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DETERMINATION OF THE CONCENTRATION OF URANIUM IN GEOCHEMICAL SAMPLES*

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ABSTRACT

Corrections for matrix absorption in energy-dispersive X-ray fluorescence analysis based on the measurement of Compton scattered radiation using a high resolution Si(Li) semi-conductor dedector is one of the important factor for the determination of the concentration of uranium in geochemical samples containing different concentrations of iron. Characteristic U L_α and U L_β X-rays were excited by Mo and Pd K X-rays. Intensities of U L_α or U L_β X-rays were measured as a function of uranium content. Correction for Compton scatter intensities minimized the matrix absorption effects. The error by regression analysis when using Mo K X-rays to excite U L_α X-rays in samples containing up to 280 ppm uranium was ± 25 ppm of which up to 11 ppm was due to counting statistics. When Pd K X-Rays were used to excite U L_β X-rays the error was up to 17 ppm.

ÖZET

Farklı miktarlarda demir içeren jeokimyasal örneklerde uranyum konsantrasyonunu yüksek resolusyonlu Si(Li) yarı-iletken dedektörü kullanarak X-ışını fluoresans analiziyle tayin etmede en önemli faktörlerden bir tanesi Compton saçılma radyasyonundan faydalanılarak matris soğurma etkisinin düzeltilmesidir. Uranyumun kendine özgü U L_α X-Işınları Molibden ve Palladyum K X-Işınları ile uyarıldı. U L_α ve U L_β X-ışınlarının şiddeti uranyum konsantrasyonunun fonksiyonu olarak bulundu. Compton saçılma radyasyonuna göre X-ışın şiddetlerinde yapılan düzeltmeyle matris soğurma etkisi ortadan kaldırıldı. Uranyum L_α X-ışınları ile uyarılmasında 280 ppm uranyum içeren örneklerde regresyon analiziyle bulunan hata ± 25 ppm olmuştur. Bu hatanın 11 ppm sayım istatistiğinden kaynaklanmaktadır. Uranyum L X-ışınlarını uyarmada Pd K X-ışınları kullanıldığı zaman bu hata 17 ppm kadar çıkmıştır.

INTRODUCTION

Energy-dispersive X-ray fluorescence analysis is finding increasing use for the measurement of mineral concentrations in the walls of boreholes, in rock specimens and in samples of material removed from boreholes.

Equipment based on a high resolution Si(Li) semiconductor detector and a low power air cooled X-ray tube is suitable for analysing geochemical samples. When producing quasi monochromatic X -rays limits of detection of a few ppm can be obtained /1,2/.

One of the main limitations in achieving the highest accuracy is interelement effects of which matrix absorption is the most important.

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The magnitude of matrix absorption effects and methods of correcting the intensity of excited characteristic X-rays for them can be optimised by careful choice of the energy of the excitation energy.

In this work the advantage of selecting the optimum energy for uranium L X-rays are described.

INTERELEMENT EFFECTS

In general, the magnitude of matrix absorption effects very considerably depending on whether the absorption coefficients for the exciting and characteristic radiations of any interfering elements which might be present are significantly different from the absorption coefficients of the principal rock forming elements. Significant differences in the magnitude of matrix absorption effects also arise according to whether the absorption edges of the interfering are above or below the absorption edges of the wanted element. This type of absorption effect is intrinsic to the sample and cannot be avoided : it can only be allowed for by compensation methods /3/.

Iron, manganese and calcium are usually the main interfering elements when determining the concentration of uranium in geochemical samples. Apart from the fact that they are all usually present at high concentrations their absorption edges are all below the energies of U L X-rays, therefore having relatively high absorption coefficients for U L X-rays.

If the energies of the Compton scattered and fluorescence X-rays are different, provided the absorption edges of the main interfering elements are not between the two energies adequate compensation can normally be achieved.

RESULTS

The X-ray tube, which had a tungsten anode, was used in conjunction with a "scatter type" excitation energy selector which was arranged to produce Pd K (21, 24 keV) and Mo K (17.5, 20 keV) Palladium K X-rays are just above the U L_2 absorption edge (20.9 keV) and are therefore ideal for exciting U L_β X-rays, and Mo K X-rays are just above the U L_1 absorption edge (17.16 keV) /4/.

The fact that the intensity of Ge K X-rays produced from the tungsten X-ray tube is approximately twice that of Mo K X-rays and four times that of PD K X-rays when operating the X-ray tube at 45 Kv and constant beam current will also improve the relative sensitivity of the measurement when using the optimum excitation energy.

