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REPORT

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A RAPID METHOD FOR THE DETERMINATION OF
URANIUM IN ORES AND CARBONACEOUS MATERIALS
BY X-RAY-FLUORESCENCE SPECTROMETRY

by

R.T. Tolmay and J.J. Jacobs

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NATIONAL INSTITUTE FOR METALLURGY

ANALYTICAL CHEMISTRY DIVISION

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Investigators R.T. Tolmay and J.J. Jacobs
Director of Division T.W. Steele

SYNOPSIS

The determination of uranium by a non-fusion method in a wide range of uranium-bearing materials, e.g., ores, coals, and resins, is described. Matrix effects are corrected for by dilution and fine grinding of the sample with coarse river sand and application of a technique for background correction. The linear calibration range is up to 1000 p.p.m. of U_3O_8.

It was found that the suitable dilution of resins with river sand and fine grinding makes it possible for up to 6 per cent U_3O_8 to be determined. Ten samples can be analysed in two-and-a-half hours. The precision and accuracy is 5 and 2 per cent at U_3O_8 concentrations of 500 and 2000 p.p.m. respectively.

The laboratory method, a listing of the computer programme required for the calibration and calculation of the U_3O_8 concentrations, and instructions for the calculation of the error in the determination are given in the appendices.

SAMEVATTING

Die bepaling van uraan deur 'n nie-smeltmetode in 'n groot verskeidenheid uraanhoudende materiale, bv. ertse, steenkool en harse, word beskryf. Daar word vir matrikseffekte gekorrigeer deur die monster met growwe riviersand te verdun en fyn te maal, en deur 'n tegniek vir agtergrondkorreksie toe te pas. Die lineêre kalibrasiebestek is tot 1000 d.p.m. U_3O_8.

Daar is gevind dat geskikte verdunning van harse met riviersand en fyn maling dit moontlik maak om tot 6 persent U_3O_8 te bepaal. Tien monsters kan binne twee en 'n halfuur ontleed word. Die presisie en akkuraatheid is onderskeidelik 5 en 2 persent met U_3O_8-konsentrasies van 500 en 2000 d.p.m.

Die laboratoriummetode, die rekenaarprogram wat nodig is vir die kalibrering en berekening van die U_3O_8-konsentrasies en instruksies vir die berekening van die fout in die bepaling word in die aanhangsels aangegee.

CONTENTS

1. INTRODUCTION

In the determination of uranium by X-ray-fluorescence spectrometry in materials such as resin and coal, an ashing stage is normally used prior to fusion or pelletization of the sample. However, because of an increase in the number of determinations required at the National Institute for Metallurgy (NIM), it was felt that attention should be given to the introduction of more direct methods.

Kikkert[1] and de Jongh[2] reported on the reduction of particle size by fine grinding and dilution with a hard material — such as quartz in the form of river sand — in order to minimize matrix effects. Fine grinding was used in the investigation reported here, but it was found that some means of correction for residual matrix variation was required.

Background intensity is dependent on matrix[3] and has been shown to be inversely proportional to mass absorption[4]. The mass-absorption coefficient is linearly related to this background between the major absorption edges[3,5]. Using these relations. Feather and Willis[6] developed a simple method for correction of the background and matrix affects on spectral peaks.

By measuring the background intensity at $35°\ 2\theta$ for the (220)-cut lithium fluoride crystal, and at the U Lα and Rb Kα peak positions for pure chemicals ranging from zinc oxide to magnesium oxide, Feather and Willis showed that linear graphs are obtained for intensities of background at $35°\ 2\theta$ versus the intensity at each of the positions for the analyte peak. It is therefore a logical assumption that the true background under the peak for a sample of unknown composition can be calculated by measurement of the background intensity at $35°\ 2\theta$ and application of these relations.

2. EXPERIMENTAL METHOD

Details of the laboratory method are given in Appendix I.

2.1. The Instrument and Instrumental Parameters Used

The instrument and instrumental parameters used in the measurements are listed in Table 1.

TABLE 1

The instrument and instrumental parameters used

Spectrometer	Philips PW 1220 with automatic control
Tube	Rh target
Voltage	60 kV
Current	40 mA
Collimator	160 μm
Bragg crystal	LiF (220)-cut
Radiation path	Air
Lower level	250 scale units
Window	500 scale units

2.2. Determination of Background Slope and Residual Intercept

Eight pure chemicals, namely zinc oxide, ferric oxide, chrome oxide, vanadium pentoxide, titanium dioxide, calcium fluoride, calcium carbonate, and magnesium oxide, were pelletized to give briquettes of infinite thickness. A rhodium target tube was used for measurement[7] of the intensities at an interference-free background of $35°\ 2\theta$ for (220)-cut lithium fluoride crystals and at the U Lα and Rb Kα analytical lines. Graphs were drawn by plotting of the background intensity at the spectral peak position versus the intensity at the interference-free background (see Figure 1).

The background under the spectral peak is given by the linear equation

$$Y = MX + C, \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (1)$$

where Y is the background under the spectral peak,
          M is the slope,
          X is the background at a position where it is free from interference, and
          C is the residual background.

