Spectrophotometric Determination of Uranium with Sodium 2'',6''-dichloro-4'-hydroxy-3,3'-dimethylfuchsone-5,5'-dicarboxylate

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For the colorimetric determination of uranium, various organic reagents have been used : sodium salicylate[1], tannic acid[2], thioglycollic acid[3], oxine[4-6], chromotropic acid[7-9], dimethyldithiocarbamate[10], dibenzoylmethane[11-15], morin[16], acetylacetone[17], thorin[18], neothorin[19] and arsenazo[20-21].

In this paper, a new method is described for the colorimetric determination of small amounts of uranium. It is based on the colored complex formation between uranyl ions and sodium 2'', 6''-dichloro-4'-hydroxy-3,3'-dimethylfuchsone-5, 5'-dicarboxylate. This compound has recently been used for the determination of beryllium, iron and copper and observations suggested a possibility that it could also be used for uranium[22].

Experimental

The spectrophotometer and photoelectric photometer were the same as those used in our previous work[22].

Ion Exchange Resin.—Tube, 10 mm. in diameter, with a high-porosity glass filter disk fused to the lower end was used. The resin was a quaternary ammonium anion exchange type, a modification of Amberlite IRA-410. Before use, the resin was converted into the sulfate form by treating it with 10% sulfuric acid. The treated resin was washed with distilled water until the effluent solution was neutral. The resin was added to the tube with distilled water to give a column height of 15 cm.

Uranium Standard Solution.—A standard stock solution of uranium was prepared by dissolving uranyl nitrate in distilled water. The solution contained 100 γ of uranyl ions per milliliter.

Reagent Solution.—A 0.2% reagent solution was prepared by dissolving sodium 2'',6''-dichloro-4'-hydroxy-3,3'-dimethylfuchsone-5, 5'-dicarboxylate in 99% ethanol.

***p*-Nitrophenol Indicator.**—A 0.4% solution was prepared by dissolving *p*-nitrophenol in distilled water.

All other chemicals were of analytical reagent grade.

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Separation of Interfering Ions.—Uranium was separated from other ions according to Fisher's procedure[23].

Procedure for Determination of Uranium.—Pipet 23 ml. of a slightly acidified sample solution, which has been adjusted so as to contain 1 to 10 γ uranium per milliliter, and one drop of *p*-nitrophenol indicator solution to a 25 ml. volumetric flask. Add 0.05 N sodium hydroxide solution dropwise until the indicator just turns yellow, then discharge yellow color by careful addition of 0.05 N hydrochloric acid dropwise. The resultant solution should be adjusted to pH 5.2 ± 0.4. Add one milliliter of the reagent solution, shake well, make up to the mark with distilled water and mix thoroughly. Measure the absorbance at 610 mμ, after ten minutes, using distilled water as reference. Determine the weight or the concentration of uranium in the sample from a calibration curve prepared by the same procedure used for the sample.

Results and Discussion

Absorption Spectra.—Color reactions between many ions and sodium 2'',6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate were recorded in our previous paper[22]. Uranyl ions react with the compound to give a blue complex in dilute acid solution. Absorption spectra of the compound in a solution and of its uranyl complex are shown in Fig. 1.

The maximum absorption of the uranyl complex solution occurs at 610 mμ. The reagent solution has little or no absorption at this wavelength. A large excess of the reagent must be avoided because its solution has a slight absorption at 610 mμ when the concentration is greater than about 80 p.p.m. It is not necessary, however, to use the same concentration of the reagent for standards and unknowns, when the concentration of unreacted reagent is in range of 80 to 40 p.p.m.

