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**REPORT**

NIM

**No. 2026**

**THE DETERMINATION OF URANIUM IN  
PYRITE SAMPLES**

by

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**NATIONAL  
INSTITUTE  
for  
METALLURGY**

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18th September, 1979



# NATIONAL INSTITUTE FOR METALLURGY

ANALYTICAL CHEMISTRY DIVISION

## REPORT

No. 2026

THE DETERMINATION OF URANIUM IN PYRITE SAMPLES

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Programme No. 504  
Project No. 05177  
Project Report No. 8

18th September, 1979

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ISBN 0 86999 471 9

## SYNOPSIS

An existing method for the determination of uranium in rocks and minerals is examined for the determination of uranium in materials containing pyrite.

The results are comparable with those obtained by a spectrophotometric method, the precision (relative standard deviation) of the method for standards with  $U_3O_8$  contents of 1500 and 300 p.p.m. being 0,03 and 0,08 respectively when prepared in pyrite, and 0,15 and 0,06 respectively when made up with inert diluent.

Full details of the procedure are given in accompanying appendices.

## SAMEVATTING

'n Bestaande metode vir die bepaling van uraan in gesteentes en minerale word ondersoek vir die bepaling van uraan in materiale wat piriet bevat.

Die resultate is vergelykbaar met dié wat volgens 'n spektrofotometriese metode verkry is. Die presisie (relatiewe standaardafwyking) van die metode vir standarde met 'n  $U_3O_8$ -inhoud van 1500 en 300 d.p.m. is onderskeidelik 0,03 en 0,08 wanneer dit in piriet berei word, en onderskeidelik 0,15 en 0,06 wanneer dit met 'n trae verdunmiddel opgemaak word.

Volledige besonderhede van die prosedure word in bygaande aanhangsels verstrekk.

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## 1. INTRODUCTION

Two samples (AC 362/5 and AC 362/6) containing uranium in a pyrite matrix were submitted for analysis, since previous results from other laboratories and from the National Institute for Metallurgy (NIM) had shown appreciable scatter. The initial results obtained at NIM with X-ray-fluorescence spectrometry (XRF)<sup>1</sup> and a spectrophotometric method<sup>2</sup> had given results indicating a  $U_3O_8$  concentration of approximately 1700 and 1400 p.p.m. respectively. Possible sources of error could be differences in mass absorption and matrix effects with XRF spectrometry, and interferences from iron or errors in dilution, or both, with the spectrophotometric method. These possibilities were therefore investigated.

## 2. EXPERIMENTAL METHODS

Calibration standards were prepared for  $U_3O_8$  in pyrite and in an inert diluent so that an assessment could be made of whether the compensation for matrix effects had been adequate. In addition, duplicate synthetic standards of pyrite with a known  $U_3O_8$  content were prepared for wet-chemical analysis by the spectrophotometric method.

### 2.1. Preparation of Samples and Standards for Analysis by XRF

Samples for analysis were prepared as follows. The sample as received was spread out on glazed paper, and dip samples were taken until 2 g of the sample had been collected. The material collected was then transferred to a clean Vitreosil dish of 7 cm diameter and spread out in an even layer.

#### 2.1.1. Ignition of the Samples Prepared in Pyrite

The sample in the Vitreosil dish was heated in an electric muffle furnace from room temperature to 800°C and kept at this temperature for 1 hour, the chimney of the muffle furnace being left open so that there was an oxidizing atmosphere to convert the pyrite to iron oxide. After 1 hour, the dish was taken out and cooled to room temperature.

#### 2.1.2. Fusion of the Samples Prepared in Pyrite

The ignited pyrite in the Vitreosil dish and 6 g of the flux normally used for uranium analysis (1 part of fluorspar to 2.5 parts of lithium tetraborate) were mixed intimately with a narrow-bladed spatula. The mixture was transferred quantitatively to a graphite crucible, placed in an electric furnace at 400°C, and heated to 1100°C for 1 hour. After the crucible had cooled to room temperature, the fusion bead was removed, weighed, and then pulverized and briquetted<sup>3</sup> (see Appendix I).

#### 2.1.3. Uranium Standards Used in XRF

The masses of pyrite (with a  $U_3O_8$  concentration of 16 p.p.m.) and of pitchblende standard used are given in Table 1.

