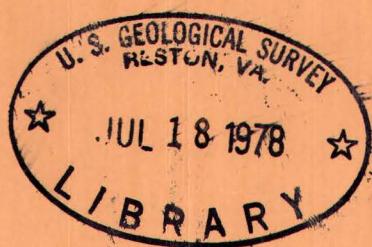


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Short Routine Direct Method for the Fluorimetric Determination of Uranium in Phosphate Rock



Trace Elements Investigations Report 134

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Unclassified.

UNITED STATES DEPARTMENT OF THE INTERIOR
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SHORT ROUTINE DIRECT METHOD FOR THE FLUORIMETRIC
DETERMINATION OF URANIUM IN PHOSPHATE ROCKS

by

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December 1950

USGS-TEI Rept. 134
Consisting of 7 pages
Issued to (see below)

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ABSTRACT

A short routine direct fluorimetric procedure for the determination of up to 0.06 percent uranium in phosphate rocks is described. The procedure employs a simple acid leach for preparing the solution, and the uranium is determined directly on a 1.8-mg aliquot. The results obtained by using this simple procedure on several thousand samples are discussed. The quenching of the uranium fluorescence by foreign elements was found to be negligible, for all practical purposes, and results on western phosphates may be corrected by using an empirically determined quenching factor.

INTRODUCTION

Need for faster routine uranium analyses of phosphate rocks made it necessary to reappraise previous methods for the purpose of introducing as many short cuts as possible consistent with the accuracy sought.

The fastest procedure used in the Geological Survey is the dilution technique which employs microgram amounts of samples in

conjunction with very sensitive fluorimeters.^{1/} This dilution technique is necessary for most types of materials to avoid quenching of the uranium fluorescence by foreign elements in the sample. However, microgram amounts of samples are unnecessary for the analysis of phosphate rocks because in them the concentration of quenching elements is relatively small.

The use of larger samples has definite advantages for routine analysis. With a larger sample, the ratio of fluorescence intensities of samples to the blank value is greater. Consequently, variations in the blank value of ball-mill ground flux result in no significant uncertainty in the analysis. Also, a higher level of accidental contamination resulting from improperly cleaned glassware or air-borne dusts may be tolerated. In our opinion, the ideal direct method should employ a sufficiently large sample to avoid the enumerated difficulties and still be small enough so that quenching of the uranium fluorescence by foreign elements will not be significant.

In the preparation of the solution for analysis it has been assumed heretofore that complete decomposition of the sample is necessary. Lacking any information to the contrary it is the only safe procedure to follow. However, the uranium in phosphate rocks yields to simpler and faster methods of attack. The fastest solution procedure for a large number of samples is a simple acid leach. This method was investigated and gave excellent dissolution of all the uranium-bearing components of the rock.

^{1/} Fletcher, Mary H., U. S. Geol. Survey Trace Elements Investigations Rept. 130 (in preparation).

The final procedure evolved for testing phosphate rocks integrates all of the foregoing considerations and simplifications. An aliquot of the (18 + 82) HNO_3 acid leach representing a 1.8-mg sample is evaporated in a 30-ml platinum crucible or other suitable container and fused directly over a burner with 3 g of fluoride carbonate flux previously described.^{2/} The fluorescence of the disc is measured in the reflection fluorimeter described by Fletcher and May.^{3/} These measurements may also be made with the transmission instrument.^{4/}

EXPERIMENTAL WORK

Preliminary tests on about 30 samples indicated that the short procedure described in this paper was applicable to phosphate rock. Then the method was adopted tentatively for routine uranium determination on phosphate rock. Several thousand samples typical of the deposits being tested by the Geological Survey were analyzed for uranium by this procedure over an extended period of time.

Concurrent with the chemical analyses, the uranium content of these samples was determined by independent methods. The results by beta-gamma count of total radioactivity were used as the main criteria for a "correct"

^{2/} Fletcher, Mary H., U. S. Geol. Survey Trace Elements Investigations Rept. 130 (in preparation).