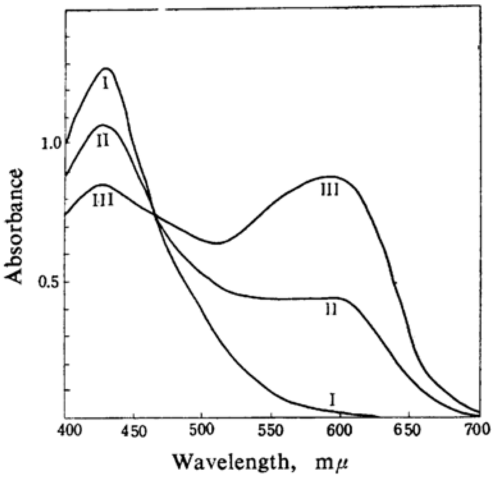

Fig. 1. Absorption spectra of the reagent solution and of its uranyl complex. pH 5.2.

I : Reagent 80 p.p.m.

II : Reagent (80 p.p.m.) + U(4.0γ/ml.)

III: Reagent (80 p.p.m.) + U(8.0γ/ml.)

Molar Ratio.—The colored complex in solution was found to have a molar ratio of 2 to 1, reagent to uranyl ions. The mole ratio method[24] and the continuous variation method[25-26] were used to establish the molar ratio. The continuous variation method was applied by mixing *X* ml. of 3.7×10^{-3} M reagent solution and $(1.00-X)$ ml. of uranyl solution of 3.7×10^{-3} M and diluting to 25 ml. after adjusting to pH 5.2. The results are shown in Figs. 2 and 3.

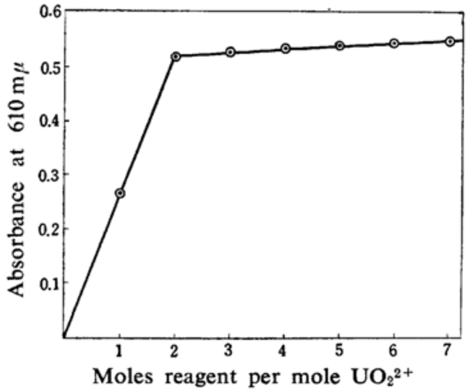

Fig. 2. Mole ratio method showing a ratio of 2 to 1, reagent to UO_2^{2+}, in the colored complex. pH 5.2.

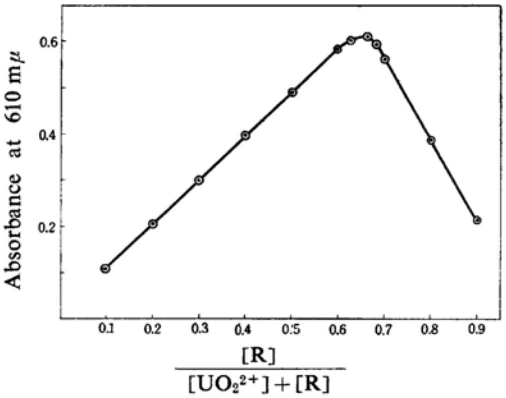

Fig. 3. Continuous variation method showing a ratio of 2 to 1, reagent to UO_2^{2+}, in the colored complex. pH 5.2.

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Effect of pH.—The effect of pH on the color reaction was examined by measuring the absorbance of a colored solution, at 610 mμ, containing 3.52 p.p.m. of uranium and 80 p.p.m. of the reagent, the pH being adjusted by adding dilute hydrochloric acid or dilute sodium hydroxide solution. The uranyl complex has a maximum intensity in the pH range 4.8 to 5.8 as shown in Fig. 4.

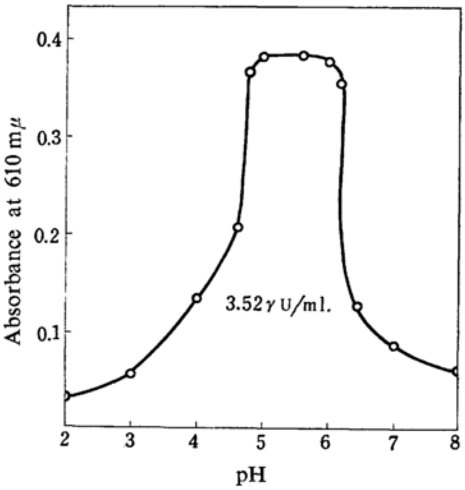

Fig. 4. Effect of pH on the uranyl complex.

