

Selective Determination of Uranium Using 1-(2-Quinolylazo)-2,4,5-Trihydroxybenzene as a Colorimetric Reagent

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Abstract: Colorimetric reaction behavior of 1-(2-quinolylazo)-2,4,5-trihydroxybenzene (QATB) has been established with uranium(VI) under various physicochemical conditions. An addition of dilute solution of uranyl ions to the dimethylformamide (DMF) solution of QATB, resulted to form a brown colored complex which was soluble if 30% DMF concentration was maintained. The brown colored complex absorbing maximum at 560 nm in the pH range 6.5-7.5. Beer's law was valid over concentration range 0.0-14.0 ppm, with molar absorptivity and Sandell's sensitivity of $1.9 \times 10^4 \text{ L.mol}^{-1} \text{ cm}^{-1}$ and $0.0125 \mu\text{g cm}^2$, respectively. The molar composition of the complex was 1:2 (M:L) as determined by Job's method of continuous variation. The tolerance limits for interfering ions are discussed. All variables were studied in order to optimize the reaction conditions. The efficiency of the proposed method is shown by the successful determination of traces of uranium in some ores.

Keywords: Spectrophotometry, QATB, Uranium, Ores

Introduction

It is well known that uranium is toxic as well as being radioactive; the safety profiles for uranium compounds are well established^{1,2}. Because uranium is a relatively mobile element in many surface or near-surface environments, its geochemical exploration methods require the measurement of the trace quantities of the metal ion in water samples^{3,4}, along with that in plants, soils and rocks. The uranium concentration of sea water is about $3.3 \mu\text{g/L}$ ^{4,5} in fresh-water or even lower. Thus, highly sensitive methods are required for pre-concentration and determination of uranium in water samples collected for prospecting purposes.

Numerous method for the spectrophotometric determination of uranium based on the use of balmic acid, morin, sodium fluoride, pyrogallol red, pyrogalllic acid *etc.*, have been reported⁶⁻¹³, but most of them require a solvent extraction step and entail various disadvantages in terms of reproducibility, simplicity, rapidity and sensitivity. Heterocyclic azo compounds have attracted much attention as they are sensitive chromogenic reagents in addition to being important complexing agents. These dyes have been useful in the spectrophotometric determination due to its good selectivity and sensitivity over a wide range of pH and because they are relatively easy to synthesize and purify.

This paper reports, 1-(2-quinolylazo)-2,4,5-trihydroxybenzene (QATB) as an analytical reagent for the micro determination of uranium(VI), whereas a very limited number of heterocyclic azo dyes find their uses for the determination of uranium(VI). Comparatively this reagent has been found a selective reagent for uranium(VI).

Experimental

A Bausch and Lomb Spectronic 2000 spectrophotometer with 10 mm matched glass cells was used for recording spectra and a Beckman pH meter was used for pH measurements.

Reagents and solutions

All the chemicals were of analytical grade. Doubly distilled water was used throughout the experiment for the dilution of the reagents and samples. Standard uranium(VI) solution of uranyl ion was prepared by dissolving appropriate amount of uranyl nitrate (AnalaR) in double distilled water. The solution was standardized as uranyl oxinate¹⁴.

1-(2-Quinolylazo)-2,4,5-trihydroxybenzene (QATB) as synthesized earlier¹⁵, was used as a 1×10^{-3} M solution prepared by dissolving 0.281 g of freshly distilled dimethyl-formamide (DMF). Solutions more than a week old were discarded. Dilute solution of sodium hydroxide, sodium acetate and hydrochloric acid were prepared and used for pH adjustment.

Determination of uranium(VI)

To a suitable volume of sample containing 20.0-120.0 μg of uranyl ions, 2 mL of 2×10^{-3} M QATB solution in DMF was added followed by addition of 2 mL of 1×10^{-3} KCN solution. 1.0 mL of 1 M sodium acetate was added and made up the volume to 10 mL, maintaining 40% DMF concentration in the final solution. The absorbance at 560 nm was measured against a corresponding reagent blank prepared under similar conditions.

