

GUAIACOL AS A NEW REAGENT FOR THE SPECTROPHOTOMETRIC
DETERMINATION OF URANIUM

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Guaiacol, i.e. o-hydroxyanisole, gives a distinct color reaction with U(VI) suitable for spectrophotometric determination of the metal. The complex formed in the reaction has an absorption maximum at 352 nm. Optimum pH for the color development ranges from 6.5 to 8.5. The molar absorptivity and Sandell's sensitivity of the method were found to be $3.75 \times 10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and $0.063 \text{ } \mu\text{g} \cdot \text{cm}^{-2}$, respectively. Many anions and cations do not interfere up to 100 ppm. The method has been made very specific by selective extraction of U(VI) with TBP from a mixture of different cations and anions in the presence of 60% NH_4NO_3 as salting out agent followed by developing the color in the non-aqueous phase by adding guaiacol in methanol at pH 6.5 to 8.5. An amount as low as 30 μg of uranium(VI) per 10 ml of the solution could be satisfactorily determined with an RSD of $\pm 2.0\%$. The method was applied to rock samples after U(VI) had been extracted from a sample solution into 25% TBP in hexane. Results obtained by the new method compare very well with those of conventional fluorimetric and radiometric assays. The features of the method include excellent precision, rapidity, good selectivity, and ease of performance.

INTRODUCTION

Uranium is a chromogenic element and therefore a number of photometric methods using different reagents have been known for its determination. Among the reagents used for the determination of uranium, mention may be made of hydrogen peroxide¹, thiocyanate², ferrocyanide³, resorcinol⁴, sulfosalicylic acid⁵, pyrogallol⁶, azide⁷, ascorbic acid⁸, ammonium thioglycollate⁹, acetylacetone¹⁰, 8-hydroxyquinoline¹¹, morin¹², dibenzoylmethane¹³, and arsenazo-III^{14,15}. Of these reagents dibenzoylmethane, morin, and arsenazo-III are quite sensitive although not sufficiently selective. Others are neither selective nor sensitive. In the course of syntheses and physicochemical studies of complex uranates¹⁶⁻¹⁹ in our Laboratory and as part of our interest in the reaction of uranium with various phenolic derivatives, it was observed that o-hydroxyanisole, commonly known as guaiacol, rapidly reacted with uranium(VI) in methanol under slightly alkaline conditions to give a yellowish-orange color suitable for spectrophotometric determination of uranium on ppm level. It was therefore decided to explore its applicability for determination of the metal. The efficacy of guaiacol as a reagent for spectrophotometric determination of uranium is reported in this paper. Also highlighted are the advantages of the new method in terms of reproducibility, stability of the complex, and operational simplicity. The reagent is easily available and non-toxic.

EXPERIMENTAL

Preparation of reagents

Reagent grade chemicals were used throughout the investigation.

10% v/v guaiacol in methanol: dissolve 10 ml of guaiacol in methanol and make up the volume to 100 ml with methanol. The solution once made is stable for 1 week.

0.01M $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: Dissolve 0.5 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water in a 100 ml volumetric flask and fill up with distilled water. Uranium content of the stock solution was ascertained gravimetrically²⁰. Prepare appropriate dilute solutions from this solution.

25% v/v tributylphosphate in hexane: dissolve 25 ml of TBP (previously washed with sodium hydroxide) in 50 ml of hexane and dilute to 100 ml with hexane.

60% m/v NH_4NO_3 in water: Dissolve 60 g of NH_4NO_3 in 50 ml of distilled water and dilute the solution to 100 ml with distilled water.

1.0% EDTA: Dissolve 1.0 g of disodium salt of ethylenediaminetetraacetic acid in 100 ml of distilled water.

Ammonia solution: Aqueous ammonia (density 0.9 g cm^{-3}) was diluted with an equal volume of distilled water and used for pH adjustment.