TABLE 1

*Calibration by XRF of uranium standards in pyrite*

Pyrite g	Pitchblende g	Bead g	$U_3O_8$ content, p.p.m.	
			Briquette	Synthetic sample
1,974 15	0,034 45	6,823	61	222
1,974 90	0,035 30	6,894	62	227
1,923 50	0,084 20	6,916	146	520
1,925 65	0,084 25	6,886	147	520
1,836 55	0,167 95	6,812	297	1022
1,836 65	0,167 45	6,917	291	1020
1,752 20	0,250 05	6,940	433	1516
1,757 55	0,250 85	6,942	435	1516
1,679 30	0,334 55	6,982	576	2011
1,676 90	0,344 20	6,894	583	2012

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Uranium standards were also prepared in a lighter matrix, which consisted of silica, alumina, and ferric oxide in the ratio 15:4:1. The quantities of inert diluent and uranium standard used are given in Table 2.

TABLE 2

*Calibration by XRF of uranium standards in inert diluent*

Inert diluent, g	U <sub>3</sub> O <sub>8</sub> standard, g	Bead, g	U <sub>3</sub> O <sub>8</sub> content, p.p.m.	
			Briquette	Synthetic sample
1,960 10	0,034 45	7,332	57	208
1,971 15	0,036 84	7,436	60	221
1,923 55	0,085 00	7,469	137	509
1,930 00	0,084 35	7,509	135	504
1,849 30	0,167 10	7,491	268	997
1,833 75	0,165 90	7,420	269	998
1,748 55	0,252 70	7,530	404	1518
1,747 15	0,253 00	7,395	412	1521
1,671 00	0,333 30	7,459	537	2000
1,670 80	0,340 10	7,504	545	2034

2.2. Preparation of Samples in Synthetic Pyrite for Wet-chemical Analysis

Known amounts of a sample of pitchblende (internal reference material No. A366) having a U<sub>3</sub>O<sub>8</sub> concentration of 1,2028 per cent were added to aliquot portions of pyrite with a U<sub>3</sub>O<sub>8</sub> concentration of 16 p.p.m. The mixtures prepared in this way had nominal U<sub>3</sub>O<sub>8</sub> values of 320, 617, and 1820 p.p.m. respectively. No mixing was envisaged, since the whole of each standard sample was to be analysed.

The masses used are given in Table 3.

TABLE 3

*Preparation of standards*

Standard	A 366 g	Pyrite g	Calc. U <sub>3</sub> O <sub>8</sub> p.p.m.
1	0,050 50	1,950 50	319
	0,050 60	1,950 50	320
2	0,100 15	1,900 25	617
	0,100 15	1,900 25	617
3	0,300 70	1,700 80	1820
	0,300 70	1,700 80	1820
4	Nil	2,000 0	16
	Nil	2,000 0	16

2.3. Procedure for Determination of XRF

The operating conditions are given in Appendix I (Table I-1). The intensities were measured at the background and at the U L $\alpha$  and Rb K $\alpha$  peaks. The measured count rate for the background was corrected for spectral overlap by the U L $\alpha$  peak, this peak being corrected for the spectral overlap left by the Rb K $\alpha$  peak. The intensity function was calculated according to Jacobs *et al.*<sup>1</sup> and related to the concentrations of the standards. The intensity function of the samples was read off this graph and converted to units indicating concentration.

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2.4. Precision and Accuracy of the Method

Duplicate analyses were carried out on both samples, use being made of standards with matrices of pyrite and inert diluent respectively. The results are given in Table 4, which also shows the reproducibility for the wet-chemical analyses of these samples.

TABLE 4

$U_3O_8$  values (p.p.m.) based on different calibration methods

Pyrite Sample no.		Inert diluent Sample no.		Wet-chemical analysis Sample no.	
AC 362/5	AC 362/6	AC 362/5	AC 362/6	AC 362/5	AC 362/6
1432	307	1439	276	1389	287
1412	276	1418	312	1427	278
1392	289	1394	277	1444	287
1486	271	1438	312	1474	284
1523	301	1492	265	1444	
1488	246	1477	304	1474	
1435	303	1455	305		
1492	325	1500	300		
1462	293	1478	275		
1458	290	1454	291	Average	
2,88	0,793	0,241	0,619	R.S.D.	
1,87	0,173	0,187	0,173	R.S.D. <sub>d</sub>	
2,19	0,774	0,152	0,594	R.S.D. <sub>(S+P+C)</sub>	

R.S.D. = Relative standard deviation.

