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8-HYDROXYQUINOLINE COLORIMETRIC METHOD FOR THE
DETERMINATION OF MICROGRAM QUANTITIES OF URANIUM

ABSTRACT

Uranium is determined quantitatively in microgram amounts by measuring the optical density of the chloroform extract of uranyl 8-hydroxyquinolate from neutral uranyl solutions at 380 mμ using a Beckman spectrophotometer.

D. A. Lee and R. W. Woodard

Oak Ridge, Tennessee
November 19, 1947

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8-HYDROXYQUINOLINE COLORIMETRIC METHOD FOR THE
DETERMINATION OF MICROGRAM QUANTITIES OF URANIUM

Uranyl ion forms a highly colored chelate compound with 8-hydroxyquinoline which is soluble in chloroform. Twenty-five to seven hundred micrograms of uranium can be determined quantitatively by its use. *in how much matrix?*

In a study of the exchange of uranous and uranyl ions¹ it was necessary to determine the amount of uranium plated on the discs for counting. This was done by evaporating an aliquot of the uranous-cupferride-chloroform solution to dryness, destroying the organics with perchloric acid, adjusting the pH, extracting the uranyl-"oxine" compound with chloroform, and reading the optical density of this solution on a Beckman spectrophotometer.

8-Hydroxyquinoline in chloroform is a very sensitive reagent for the colorimetric determination of several cations.² A. A. Smales³ has separated and determined small amounts of uranium and iron by this method.

According to Smales the optimum pH for extracting the uranium compound is from 7 to 9 using an acetate buffer. It was found there was no need for the buffer in this specific work, and that uranium is 100% extractable at an initial pH of 3.2 to 8. The extractions carried out at pH values near either end of this range are colored in the second pass while extractions at a pH of 4 to 7 are colorless after the first pass.

This optimum range was determined by a series of extractions made at different pH's. Each sample was extracted three times with 5 ml 8-hydroxyquinoline in chloroform.

1. Woodard, et. al., Y-30
2. Moeller, T., Ind. Eng. Chem. Anal. Ed., 15, 346 (1943)
3. Smales, A. A., Imperial Chemical Industries Limited Billingham Division, Br.-412 (1944) "Separation and Determination of Small Amounts of T and Fe by Means of 8-Hydroxyquinoline."

Table 1

<u>pH Before Extraction</u>	<u>pH of Water Layer After Extraction</u>	<u>Percent U Extracted</u>
2.9	3.9	95
3.25	4.4	102
5.4	5.2	98
6.5	6.5	97
7.1	6.8	100
8.5	7.0	96

Smales reported that 100% of the uranium at a pH of 9 could be extracted. When the 8-hydroxyquinoline is in the chloroform used for extraction at higher pH's insufficient oxine will leave the organic phase and enter the aqueous phase to react with the uranium, thereby causing incomplete extraction. To overcome this Smales added an alcohol solution of oxine to the acid sample, raised the pH to 9, and extracted with chloroform. Adding this extra operation is unnecessary if the extraction is made at a lower pH.

Acetate interferes with the complete extraction of uranium below a pH of 7. At a pH of 5.2 with ammonium acetate (10 ml 1M) and hydrochloric acid, 15% of the uranium was extracted. This is probably due to an uranium acetate complex which will tie up the uranyl ion and will not release it to the 8-hydroxyquinoline until a pH of 7 is reached.

Smales used a photometer with a filter and read the density at 436 mμ. From the absorption spectra curve in figure 1, the density at 436 mμ is only about one-half that at 580 mμ; thus the latter is to be preferred.

In figure 2 the color intensity is shown to be proportional to the concentration of uranium over the workable range of the spectrophotometer. The molar extinction coefficient is .7219.

Since many cations form colored compounds with 8-hydroxyquinoline, uranium should be separated from interfering ions or the interfering ions "masked" by a suitable reagent, for example, malonic acid for aluminum. Nitrates, chlorides, perchlorates, and moderate amounts of sulfate do not interfere.

Materials

Reagent grade chemicals were used.

0.2 g 8-hydroxyquinoline (oxine) in 100 ml chloroform.

60 ml pear-shaped separatory funnels.

25 ml volumetric flasks.

1 cm corex absorption cells.

Beckman Spectrophotometer.

Procedure

1. Evaporate a suitable aliquot to dryness (50 to 500 γ U).
2. Add 1 ml HNO_3 and 1 ml HCl . Evaporate to dryness.
3. Add $1/2$ ml HNO_3 and $1/2$ ml HClO_4 . Evaporate until no more fumes are given off.
4. Add 5 ml distilled water. Warm on a steam bath. Cool. Adjust pH if necessary with NaOH . (pH = 3.5 - 7.0).
5. Transfer the sample quantitatively to a 60 ml separatory funnel.
6. Place 10 ml H_2O in a 60 ml separatory funnel and run a blank along with the sample.
7. Add 5 ml of the "oxine" solution. Shake for one minute. Drain the chloroform layer into a 25 ml volumetric flask. Extract three times or until colorless.

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8. Dilute to volume with chloroform and mix.
9. Fill a 1 cm corex absorption cell $2/3$ full. Use the blank in the first cell as a reference.
10. Read the optical density on the Beckman spectrophotometer at 380 m μ with a minimum slit width, using a Tungsten lamp.
11. Optical density $\times 821 = \gamma U$ per 25 ml.

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FIGURE 2