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# THE DETERMINATION OF LOW CONCENTRATIONS OF URANIUM IN ORES AND SOLID MILL PRODUCTS BY X-RAY FLUORESCENCE SPECTROMETRY

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THE DETERMINATION OF LOW CONCENTRATIONS OF  
URANIUM IN ORES AND SOLID MILL PRODUCTS  
BY X-RAY FLUORESCENCE SPECTROMETRY

by

J.B. Zimmerman\* & V. Reynolds\*\*

ABSTRACT

A direct X-ray fluorescence method for the rapid determination of uranium in low-grade ores and rocks of variable matrix, is described.

Accuracy and precision are comparable to the optical fluorescence method down to the 0.01% uranium level.

The effects of matrix composition on uranium intensities are eliminated by a double-dilution technique, in which the dilutions are kept small to minimize intensity losses.

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LA DETERMINATION DE FAIBLES CONCENTRATIONS D'URANIUM  
DANS DES MINERAIS ET DES PRODUITS SOLIDES D'USINE  
A L'AIDE DE LA SPECTROMETRIE DE FLUORESCENCE X

par

J.B. Zimmerman\* et V. Reynolds\*\*

RESUME

Les auteurs ont décrit une méthode directe de fluorescence X afin de déterminer rapidement la quantité d'uranium dans des minerais de faible teneur et des roches provenant de matrice différente.

L'exactitude et la précision sont comparables à la méthode de fluorescence optique jusqu'au niveau minimum d'uranium de 0.01%.

Les effets de la composition de matrice sur les quantités d'uranium sont éliminés par la méthode de double dilution. Les dilutions y sont maintenues à un niveau le plus bas afin de minimiser les pertes d'intensité.

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2. Comparison of Results of Analysis by the Double Dilution Method with Known Uranium Values.
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## INTRODUCTION

The direct determination of low concentrations of uranium in rock, ores and exploration samples by X-ray fluorescence has two main advantages over conventional methods; 1) the need for prior chemical treatment of the sample is eliminated, and 2) the speed of analysis is greatly increased. However there are some disadvantages as well, namely, radiation intensity is low when the element concentration is low, and matrix effects, which can cause absorption or enhancement of the intensity of the element of interest, are unpredictable.

This report describes a double-dilution method which effectively corrects for the matrix effects while minimizing intensity losses by keeping the dilution small. The method is uncomplicated, and requires only the mechanical preparation of two specimen pellets containing only slightly different weight fractions of the sample.

APPARATUS AND REAGENTS

- 1) Philips X-ray fluorescence spectrometer PW 1220, with associated electronic components
- 2) Herzog pressure and time controlled pellet press
- 3) Shatterbox pulverizer
- 4) Pica blender and plastic vials
- 5) Aluminum Spex caps
- 6) Somar powder binding agent
- 7) Silica - 300 mesh floated powder

INSTRUMENTAL

- 1) Excitation - 65 kV 20 ma Molybdenum tube
- 2) Detector - Scintillation
- 3) Crystal - LiF 220
- 4) Analytical line - Uranium  $L\alpha$   $37.31^{\circ}2\theta$
- 5) Background angle -  $36.63^{\circ} 2\theta$

#### METHOD

The method requires the accurate weighing of two different aliquots of sample powder which has been blended with Somar binding agent, the adjustment of the aliquots to the same weight with silica powder, the blending of the silica-diluted aliquots in the Pica blender and the pressing of the blended powders in Spex caps at 20 tons per square inch pressure.

X-ray intensities for the uranium  $L\alpha$  line and the background are obtained by taking counts for 100 seconds at the appropriate angles.

A correction factor, based on Tertian's method (1), is calculated from the difference in the net intensities obtained from the two aliquots, and is applied to the net intensity of the larger aliquot. The uranium concentration of the sample is then calculated by multiplying the net intensity of the larger aliquot by the appropriate dilution and calibration factor.

#### SAMPLE PREPARATION

- 1) Weigh 10.00 g of sample and 1.00 g of Somar powder into a plastic vial and blend in the Pica blender for three minutes.
- 2) Grind 4.00 g of blended sample plus 2.00 g of minus 300 mesh silica powder; and 5.00 g of blended sample plus 1.00 g of the same silica powder in the Shatterbox for three minutes.

Note each specimen weighs 6.00 g.



3) Press the specimens in Spex caps in the Herzog press at 20 tons per square inch for 40 seconds.

#### BACKGROUND CORRECTION

The counting procedure determines the net intensity for the uranium in the specimen by counting at the uranium  $L\alpha$  line and subtracting the background intensity. The background is calculated by taking an intensity measurement at  $0.68^\circ 2\theta$  removed from the uranium  $L\alpha$  line on the short wave-length side and multiplying this intensity by 0.932. This factor was determined from intensity measurements made at  $2\theta$  angles on both sides of the uranium  $L\alpha$  line, on standards free from interference.