Apparatus: An ELICO pH meter model LI-120 equipped with combination electrodes was used for pH measurements.

Varian (634-S) double beam digital spectrophotometer equipped with 1.0 cm quartz cuvettes was used for ab-

sorbance measurements. Laser Raman spectra were recorded on a SPEX Ramalog model 1403 spectrometer.

Reaction conditions

Absorption spectra: Two solutions, one containing known amounts of U(VI) and guaiacol, and the other containing only guaiacol both at pH 8.0, were prepared.

The absorption spectra of the complex against the reagent blank and the reagent blank against methanol were recorded in the wavelength region of 330-450 nm.

Effect of pH: Solutions containing known amounts of U(VI) and guaiacol were prepared in the pH range of 1.5-8.0 and the absorbances measured at 352 nm.

Effect of reagent concentration: Two sets of solutions, one set containing a fixed amount of U(VI) and varying amounts of guaiacol, and the other set containing only guaiacol (corresponding blank) were prepared at pH 8.0. The absorbances were measured at 352 nm against the corresponding reagent blank.

Adherence to Beer's Law: Solutions containing a fixed amount of the reagent and varying amounts of U(VI) were prepared at pH 8.0 and the absorbances were measured at 352 nm.

Effect of foreign ions: Solutions containing 100 μg of U(VI), a 1000 fold excess of guaiacol, and varying amounts of foreign ions were prepared and the absorbances measured against the corresponding reagent blank at 352 nm. Total volume of the solution in direct measurement was 10 ml and that in extractive system was 25 ml.

Choice of solvents: As guaiacol is insoluble in water, the present study could not be conducted in an aqueous medium. Experiments involving solvents like

chloroform, carbon tetrachloride, hexane, benzene, ethyl alcohol, methyl alcohol etc., in which guaiacol is soluble, were conducted and the most satisfactory results were obtained with methanol as the solvent. A 40:60 water:methanol medium gave equally satisfactory results.

Recommended procedures

1. Direct determination

Take 2 ml aliquot containing 5 to 800 μg of U(VI) into a 10 ml volumetric flask and add 5 ml of 10% guaiacol solution in methanol. Adjust the pH of the solution to 8.0 with a few drops of dilute ammonia solution and make up the volume to the mark with guaiacol solution in methanol. Prepare a reagent blank similarly without using uranium and measure the absorbance of the complex against the reagent blank. Deduce the amount of uranium from a previously prepared calibration graph.

2. Extractive spectrophotometric determination

Take an aliquot containing 15 to 800 μg of U(VI) in the presence of interfering ions into a 100 ml separating funnel. Add to it 1 ml of 1% EDTA, 25 ml of 60% NH_4NO_3 solution and 5 ml of 25% TBP in hexane.

Shake the mixture for 2 min and keep for phase separation. Remove the aqueous phase, wash the organic phase with distilled water and discard the aqueous phase. Add 15 ml of guaiacol solution in methanol and adjust the pH of this solution to 8.0 with ammonia solution. Shake it for a few seconds. Yellowish-orange color develops immediately. Transfer the methanol-TBP solution to a 25 ml volumetric flask and make up the volume to the mark with methanol. Measure the absorbance at 352 nm

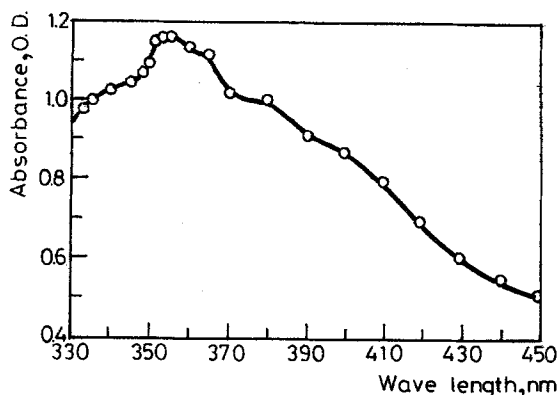


Fig. 1. Absorption spectrum of the complex against reagent blank (methanol)

against a similarly prepared reagent blank. Prepare a calibration graph between the amount of uranium taken and the corresponding absorbance by taking 15 to 800 μg of U(VI) and carrying through the procedure.

