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THE DETERMINATION OF URANIUM IN CONCENTRATES **BY THE FLUOROPHOTOMETRIC METHOD**

by

J. B. ZIMMERMAN, F. T. RABBITTS, and E. D. KORNELSEN RADIOACTIVITY DIVISION

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ABSTRACT

The quantitative determination of uranium in minerals and ores, based on the fluorescence emitted by uranyl fluoride when irradiated with ultraviolet light, has been extended to the analysis of gravity and chemical concentrates for uranium. Two important modifications to the previous method have been introduced. Firstly, a modified micropipette is used to minimise pipetting errors; and, secondly, a sufficiently large number of determinations is obtained to give a good statistical average. The method is rapid and simple. Interferences are usually negligible, but, if appreciable, can be eliminated by a simple separation. Good precision and accuracy can be attained.



THE DETERMINATION OF URANIUM IN CONCENTRATES

BY THE FLUOROPHOTOMETRIC METHOD

by

J. B. Zimmerman, F. T. Rabbitts and E. D. Kornelsen

INTRODUCTION

The fluorophotometric method for the determination of uranium has been used in this laboratory on a routine basis for several years. The procedure has been described in detail by one of the authors (3). It has been applied successfully to determine uranium in minerals and ores containing up to one per cent U_3O_8 and in solutions containing up to one gram U_3O_8 per litre. Higher grade samples have been analysed by the cellulose column method (2).

In April, 1953, an investigation was begun to determine the possible application of the fluorophotometric method to the analysis of high-grade gravity and chemical concentrates for uranium. The first important change was the introduction of a modified micropipette (Figure 1) to minimise pipetting errors. This pipette, which will be described subsequently, is of the overflow transfer type. Hence, there is no adjustment of a meniscus to a calibration mark and, therefore, this possibility of human error is eliminated. In addition, the same pipette is used to measure aliquots of the standard and also of the unknown sample. The measurement becomes, therefore, entirely relative and the accuracy of calibration of the pipette is not important.



The second important change comprises the taking of a sufficient number of original samples and the carrying out of enough determinations on each of these to obtain a good statistical average. For example, with a concentrate containing 25 to 50% $U_3 O_8$, four original samples are taken and weighed. These are dissolved and diluted suitably. From the final dilution of each sample are taken ten aliquots of the unknown. Ten aliquots of standard sample are also measured out. The twenty aliquots plus two blanks form a "plate" (Figure 2) and after drying and adding flux, they are all fused at one time on the burner. Hence, for the original concentrate, forty determinations are run together with forty standards and eight blanks. In this way a good statistical average is obtained. The procedure is, of course, longer than that for low grade materials, but much shorter than the conventional cellulose column or hydrogen sulphide-cupferron volumetric procedure. Because of the very high dilution ratio employed, interference by other elements is eliminated in most cases and hence no separation procedures are required. In a few special cases, where interference (quenching or enhancing of the fluorescence) may be possible, a simple extraction procedure for uranyl nitrate may be used with ethyl acetate as the solvent and aluminum nitrate as the salting agent (4). Since the procedure has fewer steps, there is much less possibility of losses occurring than in the conventional volumetric procedures.

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SPECIAL REAGENTS AND APPARATUS

In addition to the reagents and apparatus described in Mines Branch Memorandum Series No. 114 (3), the only equipment required is the modified micropipette illustrated in Figure 1. This is made as follows:- A 100-lambda self-adjusting transfer type micropipette⁴ is modified by cutting off the glass tubing forming the overflow chamber. A larger, more conveniently sized overflow chamber is obtained by attaching a piece of glass tubing (75 mm long and 10 mm 0.D.) to the micropipette with a short length of Tygon tubing, as shown. The overall length of the modified pipette is now 130 mm. The upper end of the overflow chamber is tapered to accommodate a rubber bulb 60 mm long and 35 mm 0.D.⁴⁴. A small air vent 2 mm in diameter is made in the top of the bulb so that the air pressure in the bulb can be controlled by the forefinger. This micropipette is simpler to manipulate than, for example, the Mohr type.

The fluorimeter used in this laboratory is the M.I.T. Model 3 as described in Mines Branch Memorandum Series No. 114 (3). The fusion burner is also described in that publication. It should be emphasised that success in the fluorimetric method

Mo. 283-A, made by Microchemical Specialities Co., 1834
University Ave. Berkeley 3, California, U. S. A.
Max
Central Scientific Co., No. 8775, 1/2 oz size.