#### CALIBRATION FACTOR

The calibration factor (the reciprocal of the slope of a curve when corrected intensity is plotted against concentration) is developed from two well-analyzed samples, prepared as indicated in METHOD. In the example shown, sample "A" contained 0.45% U and sample "B" 0.18% U. Table 1 shows the intensity measurements for the two specimens prepared from samples "A" and "B", the correction factor "Q" according to the double dilution method, and the corrected net intensity for the specimen containing the larger aliquot of sample.

TABLE 1  
 Calculation of Corrected X-ray Intensity  
 by the Double Dilution Method

Sample	Specimen	Peak Intensity C/Sec	Background Intensity C/Sec	Net Peak Intensity C/Sec	"Q" Net 1. Net I <sub>2</sub> -Net 1,	Corrected Peak Intensity Net I <sub>2</sub> x Q C/Sec
"A" 0.45% U	1	4910.99	333.26	I <sub>1</sub> : 4577.73		
	2	5711.03	323.54	I <sub>2</sub> : 5387.49	5.653	30455.48
"B" 0.18% U	1	2029.35	310.44	I <sub>1</sub> : 1718.91		
	2	2305.80	298.09	I <sub>2</sub> : 2007.71	5.952	11949.89

The corrected peak intensities shown in Table 1 require correction by a factor "d" and for the dilution of the original 10g of sample to 11 g with Somar binding agent.

The "d" correction depends upon the ratio of the weight fraction of the original sample in the two specimens and is represented by  $\frac{1-n}{n}$

$$\text{Where 'n' is } \frac{4\text{g of blended sample}}{6\text{g total}} \Bigg/ \frac{5\text{g of blended sample}}{6\text{g total}} = 0.800,$$

$$\text{Then 'd' = } \frac{1-0.800}{0.800} = 0.250$$

The completely corrected intensities for the standards shown in Table 1 are, therefore:

$$\text{"A" sample } (30455.48)(0.250)(1.100) = 8375.26 \text{ net C/sec}$$

and

$$\text{"B" sample } (11949.89)(0.250)(1.100) = 3286.22 \text{ net C/sec}$$

The calibration factor  $\left( \frac{\text{U conc}}{\text{Completely corrected intensity}} \right)$  derived

$$\text{from sample "A" is } \frac{0.45\% \text{U}}{8375.26 \text{ C/sec}} = 0.0000537 \% \text{ U/C/sec}$$

$$\text{and from sample "B" } \frac{0.18\% \text{U}}{3286.22 \text{ C/sec}} = 0.0000548 \% \text{ U/C/sec}$$

For the calculation of the uranium concentration in unknown samples, prepared according to the described procedure, the average of the two factor determinations (0.0000543) is used to convert the corrected intensity of the larger aliquot of an unknown sample to percent uranium concentration of the sample.

COMPARATIVE ANALYSIS

To test the applicability of the double dilution method to the determination of uranium in low-grade samples, a range of samples of known uranium concentration was prepared and assayed by the described procedure.

The known uranium concentration and the X-ray analysis are compared in Table 2.

TABLE 2

Comparison of Results of Analysis by the Double Dilution Method With the Known Uranium Values, on Standard Low-grade Samples

Sample	Known Uranium Concentration % U	Double Dilution Method % U	Ratio <u>Dilution</u> Known
A	1.02	0.99	0.97
B	0.45	0.46	1.02
C	0.176	0.189	1.07
D	0.022	0.025	1.14
E	0.004	0.005	1.25

PRECISION

An estimate of the precision of the method was made by analyzing five pairs of pellets prepared from a uranium ore sample containing 0.173% U and 13.0% Th. The average intensities for four runs of 100 seconds each were used to calculate the uranium concentration in the sample. The five results are shown in Table 3.

TABLE 3  
Precision of Analysis for Uranium in  
Low Grade Ore Samples.

Replica Sample	Percent Uranium
A	0.175
B	0.179
C	0.177
D	0.178
E	0.176

From the data in Table 3, the average uranium concentration is 0.177 percent, the standard deviation  $\pm 0.005$  percent uranium and the recovery based on the known uranium value 1.03.

#### CONCLUSIONS

The X-ray double dilution method described in this report has two main advantages for the determination of uranium in low-grade uranium ore samples. For complex ores which are difficult to take into solution, it is much less time consuming than the conventional fluorimetric method. One sample can be prepared and analyzed in thirty minutes by the double dilution method while a day or more may be required to chemically prepare a suitable solution for fluorimetric analysis. The method provides a positive correction for absorption and enhancement in ores of variable matrix.

The precision and accuracy of the method is comparable to the fluorimetric method when sufficient counting time is used to accumulate a statistically significant number of counts, this being a requirement for the accurate determination of the relatively large "Q" factor resulting from the described dilution procedure.

The lower limit of detection, calculated to be approximately 0.004% uranium falls short of that for the fluorimetric method, which has the ability to determine uranium several orders of magnitude lower. The X-ray method would have a useful application for the analysis of uranium in ore samples down to 0.01 wt.%.

Reference

- 1) Tertian R., "Advances in X-ray Analysis" Vol 12, p. 546,  
Plenum Press 1969.