R.S.D.<sub>d</sub> = Relative standard deviation due to drift.

R.S.D.<sub>(S+P+C)</sub> = Relative standard deviation due to sample homogeneity (S), error in preparation (P), and error in counting (C).

$$\text{where } R.S.D._{(S+P+C)} = \sqrt{R.S.D.^2 - R.S.D._d^2}$$

Two uranium standards — with  $U_3O_8$  concentrations approximately equal to that of a 2 g sample diluted to 6 g with flux — were selected and measured 8 and 9 times respectively so that the stability of the instrument could be evaluated. The results are given in Table 5.

TABLE 5

Measurement of two uranium standards for evaluation of stability of the instrument

$U_3O_8$ concentration in standard, p.p.m.	433	147
Reading 1	419,7	142,6
Reading 2	423,4	145,1
Reading 3	427,8	150,4
Reading 4	441,1	146,5
Reading 5	415,7	148,8
Reading 6	434,4	147,9
Reading 7	422,7	149,4
Reading 8	419,1	148,4
Reading 9	425,1	-
Average	425,5	147,4
Standard deviation	8	2,5
R.S.D.	0,187	0,173

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The synthetic uranium standards prepared in pyrite (see Table 1) were also analysed spectrophotometrically. These results are compared with the calculated  $U_3O_8$  concentrations in Table 6.

TABLE 6

*Comparison of spectrophotometric and calculated values for  $U_3O_8$  in synthetic pyrite*

$U_3O_8$ concentration, p.p.m.			
Spectrophotometric		Calculated	
305	} 295	320	} 320
286		319	
617	} 617	617	} 617
617		617	
1787	} 1819	1820	} 1820
1852		1820	

### 3. DISCUSSION

From Table 4, it is evident that there is very little difference between the calibrations for the pyrite and the diluent matrices. The calibration for the inert diluent gives a slightly better precision than that for the pyrite, since the count rate for the  $U\ L\alpha$  spectral line in the light matrix of inert diluent is higher than that for the same  $U_3O_8$  concentration in the heavier matrix of pyrite. The error in the counting statistics is therefore smaller for the standard made up with inert diluent. (Comparison of calibrations in Table 4 shows that the relative standard deviations are 0,288 and 0,241 for standards made up with pyrite and inert diluent respectively.) Comparison of the average values for  $U_3O_8$  concentration are virtually identical, i.e., 1458 and 1454, and 290 and 291 p.p.m. respectively.

The measurements for evaluation of instrumental drift (Table 5) show a relative error of less than 2 per cent, the remainder of the relative error being due to differences in homogeneity, preparation of the samples, and errors in the counting statistics. Table 4 shows that this remainder is more or less equal to that due to instrumental drift at high concentrations of uranium (1400 p.p.m.). At a concentration of 300 p.p.m., counting errors constitute the greater portion of the total error.

The average figures for the wet-chemical analyses of the samples (Table 5) compare favourably with those obtained by XRF, i.e., with 1 per cent for the higher value and 2 per cent for the lower value. The spectrophotometric method shows very good agreement with the theoretical calculated values for the synthetic pyrite standards as given in Table 6.

The first reported  $U_3O_8$  concentration (1709 p.p.m.) obtained with XRF was based on the calibration of only one standard; therefore, if this standard were faulty, all the results would be incorrect.

Good agreement exists between the wet-chemical and XRF analyses of the synthetic standards prepared in pyrite for calibration by XRF. Subsequent repeated analyses based on the single calibration standard that was used for the initial suspect analysis gave values of 1521 and 1577 p.p.m., i.e., higher than those obtained in these tests. It was shown that this difference could be attributed to low counts obtained for the calibration standard used. No explanation can be offered for the first high value obtained with XRF.