Twenty-six geochemical samples which had a particle size of less than 200 mesh contained up to 280 ppm uranium with iron contents varying from 5 to 22 per cent were provided. The samples also contained variable and unknown concentrations of rubidium. As it was not possible to completely resolve U L_α (13.438, 13.613 keV) from Rb K_α (13.335, 13.394 keV) X-rays, it was necessary to correct the U L_α measurement for variations in rubidium content by subtracting 27% of the measured Rb K_α X-ray intensity for each sample.

Determination of concentration of uranium

Characteristic U L_α X-rays were excited by Mo K X-rays produ-

ced in a "scatter type" excitation energy selector with the X-ray tube which had a tungsten anode and was operated at 45 kV 400 u A. Characteristic U L_α and U L_β X-rays were then excited by Pd K X-rays produced under the same operating conditions.

The measurement times were automatically adjusted so that for each set of measurement a constant number of Compton scattered incident X-rays were detected, 120,000 for Mo K X-rays, and 200,000 for Pd K X-rays. The measurement times in both cases varied from 200 - 350 seconds depending on the iron content of the samples.

Figs. 1-3 give the intensity of U L_α or U L_β X-rays (c/sec) as a function of uranium content for the three measurements. The U L_α reading was adjusted by substracting 27% of the Rb K_α channel reading to allow for the overlap of their unresolved peaks. It is seen that matrix absorption effects are approximately of the same magnitude in each case.

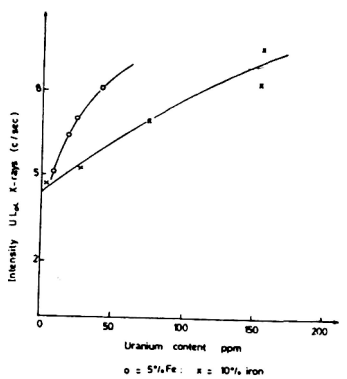

Fig. 1. Intensity U L_α X-rays (c/sec) excited with Pd K X-rays as a function of uranium content.

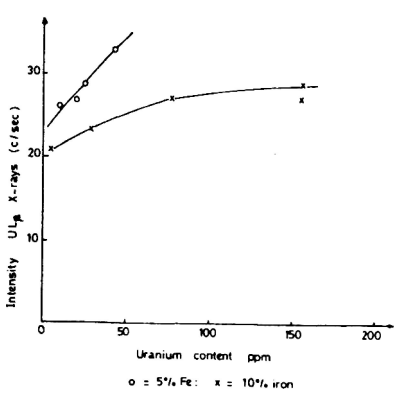

Fig. 2. Intensity U L_β X-rays (c/sec) excited with Pd K X-rays as a function of uranium content.

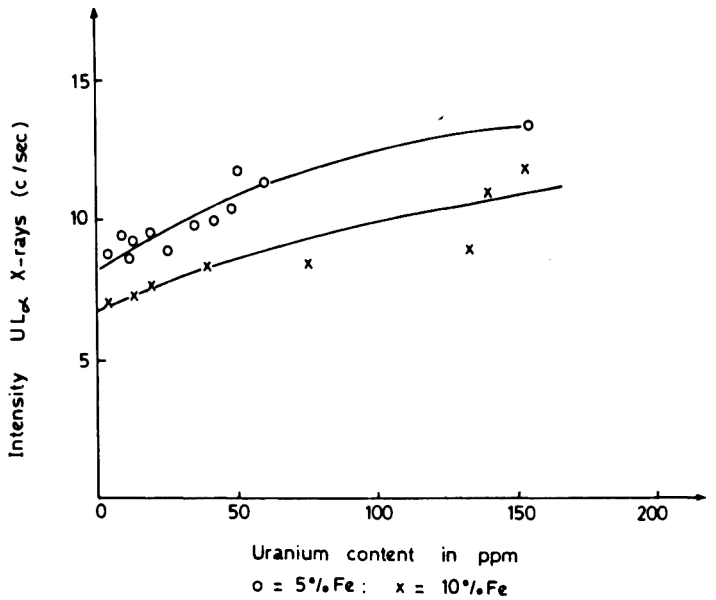

Fig. 3. Intensity U L_α X-rays c/sec excited with Mo K X-rays as a function of uranium content.

Fig. 4 gives the observed intensity of U L_α or U L_β for the selected number of Compton scattered incident X-rays and it is seen that straight line calibration graphs are obtained in each case. (The U L_α reading being adjusted as described above).

Table-1 shows the errors due to counting statistics (95% C.L.) for all three measurements. It is seen that both the U L_α determinations are approximately the same and are better than the U L_β determination. The reason that there is little or no advantage in using Mo K rather than Pd K X-rays to excite U L_α is mainly due to the fact that there is a corresponding increase in the number of unresolved Rb K_α X-rays appearing in the U L_α channel.

