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FLUORIMETRIC DETERMINATION OF URANIUM IN SHALES, LIGNITES, AND MONAZITES AFTER ALKALI CARBONATE SEPARATION

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ABSTRACT

Comparative data are presented on separations of microgram amounts of uranium from milligram amounts of various metal ions with Na_2CO_3-K_2CO_3, Na_2CO_3-K_2CO_3-H_2O_2, and Na_2CO_3-NaClO. The Na_2CO_3-K_2CO_3 separation procedure is applied to the analysis of shales, lignites, and monazites. This method will determine as little as 0.001 percent uranium in shales and lignites and 0.01 percent uranium in monazites.

INTRODUCTION

Several fluorimetric procedures, based essentially on two techniques, have been developed in the Geological Survey and are used for the analysis of uranium in a wide variety of material. One technique (Grimaldi and Levine, 1948) involves a preliminary isolation of uranyl nitrate by solvent extraction from milligram amounts of sample. The second technique (Fletcher, 1951), based on Price's dilution method (1945), involves no preliminary isolation of uranium and employs microgram amounts of sample. Each method has its advantages and disadvantages for routine work which need not be discussed here.

The Geological Survey is constantly searching for new methods or modifications that can be used to advantage in the determination of small amounts of uranium, even if applicable only to certain types of samples. This continuing investigation of methods of analysis for uranium involves, among other things, evaluating known techniques and methods and devising new applications of known facts for special purposes.

Precipitation with alkali carbonate is a standard procedure for the separation of iron and other elements, that form insoluble hydroxides or carbonates, from uranium which stays in solution as a complex carbonate. It is a popular method of separation in procedures for the determination of macro amounts of uranium but is rarely used when micro amounts of uranium are to be determined. The neglect of this method in trace analyses is partly due to the lack of available data on the performance of this separation when small amounts of uranium are involved.

The purpose of this study was to obtain data on the carbonate separation method that might be applicable to the Survey's work. The separation proved to be remarkably efficient and, in conjunction with fluorimetric estimation of uranium, it was made the basis of a simple method for the determination of small amounts (1×10^{-8} g and more) of uranium in shales, lignites, and monazites. This method will determine as little as 0.001 percent uranium, as the lower limit, in shales and lignite samples and 0.01 percent uranium as the lower limit in monazite samples.

EXPERIMENTAL DATA AND DISCUSSION

Preliminary tests were made to determine the efficiency of the carbonate separation of uranium from various metal ions. In these tests sulfates of the test metals were used in amounts equivalent to 15 mg or less of each metal oxide. This amount was determined by the fact that the carbonate precipitation method proposed in this report employs solutions containing no more than 15 mg of each sample.

The procedures used on the test samples follow:

In the first experiments (method 1) a 5-ml aliquot of a solution, containing a known weight of metal sulfate, 0.05 ml of H_2SO_4, and 2.25 γ of U, was transferred to a glass-stoppered test tube. Five milliliters of mixed carbonate solution (made by dissolving 10 g Na_2CO_3 and 10 g of K_2CO_3 in 100 ml H_2O) were then added from a pipette and the glass-stoppered tube shaken to give a uniform mixture. The tube was placed in a beaker of hot water for half an hour at a temperature of about 80°C. The tube was then removed, and the solution allowed to cool to room temperature for one hour. Next the solution was filtered through a dry filter paper (Whatman No. 42) and collected in a dry test tube. An 0.8-ml aliquot of the filtered solution was transferred to a platinum container (3.5-cm diameter) and the solution evaporated on the steam bath. Two grams of fluoride flux (9 parts by weight NaF, 45.5 parts by weight Na_2CO_3, and 45.5 parts by weight K_2CO_3) were added and the mixture fused over a burner at a temperature not exceeding 700°C. Heating and mixing were continued for two minutes after the flux melted. The fluorescence of the disc was then measured in a fluorimeter designed by Fletcher and May (1950). The carbonate precipitate was dissolved in nitric acid and tested for occluded uranium by the uranyl nitrate extraction procedure (Grimaldi and Levine, 1948).

In another set of experiments (method 2) the carbonate precipitation was made after the addition of 1 drop of 30 percent H_2O_2 to the test solutions which had been made as before. In still another set of experiments (method 3) the carbonate precipitation was made with 5 ml of mixed carbonate solution containing 0.5 percent by weight of NaClO. The NaClO was added to test the behavior of those elements that are oxidized to higher valence states.

Table 1 shows the results obtained. None of the low results obtained (method 1, Na_2CO_3-K_2CO_3) was due to loss of uranium by occlusion in the carbonate precipitate but rather was due to quenching of the uranium fluorescence by the small amounts of the test elements escaping precipitation. Most of the carbonate filtrates were colored when low results were obtained.