### 4. CONCLUSION

It has been shown that, with XRF spectrometry, the values that can be obtained for  $U_3O_8$  in a pyrite matrix are consistent with spectrophotometric values (by the bromo-PADAP method)<sup>2</sup>, irrespective of whether the calibration is carried out in a matrix of inert diluent consisting of pyrite, or of silica, ferric oxide, and alumina. Prior roasting of the sample is necessary to ensure a good fusion.

Laboratory Method no. 92/72<sup>3</sup> is therefore applicable to the determination of uranium in pyritic iron with some slight modification. The modified method is given in Appendix I.



## URANIUM IN PYRITE SAMPLES

### 5. REFERENCES

1. JACOBS, J.J., AUSTEN, C.E., and STEELE, T.W. The determination of uranium in solids and solutions by X-ray fluorescence spectrometry using a background-ratio method with an empirically derived exponent, to correct for matrix effects. Randburg, National Institute for Metallurgy, *Technical Memorandum 10065*. Mar. 1977. (Unpublished.)
2. COOK, E.B.T., SHELTON, B.J., and STEELE, T.W. The spectrophotometric determination of total uranium in silicate ores and leach liquors by use of bromo-PADAP. Randburg, National Institute for Metallurgy, *Report no. 1840*. Jul. 1976.
3. JACOBS, J.J., AUSTEN, C.E., and STEELE, T.W. The determination of uranium in solids and solutions by X-ray fluorescence spectrometry using a background-ratio method with an empirically derived exponent, to correct for matrix effects. Randburg, National Institute for Metallurgy, *Laboratory Method no. 92/72*. Mar. 1977. (Unpublished.)

## APPENDIX I

## THE DETERMINATION OF URANIUM IN PYRITE CONCENTRATES BY X-RAY-FLUORESCENCE SPECTROMETRY AND A BACKGROUND-RATIO METHOD WITH AN EMPIRICALLY DERIVED EXPONENT (LABORATORY METHOD NO. 92/76)

## 1. OUTLINE

A mass of pyritic concentrate is burnt off in a flat silica dish under oxidizing conditions in a furnace at 800°C for 1 hour. After being allowed to cool, the sample is mixed with flux, transferred to a graphite crucible, and fused for 1 hour at 1100°C. The fused material is cooled, and the fusion bead is weighed, pulverized, and briquetted.

The measurement of uranium then follows the method described in Laboratory Method n.o. 92/72 (revised)<sup>1</sup>, calibration being with synthetic standards of uraninite in a matrix of either pyrite or inert diluent. Standards prepared in pyrite must be taken through an oxidation step in the same way as the samples.

Corrections are made for spectral interferences, after which matrix effects are taken into account<sup>2</sup>, the exponent-background technique<sup>3</sup> being used.

## 2. APPLICATION

The method is applicable to samples of pyritic concentrates having  $U_3O_8$  contents ranging from 0 to 10 000 p.p.m.

## 3. APPARATUS

(1) *Dishes*

Flat silica dishes of 7 cm diameter.

(2) *Crucibles*

Graphite crucibles of the following dimensions. Outer: diameter 6 cm, height 4 cm; inner: diameter 3 cm, height 3 cm, with slightly tapered bottom.

(3) *High-temperature furnace (1100 °C)*(4) *Low-temperature Furnace*

Must have air flow to create oxidizing conditions.

(5) *Top-loading Mass Meter*

Accurate to 2 mg.

(6) *Siebtechnik Mill*

Colmonoy or tungsten carbide bowl (10 cm<sup>3</sup>).

## 4. REAGENTS

(1) *Binder for Briquettes*

Dissolve 83,3 g of ethyl cellulose in 1000 cm<sup>3</sup> of acetone, using an electric stirrer.

(2) *Flux*

Mix chemically pure anhydrous lithium tetraborate and chemically pure fluorspar in a ratio of 2,5:1. (Note 1.)

(3) *Inert Diluents*

Mix silica, alumina, and ferric oxide in a ratio of 15:4:1. Use the mixture as a base for uranium standards.

(4) *Pyrite Matrix Low in Uranium*

## 5. AMOUNT OF SAMPLE

The amounts of sample and inert diluent are given in Table I-1.