U Lα background = y = 0,753x + 6,5934
Rb Kα background = y = 0,704x + 9,2583
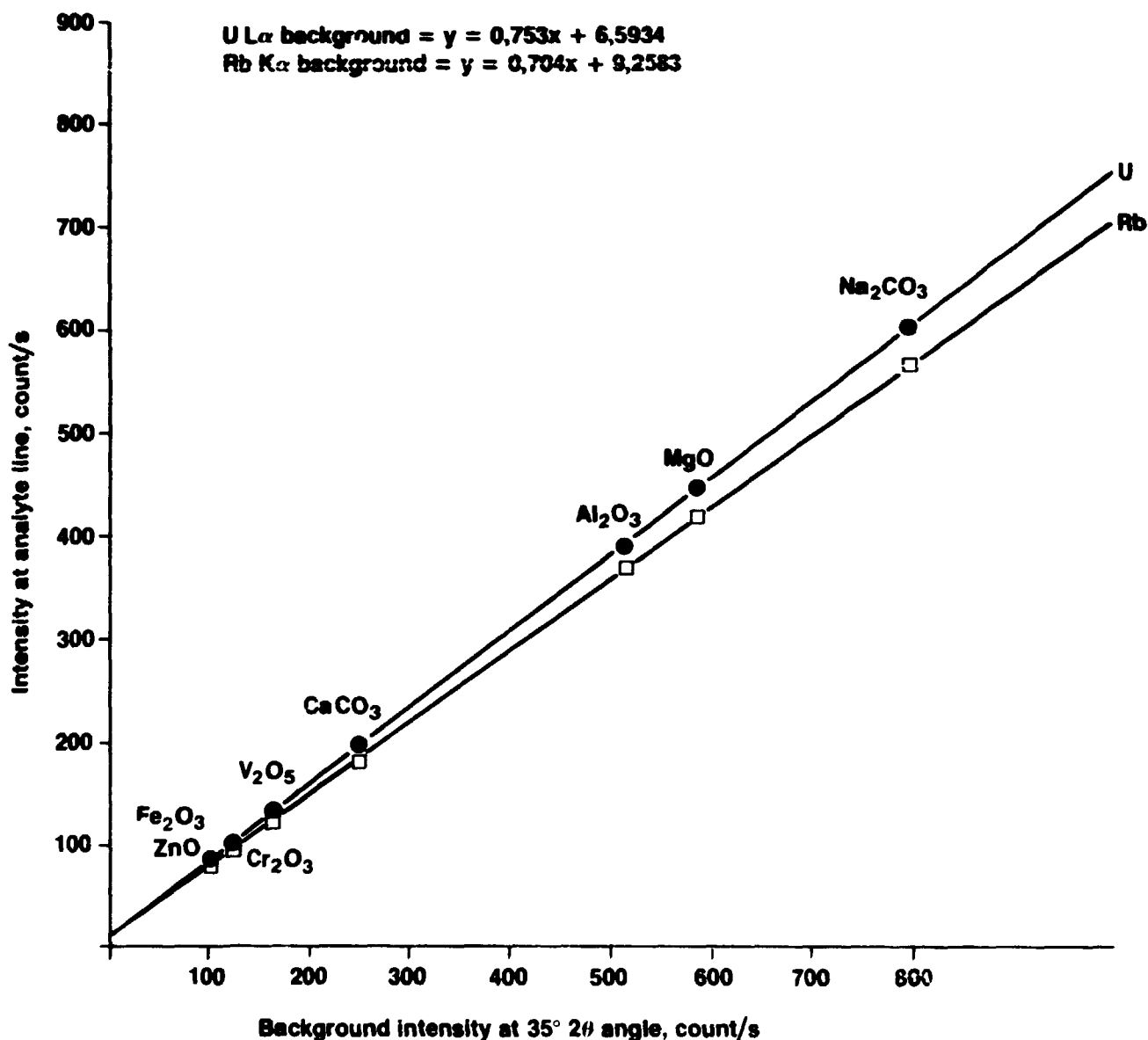
FIGURE 1. Background intensity at the spectral peak position versus intensity at the interference-free background

The values for *M. C.* and the correlation factor for line regression of the U Lα and Rb Kα backgrounds are given in Table 2. As can be seen, there is a slight positive intercept, which is due to electronic noise and possible scatter from the sample-changer. This intercept will be referred to as residual background.

TABLE 2

Values for the slope, residual background, and correlation factor for line regression of the U Lα and Rb Kα background

	U Lα bkgd	Rb Kα bkgd
Slope	0,753	0,704
Residual bkgd (intercept)	6,593 4	9,258 3
C.O.C.	0,999 96	0,999 94

Bkgd = background
C.O.C. = coefficient of correlation

2.3. Tests on Grinding and Pelletization

Grinding of 2 g of sample with 6 g of sand, 1 g of Hoechst polyvinyl sulphonate, and 1 g of boric acid was carried out in a 10 cm³ tungsten carbide bowl. After the material had been pelletized, it appeared to be incompletely ground and gave low intensities. It was therefore decided that a 100 cm³ Colmonoy bowl and different grinding times should be tried.