Some additional observations relating to the data in table 1 should be pointed out. We note that the elements Y, Zr, V, As, Sm, and Gd are completely soluble and that Co, Ce, Nd, Pr, and Al are slightly soluble in carbonate solutions. This solubility is not due solely to the complexing action of carbonate. The amount of sulfate present in the solutions tested was found to increase the solubility of some metals. For example, in the absence of sulfate, all the zirconium is precipitated as is almost all of the cobalt.

Table 1.--Efficiency of the carbonate separation method under various test conditions

gn element taken	Uranium taken (γ)	Apparent uranium recovery as determined by fluorescence (γ)			Uranium found in residue from Na_2CO_3-K_2CO_3 Method 1	Solubility of the element in Na_2CO_3-K_2CO_3 Method 1
		Na_2CO_3-K_2CO_3 Method 1	Na_2CO_3-K_2CO_3 H_2O_2 Method 2	Na_2CO_3-K_2CO_3 NaClO Method 3		
Fe_2O_3	2.25	2.25	2.25	2.25	None	Insoluble
Al_2O_3	2.25	2.25	2.15	2.25	"	Somewhat soluble
Cr_2O_3+5 mg Fe_2O_3	2.25	2.25	0.90	0.75	"	Insoluble
CaO	2.25	2.25	2.25	2.25	"	Insoluble
MgO	2.25	2.25	2.10	2.25	"	Insoluble
ZrO_2	2.25	2.25	2.25	2.25	"	Completely soluble
V_2O_5	2.25	2.22	2.25	2.25	"	Completely soluble
MnO	2.25	2.10	2.25	1.95	"	Very slightly soluble
CoO	2.25	1.05	0.75	0.45	"	Slightly soluble
CoO+5 mg Fe_2O_3	2.25	2.25	2.25	1.95	"	Insoluble
NiO	2.25	2.25	2.10	2.25	"	Insoluble
ZnO	2.25	2.25	2.25	2.25	"	Insoluble
ZnO+5 mg Fe_2O_3	2.25	2.25	2.25	2.25	"	Insoluble
As_2O_3 (as arsenate)	2.25	2.25	2.25	2.25	"	Completely soluble
La_2O_3	2.25	2.22	1.35	2.25	"	Insoluble
Y_2O_3	2.25	2.10	2.25	2.25	"	Completely soluble
Y_2O_3+5 mg Fe_2O_3	2.25	2.25	2.25	2.25	"	Y completely soluble
Ce_2O_3	2.25	1.50	1.80	2.18	"	Slightly soluble
Ce_2O_3+5 mg Fe_2O_3	2.25	1.50	1.95	2.25	"	Ce slightly soluble
Nd_2O_3	2.25	2.03	--	2.25	"	Slightly soluble
Pr_2O_3	2.25	1.95	--	1.95	"	Slightly soluble
Sm_2O_3	2.25	2.10	--	2.05	"	Completely soluble
Gd_2O_3	2.25	2.10	--	2.10	"	Completely soluble

Of the elements which are not precipitated, Y, Zr, V, As, Sm, Gd, and Al do not quench the uranium fluorescence. It might be generalized that the cerium earths are bad quenchers, whereas the yttrium earths do not quench the uranium fluorescence seriously. Mn, Co, and Cr are elements which apparently seriously quench the uranium fluorescence.

The behavior of copper (cupric) in the carbonate precipitation is erratic. In a few of our tests, copper was completely precipitated as CuO. However, the conditions for complete precipitation of copper appear to be exceedingly critical, and the precipitation is usually incomplete with much of the copper remaining in solution as a blue complex. To insure the complete precipitation of copper, we have found it desirable to reduce the copper to Cu_2O with hydroxylamine hydrochloride. This reagent is introduced only in those cases where a blue solution persists after the boiling with alkali carbonate.

The blue color of the soluble copper complex is barely perceptible at about 50 γ of Cu in 10 ml of solution. Tests summarized in table 2 show that if the quantity of copper is insufficient to yield a blue color after the carbonate precipitation (that is, < 50 γ Cu) no hydroxylamine need be added; this amount of copper will not result in any quenching of the uranium fluorescence using the general procedure. When hydroxylamine is used, the data in tables 2 and 3 show that no loss of uranium occurs by occlusion in the cuprous oxide precipitate. We have also confirmed the fact that the introduction of hydroxylamine causes no significant change in the behavior of the elements listed in table 1.