## 6. PREPARATION OF THE SAMPLE

## 6.1. Oxidation and Fusion Procedure

- Measure out the appropriate amount of pyritic concentrate and diluent as given in Table I-1.
- Transfer the sample to a flat silica dish, 7 cm in diameter, and spread the sample out in the dish so that it presents a large area.
- Put the dish in a low-temperature furnace at an initial temperature of 400°C, and allow the temperature to rise to 800°C for 1 hour.
- After 1 hour, remove the dish with its contents from the furnace, and cool.

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- e. Mix the contents of the dish thoroughly with 6 g of flux.
- f. Transfer the mixture to a marked graphite crucible and heat in the high-temperature furnace for 1 hour at 1100°C. (Note 2.)
- g. Remove the crucible from the furnace, and allow it to cool to room temperature.
- h. Put the fusion bead into the same 50 cm<sup>3</sup> beaker, and determine the mass of the fusion bead with a top-loading mass meter.
- i. Transfer the fusion bead to a 10 cm<sup>3</sup> Siebtechnik bowl and grind for 4 minutes.
- j. Transfer the finely divided powder from the Siebtechnik mill to a 50 cm<sup>3</sup> beaker.
- k. Briquette and mark the ground fusion bead as described in Section 6.2.

### 6.2. Briquetting Procedure

- a. Transfer the powdered fusion bead to a briquetting die.
- b. Add 1 cm<sup>3</sup> of binder solution and mix well with a spatula until most of the solvent has evaporated.
- c. Form a briquette by pressing at 5 t for 2 minutes.
- d. Identify the briquette by marking it with a wick pen or by other suitable means.

TABLE I-1

*Amounts of solid sample and inert diluent*

Est. U <sub>3</sub> O <sub>8</sub> content p.p.m.	Mass of sample g	Mass of inert diluent (or pyrite matrix) g
0 to 200	2	Nil
>200 to 4 000	2	Nil
4 000 to 8 000	1 to 2	1 to nil
8 000 to 10 000	0.8 to 1	1.2 to 1

## 7. PREPARATION OF CALIBRATION STANDARDS

### 7.1. Standards in Pyrite Matrix

- a. Prepare 2 g of uranium standards to cover the range 0 to 9000 p.p.m. of U<sub>3</sub>O<sub>8</sub> by mixing pyrite (low in uranium) with a siliceous uraninite standard or U<sub>3</sub>O<sub>8</sub> in a siliceous base.
- b. Calculate the U<sub>3</sub>O<sub>8</sub> content of the uranium standard in the pyrite matrix as follows:

$$U_r = \frac{W_1}{W_1 + W_2} \cdot R + \frac{W_2}{W_1 + W_2} \cdot S.$$

where  $U_r$  is the U<sub>3</sub>O<sub>8</sub> content of the disc (p.p.m.) in a mixture of pyrite and uraninite,  
 $W_1$  is the mass of the pyrite matrix,  
 $W_2$  is the mass of the uraninite standard,  
 $R$  is the U<sub>3</sub>O<sub>8</sub> content of the pyrite matrix (p.p.m.), and  
 $S$  is the U<sub>3</sub>O<sub>8</sub> content of the uraninite standard (p.p.m.).

- c. Calculate the uranium content of the briquette obtained after fusion as follows:

$$U_b = U_r \times (W_1 + W_2)/M.$$

where  $U_b$  is the U<sub>3</sub>O<sub>8</sub> content of the briquette (p.p.m.), and  
 $M$  is the mass of the fusion bead.

### 7.2. Standards in Matrix of Inert Diluent

- a. Prepare uranium standards in inert diluent to have a total mass of 2 g and to cover the range 0 to 9000 p.p.m. of U<sub>3</sub>O<sub>8</sub>.

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- b. Calculate the  $U_3O_8$  content of the uranium standard as follows:

$$U_r = \frac{W_2}{W_1 + W_2} \times S,$$

where  $W_1$  is the mass of inert diluent,

$W_2$  is the mass of the uranium standard, and

$S$  is the  $U_3O_8$  content of the uraninite standard (p.p.m.).

- c. Calculate the  $U_3O_8$  content of the briquette obtained after fusion as follows:

$$U_b = U_r \times (W_1 + W_2)/M,$$

where  $M$  is the mass of the fusion bead.

### 7.3. Blank Briquettes

- a. Prepare blank briquettes with 2 g of inert diluent or 2 g of pyrite as the matrix. For pyrite, follow the oxidation procedure described in Section 6.1, and then the fusion procedure.