A series of samples — three groups of six samples each — were prepared by grinding for 50, 100, and 150 s and briquetting at 2 t for 2 min.

The samples were read on the spectrometer, and the ratio $(P-B)/B$, where P is the count at the peak position and B the count at the background position, was determined. A monitor disc was used in the determination of the instrumental variation. The relative standard deviations for the monitor and each group of six pellets milled for different times are shown in Table 3.

TABLE 3

Relative standard deviation for the monitor and three groups
of six pellets each milled for different times

	Monitor	50 s	100 s	150 s
Mean	0,500 96	0,496 64	0,492 74	0,499 73
R.S.D.	0,033 3	0,029 9	0,026 6	0,051 6

R.S.D. = relative standard deviation

A grinding time of 100 s gave the best precision, and was therefore used in subsequent tests. The results for samples milled for 150 s showed greater scatter, probably because of breakdown of the polyvinyl sulphonate by the excessive heat generated during grinding.

2.4. Interfering Elements

The spectral lines given in Table 4 can interfere with the determination of uranium. The background at $35°$ 2θ is virtually free of interference unless thorium is present in large amounts.

TABLE 4

Interfering elements at U Lα position and background at $35°$ 2θ

Interfering element	Line	2θ angle	R.I.	Where interference (ΔI) would be apparent
Y	$K\alpha_{1+2}$	33,90	150	
Ra	$L\beta_2$	34,11	20	
Ra	$L\beta_{1+5}$	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	U background at $35°$ 2θ
Th	L_n	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	
Br	$K\beta_2$	37,71	2	
Bi	$L\beta_5$	37,93	1	
Au	$L\alpha_1$	37,97	10	U Lα analytical line
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

If the composition of the sample is not known, a powder sample or briquette should be scanned and the interfering elements identified and corrected for as follows.

    (a) The discriminator should be adjusted to include the full energy range of the required determination. (This range must include the energy of the suspected interfering elements and possible background positions.)

    (b) The X-ray peaks should be identified and Table 4 used to show whether any of the peaks interfere on the U $L\alpha$ or background positions.

    (c) Interference should be corrected for as follows:

$$\Delta I = F_E \cdot I_{net} \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (2)$$

where ΔI is the increase in counts per second due to interfering elements,
          I_{net} is the net intensity in counts per second for the interfering peak, and
          F_E is a constant, also called a lift factor.

F_E is determined by measurement of the net intensities at the analytical lines of the interfering element and of the analyte element, i.e.,

$$F_E = A/B,$$

where A is the net intensity at the analytical line of the analyte element, and
          B is the net intensity at the analytical line of the interfering element.

3. PREPARATION OF SAMPLE AND STANDARD DISCS

For the sample discs, up to 2 g of sample material was ground with 6 g of sand, 1 g of boric acid, and 1 g of Hoechst polyvinyl sulphonate for 100 s in a Colmonoy bowl. Where less than 2 g of sample was taken, river sand was added to make up the difference to 2 g. The entire mass was then briquetted at 5 t for 2 min. The standard discs were prepared from different uranium-bearing reference materials. The masses of reference materials and of sand and binder used are given in Table 5.

TABLE 5

Masses of materials used in the preparation of calibration standards

Std no.	Type of material	Mass of material g	Mass of sand and binder g	Calculated U_3O_x in disc p.p.m.
A330	Uraninite	2	8	1318
A330	Uraninite	1	9	659
A445	Uraninite	2	8	450
A445	Uraninite	1	9	225
A87	Torbernite	2	8	783
A87	Torbernite	1	9	291
A333	Uraninite	2	8	98
A333	Uraninite	1	9	49

The standards were loaded in the first 10 positions and the samples in positions 11 to 120 in the automatic loader (see Table 1).

4. CALIBRATION

The computer programme listed in Appendix II was used for calculation of the ratios $(P-B)/B$ corrected for residual background. These ratios were used with the U_3O_x concentration in the standard discs for calculation of the slope and intercept of the calibration graph (see Table 6).

TABLE 6

Results of regression analysis

Slope	0.003 171
Intercept	0,051 541
C.O.C.	0,999 22

C.O.C. = coefficient of correlation

5. ANALYSIS OF SAMPLES

After the slope and intercept of the calibration graph has been calculated, the computer automatically stores these values for later use in the calculation of the U_3O_x concentrations in the sample discs.

6. RESULTS

Analyses were carried out on sample discs prepared by the sand-grinding method (see Section 3), as well as by the fusion–exponent method[2], which was used for comparison of the results for ores and carbonaceous materials (Table 7). The analyses of the resin, which involved destruction of the sample by wet oxidation and measurement of the U_3O_x concentration in solution, were compared with those obtained by the sand-grinding method (Table 7).