The data in table 2 were obtained as follows: 5 ml portions of solutions containing 4.5 γ U (uranyl nitrate), varying amounts of copper sulfate, and 0.1 ml of (1 + 1) H_2SO_4 were treated as previously described (p. 6, method 1). After heating for 10 minutes in the bath, 0.05 ml of a 20 percent aqueous solution of $NH_2OH \cdot HCl$ (20 g per 100 ml of H_2O) was added to some of the samples. The heating was continued for 20 minutes for all the samples. The samples were cooled for one hour. The uranium content was then determined as before.

Table 2.--Elimination of interference of copper with hydroxylamine hydrochloride

CuO taken (γ)	Uranium taken (γ)	$NH_2OH \cdot HCl$ added (ml of 20 percent solution)	Uranium found (γ)
1.5	4.5	0.05	4.5
15	4.5	0.05	4.5
75	4.5	0.05	4.5
150	4.5	0.05	4.6
750	4.5	0.05	4.6
7500	4.5	0.05	4.6
None	4.5	None	4.5
1.5	4.5	None	4.6
7.5	4.5	None	4.6
15	4.5	None	4.7
75	4.5	None	4.6

Of the three methods used to obtain data in table 1, fluorimetric results based on carbonate-peroxide separation (method 2) are poorest. The carbonate-hypochlorite method (method 3) is better than the simple carbonate method (method 1) for samples containing rare earths and would be the method of choice were it not for the serious interference of chromium. Of the elements tested in the simple carbonate method (method 1) only cerium, cobalt, and copper can interfere when uranium is determined fluorimetrically. The interference of copper is readily overcome by use of hydroxylamine.

In determining uranium in shales, lignites, and monazites we selected the simple carbonate separation for the following reasons:

1. Shale and lignite samples do not contain sufficient cerium or cobalt to interfere in a fluorescence method based on 1.2 mg of sample.

2. Although cerium would normally quench the uranium fluorescence in a 1.2-mg sample of monazite, the fact that the uranium content of monazite is usually greater than 0.1 percent enables us to use a sufficiently small sample (0.12 mg) to eliminate any quenching due to cerium. For the 0.12-mg sample used in the procedure for monazite, cerium will not interfere when the monazite contains 0.01 percent uranium or more.

PROCEDURE FOR SHALES AND LIGNITES

The procedure used for shales and lignites follows:

1. Weigh 0.15 g of sample (minus 80 mesh) into a 70-ml platinum dish.
2. Ignite the sample gently to remove organic matter. Cool and moisten the sample with water.

3. Add 1 ml (1 + 1) H_2SO_4 and cautiously add 5-10 ml HF. Digest sample on the steam bath and then evaporate the solution to remove water.

4. Bring the sample to fumes of sulfuric and fume for several minutes. Cool.

5. Cautiously add 25 ml of water, digest the sample on steam bath stirring to effect solution. Cool to room temperature.

6. Transfer the contents of the dish to a 50-ml glass-stoppered graduated cylinder. Make to 50 ml with water. Mix.

7. Take a 5-ml aliquot and transfer the solution to a 25-ml glass-stoppered test tube.

8. Add 5 ml of mixed carbonate solution (10 g Na_2CO_3 + 10 g K_2CO_3 per 100 ml of water) and mix.

9. Place the stoppered tube in a beaker of hot water and let stand for 30 minutes at 80-90°C. If, after 10 minutes of heating, a blue solution is evident, cool, add 0.05 ml of 20 percent hydroxylamine hydrochloride solution (made by dissolving 20 g $NH_2OH \cdot HCl$ in 100 ml H_2O) and resume the heating for another 20 minutes.

10. Remove the tube from the bath and allow the solution to cool for an hour at room temperature.

11. Filter part of the solution through a dry filter paper (Whatman No. 42) into a dry test tube. The filter paper may be conveniently held in place by the test tube itself.

12. Take an 0.80-ml aliquot and transfer the solution to a standard platinum container (average diameter about 3.5 cm) and evaporate the solution on the steam bath.

13. Add 2 g of flux (9 parts by weight NaF, 45.5 parts by weight Na_2CO_3, and 45.5 parts by weight K_2CO_3).

14. Heat over a burner until the flux melts and then for an additional 2 minutes, mixing and swirling the contents to assure a uniform melt. The temperature of the container should not be allowed to exceed 700°C during the heating period.

15. Place the dish on an asbestos pad to cool.

16. Measure fluorescence of the disc in the fluorimeter (Fletcher and May, 1950) and convert to percent uranium by reference to a standard curve. The standard curve is prepared by fusing various amounts of uranium with the fluoride flux and measuring the fluorescence intensity of the discs.

PROCEDURE FOR MONAZITE

The procedure for monazite differs only in the method of preparing the solution and in the final size of sample taken.

