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A COMPARISON OF PIXE AND NEUTRON ACTIVATION TECHNIQUES FOR THORIUM AND URANIUM ORE ANALYSIS

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ABSTRACT

Proton induced X-ray emission (PIXE) and neutron activation analysis (NAA) techniques are used to estimate the concentrations of trace quantities of thorium and uranium in powdered rock or ore samples. The accuracy of the two methods is compared in both a carbon matrix and a variety of ore matrices over the concentration range 1 to 10 000 μg g^{-1}. Under the test conditions the PIXE and NAA concentration estimates for any individual sample in this range are found to be the same within a 3σ standard error of 9 per cent.

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X-RAY EMISSION ANALYSIS; PROTONS; NEUTRON ACTIVATION ANALYSIS; COMPARATIVE EVALUATIONS; URANIUM ORES; TRACE AMOUNTS; DELAYED NEUTRON ANALYSIS; QUANTITATIVE CHEMICAL ANALYSIS; CHEMICAL COMPOSITION; THORIUM ORES

CONTENTS

1. INTRODUCTION

This report describes some nuclear analytical techniques available at Lucas Heights for trace uranium and thorium detection; proton induced X-ray emission (PIXE) [Cohen et al. 1978], delayed fission neutron analysis (DNA) and standard neutron activation analysis (NAA). At Lucas Heights, DNA has been in routine use for five years as a fully operational commercial service [Wall 1978] and the technique is well documented (e.g. review paper by Binney and Scherpelz 1978). Work on NAA for thorium continues to be reported in various applications [Steinnes 1976], although the methods are well known. The PIXE technique for thick ore samples is only a recent development at Lucas Heights and has not reached the stage at which a commercial service can be offered.

To verify the PIXE technique for thorium and uranium determination and to check the reliability of internally and externally prepared standards, a 3 MeV Van de Graaff accelerator and the UTR-100 reactor, Moata, were used to carry out the above analytical techniques on the same batch of samples. The comparison was simplified by restricting the analysis to the trace elements thorium and uranium in matrices of either siliceous ores or carbon, and employing a single neutron irradiation for subsequent DNA and NAA. Concentrations of thorium and uranium in these matrices were analysed over the range 1 to 10^4 μg g^{-1}.

The chief advantages of these techniques are that they are non-destructive and require minimal effort for target preparation with no chemical pre-treatment. Thorium and uranium concentrations can be obtained using PIXE after a few minutes' proton irradiation. While DNA gives the uranium concentration in a shorter time than PIXE, NAA for thorium analysis involves a delay of at least two weeks after irradiation before the gamma energy peak of interest, ^{233}Pa (312 keV) can be resolved from interfering activities. The mass of irradiated samples for DNA and NAA (up to 10 g) can be three orders of magnitude larger than the mass actually exposed to the proton beam by PIXE because of the large penetration difference of protons and neutrons in the ore matrix. This tends to make DNA and NAA more sensitive and accurate than PIXE in the 1 to 100 μg g^{-1} concentration range.

2. SAMPLE PREPARATION

Most samples were prepared for analysis from additions of known weights of thorium oxide and uranium oxide to a pure carbon matrix. These are called 'standards' in this report. In addition, some certified geochemical materials [Abbey et al. 1975; Flanagan 1973; Ingles et al. 1977], referred to as 'ores' in the text, were also prepared.

After thorough mixing, the powders were placed into pure (99.9 per cent) aluminium caps (13 mm diameter) and pelletised at 14 MPa for 60 s to an approximate thickness of 2 mm. The final pellets with their flat, well-defined front faces were convenient for mounting on the long target sticks for the PIXE measurements. The geometry of these samples was also ideal for NAA; however, their 2 mm thickness eliminated only first order corrections for neutron self-shielding and gamma self-absorption. Standard thorium/uranium and ore samples were prepared to cover the concentration range 1 to 10^4 μg g^{-1}. Depending on the matrix density the net sample masses were in the range 200 to 500 mg.

