*The Spectrophotometric Determination of Uranium with Dibenzoylmethane**

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Recently, many organic reagents which are very sensitive to uranium, such as dibenzoylmethane[1], PAN[2] and arsenazo[3], have been used for the spectrophotometric determination of uranium. In general, however, these reagents are liable to be affected by diverse ions. Accordingly, it is preferable to separate uranium from diverse ions by extraction prior to its spectrophotometric determination.

Of these chromogenic reagents, dibenzoylmethane can be advantageously used for the direct color development in the organic phase; thus the time for the analysis may be shortened and, at the same time, the possible loss of uranium during stripping may be prevented. From this point of view, several kinds of extractant, such as tetrapropylammonium nitrate (in methyl isobutyl ketone)[4], tri-*n*-octylphosphine oxide (in cyclohexane)[5] and tributyl phosphate (in ethyl acetate[6], or in isooctane[7], or in no diluent[8]), in combination with the use of dibenzoylmethane, have been reported. Some of these, however, involve procedures too complicated for routine use, or are too greatly subject to interference from diverse ions.

This paper describes a simple direct spectrophotometric determination of uranium with dibenzoylmethane in combination with tributyl phosphate, which is selected as the extractant of uranium because of its popularity.

* The main part of this work was done while the writer was at the School of Chemistry, University of Minnesota, U. S. A.

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2) K. L. Cheng, ibid., **30**, 1027 (1958).
3) H. P. Holcomb and J. H. Yoe, ibid., **32**, 616 (1960).
4) W. J. Maeck et al., ibid., **31**, 1130 (1959).
5) C. A. Horton and J. C. White, ibid., **30**, 1779 (1958).
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Experimental

Apparatus.—Absorbance measurements were made with a Beckman Model B spectrophotometer using 1-cm. glass cells.

Reagents.—*Standard Uranium Solution.*—A stock solution containing 100 μg. of uranium per ml. was prepared by dissolving uranyl nitrate in water. The standardization was made by titration with a standard potassium dichromate solution after the reduction of uranium with zinc amalgam. Dilutions of this solution were made as required.

Dibenzoylmethane Solution.—A 1% solution was prepared by dissolving 1 g. of dibenzoylmethane in 100 ml. of 95% ethyl alcohol.

Tributyl Phosphate Solution.—A 30% tributyl phosphate solution was prepared by mixing 300 ml. of tributyl phosphate with 700 ml. of benzene. This solution was washed first with a 5% sodium hydroxide solution and then with a 1 N nitric acid solution.

Aluminum Salting Agent.—An aluminum salting agent was prepared by dissolving 500 g. of aluminum nitrate nonahydrate and 70 ml. of concentrated nitric acid in enough water to make 1 l. of solution.

The other solvents and reagents were of an analytical reagent grade and were used without further purification.

Procedure.—*Extraction of Uranium.*—*a*) Samples which do not contain interfering ions.—Bring the nitric acid concentration of the sample solution to approximately 1N and then make it up to a definite volume with 1N nitric acid. Transfer 5 ml. of the sample solution to a 50-ml. separatory funnel. Add 5 ml. of a salting agent and 3 ml. of a tributyl phosphate solution. Shake vigorously for about 1 min. After it has settled, discard the aqueous layer and, if necessary, wash the organic layer with 2~3 ml. of a 10% sodium nitrate solution (1 N in acid) and discard the aqueous layer. Run the organic layer through a small plug of filter paper in the stem of the separatory funnel into a dried small vessel (e. g., a weighing bottle).

b) Samples containing chromium(VI) and cerium(IV).—Bring the nitric acid concentration of the sample solution to approximately 1 N in a definite volume. Transfer 5 ml. of the sample

solution to a small beaker. Add 1~2 ml. of a 10% sodium nitrite solution and warm this solution at 80~90°C until small bubbles of colored gas disappear. After cooling, transfer the solution into a 50-ml. separatory funnel and treat this solution as in a).

c) Samples containing thorium (IV) and zirconium (IV).—Bring the nitric acid concentration of the sample solution to approximately 1 N in a definite volume. Transfer 5 ml. of the sample solution to a 50-ml. separatory funnel. Add 3~5 ml. of a 1 M potassium fluoride solution. When 5 ml. of a potassium fluoride solution is used, the amount of salting agent should be doubled. In this case, solid aluminum nitrate nonahydrate is preferable. Treat this solution as in a).