1. Weigh 0.0800 g of representative finely ground monazite into a platinum crucible.

2. Add 0.6 g of flux (2 parts by weight NaF and 3 parts by weight $K_2S_2O_7$).

3. Fuse the sample over a low burner until a clear melt is obtained (about 30 seconds). Cool.

4. Add 0.4 ml of concentrated H_2SO_4. Heat gently and at a low temperature until all the fluorine is removed and a clear pyrosulfate melt is obtained. This fusion proceeds through several stages. In the first stage some frothing is apparent until the pad disintegrates.

The melt is usually colored and muddy at this point. In the second stage the melt thickens appreciably and becomes lighter in color, In the final stage a clear pyrosulfate melt is obtained. The total time for the complete process takes about 3 1/2 minutes. Cool.

5. Add 10-15 ml of water and 2 ml concentrated H_2SO_4. Digest the melt on the steam bath. Stir occasionally until the melt is completely disintegrated.

6. Transfer the sample to a 100-ml glass-stoppered graduated cylinder and make up to 100 ml with water. Mix. Generally a complete solution is obtained within 5 minutes. Sometimes a cloud (presumably anhydrous rare-earth sulfates) persists after 5 minutes. This is not important as long as the sample has been completely decomposed.

7. Disperse the mixture by shaking. Immediately draw off a 5-ml aliquot and transfer to a glass-stoppered test tube.

8. Proceed according to steps 8 through 11 of the procedure for shales.

9. Take a 0.3-ml aliquot and proceed as in the procedure for shales steps 12 through 16.

RESULTS OF ANALYSIS

Tables 3, 4, and 5 list the results obtained by the carbonate-fluorimetric procedure on shales, lignites, and monazites, respectively. The results for the shales and lignites agree closely with those obtained by the uranyl nitrate extraction procedure (Grimaldi and Levine, 1948). The results on monazites show good agreement with those obtained by colorimetric analysis (Grimaldi, 1946). The carbonate precipitates from the shales and lignites were also tested for uranium by the extraction procedure; uranium was not occluded.

Table 3.--Comparison of uranium analyses of shale by the carbonate-fluorimetric procedure and by the uranyl nitrate extraction procedure

Sample no.	Percent uranium		Percent uranium occluded by carbonate precipitate
	Obtained by the carbonate-fluorimetric procedure	Obtained by uranyl nitrate extraction	
1	0.006	0.005	0.000
2	0.008	0.008	0.000
3	0.005	0.005	0.000
4	0.007	0.006	0.000
5	0.005	0.006	0.000
6	0.005	0.005	0.000
7	0.006	0.006	0.000
8	0.003	0.003	0.000
9	0.005	0.005	0.000
10	0.004	0.005	0.000
11	0.005	0.005	0.000
12	0.004	0.004	0.000
13 1/	0.003	0.003	0.000
14 1/	0.014	0.015	0.000
15 1/	0.005	0.005	0.000
16 1/	0.003	0.003	0.000

1/ These samples are mineralized shales containing from 4 to 10 percent CuO. Results for uranium obtained by the procedure using hydroxylamine hydrochloride.

Table 4.--Comparison of uranium analyses of lignites by the carbonate-fluorimetric procedure and by the uranyl nitrate extraction procedure

Sample no.	Percent uranium: Obtained by the carbonate-fluorimetric procedure	Percent uranium: Obtained by uranyl nitrate extraction	Percent uranium occluded by carbonate precipitate
1	0.015	0.016	0.000
2	0.011	0.011	0.000
3	0.012	0.011	0.000
4	0.012	0.013	0.000
5	0.011	0.011	0.000
6	0.010	0.010	0.000
7	0.018	0.016	0.000
8	0.017	0.018	0.000
9	0.018	0.019	0.000
10	0.015	0.015	0.000
11	0.024	0.025	0.000
12	0.027	0.029	0.000
13	0.014	0.013	0.000
14	0.024	0.025	0.000
15	0.027	0.029	0.000

Table 5.--Results of uranium analyses of monazites obtained by the carbonate-fluorimetric method compared to those obtained colorimetrically

Sample no.	Percent uranium	
	Obtained by the carbonate-fluorimetric procedure	Obtained colorimetrically 1/
1	0.39 0.37	0.32
2	0.26 0.26	0.24
3	0.16 0.17	0.16
4	0.38	0.38
5	0.26	0.28
6	0.35	0.34
7	0.67	0.64
8	0.25 0.26	0.26
9	1.1	1.0
10	0.27	0.28
11	0.26	0.23
12	0.24	0.22
13	0.24	0.22
14	0.27	0.27

1/ Analyst, Henry Mela, U. S. Geological Survey.

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