## 8. INSTRUMENT AND INSTRUMENTAL PARAMETERS

Use the instrument and the instrumental parameters listed in Table I-2.

TABLE I-2

*Instrument and instrumental parameters*

Spectrometer	Philips PW 1220 or 1540
Generator	Philips PW 1130
Voltage	60 kV
Current	40 mA*
Tube	Mo target
Detector	Scintillation
Radiation path	Air
Collimator	160 $\mu$ m
Bragg crystal	LiF (220)-cut
Discriminator	Window to include 99% of energy at U L $\alpha$ pulse
Counting time	40 s at all $2\theta$ angles
Analytical line	U L $\alpha$ 37,30° $2\theta$
Interfering line	Rb K $\alpha$ 37,93° $2\theta$
Background U and Rb†	36,70° $2\theta$

\* The count rate of the scintillation counter must never exceed 50 000 counts per second.

† See alternative background suggested in Section 9.

## 9. INTERFERING ELEMENTS

- As the spectral lines<sup>3</sup> given in Table I-3 can interfere with the uranium determination, use an alternative background at 34,50° to 35,00°  $2\theta$ , since this is virtually free of interference compared with the background at 36,70°  $2\theta$ .
- If the composition of the sample is not known, scan a powder sample or briquette, and identify and correct for the interfering elements as follows.
- Adjust the discriminator to include the full energy range of the required determination. (This must include the energy of the suspected interfering elements and possible background positions.)
- Identify the X-ray peaks and consult Table I-3 to see whether any of the peaks interfere.

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e. Correct for interference as follows:

$$\Delta I = F_E \cdot I_{net} \dots \dots \dots (1)$$

where  $\Delta I$  is the increase in the number of counts due to interfering elements,  
 $I_{net}$  is the net intensity in counts per second for the interfering peak, and  
 $F_E$  is the lift factor.

f. Determine  $F_E$  in equation (1) by measuring the increase in the net intensity at the analytical line caused by the interfering element and the net intensity of the interfering element.

TABLE I-3

*Interfering elements at U L $\alpha$  position and background at 36,70° 2 $\theta$*

Interfering element	Line	2 $\theta$ angle	R.I.*	Where interference ( $\Delta I$ ) would be apparent
Y	K $\alpha_{1+2}$	33,90	150	} Alternative background for measurement of U L $\alpha$ peak
Ra	L $\beta_2$	34,11	20	
Ra	L $\beta_{1+3}$	34,19	1	
Pb	L $\gamma_1$	34,30	10	
Ra	L $\beta_4$	34,34	4	
Tl	L $\gamma_3$	34,36	2	
Tl	L $\gamma_2$	34,63	1	
Th	L $\eta$	34,92	1	
Tl	L $\gamma_1$	35,47	10	
Sr	K $\alpha_{1+2}$	35,85	150	
Hg	L $\gamma_1$	36,69	10	
Au	L $\gamma_3$	36,75	2	
Au	L $\gamma_2$	37,03	1	} U background at 36,70° 2 $\theta$ U L $\alpha$ analytical line
Br	K $\beta_2$	37,71	2	
Bi	L $\beta_5$	37,93	1	
Au	L $\alpha_1$	37,97	10	
Rb	K $\alpha_{1+2}$	37,99	150	
Pt	L $\gamma_3$	38,03	2	
Br	K $\beta_{1+3}$	38,25	24	
Pt	L $\gamma_2$	38,30	1	

\* R.I. = Relative intensity.

10. CALIBRATION

10.1. Determination of Background Factors for U L $\alpha$  and Rb K $\alpha$  Analytical Lines

From repeated measurements of the pressed-powder blank briquette at the 2 $\theta$  angles given in Section 8, Table I-2, evaluate the background factors  $f_U$  and  $f_{Rb}$  (Note 3) as follows:

$$f_U = P_U/b, \dots \dots \dots (2)$$

$$f_{Rb} = P_{Rb}/b, \dots \dots \dots (3)$$

where  $P_U$  is the intensity at the U L $\alpha$  position,  
 $P_{Rb}$  is the intensity at the Rb K $\alpha$  position, and  
 $b$  is the intensity at the background position.