Color Development.—Pipet 2 ml. of the extract into a 10-ml. volumetric flask. Add 1 ml. of a 1% dibenzoylmethane solution and 5 ml. of pyridine, and dilute with ethyl alcohol to the mark. Measure the absorbance at 410~425 mμ against a blank.

Results and Discussion

Effect of Salting Agent.—When uranium is extracted as the tributyl phosphate complex from a nitric acid solution, the optimum acidity is approximately 6 N[9]. However, if salting agents, e. g., sodium nitrate or aluminum nitrate, are used, uranium can be extracted quantitatively, even from a nitric acid solution of a lower acidity. In this case, the amount of pyridine used to neutralize the co-extracted acid may be reduced. The effect of the aluminum salting agent was examined while keeping other factors constant. As is shown in Fig. 1, 5 ml. of an aluminum salting agent is sufficient for the standard procedure.

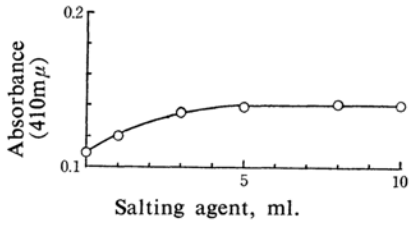

Fig. 1. Effect of salting agent.
2 p. p. m. U, extracted from 1 N nitric acid

Choice of Solvents.—An aliquot of the extract is mixed with dibenzoylmethane, a neutralizer and a diluent. The neutralizer is used to neutralize the acid extracted simultaneously in the organic phase in order to insure the full color development of the complex. Pyridine has been used almost exclusively by previous authors for this purpose.

Several kinds of solvents, such as kerosene, isooctane and ethyl acetate, have been used as a diluent for tributyl phosphate. In this method, benzene was chosen because of its high miscibility with pyridine.

Ethyl alcohol, used as the solvent for dibenzoylmethane, is useful at the same time to prevent the precipitation of a pyridinium compound, which is produced by the addition of pyridine to the extract. These solvents are miscible with each other and can be handled without special consideration because they are not extremely volatile at room temperature.

Pyridine Concentration.—Though it is known that the maximum color intensity is obtained in the "apparent" pH range of 6.5 to 8.5 in alcoholic aqueous media[1], these values can not be applied to the present organic solution because these pH values have no significance here. Therefore, the effect of the pyridine concentration on color development was studied in the extract which was obtained from a 1 N nitric acid solution with a salting agent, and in that obtained from a 6 N nitric acid solution without a salting agent. Other factors were kept constant.

As is shown in Fig. 2, with the former solution a 40~60% pyridine concentration is necessary to insure the full color development; a slight decrease in color intensity is observed with 80% pyridine. With the latter solution, a 60~80% concentration is necessary. The addition of 5 ml. of pyridine was therefore decided for the standard procedure.

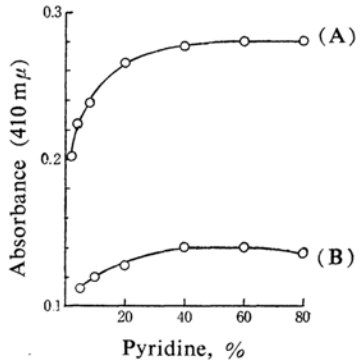

Fig. 2. Effect of pyridine concentration on absorbance.
(A) 4 p. p. m. U, extracted from 6 N nitric acid
(B) 2 p. p. m. U, extracted from 1 N nitric acid

The absorbance of the blank solution increases linearly with the increasing concentration of pyridine.