3. EXPERIMENTAL METHODS

A single batch of samples was analysed in the sequence PIXE-DNA-NAA, as described below.

3.1 PIXE

Thorium and uranium determination using PIXE has been reported in detail elsewhere [Cohen et al. 1979]. A schematic of the experimental arrangement is shown in Figure 1. A 3 MeV Van de Graaff accelerator was used to produce 2.26 MeV protons which interacted with the target to produce characteristic X-rays. The target chamber was insulated ($\geq$ 70 MΩ) from the rest of the experiment and used as a Faraday cup for charge collection and integration to give a measure of the total charge striking the target.

Up to 45 pelletised ore samples were placed on an aluminium target stick, 1 m long, which was moved through the incident proton beam by a computer-controlled stepping motor. A carbon filament for flooding insulated targets with electrons was attached to the top of the chamber. The standard samples were good thermal and electrical conductors, enabling currents as high as 500 nA to be used for an indefinite period. This was not the case for some ore samples. High current overheated the target, and charging effects (even with electron flooding) produced such high backgrounds in the X-ray spectra that the sensitivity was severely reduced. Under these conditions, the maximum target current possible was limited to approx. 350 nA. The target chamber was kept at a base pressure of 0.5 mPa. The bottom of the chamber had a 25 μm beryllium window with the detection system below.

Lower energy X-rays (< 10 keV) produced in the target were selectively absorbed by Perspex filters (6 mm thick) placed between the bottom of the chamber and the detector. The column of air (itself a filter for low energy X-rays) which lay between the chamber and the top of the detector was kept at a constant length of 3 cm; the distance from the front face of the detector to the target was 15 cm.

The detector, which was built at the Research Establishment, used an intrinsic hyper-pure n type silicon chip and had an active area of 5 mm^2 and depletion thickness of 5 mm [Beech and Eberhardt 1973]. The resolution full width at half maximum (FWHM) was 285 eV at 5.9 keV; this rose to 313 eV at the Th Lα X-ray (approx. 13 keV).

For this experiment, a 6 mm thick Perspex filter was used to absorb the lower energy X-ray continuum and the bulk of the characteristic X-rays of the matrix (Si, K, Ca, etc.). The measured efficiency of the detection system under these conditions was, relative to the no-filter situation, 34 per cent and 40 per cent for the thorium and uranium Lα peaks respectively.

3.2 Delayed Neutron Activation

When the PIXE irradiations had been completed, 42 samples were removed from the PIXE system and loaded into sample carriers for irradiation in the delayed neutron assay rig of Moata. Each sample was irradiated for 200 s in a thermal flux of 1.2×10^{12} neutrons cm^{-2} s^{-1} and counted for delayed neutron emission for 48 s. The uranium concentration in each sample was estimated by comparing the total count obtained, with that from calibrated pieces of natural uranium metal foil which had been irradiated and counted in a similar manner.

3.3 Neutron Activation Analysis

After the samples from the DNA irradiation had decayed for a period of 36 days, gamma spectra were obtained using a spectrometer with a 20 cm^3 Ge(Li) detector and 2048 or 4096 channel data sets. Each sample could be positioned and counted automatically for 10 min and a standard peak search program was used to obtain peak areas of the 311.9 keV ^{233}Pa gamma ray. The irradiation conditions were not optimal for thorium analysis by NAA but nevertheless they minimised experimental procedures.

4. RESULTS

4.1 X-ray Spectra

A typical PIXE spectrum for a 'standard' sample of 150 $\mu g\ g^{-1}$ of thorium and uranium is shown in Figure 2. Seven separate L lines were resolved for both thorium and uranium. Figure 3 is a typical spectrum for an 'ore' sample; the K series lines for strontium, yttrium and zirconium are mixed with the L series lines from lead, thorium and uranium. These spectra were background and peak fitted by the techniques described by Clayton et al. [1979], and the thorium/uranium Lα peak areas extracted and related to the nominal sample concentrations.