TABLE-1. Comparison of errors due to counting when determining the concentration of uranium.

Uranium Content (ppm)	Errors due to counting statistics (95% C.L) ppm*		
	Pd K**	Pd K***	Mo K**
20	10	14	9
100	11	16	10
200	14	17	11

* Measurement time varied from 200 - 350 seconds (clock time)
** Measuring U L_α
*** Measuring U L_β

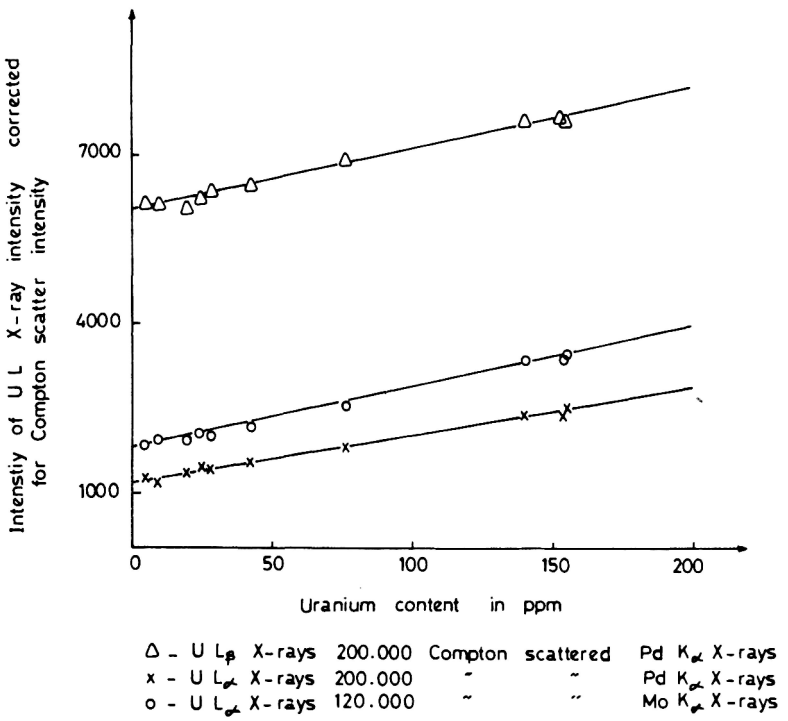

Fig. 4. Variations in the corrected intensity of U L X-rays as a function of uranium content for different energies of exciting radiation.

Table-2 gives the uranium content determined by neutron activation analysis and also the corresponding value determined by the X-ray fluorescence technique when exciting U L X-rays with Mo K X-rays. The error by regression analysis being ± 25 ppm of which up to 11 ppm is directly attributable to counting statistics.

The remaining error is probably mainly due to errors in the Rb K_α correction factor that was estimated from only a relatively small number of samples.

CONCLUSION

Using a low power X-ray tube producing quasi-monochromatic X-rays it is possible to use the intensity of Compton scattered incident X-rays to correct the measured characteristic U L X-rays for matrix absorption due to iron at concentrations varying from 5 to 22 per cent.

The error by regression analysis when using Mo K X-rays to excite U L_α X-rays in the same samples which contained up to 280 ppm uranium was ± 25 ppm of which up to 11 ppm was due to counting statistics. Corrections for variation in Rb K_α X-rays which were not completely resolved from U L_α by the Si(Li) detector were ne-

cessary.

The corresponding error when exciting U L_{β} X-rays with Pd K X-rays was up to 17 ppm in the same measurement time.

TABLE-2. Comparison of the analyses of the uranium content of the samples.

Sample Number	Uranium Content ppm	
	Neutron	XRF
1	42	28
2	277	284
3	155	150
4	35	20
5	4	8
6	19	20
7	28	20
8	60	44
9	39	30
10	13	12
11	50	64
12	11	24
13	48	35
14	140	58
15	23	25
16	14	8
17	154	139
18	4	18
19	133	150

REFERENCES

/1/ Clayton, C.G., Packer, T.W., Soc. Professional Well Log Analys. London (1974).
/2/ Link Systems Limited, XRF Division Technical Reports (1976).
/3/ Packer, T.W., Bilge, A.N., AERE, Harwell, Ind. Phys., NAQ/132/TWP/ANB(1976).
/4/ Clayton, C., Packer, T.W., "Int.Symp.Nucl.Techn.In Exp. Ext. and Proc. of Min. Resources", IAEA-SM-216/44 (1977).