Dibenzoylmethane Concentration.—As is shown in Fig. 3, 1 ml. of a 1% dibenzoylmethane solution is necessary for full color development with 2 ml. of the 3 ml. extract. However, a

9) H. A. C. McKay, *Proc. Intern. Conf. Peaceful Uses of Atomic Energy*, Geneva, 1955, 7, 314 (1956).

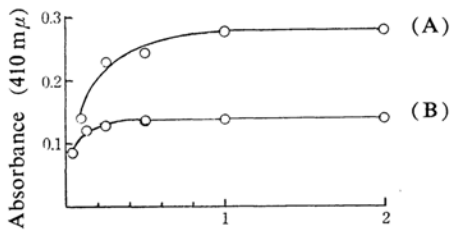

Fig. 3. Effect of dibenzoylmethane conentration on absorbance.
(A) 4 p. p. m. U (60 μg. U in aqueous solution, 2 ml. of 3 ml. extract is used for color development.)
(B) 2 p. p. m. U (60 μg. U in aqueous solution, 1 ml. of 3 ml. extract is used for color development.)

TABLE I. EFFECT OF DIBENZOYLMETHANE CONCENTRATION

U in aqueous solution μg.	Ext. used ml.	Dibenzoylmethane ml.	U found μg.
60	1	0.5	60.0
60	2	0.5	52.1
120	1	0.5	119
120	1	1.0	119
120	1+benzene 1 ml.	0.5	119
120	1+blank ext. 1 ml.	0.5	112

smaller portion of the extract may be used for samples of a higher uranium content. When 1 ml. of the 3 ml. extract is used for color development, which is frequently useful because the blank value is lowerd, 0.5 ml. of 1% dibenzoylmethane is sufficient. This value is independent of the uranium concentration in the sample solution. As summarized in Table I, this is because of the influence of excess tributyl phosphate in the organic phase. There is apparently some competition between tributyl phosphate and dibenzoylmethane in forming a complex with uranium.

Effect of the Acidity of the Sample Solution.—According to previous authors, strict control of the acidity of the aqueous solution is required in order to obtain reproducibility. In this method, where *in situ* color development is adopted, however, the change in acidity does not have any serious influence on the color intensity. This is as expected from Fig. 2. In fact, the change in the acidity of the sample solution within the range of 0.8 N and 2.0 N did not have any influence at all on the absorbance of the uranium complex in the standard procedure. This may be attributed to the fact that the amount of acid extracted simultaneously into the organic phase is not large compared with the pyridine used, while, at the same time, the excess of pyridine has little influence on the color intensity of the complex in the organic solution.

Effect of the Volume of Aqueous Solution.—In the standard procedure, the volume of aqueous solution is 10 ml., including the salting agent. In practice, however, a larger volume of aqueous solution is sometimes necessary, for instance, the complete dissolution of a precipitate. The influence of the volume of aqueous solution was studied while keeping the acidity and salting agent of the sample solution constant and using 3 ml. of tributyl phosphate.

The results reveal that when the volume of the aqueous solution is 20 ml. or 40 ml., the absorbance is 99% or 94% respectively of the absorbance from 10 ml. of the aqueous solution.

Wavelength.—The absorption spectra of the uranium complex, the thorium complex and dibenzoylmethane are shown in Fig. 4. Though

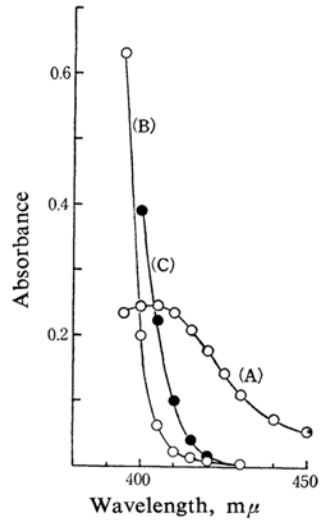

Fig. 4. Absorption spectra.
(A) 3.3 p. p. m. U
(B) Blank solution, 0.1% dibenzoylmethane
(C) 6.7 p. p. m. Th

the maximum absorption of uranium complex is observed at 400～405 mμ, the absorbance of the blank solution is fairly large at this wavelength. Moreover, as the slope of this curve is very sharp in this region, the results are liable to fluctuate when some of the factors are slightly varied. From this point of view, it is preferable to use a wavelength 410 mμ long or longer, even though the absorbance of the uranium complex decreases.