RESULTS

Absorption spectrum: The absorption spectrum of the complex is shown in Fig. 1. From the figure it is evident that the complex has a maximum absorption at 352 nm. The absorption due to the reagent is negligibly small at this wavelength. However, a reagent blank was employed in further experiments.

Effect of pH: It was found that the absorbance remained constant in the pH range of 6.5 to 8.0. The absorption above this pH decreased because of precipitation of uranium as $\text{U}_2\text{O}_7^{2-}$. Many buffer systems like pyridine, monoethanolamine and hexamine were tried separately but dilute ammonia was found to be the most effective.

Effect of reagent concentration: The absorbance increased with increasing amount of the reagent, guaiacol, and became constant when the reagent was present in a large excess (above 1000-fold molar excess over uranium).

Adherence to Beer's Law, molar absorptivity and stability of the complex: Beer's law was found to be obeyed in the range of uranium(VI) concentrations from 5 to 1200 μg per 10 ml of the solution. The molar absorptivity was found to be $3.75 \times 10^3 \text{ l.mol}^{-1}.\text{cm}^{-1}$ and the color was stable for 72 h.

Composition of the complex: The metal [U(VI)] :Ligand [guaiacol] composition was found to be 1:2 by Job's method of continuous variation.

Effect of foreign ions: In order to verify the effect of foreign ions on the newly developed method, the efficacy of the reagent was tested separately in the presence of a number of ions.

- In the direct method, the amount in ppm shown against each ion did not cause any interference with the determination of 10 ppm uranium(VI) in a solution. Al(III) (20), Ce(III) (10), Cr(III) (20), Mo(VI) (20), Ni(II) (30), Mn(II) (30), Ba(II), Ca(II) and Sr(II) (200), Th(IV) (10), Zr(10), Nb(V) (15), ClO_4^- (200), Cl^- (1000), Br^- (2000), NO_3^- (1000), SO_4^{2-} (50), $\text{S}_2\text{O}_3^{2-}$ (500), SCN^- (100), acetate (4000), BrO_3^- (1000), citrate (500), tartrate (100), EDTA (2500).
- In an extractive system, for the determination of 10 ppm of U(VI), the following concentrations of different foreign ions (ppm) did not interfere. Th (500), Zr (800), Fe (III) (2000), Cr (III) (40), Cr (VI) (10), Ce (III) (50), Ce (IV) (5), Cu (II) (100), Pb (500), Cd (200), Zn (100), Nb (50), Ta (40), Na (1000), K (1000), Ca (500), Mg (500), La (500), Ba (II) and

TABLE 1

Precision of U(VI) determination
(uranium taken = 200 μg)

Sample No.	U(VI) determined, μg	Mean, μg	RSD, %
1	203.77		
2	199.36		
3	193.71		
4	203.14		
5	198.11	200.13 \pm 3.84	1.92
6	193.71		
7	203.77		
8	201.25		
9	203.14		

Sr(II) (1000), Yt (500), W(VI) (40), V(V) (75), Al(III) (500), Ti(IV) (30), Mn(II) (45), Co(II) (500), Ni(II) (300), Au (200), Sb(V) (100), Be (100), Sn(IV) (25), Cl^- (1000), SO_4^{2-} (50), NO_3^- (1000), Br^- (100), PO_4^{3-} (70), acetate (200), tartrate (100), EDTA (2500), NO_2^- (50), SCN^- (100).

These results make us to state that the new reagent is quite effective.