TABLE 7

Comparison of analyses for fine-grinding method with those for fusion–exponent method

Type of material	Sample no.	Fine-grinding method			Fusion–exponent method			Difference in analysis %
		Mean of U_3O_x values p.p.m.	No. of determinations	R.S.D.	Mean of U_3O_x values p.p.m.	No. of determinations	R.S.D.	
Coal	8/79	412	7	0,034	431	4	0,032	−4,6
Coal	9/79	2122	7	0,016	2126	4	0,017	−0,2
Coal	1:1 of 8/79:9/79	1288	2	−	1298*	−	−	−0,8
Coal	AC380/3	1801	2	−	1860*	−	−	−3,2
Coal	AC388/2	2671	2	−	2663*	−	−	+0,3
Shale	AC388/3	263	2	−	290*	−	−	−9,4
Coal + shale	AC388/2 + AC388/3	1055	2	−	1065*	−	−	−0,8
Torbernite	A87	3055	3	0,005	3130†	−	−	−2,4
Uraninite	A90	3718	3	0,008	3750†	−	−	−0,9
Rössing ore	18/70	770	5	0,019	770‡	−	−	0,0
Wits ore	33/71	643	5	0,016	680‡	50	0,020	−4,1
Karoo ore	28/78	910	5	0,020	924§	11§	0,054§	
					902	3	0,007	+0,8
Dominion Reef ore	27/78	645	5	0,037	679	5	0,014	−3,7
Ion-exchange resin	EA769/2	5,70	2	−	5,33**	2	−	+7,5
Ion-exchange resin	EA799/1	7,01	2	−	6,96**	2	−	+0,7

* Previously reported values.
† Recommended value.
‡ Accepted value for 'in-house' reference materials.
§ Long-term variation.
** Destruction by wet oxidation and measurement in solution.

A comparison by regression analysis of the values obtained by the fine-grinding method (Y-axis) and the fusion–exponent method (X-axis) is given in Table 8, which shows that, since the slope is close to unity, there is good agreement between the two methods for a wide range of materials. The positive intercept of approximately 3,4 p.p.m. is smaller than the lower limit of detection of the method (7,5 p.p.m.), and is therefore insignificant. (See Appendix III.)

TABLE 8

*Correlation, obtained by regression analysis, between results
of fine-grinding and fusion–exponent methods*

No. of results	15
Slope	1,009 6
Intercept	3,402 8
C.O.C.	0,999 6

7. DISCUSSION AND CONCLUSIONS

Table 7 shows that, for the sand-grinding method, the precision at the 400 to 600 p.p.m. level was 5 per cent, and that at the 2000 p.p.m. level 2 per cent.

Good agreement was obtained between the method involving sand grinding and dilution and the fusion method, in which the exponent was used for the correction of matrix effects. However, care must be taken to ensure that the same minimum level of grinding is achieved and that the same grinding system is used each time. The lower limit of detection for this method (see Appendix III) was calculated to be 7,5 p.p.m. of U_3O_8, whereas that for the fusion–exponent method was 15 p.p.m. of U_3O_8.

In conclusion, the fine-grinding method is simpler, its operation is faster (two-and-a-half hours for ten samples as against four hours), it has a lower limit of detection, and it is as precise and accurate as the fusion method in which the exponent is used for background corrections. The method is applicable to a wide range of uranium-bearing materials.

8. REFERENCES

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2. DE JONGH, W.K. Heterogeneity effects in X-ray analysis. *Philips Bull.*, May 1970.
3. JENKINS, R., and DE VRIES, J.L. Practical X-ray spectrometry. Philips Technical Library. London, Macmillan, 1968.
4. HAHN WEINHEIMER, P., JOHANNING, H., and ACKERMAN, H. Relationships between mass absorption and background intensity in X-ray fluorescence spectral analysis. *Chem. Abstr.*, vol. 65. 1966. 9732(F).
5. HOWER, J. Matrix corrections in X-ray spectrographic trace element analysis of rocks and minerals. *Am. Mineralogist*, vol. 44. 1959. pp. 19.
6. FEATHER, C.E., and WILLIS, J.P. A simple method for background and matrix correction of spectral peaks in trace element determination by X-ray fluorescence spectrometry. *X-ray Spectrom.*, vol. 5. 1976. pp. 41–48.
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APPENDIX I

THE DETERMINATION OF URANIUM IN ORES AND CARBONACEOUS MATERIALS BY X-RAY-FLUORESCENCE SPECTROMETRY LABORATORY METHOD NO. 92/77

E.1. Uranium

1. OUTLINE
The method of Feather and Willis[1] is applied to materials that have been finely ground and diluted.

A mass of sample not exceeding 2 g is ground with 6 g of sand, 1 g of Hoechst polyvinyl sulphonate, and 1 g of boric acid for 100 s on a Siebtechnik mill using a 100 cm³ Colmonoy bowl and briquetted at 5 t for 2 min. Pure chemicals are briquetted at 5 t for 2 min, and are used to give the values for the background slope and the intercept (i.e., the residual background due to electronic noise).

The instrument is calibrated by the measurement of recommended and in-house standards prepared by the same method of sand grinding. The sample discs are then read against the calibration graph stored in the computer programme.