Figures 4 and 5 show the results for counts versus nominal concentrations for thorium and uranium, respectively. Good linearity over four decades of concentration (1 to 10^4 $\mu g\ g^{-1}$) was obtained for both the thorium and uranium results. The standards (X) and the ores (O), together with their least squares fitted lines, are shown separately on each graph. The lines of best fit have been adjusted to pass through the origin. The calibrated relationships are:

$$\left.\begin{array}{ll}\text{(i)} & \text{Thorium L}\alpha\text{ in carbon matrix,} \\ & \text{counts}/500\ \mu C = 14.8 \times \text{concentration } (\mu g\ g^{-1}) \\ \text{(ii)} & \text{Thorium L}\alpha\text{ in ore matrix,} \\ & \text{counts}/500\ \mu C = 16.4 \times \text{concentration } (\mu g\ g^{-1})\end{array}\right\}\ \begin{array}{l}\text{10\% difference} \\ \text{in yield}\end{array}$$

$$\left.\begin{array}{l}\text{(iii) Uranium L}\alpha\text{ in carbon matrix,}\\ \qquad \text{counts/500 }\mu\text{C} = 12.9 \text{ x concentration } (\mu\text{g g}^{-1})\\[1em] \text{(iv) Uranium L}\alpha\text{ in ore matrix,}\\ \qquad \text{counts/500 }\mu\text{C} = 14.2 \text{ x concentration } (\mu\text{g g}^{-1})\end{array}\right\}\begin{array}{l}\text{9\% difference}\\ \text{in yield}\end{array}$$

Next, the raw Lα count for each sample was fed back into relationships (i) to (iv) and the PIXE thorium or uranium concentration for that sample calculated.

The total error associated with the concentration estimates is a function of the concentration. For concentrations of approximately 10 μg g^{-1}, the statistical errors dominate, yielding a total relative error of ±30 per cent. At the 100 μg g^{-1} level, statistics are not so dominant and the total relative error is ± 10 per cent. With concentrations of 1000 μg g^{-1} or greater, experimental errors produced by the total charge reproducibility dominate and the total relative error is ± 5 per cent. All PIXE errors are quoted for the 3σ confidence level. The errors on the PIXE results quoted in Table 1 are the total of the statistical and the experimental errors for that result.

Curves of the type shown in Figures 4 and 5 show an experimentally measured lower detection limit of 3 to 4 μg g^{-1} per 100 μC for thorium and uranium analysis using PIXE. A 100 μC run at 350 nA lasted only 5 min. The longer 500 μC (24 min at 350 nA) runs were used to increase the accuracy of the lower limit estimates.

4.2 Delayed Neutron Analysis Results

The uranium analyses by DNA are shown in Table 1 compared with the nominal as-prepared values. The normal sensitivity of about 1 μg g^{-1} is obtained on a 10 g sample so the errors quoted in Table 1 reflect the unusually small mass of sample used, rather than the overall accuracy of the technique. The errors associated with this technique are predominantly statistical and are quoted for the 3σ confidence level.

4.3 Neutron Activation Analysis Results

The above results clearly show that some anomalies had occurred between uranium and thorium values as-'prepared' and as-'measured'. To obtain absolute thorium values from the NAA data, a linear least squares fit was found for the 'prepared' standard Th concentrations and the values of counts/unit mass for the ^{233}Pa peak corrected for decay, dead-time, and minor flux gradient effects. The result was an equation of the form:

$$T = (0.02324 \pm 0.0005)C + (1 \pm 4) \quad , \tag{1}$$

where T is the thorium concentration in $\mu g\ g^{-1}$ and C the ^{233}Pa peak count rate after the above corrections had been made. Statistical weights on the count rate data were taken as the inverse of the square root of the total count obtained. The line was not adjusted to pass through the origin.