Precision and accuracy: The RSD was found to be $\pm 1.92\%$ from nine replicate determinations of 200 μg uranium(VI) over a period of 9 consecutive days. The results are shown in Table 1. The accuracy of the method was found to be $\pm 1.1\%$ in the range of 200 to 800 μg of U(VI). The results are shown in Table 2. Statistical analyses were made based upon the results obtained from a series of solutions containing uranium in the range of 200 to 800 μg , because the corresponding absorbances fall in the region of lowest, photometric error of absorbance measurements of the instrument.

TABLE 2

Accuracy of uranium determination

Sample No.	Amount taken, μg	Amount determined, μg	Deviation, %
1	200	197.90	-1.05
2	400	403.47	+0.87
3	600	597.87	-0.35
4	800	803.49	+0.43

DISCUSSION

The reagent, guaiacol, works very satisfactorily for quantitative determination of uranium in solution. However, when the metal occurs in a sample in which interfering ions are present, for instance, a rock sample containing uranium, it is necessary to perform a selective extraction of the metal prior to its spectrophotometric determination. The extraction is achieved from either a neutral or a slightly acidic solution by a tributyl phosphate (TBP) solution in hexane. The extraction is carried out in the presence of ammonium nitrate and disodium salt of EDTA. While ammonium nitrate acts as a salting out agent, the disodium salt of EDTA traps the interfering ions by complexation. It has been observed that 1 ml 1% solution of EDTA disodium salt enables masking of the usual interferences. It is notable that the above mentioned extraction procedure permits a very satisfactory determination of the metal content down to a concentration of 15 μg per 25 ml of solution in the presence of most of the cations generally occurring in rock samples. It is recommended that for the determination of U(VI), the spectrophotometric experiments should be done in the presence of the extractant containing TBP since a quantitative stripping off of

the metal may not be possible. A point worth mentioning is that an excess of the reagent is needed to determine the metal. This implies that the complex formed is rather weak.

Application of the method: In order to ascertain the efficacy of the new procedures, the method was applied to six different rock samples. First uranium was separated from the sample solution as prescribed in procedure 2 and then the method was applied to determine the uranium content.

The rock sample solution was prepared by repeated treatment of 1.0 g of the sample (200 mesh) on a platinum dish with hydrofluoric and nitric acids. Organic matter was removed by fuming the residue with perchloric acid. About 1 ml of HNO_3 and 25 ml of distilled water were added to the residue and digested for 15 min. The solution was filtered through Whatman no. 1 filter paper and the filtrate stored. The residue, if any, was fused with Na_2O_2 in a nickel crucible and then extracted with dilute nitric acid solution. This extract was mixed with the filtrate. The solution was neutralized with dilute ammonia solution. A suitable aliquot was used to determine U(VI) following procedure 2 as given in this paper. Results obtained by this method were compared with those obtained from fluorimetric and radiometric analyses of the sample under study. The results agree very well, as is shown in Table 3.

Laser Raman spectrum of the solution used for determination of the metal in procedure 1, recorded at room temperature, showed a strong signal at 905 cm^{-1} . Because of large polarizability changes involved in the U-O bond, the band appeared as a strong one evidencing the occurrence of a trans-linked O=U=O center¹⁶ in the complex, as expected.

TABLE 3

Determination of uranium in rock samples.
(Average 5 replicate determinations)

Sample No.	% U ₃ O ₈		
	New method	Fluorimetric method	Radiometric method
1	3.37	3.40	3.35
2	0.26	0.29	0.28
3	0.33	0.34	0.35
4	0.20	0.17	0.19
5	0.42	0.41	0.41
6	0.20	0.18	0.21

CONCLUSION

The new method is suitable for the determination of U(VI) in rock samples assaying more than 0.01% U₃O₈. High precision and accuracy permit routine determination of uranium in rock samples using this method. Although the sensitivity of this method is not too high, it is comparable to those of the K₄Fe(CN)₆³, KSCN² and 8-quinolinol¹¹ methods and better than those of the mercaptoacetate⁹ and H₂O₂ methods¹.

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