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of uranium analysis is largely dependent on the efficiency of the gas burner. The temperature of the flame (ll50[°]C) must be high enough for fusing the flux in three and one-half minutes, and the dishes must be in a suitable burned-gas atmosphere.

PROCEDURE

Four representative samples (0.5 to 2.0 gm) are weighed into tared weighing bottles (Samples A, B, C, and D.). Each is then dissolved in a suitable manner. For refractory materials the sugar carbon-sodium peroxide attack developed by W. F. Muchlberg (1) has been found very useful in this laboratory. The filtered acid solution (usually as nitrate) is then made up to volume in a volumetric flask so that the final solution contains 5% nitric acid. After thorough mixing, an aliquot is taken and this in turn is made up to volume in 5% nitric acid in a second volumetric flask. The two dilutions are chosen so that the final solution contains 0.5 to 1.0 gamma U308 per ml. As previously mentioned a "plate" of twenty-two platinum dishes is now prepared. With the modified micropipette, ten aliquots, 100 lambda each, of Sample A are measured followed by ten aliquots, 100 lambda each, of standard (MS-ST standard dissolved in nitric acid so that one millilitre contains one gamma of $U_3 O_8$). Two dishes are left blank. The plate is dried under infra-red lamps for a few minutes. Then 800 mg (\pm 5%) of sodium fluoride (Baker and Adamson C.P.) are added to each dish with a pelletiser. The dishes are arranged on the Nichrome IV burner screen as shown

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in Figure 2 and then the contents are fused in the full heat of the burner for three and one-half minutes, the fusion being timed by stopwatch. The air and propane are shut off quickly and the molten flux is cooled rapidly by playing a stream of live steam over the dishes. As soon as the dishes are cool, they are transferred to the fluorimeter for measurement of the intensity of the fluorescence. This procedure is repeated for the B, C, and D samples.

RESULTS

The precision and accuracy of the method are good. The average mean deviation should be about plus or minus one per cent. Table 1 lists the individual determinations and average results for a number of typical samples; it will be noted that in certain cases only two or three individual determinations were carried out on these preliminary samples. Comparative results obtained by the cellulose column method are also shown. The accuracy of the method is indicated in Table 2. Column two lists the average fluorimetric results of laboratory A while columns three and four give the results obtained by two other laboratories using the hydrogen sulphide cupferron volumetric procedure. The modified fluorimetric method has also been used for samples containing up to 90% U_3O_8 .



Table 1

${\rm U}_{\rm 3}{\rm O}_{\rm 8}$ Content as Determined By the Fluorimeter and

Sample	%U308 - Fluorime	eter	%U308 - Cellulose Column		
	Individual determinations	Average	Individual determinations	Average	
1	42.15 41.46	41.80	42.24 42.38	42.31	
2	40.85 41.38 41.11	41.11	41.24 40.92	41.08	
3	45.68 45.64 46.85	46.06	45.74 45.40	45.57	
4	42.0 43.3 43.4 43.6	43.01	42.87 42.78 43.00 42.80	42.86	
5	28.4 28.2 28.5	28.37	28.57 28.70 28.58 28.42	28.57	
6	43.80 43.62 43.73	43.72	44.11 43.84 43.75 43.70	43.85	
7	45.70 45.54	45.62	45.08 45.19	45.14	

Cellulose Column Methods



Table 2

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Comparative Determinations of U308 Content by Different Laboratories

Sample	Laboratory A (Fluorimetric)	Laboratory B (HgS - Cupferron)	Laboratory C (H ₂ S - Cupferron)
	%U308	%U308	%U308
7	7.78	7.75	7.79
8	8.12	8.28	8.36
9	8.67	8.62	8.41
10	6.62	6.64	6.84
11	41.11	41.00	41.59
12	46.06	46.00	45.99
13	44.80	44.70	44.98
14	46.20	45.89	46.36

Using the Fluorimetric and Volumetric Procedures

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FIGURE I - MODIFIED MICROPIPETTE





FIGURE 2 - DISTRIBUTION OF SAMPLES, STANDARDS AND BLANKS ON BURNER