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### 10.2. Regression Analysis of Standards Data

- a. From a regression analysis of the measurement data for the standards, calculate the slope and intercept of the calibration graph.
- b. Use the values for the slope and the intercept to evaluate the results of the samples. (Note 4.)

### 11. ANALYSIS OF SAMPLES

- a. Prepare the samples and standards as described in Section 6, and measure them.
- b. Intersperse the standards in a suite of samples. (Note 5.)
- c. Calculate the  $(P-B)/B^x$  for the samples and standards. (Note 6.)
- d. Do a regression analysis of the data for the standards as described in Section 10.2, and evaluate the samples.

### 12. NOTES

1. The fluorspar must be checked for the presence of strontium, thorium, lead, and yttrium.
2. If the mixture of sample and flux effervesces or expands unduly, another graphite crucible or a lid (with its open end downward) must be used to prevent any losses during fusion.
3. Background factors are constants for the same instrument and instrumental parameters, and are therefore determined only once.
4. The calibration constant  $1/K$  is calculated by the computer programme (MINIBASIC), printed, and automatically stored in the memory of the computer (see Appendix II).
5. A few suitable controls and at least one blank sample must be inserted with every batch of samples.
6.  $x = 1,322$  for solids.

### 13. REFERENCES

1. JACOBS, J.J., TOLMAY, R.T., and STEELE, T.W. Laboratory Method no. 92/72 (revised). The determination of uranium in solids and solutions by X-ray-fluorescence spectrometry by a background-ratio method with a derived exponent. Randburg, National Institute for Metallurgy, Report no. 2025. 1979.
2. AUSTEN, C.E., TOLMAY, R.T., and STEELE, T.W. The determination of minor or trace amounts of uranium and thorium and silicate materials. Johannesburg, National Institute for Metallurgy, Laboratory Method no. 92/69. 18th Nov., 1974. (Unpublished.)
3. JACOBS, J.J., AUSTEN, C.E., and STEELE, T.W. The determination of uranium in solids and solutions by X-ray-fluorescence spectrometry using a background-ratio method with an empirically derived exponent to correct for matrix effects. Randburg, National Institute for Metallurgy, Laboratory Method no. 92/72. Mar. 1977. (Unpublished.)

## APPENDIX II

LISTING OF THE COMPUTER PROGRAMME FOR THE DETERMINATION OF  $U_3O_8$  IN SOLIDS AND SOLUTIONS

The following abbreviations are used.

BKG = Background

VAL = Value

CAL = Calibration

FAC = Factor

P = Peak.

NEW

OLD

471 373

LIST 320

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10 PRINT "U3O8 BY EXPONENT"
15 PRINT "A=U BKG RATIO"
20 PRINT "B=RB BKG RATIO"
30 PRINT "C=STD VAL"
40 PRINT "D=EXPONENT"
45 FIXED 5
50 INPUT A, B, C, D
60 PRINT "CAL 1 OR 0"
70 INPUT E
80 IF E=1 THEN 205
90 PRINT "ENTER CALFAC"
100 INPUT F
110 PRINT "ENTER BKG"
111 PRINT "ENTER U P"
112 PRINT "ENTER RB P"
113 INPUT G, H, I
120  $J=(H-G \cdot A) \cdot 0.0093$ 
130  $K=(I-G \cdot B) \cdot 0.007$ 
140  $L=(G-J) \cdot A$ 
150  $M=(H-L-K)/L \cdot D$ 
155  $N=F \cdot M$ 
160 PRINT "U3O8 PPM=",N
170 PRINT
171 PRINT
180 PRINT "CAL 1 OR 0"
185 INPUT X
190 IF X=1 THEN 205
200 GOTO 110
205 PRINT "ENTER BKG"
210 PRINT "ENTER UP"
215 PRINT "ENTER RBP"
220 INPUT G, H, I
225  $J=(H-G \cdot A) \cdot 0.0093$ 
230  $K=(I-G \cdot B) \cdot 0.007$ 
235  $L=(G-J) \cdot A$ 
240  $M=(H-L-K)/L \cdot D$ 
245  $F=C/M$ 
250 PRINT "CALFAC=", F
260 PRINT
270 PRINT
280 GOTO 110

```