2. APPLICATION
The method is applicable to ores and carbonaceous materials with U_3O_8 concentrations ranging from 200 to 5000 p.p.m., and is suitable for resins with U_3O_8 concentrations of up to 6 per cent.

3. APPARATUS
(1) Siebtechnik Mill
100 cm³ Colmonoy bowl.
(2) Herzog Press

4. REAGENTS
(1) River Sand
Must be free of uranium.
(2) Boric Acid
A.R. grade.
(3) Polyvinyl Sulphonate
Hoechst Hostapur.
(4) Pure Chemicals
ZnO, Fe_2O_3, Cr_2O_3, V_2O_5, TiO_2, CaF_2, $CaCO_3$, and MgO.

5. AMOUNT OF SAMPLE
The amounts of sample and sand used are given in Table I-1.

TABLE I-1

Amounts of solid sample and sand diluent

Est. U_3O_8 concn p.p.m.	Mass of sample g	Mass of sand g
200 to 5 000	2	6
5 000 to 10 000	1	7
10 000 to 50 000	0,2	7,8
50 000 to 100 000	0,1	7,9

6. INSTRUMENTS AND INSTRUMENTAL PARAMETERS

Use the instruments and instrumental parameters listed in Table 1-2.

TABLE 1-2

Instruments and instrumental parameters

Spectrometer	Philips PW 1220 with automatic control
Generator	Philips PW 1130
Voltage	60 kV
Current	40 mA
Tube	Rh or Mo target
Radiation path	Air
Collimator	Fine
Bragg crystal	LiF (220)-cut
Discriminator	Window to include 95% of energy at U Lα pulse
Counting time	40 s at all 2θ angles
Analytical line	U Lα 37.30° 2θ
Interference line	Rb Kα 37.93° 2θ
Background	35.00° 2θ

7. PREPARATION OF THE PURE CHEMICAL DISCS

a. Weigh out 10 g of each pure chemical on a top-loading chemical balance.

b. Briquette each of the chemicals at 5 t for 2 min.

8. PREPARATION OF THE STANDARD DISCS

a. On a chemical balance, weigh out appropriate amounts of standard sand as given in Table 1-1 into a 50 ml squat beaker.

b. Weigh out 1 g of Hoechst Hostapur (polyvinyl sulphonate) and 1 g of boric acid on a top-loading balance.

c. Mix well with a spatula, transfer to a Siebtechnik mill using a 100 cm^3 Colmonoy bowl, and mill at a 'fast' speed for 100 s.

d. Carefully remove the finely ground powder, and briquette at 5 t for 2 min.

e. Calculate the U_3O_8 concentration in the standard disc as follows:

$$U_3O_8 \text{ in calibration standard, p.p.m.} = \frac{(\text{Mass of standard taken, g}) \times (U_3O_8 \text{ in recommended standard, p.p.m.})}{\text{Total mass of disc, g}}$$

9. PREPARATION OF THE SAMPLES

a. Prepare sample discs as described in Section 7.

b. Prepare a blank disc by grinding 8 g of sand with 1 g of Hoechst Hostapur polyvinyl sulphonate and 1 g of boric acid.

10. DETERMINATION OF THE BACKGROUND SLOPE FOR U Lα AND Rb Kα ANALYTICAL LINES AND RESIDUAL BACKGROUND

a. Using the instruments and instrumental parameters listed in Table 1-2, measure the pure chemical discs at the peak positions of the U Lα and Rb Kα lines, and at the background position of 35° 2θ.

b. From a least-squares regression analysis of the intensities at 35° 2θ and at the U Lα 2θ and Rb Kα 2θ positions, calculate the slope and intercept of the background graph.

c. Alter lines 21500 and 25005 (uranium background) and lines 21505 and 25010 (rubidium background) in the computer programme listed in Appendix II.

11. ANALYSIS OF SAMPLES AND BLANK DISCS

a. Enter the programme listed in Appendix II into the computer.

b. Place the standard discs in the first 10 positions of the sample tray and the sample discs in positions 11 to 120.

c. Enter the standard U_3O_x values in lines 10 500 to 14 999.

d. Set up the instrument in the normal automatic mode to read the standards and the samples.

e. Regression analyses of data for the standards are calculated by use of the concentrations of U_3O_x (p.p.m.) in the standard discs and the ratios $(P-B)/B$,

where P is the count at the peak position, and

B is the count at the background position.

f. Samples are read and calculated according to the calibration graph obtained as described in step e.

12. REFERENCE

1. FEATHER, C.E., and WILLIS, J.P.   A simple method for background and matrix correction of spectral peaks in trace element determination by X-ray fluorescence spectrometry. *X-ray Spectrom.*, vol. 5. 1976. pp. 41–48.