Results and Discussion

Uranyl ions formed a light brown colored precipitates with an ethanolic solution of QATB. The precipitate was not soluble up to 70% ethanolic concentration. However, DMF solution of QATB also resulted to form a brown colored complex with uranyl ions which was soluble if 30% DMF concentration was maintained. The color reaction was therefore studied in 40% DMF. The absorbance spectra of $\text{UO}_2(\text{II})$ -QATB complex solution maintaining 40% DMF concentration recorded against corresponding reagent blank (QATB solution without metal ion) solution are shown in Figure 1. The complex had constant and maximum absorbance in the pH range of 6.5-7.5. For maintaining an appropriate pH of the complex solution 1 mL of 1 M sodium acetate was sufficient. For attaining maximum sensitivity, at least 5-times molar excess of reagent was required and hence in subsequent studies, 10-times molar excess of reagent was used. Under these optimum conditions, various physicochemical constants were established and are given in Table 1. A comparative study of the sensitivities of various spectrophotometric reagents known for uranium given in Table 2, shows, that the present reagent has a good sensitivity for the micro determination of uranium.

Effect of diverse ion

In the determination of uranium(VI) at the 4.76 $\mu\text{g/mL}$ level; chloride, bromide, iodide, nitrite, sulphate, sulphite, alkaline earths, lanthanides, aluminum(III), indium(III), antimony(III), bismuth(III), chromium(III), platinum metals (except palladium(II)) did not interfere at all. However, thorium(IV) and rare earths up to 1000 fold do not interfere in the determination. EDTA and borax were found to interfere. Under the appropriate conditions found for uranium(VI), cyanide and iodide are tolerated in fair concentration and have been used to mask of interfering transition metals.

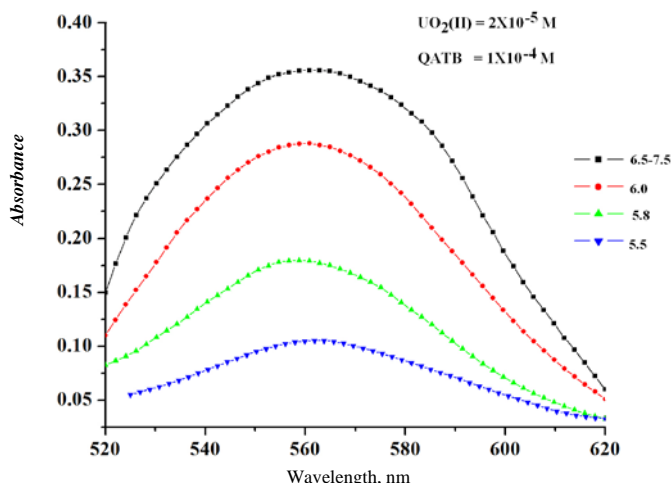


Figure 1. Absorption spectra of $\text{UO}_2(\text{II})$ -QATB complex at different pH

Table 1. Physicochemical characteristics of $\text{UO}_2(\text{II})$ -QATB complex

Characteristics	$\text{UO}_2(\text{II})$ -QATB complex
λ_{max} , nm	560
pH range	6.5-7.5
Reagent required for full complexation, mol	5
Beer's law range, ppm	0.00-14.0
Sandell's sensitivity, $\mu\text{g cm}^{-2}$	0.0125
Molar absorptivity (ϵ), $\text{l mol}^{-1}\text{cm}^{-1}$	1.9×10^4
Composition (M:L) by job's method	1 : 2
Optimum concentration range, ppm	2.0 – 12.0

Table 2. Comparison of sensitivities of various spectrophotometric reagents for uranium(VI)

Reagent	λ_{max} , nm	Molar absorptivity, $\text{L.mol}^{-1}\text{cm}^{-1}$	References
2-Hydroxy-3-methoxybenzaldehyde isonicotinoyl hydrazone	374	1.05×10^4	16
2-(2-Thiazolylazo)- <i>p</i> -cresol	588	1.31×10^4	17
Pyrocatechol violet	650	9.5×10^4	18
1,4-Dihydroxy-9,10- anthracenedione	600	1.19×10^4	19
<i>o</i> -Chlorophenyl fluorone	560	1.42×10^4	20
5-(<i>p</i> -Carboxyphenylazo)-8- hydroxyquinoline	470	4.39×10^4	21
5-(2- Carboxyphenylazo)-8-quinolinol	524	1.035×10^4	22
5,14- <i>N</i> , <i>N'</i> - Hydroxyphenyl – 4, 15-dioxo-1,5,14,18 –tetraazo hexacosane	390	1.0×10^4	23
2-Hydroxy-1-naphthaldehyde isonicotinoyl hydrazone	430	9.6×10^3	24
Di-2-pyridyl ketone benzoyl hydrazone	377	2.02×10^4	25
Diacetyl monoxime isonicotinoyl hydrazone	364	1.63×10^4	26
1-(2-Quinolylazo)-2,4,5-trihydroxybenzene	560	1.9×10^4	This work

