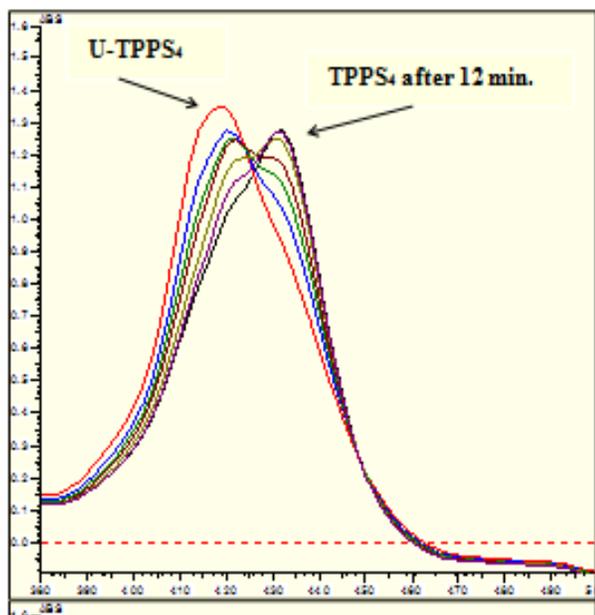


Fig.2. The visible region of the titration U-TPPS₄ with time at $\lambda 414$ and $\lambda 433$, pH 2.5, T=25 °C.

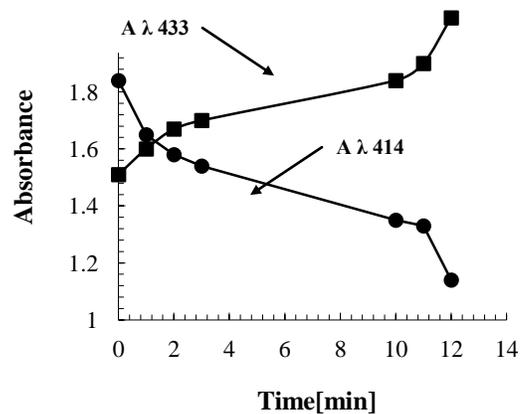


Fig.3a. The change in absorbance at $\lambda 414$ and $\lambda 433$ nm over time of U-TPPS₄ ($5 \times 10^{-5} \text{M}$) upon exposed to the visible light, pH 2.5, T 25 °C.

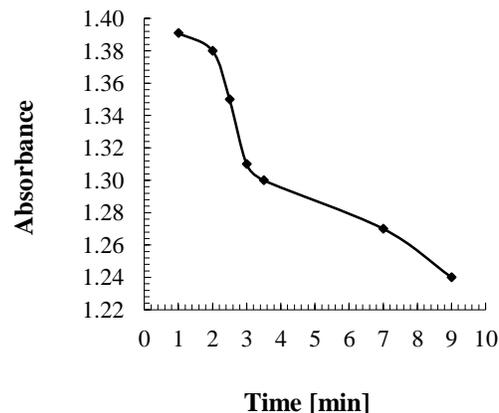


Fig.3b. The change in absorbance spectra of U-TPPS₄ (10^{-5}M) upon exposed to the U.V-Vis light lamp at pH 2.5, decomposition time 1.5-12 min. at $\lambda 420$ nm.

3.3 Analytical applications

TPPS₄ is very sensitive as a chromogenic reagent and could be applied for spectrophotometric determination of metal ion under study. In the presence of 10^{-5}M TPPS₄ at pH 2.5 (in acetate buffer), the absorbance of the formed metal complex exhibits a maximum value. Under the conditions employed, the calibration graphs was linear in the range $(0.01-120) \mu\text{g l}^{-1}$ for u ion **fig. 4**. The sensitivity for the 0.003 absorbance (sandell's



index) was 2.95 ng cm^{-2} , thus the sensitivity is superior to that . Obtained previously for other porphyrins [7, 23].

Application of TPPS₄ allowed the determination of small amounts of uranium with a detection limit of $2 \times 10^{-9} \text{ M}$. The

precision for three replicate measurements at $0.08 \mu\text{g ml}^{-1}$ concentration level was in the rang 1.4-2.0% RSD. The total uranium concentration was found in the tap water sample is $11.02 \mu\text{g l}^{-1}$ (ion added + u ion in water) and the different was $0.02 \mu\text{g l}^{-1}$ in water sample, RSD % (n=5) is 2.3.

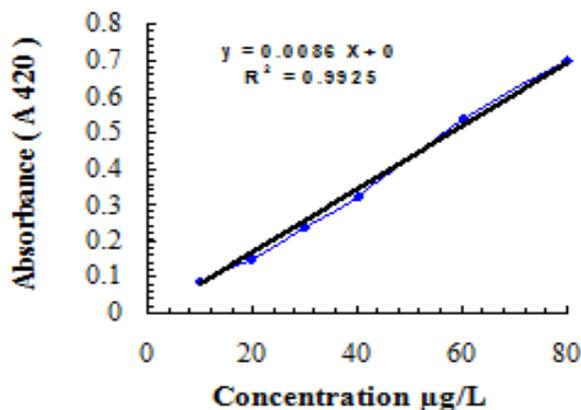


Fig.4. Calibration curve of U- TPPS₄

The effect of foreign ions was investigated for determination of uranium ion using TPPS₄ as a color reagent. The method shows a good tolerance to the great excess of alkali and alkaline earth metals.

No significant interferences from common inorganic anions, such as chlorides nitrates and sulfates, were also found. The effect of the presence of some heavy metals was examined up to their 50-fold. However, Co (II), Zn (II) and Cu (II) caused

more than 80% suppression of uranium complex formation even when they were at similar concentration level owing to formation of their complexes with TPPS₄ by metal substitution.

Table 1: Spectrophotometric Determination of Metal Ion with Porphyrin Reagents

Metal ion	Reagent	Condition	Absorption Spectra λ_{max} , $\epsilon (\times 10^5)$	Range of determination	interference	Refs
Cu(II)	TPPS ₃	pH4(100°,1min)	434 , 4.8	6-60 ng l^{-1}	Zn	[24]
Zn(II)	TPPS ₄	pH 7.1+ Imidazole+Cd room temp 30 min	425 , 4.5	10-150 ng l^{-1}	Mn(II),Co(II), Fe(II)	[16]



Pb(II)	TPPS ₄	pH4+ ascorbic Acid(100.7min)	411 , 2.2	–	Cu(II), Hg(II)	[23]
Ni(II)	TPPS ₄	pH8-9+(Cd(II) + imidazole(100°C)	418 , 2.3	Up to 150 ngI ⁻¹		[20]
U ion	TPPS ₄	pH 3.0+NH ₂ OH.HCl	420 , 2.2	0.01-120µgl ⁻¹	This work	
Cd	T ₄ BPP	pH 10.0 by HPLC	436	0.01 – 120 µgl ⁻¹		[26]
Hg	T ₄ BPP	10.0 by HPLC	449	0.01 -120 µgl ⁻¹		[26]

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