Stability.—The yellow color develops instantaneously on the addition of the reagent and

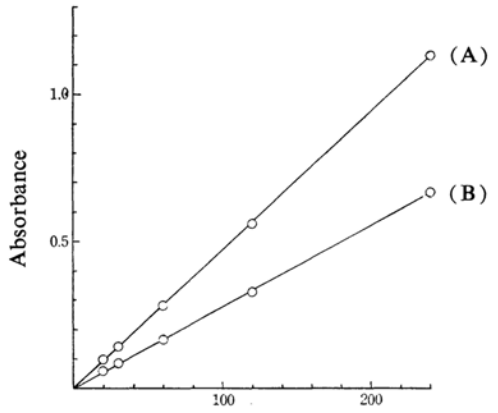

Fig. 5. Calibration curves.
(A) 410 mμ (B) 425 mμ

pyridine and is stable for at least 20 hr. at room temperature, provided the container is sealed.

Beer's Law.—Beer's law is obeyed up to 240 μg. of uranium in the aqueous solution, as Fig. 5 shows.

Diverse Ions.—In order to simplify the method, it is desirable to use the extract directly for color development without any washing procedure. The results obtained by this procedure are shown in Table II. When large amounts of a foreign ion, e. g., iron, are present in the sample solution, it is better to wash the extract with 2~3 ml. of a 10% sodium nitrate solution (1 N nitric acid) in order to reduce the interference, which may be attributed, in part, to the contamination of the extract with the aqueous suspension in the organic phase. The presence of chloride and iron ions in the same solution should be avoided. Bismuth may be present up to 3 mg. when measuring the absorbance at 425 mμ.

The interference of chromium(VI) and cerium(IV) can be minimized or eliminated by reduction with a proper reductant. For this purpose, sodium nitrite and sodium sulfite were each tried. At a low cerium(IV) concentration, sodium sulfite can be used without any difficulty. At a high concentration (e. g., 50 mg. Ce), however, a precipitate, presumably cerium(III) sulfate, is sometimes produced. When sodium nitrite is used as a reductant, caution should be taken to expel the colored gas which is liberated by the addition of nitrite; otherwise it is extracted into the organic phase and produces a positive error. In order to expel this gas completely, the solution is warmed at 80~90°C for several minutes until the fine bubbles disappear.

Thorium and zirconium interfere seriously because they are extracted into the organic phase and react with dibenzoylmethane. The absorption of these complexes decreases rapidly at longer wavelengths (shown in Fig. 4 for thorium). Masking these ions with fluoride is effective to some extent, even in the presence of a large number of aluminum ions, which form a stable complex with fluoride ions. Thus, the interference up to 2 mg. of each of these ions can be minimized. The results of the reduction and the masking experiments are shown in Table III.

TABLE II. EFFECT OF DIVERSE ION
(50 μg. of U(VI) present)