APPENDIX II

COMPUTER PROGRAMME FOR USE WITH LABORATORY METHOD NO. 92/77

```
5 PRINT"U3O8 USING SAND GRINDING AND FEATHER AND WILLIS METHOD"
6 PRINT"FOR BACKGROUND CALCULATION AND MATRIX CORRECTION"
7 PRINT"PROGRAMMED BY R.T.T.----------------19/10/79
8 PRINT"PLACE STD DISCS IN HOLDER NUMBERS 1 TO 10"
9 PRINT"PLACE SAMPLES IN HOLDER NUMBERS 11 TO 120"
10 PRINT"ENTER STANDARD VALUES IN DATA LINES 10500 TO 14999"
11 DIMA(10),M(10)
20 H6=7
470 REM CALB LDR,GONIOM
480 T=-122
490 T1=XRR(T)
500 T1=XRR(0)
510 IFT1=-1THEN500
520 IFT1<>-2THEN550
540 STOP
550 IFT1<>-3THEN580
560 PRINT"LDR IN MAN,SET TO AUTO THEN IN 1"
565 INPUTT
570 GOTO480
580 PRINT"IN GONIOM STRT ANG AS A -VE"
590 INPUTT
595 T=INT(T*100)
600 T2=XII(T)
610 T2=XII(0)
620 IFT2=-1THEN610
630 IFT2<>-2THEN660
630 STOP
660 REM
662 T=21
665 GOSUB15000
670 GO TO 20000
10090 REM REGRESSION ANALYSIS OF STANDARDS
10100 L=1
10110 READ M(L)
10120 L=L+1
10130 IF L<=X THEN 10110
10140 PRINT"DATA IN"
10141 X1=0
10142 X2=0
10143 Y1=0
10144 Y2=0
10145 W=0
```

```
10150 FOR Q=1 TO X
10160 X1=X1+M(Q)
10170 X2=X2+M(Q)↑2
10180 Y1=Y1+A(Q)
10185 Y2=Y2+A(Q)↑2
10190 W=W+M(Q)*A(Q)
10200 NEXT Q
10210 X3=X1/X
10220 Y3=Y1/X
10230 N=(X*W-X1*Y1)/(X*X2-X1↑2)
10240 C=(Y3-N*X3)
10250 R=(X*W-X1*Y1)/SQR((X*X2-X1↑2)*(X*Y2-Y1↑2))
10260 PRINT"NØ ØF STANDARDS              ="X
10270 PRINT"SLØPE                        ="N
10280 PRINT"INTERCEPT                    ="C
10290 PRINT"CØEFF. ØF CØRRELATIØN        ="R
10300 RETURN
10499 REM LINES 10500 TØ 14999 RESERVED FØR STANDARD VALUES
15000 REM PØS LDR
15010 T2=XEE(0)
15012 IFT2=-1THEN15010
15014 T2=XEE(T)
15020 T2=XEE(0)
15030 IFT2=-1THEN15020
15040 IFT2<>-2THEN15060
15050 STØP
15060 RETURN
15070 REM PARS LIFT & DØWN HLDR & LID
15090 T2=XAA(T)
15091 IFT2=-2THENSTØP
15092 T2=XKK(5)
15094 T2=XKK(0)
15096 IFT2=-1THEN15094
15097 IFT2=-2THENSTØP
15100 T2=XAA(0)
15110 IFT2=-1THENPRINT"ERR GRAB"
15120 IFT2<>-1THEN15130
15125 T2=XII(1)
15130 RETURN
15140 REM PØS SMPL CHM
15142 IFT-H6<0THENLETT4=T-H6+4
15143 IFT-H6>0THENLETT4=T-H6
15144 T4=T4*2+1
15145 IFH6=7THENLETT4=7
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```
15146 H6=T
15150 T2=XFF(T)
15160 T2=XFF(T)
15170 IFT=-1THEN15160
15180 IFT2<>-2THEN15190
15185 STØP
15190 T4=XKK(T4)
15194 T4=XKK(0)
15195 IFT4=-1THEN15194
15196 IFT4<>-2THEN15200
15197 STØP
15200 RETURN
15210 REM STATUS WELL?
15230 T2=XEE(0)
15235 IFT2=4THEN15260
15240 PRINT"STATUS AT WELL WRØNG"
15260 RETURN
15270 REM TØ LIFT HØLDER
15282 T=1
15290 GØSUB15070
15310 RETURN
15320 REM DØWN HLDR
15330 T=2
15340 GØSUB15070
15360 RETURN
15470 REM PARS DETECTØRS
15480 T2=XCC(T)
15490 IFT2<>-2THEN15510
15500 STØF
15510 T4=XKK(2)
15530 T4=XKK(0)
15540 IFT4=-1THEN15530
15550 IFT4<>-2THEN15570
15560 STØP
15570 RETURN
15610 REM SCINT CNTR
15620 T=2
15630 GØSUB15470
15640 RETURN
15690 REM PARS CØLLM
15700 T2=XDD(T)
15710 T2=XDD(T)
15730 IFT2<>-2THEN15750
15740 STØP
15750 RETURN
15760 REM FINE CØLLM
15770 T=1
15780 GØSUB15690
15790 RETURN
15840 REM PARS FILT,VAC,SPIN
15850 T2=XDD(T)
```

```
15880  T4=XKK(T3)
15890  T4=XKK(0)
15900  IFT4=-1THEN15890
16000  IFT4<>-2THEN16020
16010  STØP
16020  RETURN
16030  REM FILT ØUT
16040  T=3
16050  T3=5
16060  GØSUB15840
16070  RETURN
16130  REM VAC ØFF
16140  T=5
16150  T3=2
16160  GØSUB15840
16170  RETURN
16280  REM SPIN ØN
16290  T=8
16300  T3=1
16310  GØSUB15840
16320  RETURN
16330  REM PARS CRYST/ØRD
16340  T2=XEE(T)
16350  IFT2<>-2THEN16370
16360  STØP
16370  T4=XKK(5)
16390  T4=XKK(0)
16400  IFT4=-1THEN16390
16410  IFT4<>-2THEN16430
16420  STØP
16430  RETURN
16600  REMCRYST 3-1
16610  T=5
16620  GØSUB16330
16630  RETURN
16680  REM K.V.
16700  T2=XGG(T)
16710  T3=5
16720  T4=XKK(T3)
16730  T4=XKK(0)
16740  IFT4=-1THEN16730
16750  IFT4<>-2THEN16770
16760  STØP
16770  IFT2=-1THEN16700
16780  IFT2<>-2THEN16795
16790  STØP
16795  IFINT(T2)<>INT(T)THEN16700
16800  RETURN
16810  REM M.A.
16820  T2=XHH(T)
16830  T3=5