^{3/} Fletcher, Mary H., and May, Irving, An improved fluorimeter for the determination of uranium in fluoride melts: U. S. Geol. Survey Trace Elements Investigations Rept. 120, 1950.

^{4/} Fletcher, Mary H., May, Irving, and Slavin, Morris, A transmission fluorimeter for use in the fluorimetric method of analysis for uranium: U. S. Geol. Survey Trace Elements Investigations Rept. 104, 1949.

analysis. This counting was done under the supervision of Francis J. Flanagan of the U. S. Geological Survey and has proved to be a very reliable method for uranium determinations on phosphate rocks. About 10 percent of the samples counted were spot-checked by one or more of the refined chemical methods described by Grimaldi and Levine,^{5/} and Fletcher.^{6/}

Data for the feasibility of simple acid attack were obtained by determining uranium in 100 samples by more conventional methods after complete decomposition of the sample and after simple acid leach. The acid insoluble residues from 600 samples were also tested and found to be free from uranium.

DISCUSSION

The short procedure is not perfect, by any means, but represents the best compromise at this time between speed, accuracy sought, simplicity, and convenience. Analysis of the results obtained with the short procedure on several thousand samples from the Florida phosphate deposits has shown that quenching of the uranium fluorescence by foreign elements has not been eliminated altogether.

^{5/} Grimaldi, F. S., and Levine, Harry, The rapid fluorimetric determination of uranium in low-grade ores: U. S. Geol. Survey Trace Elements Investigations Rept. 47, 1948.

^{6/} Fletcher, Mary H., U. S. Geol. Survey Trace Elements Investigations Rept. 130 (in preparation).

1. In 90 percent of these samples the quenching amounted to less than 10 percent, and most of the samples showed no detectable quenching.
2. In 8 percent of the Florida samples the quenching was between 10 and 20 percent; in most of them it was less than 15 percent.
3. The last 2 percent of the samples showed quenching of the order of 20 to 25 percent.

When it is considered that phosphate rocks rarely contain more than 0.02 percent U, errors due to quenching certainly can be tolerated, when they are of the magnitude cited. For example a sample containing .015 percent U would be reported as .012 percent U if the quenching amounted to 20 percent.

Analysis of the results obtained with the short procedure on more than a thousand samples of western phosphate deposits showed the following:

1. In 90 percent of these samples the quenching amounted to 15 percent or less; the average quenching in this group amounted to 12 percent.
2. In 8 percent of these samples the quenching amounted to 15 to 20 percent.
3. In the last 2 percent of the samples the quenching amounted to 20 to 25 percent.

Quenching is more serious in western phosphates, but it is also relatively constant in amount. Advantage may be taken of this fact

to correct results on western phosphates by use of an empirical factor. The factor used in this laboratory is 1.18. Thus:

$$\% \text{ U given by short procedure} \times 1.18 = \text{"true"} \% \text{ U.}$$

The empirical correction factor was used to improve the results on 500 more samples of western phosphates and the corrected figures were indistinguishable from results obtained by more reliable methods.

Our laboratory's experience with simple acid leaching of phosphate rocks for the preparation of the solution for analysis has been remarkable in its success. Out of 4,000 samples of Florida and western phosphate deposits only 4 samples so far have failed to yield completely to attack by (18 + 82) HNO_3 . These 4 were unusual samples (the uranium-bearing mineral proved to be a different mineral than the one usually associated with phosphate rocks), but even these samples yielded to attack by (1 + 1) HNO_3 .

When thousands of samples have to be analyzed routinely by relatively unskilled technicians and speed is an important consideration, a certain fraction of the analyses reported will be in error no matter what procedure is used, and the irreducible minimum of errors will increase with the complexity of the analytical procedure. The results obtained here by this short procedure have been better on the whole than when more refined methods of analysis were used.