Uranium(VI) can therefore be determined selectively in presence of many base metals as well as noble metals. Table 3 represents the tolerance limits in ppm of various ions in solution that caused a deviation smaller than $\pm 2\%$ in absorbance for the determination of uranium(VI).

Table 3. Tolerance limits of diverse ions in the determination of 4.76 $\mu\text{g/mL}$ of uranium(VI)

Foreign ions	Tolerance limits, ppm	Masking agents
F^-	50	-
Cl^-	600	-
Br^-	600	-
I^-	500	-
CNS^-	200	-
CN^-	100	-
$\text{S}_2\text{O}_3^{2-}$	400	-
Oxalate	20	-
Citrate	20	-
Tartrate	20	-
PO_4^{3-}	50	-
Mo(VI)	25	-
W(VI)	10	-
V(V)	20	Masked by CN^-
Cd(II)	40	-
Hg(II)	40	-
Mn(II)	10	-
Fe(II)	10	Masked by CN^-
Cu(II)	5	Masked by CN^-
Zn(II)	4	-
Ag(II)	10	Masked by I^-
Pd(II)	20	Masked by I^-
Pb(II)	20	Masked by CN^-

Application for determining uranium(VI) in various synthetic ores

Synthetic mixtures of the ores were prepared by mixing the compounds in the same ratio equivalent to the composition of the corresponding ore and dissolving them in concentrated HCl. The mixture were evaporated to dryness and dissolved in distilled water. The amount of U(VI) was determined following the recommended procedure given above. Synthetic mixtures of important alloys used for various purposes were prepared by mixing appropriate amounts of components and were also analyzed following the recommended procedure. The results of the analysis are given in Table 4.

Table 4. Estimation of uranium(VI) in synthetic samples of uranium ores

Ores/ Alloys	Amount of uranium taken, ppm or (% composition in ore)	Uranium(VI) found, ppm	Mean value, ppm	% Recovery	Standard Deviation (σ)
Pitchblende	U(VI) 47, Pb(II) 3.0, As(II) 0.9, Ca(II) 0.5	46.7, 46.8, 47.5, 46.5, 48.0, 47.3	47.133	100.28	0.568
Monazite	U(VI) 48, Pb(II) 3.5, As(II) 1.2, Ca(II) 1.0	48.5, 48.8, 47.7, 47.5, 48.4, 48.6	48.25	100.52	0.524

Contd...

Carnotite $K_2(UO_2)_2(VO_4)_2 \cdot 1-3H_2O$	U(VI) 52, K(I) 9.0, V(V) 12	52.5, 52.7, 51.4, 52.6, 51.5, 52.3	52.166	100.32	0.572
Autunite $Ca(UO_2)_2(PO_4)_2 \cdot 10-12H_2O$	Ca(II) 5.0, U(VI) 52.0	53.0, 52.7, 51.4, 51.6, 52.5, 52.8	52.333	100.64	0.668
Torbernite $Cu(UO_2)_2(PO_4)_2 \cdot 10H_2O$	U(VI) 48.0, Cu(II) 6.4	48.8, 49.0, 47.5, 47.3, 48.5, 48.4	48.25	100.52	0.695

Conclusion

It has been demonstrated that QATB is an excellent analytical reagent for the spectrophotometric determination of Uranium(VI) in ores/alloys samples. QATB is more simple, sensitive and cheap than most other reagents reported earlier. Nearly all anions and most of the cations do not interfere with the chromogenic reaction. Under the appropriate conditions found for Uranium(VI), cyanide and iodide are tolerated in fair concentration and have been used to mask of interfering transition metals. The colour reaction is fast and the complex is stable which makes it easy to obtain accurate and precise results.

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