```

```
16840 T4=XKK(T3)
16850 T4=XKK(0)
16860 IFT4=-1THEN16850
16870 IFT4<>-1THEN16890
16880 STØP
16890 IFT2=-1THEN16820
16910 IFT2<>-2THEN16925
16920 STØP
16925 IFINT(T2)<>INT(T)THEN16820
16930 RETURN
16940 REM GØNIØM
16942 T3=(T-1)*100
16943 T2=XII(T3)
16944 T2=XII(0)
16945 IFT2=-1THEN16944
16946 IFT2<>-2THEN16950
16947 STØP
16950 T=T*100
16960 T2=XII(T)
16970 T2=XII(0)
16980 IFT2=-1THEN16970
16990 IFT2<>-2THEN17010
17000 STØP
17010 RETURN
17020 REM READ/TRANSF DATA
17022 K1=0
17024 K1=K1+1
17026 T2=XJJ(S1/2)
17028 T2=XJJ(0)
17030 IFT2=-1THEN17028
17032 IFT2=-2THENSTØP
17034 T3=XLL(1)
17036 IFT3=-1THEN17034
17038 IFT3=-2THENSTØP
17040 IFT3=0THEN17026
17042 Y(K1)=T3
17044 IFK1=1THEN17024
17046 K2=0
17048 K2=K2+1
17052 Y1=ABS(Y(K1)-Y(K2))
17054 IFY1<3*SQR(Y(K2))THEN17062
17056 IFK2<K1-1THEN17048
17058 IFK1<5THEN17024
17060 PRINT">5 CNTS REJ"
17062 T3=Y(K1)+Y(K2)
17064 T3=T3/S1/(1-T3/S1*(1.5/1E6))
17070 RETURN
20000 PRINT"INSTRUMENT PARAMETERS"
20010 PRINT"TUBE K.V.";
20020 INPUTZ1
```

```
20025 W3=0
20030 PRINT"TUBE M.A.";
20040 INPUTZ2
20050 PRINT"FILTER--4=IN,3=OUT";
20060 INPUTZ3
20070 PRINT"COLLM--1=FINE,2=COARSE";
20080 INPUTZ4
20090 PRINT"CRYSTAL--1=1.1,3=2.1,5=3.1";
20100 INPUTZ5
20110 PRINT"DETECTOR--2=SC,1=FLOW,3=FL+SC";
20120 INPUTZ6
20130 REM VAC ALWAYS OFF
20140 Z7=5
20150 REM SPIN ALWAYS ON
20160 Z8=8
20170 PRINT"ENTER U PEAK ANGLE,RB PEAK ANGLE "
20180 INPUTZ9,X9
20190 PRINT"EKG ANGLE";
20200 INPUTZC
20210 PRINT"COUNTING TIME";
20220 INPUTS1
20222 GOSUB20800
20230 PRINT"NO OF STANDARDS"
20240 INPUT X
20241 PRINT"NO OF SAMPLES"
20242 INPUT S
20243 Q=S+10
20250 J=0
20260 J=J+1
20270 T=J
20280 GO SUB 15000
20290 GO SUB 15270
20300 T=11
20310 GO SUB 15000
20320 T=122
20330 GO SUB 15000
20340 GO SUB 15210
20350 T=1
20360 GO SUB 15140
20370 GO SUB 15320
20380 T=3
20390 GO SUB 15140
20392 IFJ>1THEN20400
20400 T=Z9
20410 GO SUB 16940
20420 GO SUB 17020
20421 PRINT
20430 PRINT"STANDARD NO ="J
20435 PRINT"ULA PEAK    ="T3
20440 P3=T3
20445 T=X9
```

```
20450 GØ SUB 16940
20455 GØ SUB 17020
20460 PRINT"REKA PEAK  ="T3
20465 P4=T3
20470 T=20
20475 GØ SUB 16940
20480 GØ SUB 17020
20485 PRINT"EKG AT 35  ="T3
20490 P2=T3
20500 GØ SUB 21500
20505 IF J>1 THEN 20515
20514 J=1
20515 T=1
20520 GØ SUB 15140
20525 GØ SUB 15270
20530 T=J
20540 GØ SUB 15000
20542 GØ SUB15320
20545 IF J<X THEN 20260
20560 GØ SUB 10090
20570 GØ TØ 22000
20800 REM SET INSTRM PARAM
20810 T=Z1
20820 GØSUB16680
20830 T=Z2
20840 GØSUB16810
20850 T3=10
20860 T=Z3
20870 GØSUB15840
20880 T=Z4
20885 GØSUB15840
20890 T=Z5
20900 GØSUB16330
20910 T=Z6
20920 GØSUB15470
20930 T=Z7
20940 GØSUB15840
20950 T=Z8
20960 GØSUB15840
20970 RETURN
21430 REM CLS DN
21440 T=4
21450 GØSUB16810
21460 T=20
21470 GØSUB16680
21475 T=XII(1)
21480 RETURN
21490 REM CALCULATIØ ØF RATIØ
21500 B=P2*0.753+6.5934
21505 P5=(P4-(P2*0.704+9.2683))*0.007
21510 P6=P3-B-P5
21515 P7=P6/B
21525 PRINT"RATIØ ="P7
21530 A(J)=P7
21535 RETURN
22000 J=10
22003 J=J+1
22005 T=J
22010 GØ SUB 15000
```

```
22015 GØ SUB 15270
22020 T=11
22025 GØ SUB 15000
22030 T=122
22035 GØ SUB 15000
22040 GØ SUB 15210
22045 T=1
22050 GØ SUB 15140
22055 GØ SUB 15320
22060 T=3
22065 GØ SUB 15140
22070 T=Z9
22075 GØ SUB 16940
22080 GØ SUB 17020
22085 PRINT
22090 PRINT
22095 PRINT"SMP NØ = "J
22100 PRINT"ULA PEAK     ="T3
22105 P3=T3
22110 T=X9
22115 GØ SUB 16940
22120 GØ SUB 17020
22125 PRINT"BEKA PEAK    ="T3
22130 P4=T3
22135 T=Z0
22140 GØ SUB 16940
22145 GØ SUB 17020
22150 PRINT"BKG AT 35    ="T3
22160 P2=T3
22170 IF J>1 THEN22175
22175 GØ SUB25000
22180 T=1
22185 GØ SUB 15140
22190 GØ SUB 15270
22195 T=J
22200 GØ SUB 15000
22205 GØ SUB 15320
22210 IF J<Q THEN 22003
22215 GØ SUB 21430
22220 GØ TØ 30000
25000 REM CALCULATIØN ØF RESULTS
25005 B=P2*0.753+6.5934
25010 P5=(P2*0.704+92683)*0.007
25015 P6=P3-B-P5
25020 P7=P6/P
25025 P8=(P7-C)/N
25035 PRINT"RATIØ     ="P7
25040 PRINT"PPM U3Ø8 ="P8
25045 RETURN
30000 END
```