DETAILED PROCEDURE FOR PHOSPHATE ROCKS

1. Weigh out a 0.15-g sample into a 125-ml Erlenmeyer flask.
2. Add, by means of a graduate, 50 ml of carefully measured (18 + 82) HNO_3 .
3. Cover the flask with a small glass and heat the solution just to boiling on a hot plate. Boil gently for 2 minutes. Cool.
4. Take a 0.6-ml aliquot of the supernatant liquid by means of a 1-ml graduated pipette and transfer this amount to a clean 30-ml platinum crucible.
5. Evaporate the solution to dryness on the steam bath. Gently ignite the residue.
6. Add 3 g of the carbonate fluoride flux (9 parts NaF , 45.5 parts K_2CO_3 , and 45.5 parts Na_2CO_3 by weight).
7. Heat on a low burner flame until the flux melts. The crucible should not be heated at any time above incipient red heat.
8. Heat for an additional 2 minutes at the lowest temperature at which the flux stays molten swirling and mixing the contents of the crucible to obtain a uniform bead. Place the crucible on an asbestos pad to cool and then store in a desiccator for 30 minutes.
9. Read the fluorescence on the fluorimeter. Obtain the percent uranium by reference to the standard curve, figure 1.
10. For Florida phosphates, report what is obtained. For western phosphates, multiply the percent U by 1.18 for your report.

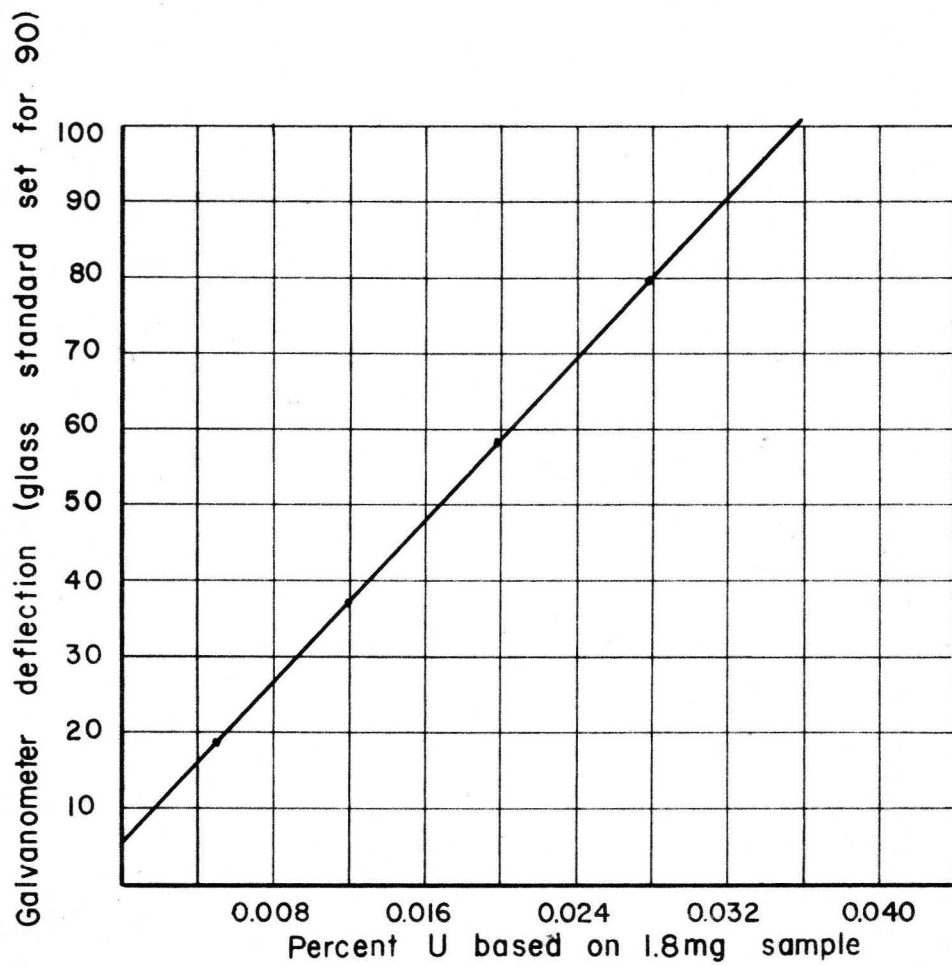


Figure 1 — Working curve