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THE FLUORIMETRIC DETERMINATION OF URANIUM IN NONSALINE AND SALINE WATERS

By
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This preliminary report is released without editorial and technical review for conformity with official standards and nomenclature, to make the information available to interested organizations and to stimulate the search for uranium deposits.

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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ABSTRACT

The procedure determines about 10^{-8} percent uranium using 500-ml samples of water. Uranium is concentrated by precipitating uranyl phosphate using aluminum phosphate as a carrier. The aluminum phosphate is dissolved in nitric acid, salted with aluminum nitrate, and the uranium is extracted with ethyl acetate. A portion of the ethyl acetate is evaporated in a standard platinum dish and a fluorescing disc is prepared with a mixed fluoride flux. Fluorescence measurements are made with a fluorimeter. One precipitation with $AlPO_4$ collects more than 95 percent of the uranium. The uranium content of various ocean waters tested ranged from 2.3×10^{-7} to 3.4×10^{-7} percent uranium.

INTRODUCTION

In the determination of uranium in waters containing slightly more than 10^{-8} percent uranium, it is frequently necessary to concentrate the uranium prior to its estimation by the fluorescence method using fluoride phosphors. The uranium in waters of low salinity can be concentrated by simple evaporation of the water, but this method is not as useful for saline waters, where the problem is not only to concentrate the uranium but to separate it from large amounts of salts that would cause subsequent analytical difficulties.

Hernegger and Karlik (1934) isolated uranium from sea water by precipitating the uranium with ammonium hydroxide using a small amount of ferric iron as a carrier. This carrier has also been used by others (Lahner, 1939; Hoffman, 1939; and Urry, 1941) for concentrating uranium from rocks and from ocean sediments. Other useful collectors for uranium include aluminum hydroxide (Urry, 1941, and Orlemann, 1945) and aluminum phosphate (Tschernichow, 1934).

Aluminum phosphate has certain advantages as a carrier for uranium. Especially important is the ease with which aluminum phosphate can be dissolved with dilute acids even after it is aged or ignited. We have found aluminum phosphate to be an efficient collector even for less than microgram amounts of uranium.

This paper presents a simple fluorimetric method for the determination of uranium in naturally occurring waters. Preliminary concentration of uranium is made by precipitating uranyl phosphate using aluminum phosphate as a carrier. After dissolving the aluminum phosphate in nitric acid and salting the solution with aluminum nitrate, the uranyl nitrate is isolated by extraction with ethyl acetate (Grimaldi and Levine, 1948). The relative fluorescence of the disc is measured in a fluorimeter (Fletcher and May, 1950). The procedure is designed to determine 10^{-8} g of uranium as a lower limit and uses 100- to 500-ml samples of water. This work was done on behalf of the Division of Raw Materials of the Atomic Energy Commission.

EXPERIMENTAL DATA

The procedure recommended in this paper is based on two operations--the coprecipitation of uranium with aluminum phosphate, and the isolation of uranyl nitrate by ethyl acetate extraction from solutions salted with aluminum nitrate. The reliability of the extraction process has been demonstrated and is a standard procedure in this Geological Survey laboratory for the isolation of uranium from many naturally occurring materials prior to the estimation of uranium by the fluorescence method. Our major aim in this report is to show that aluminum phosphate is an efficient collector for uranium.

Data on the efficiency of aluminum phosphate as a carrier for uranium was obtained by several more or less independent techniques.

Nonsaline waters

The following techniques were used in testing nonsaline waters:

1. Known amounts of uranium were added to separate 500-ml aliquots of distilled water. Analysis for uranium was then made according to the recommended procedure of this report. The recoveries are given in table 1, column 3.

2. The amount of uranium left in the filtrates after the precipitation and filtration of the aluminum phosphate was determined. This was accomplished in the following manner: The filtrates were evaporated to dryness and the ammonium salts were destroyed by aqua regia. Chlorides were converted to nitrates by evaporation with nitric acid, and the nitric acid solutions obtained were extracted with ethyl acetate after

adding the requisite amount of aluminum nitrate for salting. The uranium in the ethyl acetate layers was determined fluorimetrically and the results, corrected for the small amount of uranium introduced by the reagents, are given in table 1, column 4. It is seen from the tests on the filtrates that more than 95 percent of the uranium is collected by the aluminum phosphate. Some samples showed slightly low overall recoveries of uranium. These errors are inherent in the fluorimetric procedure. For instance, it is sometimes difficult to burn the ethyl acetate without a slight loss. Some quenching of the uranium fluorescence occurs because of platinum that may be dissolved from the fusion vessel. This may occur if there is accidental overheating during the preparation of the standard disc.