A pH of 5.2±0.4 should be used when making absorbance measurements of the complex.

Several buffer solutions were tried: borax-succinic acid, acetate-acetic acid, phthalate, and phosphate buffers were unsatisfactory. All lowered the color intensity of the complex. Dilute hydrochloric acid and sodium hydroxide solution were satisfactory for pH adjustment with *p*-nitrophenol as indicator.

Rate of Color Formation.—Within the optimum pH range (5.2±0.4), the color intensity reaches a maximum in ten minutes and remains unchanged for about an hour. It is necessary, therefore, to allow the colored solution to stand at least ten minutes and then to measure the absorbance within an hour.

Effect of Temperature.—There is no variation in the absorbance of the colored complex over a temperature range 15 to 30°C.

Interfering Ions.—The reagent was tested on a spot plate[22]. Twelve ions were found to interfere: Al^{3+}, Be^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Ga^{3+}, Gd^{3+}, Nd^{3+}, Ni^{2+}, Pr^{3+}, Sc^{2+} and Y^{3+}. The effect of some common ions on the determination of uranium is shown in Table I. The limiting concentration was taken to be one that causes a deviation of more than 0.01 unit in the absorbance of a solution containing 5.28 γ uranium per milliliter.

TABLE I. EFFECT OF DIVERSE IONS

Ion	Added as	Limiting concentration, γ ions per milliliter
Al^{3+}	sulfate	0.02
Be^{2+}	chloride	0.02
Ca^{2+}	chloride	>1500
Cu^{2+}	sulfate	1
Cr^{3+}	sulfate	150
Fe^{2+}	Mohr's salt	2
Fe^{3+}	iron alum	0.8
Ni^{2+}	nitrate	80
Mg^{2+}	chloride	>1500
Zn^{2+}	chloride	>1000

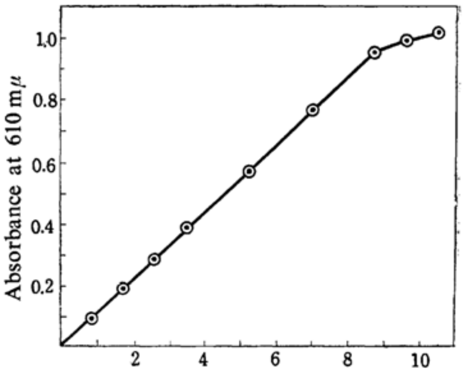

Fig. 5. Beer's law curve. pH 5.2.

TABLE II. DETERMINATION OF URANIUM

Solution analyzed		Added γ/50 ml.	Found U* γ	Error %
1	Al^{3+}	200		
	Be^{2+}	50		
	Fe^{2+}	200		
	Fe^{3+}	200		
	U	132.0	130.0	−0.2
2	Al^{3+}	1000		
	Be^{2+}	200		
	Fe^{3+}	500		
	U	176.0	169.6	−3.6
3	Al^{3+}	1000		
	Be^{2+}	500		
	Cu^{2+}	1000		
	Cr^{3+}	1000		
	Fe^{2+}	1000		
	Ni^{2+}	1000		
	U	44.0	45.8	+4.1

* These values are the averages of 5 replicate determinations.

Several methods were tried to eliminate interfering ions. The method proposed by Fisher[23] was adopted. It makes use of an anion exchange resin as mentioned in this paper. Ferric ions are reduced to ferrous ions with sulfurous acid before passing the sample solution through the resin column.

Beer's Law.—Beer's law is obeyed up to about 8.8 γ of uranium per milliliter (See Fig. 5).

Determination of Uranium in Synthetic Solutions Containing Other Ions.—The determination of uranium in the presence of certain other ions was made. The results are given in Table II.

Summary

A procedure has been developed for the spectrophotometric determination of small amounts of uranium with sodium 2'',6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5,5'-dicarboxylate. Beer's law is obeyed up to about 9 γ of uranium per milliliter. The accuracy and precision are satisfactory. Interference of foreign ions is eliminated by using an anion exchange resin.

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