Ion	Added mg.	Added as	U recovered, μg. 410 mμ	420 mμ	425 mμ
Cd(II)	50	NO_3	50.0	49.9	
Co(II)	50	ClO_4	51.1	50.9	
Cu(II)	50	NO_3	50.4	50.9	
Hg(II)	50	NO_3	49.4	49.2	
Mn(II)	50	SO_4	51.1	50.6	
Ni(II)	50	NO_3	50.5	51.2	
Pb(II)	50	NO_3	51.1	51.0	
Zn(II)	50	NO_3	49.5	49.5	
La(III)	50	NO_3	52.1	51.6	
Bi(III)*1	1.0	NO_3	51.3	50.6	
	3.0	NO_3	56.4	53.1	51.7
Fe(III)	50	NO_3	51.9	53.4	
	100*2	NO_3	51.5	53.4	
Fe(III) Cl⁻	10 20	NO_3 NaCl	54.8	54.3	
Ti(IV)	50	SO_4	48.1	48.5	
V(V)	50	VO_3^-	50.2	50.2	
Mo(VI)	50	MoO_4^{2-}	52.2	51.9	
W(VI)*3	50	WO_4^{2-}	49.8	51.1	
Cl^-	100	NaCl	50.0	50.6	
SO_4^{2-}	100	Na_2SO_4	50.0	50.6	
ClO_4^-	100	$NaClO_4$	49.6	50.3	
OAc^-	100	NaOAc	48.2	48.9	
PO_4^{3-}	100	Na_3PO_4	44.2	45.5	
	100*4	Na_3PO_4	48.6	49.8	
F^-	175	KF	48.5	49.6	
	290*4	KF	49.1	49.8	
F^- SO_4^{2-}	290*4 250	KF H_2SO_4	47.0		47.2
	290*5 250	KF H_2SO_4	49.4		48.9

*1 Precipitate is produced in organic phase upon standing.
*2 Washed with 2 ml. of 10% sodium nitrate solution.
*3 Precipitate is produced in aqueous phase upon standing.
*4 5 g. of aluminum nitrate nonahydrate was used.
*5 9 g. of aluminum nitrate nonahydrate was used.

TABLE III. REDUCTION AND MASKING OF DIVERSE IONS

(50 μg. of U(VI) present)

Ion	Added mg.	Added as	Reductat or masking agent	U recovered, μg. 410 mμ	425 mμ
Cr(VI)	50	CrO_4^{2-}	None	Approx. 260	
	50	CrO_4^{2-}	$NaNO_2$	50.3	
	50	CrO_4^{2-}	Na_2SO_3	50.2	
Ce(IV)	5.0	SO_4	None	59.4	
	50	SO_4	$NaNO_2$	52.7	51.4
	50*	SO_4	Na_2SO_3	55.1	
Th(IV)	0.1	NO_3	None	67.2	
	1.0	NO_3	KF 3 ml.	70.1	50.7
	2.0	NO_3	KF 5 ml.	73.1	51.4
Zr(IV)	0.1	NO_3	None	76.5	
	1.0	NO_3	KF 3 ml.	60.9	50.3
	2.0	NO_3	KF 5 ml.	67.3	52.9

* Precipitate is produced in aqueous solution upon standing.

The Determination of Uranium in Ores.—The above-mentioned procedure was applied to the determination of uranium in uranium ores and in monazite.

For uanium ore, 1 g. of sample was decomposed with aqua regia. After filtration, uranium was precipitated with ammonium hydroxide. The precipitate was dissolved in enough nitric acid to make exactly 50 ml. or 250 ml. of a 1~1.5 N nitric acid solution.

For monazite, 1 g. of sample was decomposed with 10 ml. of fuming sulfuric acid. After cooling, the solution was poured into cold water. After filtration, the filtrate was transferred to a 250-ml. volumetric flask and made up to volume with water.

Using an aliquot of these stock solutions, uranium was determined according to the above-mentioned procedure. In the case of monazite, 1 ml. of nitric acid (1 : 1), 1 ml. of a 10% sodium nitrite solution*, and 5 ml. of a 1 M potassium fluoride solution for 5 ml. of sample solution were used.

The absorbance measurements were made at 410 mμ and 425 mμ respectively. The results shown in Table IV show good agreement with the values obtained by the authorized method.

TABLE IV. ANALYSIS OF URANIUM ORE AND MONAZITE

Sample	U* Content, U_3O_8, %	U Found, U_3O_8, %	No. of Detns.
Uranium ore (sedimentary) No. 1	0.321	0.344	12
Uranium ore (sedimentary) No. 2	0.057	0.057_2	5
Monazite	0.286	0.300	5

* Results of the co-operative analysis at 11 laboratories.

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* When sodium sulfite was used a white precipitate was produced in the organic phase after neutralizing the extracts with pyridine. This could be prevented by expelling the excess of sulfur dioxide before extraction.