3. Naturally occurring waters were used in 500-ml aliquots and uranium was determined by alternate methods. In one method the procedure of this report was used. In the other, concentration of uranium was made by simple evaporation of the water, and the uranium was extracted directly without prior precipitation with aluminum phosphate. The results by the two methods are given in table 2. The agreement is good and no worse than the reproducibility of either method.

Saline waters

The techniques used for saline waters follow:

1. Known amounts of uranium were added to 500-ml aliquots of a synthetic solution made to approximate the composition of ocean water. Uranium was then determined by the recommended procedure, and the amounts found are given in table 3.

2. In another set of experiments, true ocean waters were used. Quadruplicate uranium determinations were made on a sample of water obtained from the surf at Ocean City, Maryland (table 4). The filtrates from the aluminum phosphate precipitates were further treated as follows: On filtrates 1 and 2 the aluminum phosphate precipitation was repeated and the precipitate analyzed for uranium to determine if the second precipitation would recover more uranium. Known amounts of uranium were added to filtrates 3 and 4, the aluminum phosphate precipitation repeated, and the precipitate analyzed for uranium. The results of determinations on these four filtrates are given in table 4.

The results of tests on Ocean City water after the addition of known amounts of uranium are given in table 5.

Table 6 gives the location and uranium content of waters collected off the coast of Florida.

It is of interest to note that the uranium content of both the Ocean City water and the waters from the Gulf is greater than what has been generally found in other ocean waters by earlier investigators (Hernegger and Karlik, 1934; Koczy, 1950). This may be because of purely local conditions. Our results are in line with the recent results of Nakanishi (1951).

Table 1.--Uranium found in distilled water after the addition of known amounts of uranium.

Sample no.	Micrograms of uranium added	Micrograms of uranium found 1/	Micrograms of uranium found in filtrates from $AlPO_4$ separation
1	0.09	0.11	<0.01
2	0.09	0.09	
3	0.30	0.32	<0.01
4	0.45	0.44	
5	0.45	0.40	0.02
6	1.2	1.4	
7	1.8	1.6	0.01
8	1.8	1.7	
9	9.0	8.3	0.01
10	9.0	8.5	
11	18	17	0.04
12	36	34	
13	36	35	<0.01

1/ In samples 7-13 a correspondingly smaller aliquot of the ethyl acetate extract was used for the determination of uranium because the normal aliquot yields fluorescence intensities beyond the range of the working curve.

Table 2.--Comparisons of results of two methods of fluorimetric uranium determination on naturally occurring nonsaline waters.

Sample no.	Percent uranium $AlPO_4$ concentration of U	Percent uranium 1/ no $AlPO_4$ concentration of U
1	2.8×10^{-6}	3.0×10^{-6}
2	5.2×10^{-6}	4.6×10^{-6}
3	1.1×10^{-6}	1.1×10^{-6}
4	2.8×10^{-7}	3.0×10^{-7}

1/ Analyst, A. M. Sherwood, U. S. Geological Survey

Table 3.--Uranium analyses of synthetic sea-water solutions containing known amounts of uranium.

Sample no.	Micrograms of uranium added	Micrograms of uranium found
1	0.36	0.35
2	0.72	0.70
3	1.80	1.77
4	1.80	1.79
5	1.80	1.80
6	3.60	3.30
7	3.60	3.34

Table 4.--Test of procedure on a sea-water sample from the surf at Ocean City, Md.

Sample number	Micrograms of uranium added	Micrograms of uranium found	Micrograms of uranium found in 2d $AlPO_4$ ppt.
1	None	1.1	
2	None	1.2	
3	None	1.1	
4	None	1.2 (average 1.15 1/)	
Filtrate from 1	None	--	0.01
Filtrate from 2	None	--	0.01
Filtrate from 3	0.45	--	0.48
Filtrate from 4	1.80	--	1.74

1/ This corresponds to 2.3×10^{-7} percent uranium in the water from Ocean City, Md.