#READY

APPENDIX III

CALCULATION OF THE ERROR IN LABORATORY METHOD NO. 92/77

1. METHOD

These calculations are used with the method of Feather and Willis[1], which is applied to materials that had been finely ground and diluted.

Let R represent the ratio $(P-B)/B$,

where P is the count at the peak position, and

B is the count at the background position.

Then

$$R = \frac{p - L_{Rb} - (F_u \times b) + I_u}{(F_u \times b) + I_u},$$

where p is the net corrected U Lα peak,

L_{Rb} is the lift factor on the U Lα peak caused by overlap of the Rb Kα analytical line.

F_u is the background factor,

b is the background intensity, and

I_u is the intercept of the background graph (i.e., the residual background due to electronic noise).

The error in R, σ_R, is given by the equation

$$\sigma_R \approx \frac{R}{T}\sqrt{\frac{p_u + L_{Rb} + (F_u^2 \times b) + I_u}{[p_u - L_{Rb} - (F_u \times b) + i_u]^2} + \frac{(F_u^2 \times b) + I_u}{[(F_u \times b) + I_u]^2}}.$$

where p_u is the gross U Lα intensity, and

T is the counting time, s.

By use of data obtained on a standard containing 1054 p.p.m. of U_3O_8,

$$\sigma_R \approx 0,0239.$$

The lower limit of detection (L.L.D.) can be expressed as follows:

$$L.L.D. \approx \frac{\sigma_R}{M}$$

where M is the slope of the calibration curve (see Table 6 of the Report.)

Therefore

$$L.L.D. \approx \frac{0,023\ 9}{0,003\ 171}$$

$$\approx 7,5 \text{ p.p.m.}$$

2. REFERENCE

1. FEATHER, C.E., and WILLIS, J.P. A simple method for background and matrix correction of spectral peaks in trace element determination by X-ray fluorescence spectrometry. *X-ray Spectrom.*, vol. 5. 1976. pp. 41–48.