Table 5.--Uranium found in sea water from Ocean City, Md., after addition of known amounts of uranium.

Test no.	Amounts of sea water taken (ml)	Amount of uranium (micrograms)			
		Present in the sea water	Added	Total present	Total found
1	500	1.15	0.90	2.05	2.1
2	500	1.15	0.90	2.05	1.9
3	500	1.15	2.2	3.35	3.1
4	500	1.15	2.2	3.35	3.1
5	500	1.15	9.0	10.15	9.5
6	500	1.15	9.0	10.15	9.6
7	500	1.15	18	19.15	18
8	500	1.15	18	19.15	18

Table 6.--Uranium found in water samples from the coast of Florida (Gulf of Mexico and near the Indian River Estuary).1/

Sample no.	Location	Depth in fathoms	Percent uranium	Micrograms of	
				uranium added	uranium found
1	Lat. 26°31'N. Long. 83°10'W.	Sample 0 Water 25	3.2×10^{-7}		
2	Lat. 26°39'N. Long. 82°31'W.	Sample 0 Water 11	3.4×10^{-7}		
3	Lat. 28°1.5'N. Long. 80°32.5'W.	Sample 0 Water 5	3.0×10^{-7}		
4	Lat. 28°2.5'N. Long. 80°32.2'W.	Sample 0 Water 8	3.0×10^{-7}		
Filtrate from 1				1.35	1.35
Filtrate from 3				1.35	1.35

1/ Collected by Albert Collier, U. S. Fish and Wildlife Service.

GENERAL PROCEDURE FOR THE DETERMINATION OF URANIUM IN NONSALINE AND SALINE WATERS

Sampling

In sampling waters it is good practice to add acid (about 8 ml of HNO_3 per gallon of water) immediately after collection. If the water sample contains sediment, the sediment should be separated by decantation or by filtration through a porous filter before adding acid to the water. Unacidified water samples tend to decrease in uranium concentration during storage because some of the uranium may be precipitated or adsorbed on the glass (Koczy, 1950).

Procedure

1. Transfer a 500-ml aliquot of water to an 800-ml beaker.

2. Add 3 ml of HNO_3, aluminum nitrate solution equivalent to 20 mg Al_2O_3, and 5 ml of $(NH_4)_2HPO_4$ solution [1cc = 12 mg $(NH_4)_2HPO_4$]. Heat to boiling to remove CO_2.

3. Add ammonium hydroxide until methyl red indicator is just yellow.

4. Digest the precipitate on the steam bath for about 10 minutes. Stir in paper pulp.

5. Filter the solution on a fast paper and wash the precipitate with 1 percent NH_4NO_3 solution.

6. Transfer the precipitate and paper to a clean 25-ml porcelain crucible and ignite at low temperature to remove carbon.

7. Add 5 ml of (15 + 85) HNO_3 and warm gently to dissolve the salts (avoid significant evaporation of the solution).

8. Add 9.5 g $Al(NO_3)_3 \cdot 9H_2O$ and warm to dissolve the salt.

9. Pour the solution into a dry 30-ml glass-stoppered graduated test tube. Do not wash the crucible.

10. Add 10 ml of ethyl acetate by pipet or buret and shake the mixture for about 30 seconds. Allow the layers to separate for a few minutes.

11. Filter about 8 ml of the ethyl acetate through a dry paper into a dry test tube.

12. Transfer a 2-ml aliquot (more or less may be necessary depending on the uranium content of the water) of the filtered ethyl acetate into a standard platinum container (average diameter about 3.5 cm). Place the dish on four layers of water-soaked paper which rest in a pan containing about 1/16 inch of water and ignite the ethyl acetate with a lighted splinter. After the ethyl acetate has burned off, gently ignite the dish.

13. Add 2 g of the mixed fluoride flux (prepared by grinding or mixing together 9 parts NaF, 45.5 parts Na_2CO_3 and 45.5 parts K_2CO_3, by weight).

14. Heat over a burner until the flux melts and then for an additional 2 to 4 minutes, mixing and swirling the contents to assure a uniform melt. All heating should be done at the lowest temperature at which the flux stays molten. The temperature of the melt should not be allowed to exceed 700 C during the heating period.

15. Measure the relative fluorescence of the melt on the fluorimeter.

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