The results for NAA thorium determinations are shown in Table 1. Again the statistical errors dominate and are quoted for the 3σ confidence level.

The use of the ^{233}Pa 312 keV energy as a thorium indicator for the NAA and a 36-day decay period ensured that interferences from other matrix elements at this gamma ray energy were negligible. The aluminium caps described in Section 2 were found to have a trace amount (0.3 $\mu g\ g^{-1}$) of thorium and this was taken into account in the final analysis.

5. COMPARISON OF METHODS

Table 1 summarises all results for PIXE, DNA and NAA compared with the nominal concentrations. The agreement in most cases is excellent and well within the errors quoted. Inaccuracies in some of the nominal concentrations of our prepared samples were verified by both PIXE and NAA techniques. For example, sample 7, nominally 250 $\mu g\ g^{-1}$ thorium, was measured by PIXE to be 408 ± 30 $\mu g\ g^{-1}$ and NAA 400 ± 50 $\mu g\ g^{-1}$. Similar results were obtained for samples 12, 20 and 42. Figure 6 is a plot of PIXE versus DNA and NAA results and is a graphical display of Table 1. The errors in the plot are the total (statistical and experimental) errors for the PIXE results and the 3σ statistical errors for the DNA and the NAA results. The mean of the ratio of PIXE to the neutron activation results for the whole of Table 2 is 1.01, with a standard deviation of 18 per cent. For any individual sample, the PIXE and NAA estimates are the same, within a 3σ standard error of 9 per cent.

The bulk of the discrepancies in Table 1 occur with the PIXE measurements. This technique is very sensitive to sample homogeneity and particle size and is a 'surface only' analysis. The proton range in most samples is only approx. 50 μm for a 2 mm diameter beam, implying that there were only approx. 20 one-micron radius particles of thorium and uranium in the irradiated volume of a 10 μg g^{-1} silicon matrix sample. This demonstrates the severe statistical limitations that the particle size and sample homogeneity can produce for small trace element concentrations. NAA does not suffer from this effect because a sample mass larger by three orders of magnitude is irradiated.

The problem of adjacent peak interferences [Cohen et al. 1979] can also be serious for PIXE ore analysis. Rubidium and strontium commonly occur in rock samples and their Kα lines interfere with the thorium and uranium Lα lines. This increases the uncertainty in the thorium and uranium concentration estimates. When rubidium and strontium are present with concentrations greater than 10 to 15 times the thorium or uranium concentrations, then the Lα peaks are completely obscured and other L series lines for thorium or uranium have to be used to obtain a concentration estimate.

Although a few interferences were detected using NAA for the thorium analyses in the samples described above, it is well known that the NAA method has its limitations, especially for ores with high Co, Sc, Cr and Hf concentrations. The low irradiation dose of 2.4×10^{14} neutrons cm^{-2} for the DNA and subsequent NAA analysis was the result of using the AAEC's commercial DNA rig which is optimised for uranium analysis [Wall 1978]. An alternative rig, in which 40 samples for thermal NAA (or 20 samples for epicadmium NAA), can be simultaneously irradiated for a total dose of 3×10^{16} neutrons cm^{-2}, has been tested using Moata [Wall 1980]. Several ores with the NAA interferences mentioned above have been encountered. A sensitivity of (1 ± 0.2) μg g^{-1} thorium could be obtained in interference free cases.

6. CONCLUSION

The present work has demonstrated the viability of the three techniques PIXE, NAA and DNA, and has shown that there is no systematic error in any of the methods over the range of thorium and uranium concentrations, 1 to 10^4 µg g^{-1}. The thorium and uranium concentration estimates by PIXE and NAA gave the same value within a 3σ standard error of 9 per cent.

7. ACKNOWLEDGEMENTS

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TABLE 1

VALUES FOR THORIUM AND URANIUM ANALYSIS ($\mu g\ g^{-1}$)

BY PROTON INDUCED X-RAY AND NEUTRON ACTIVATION

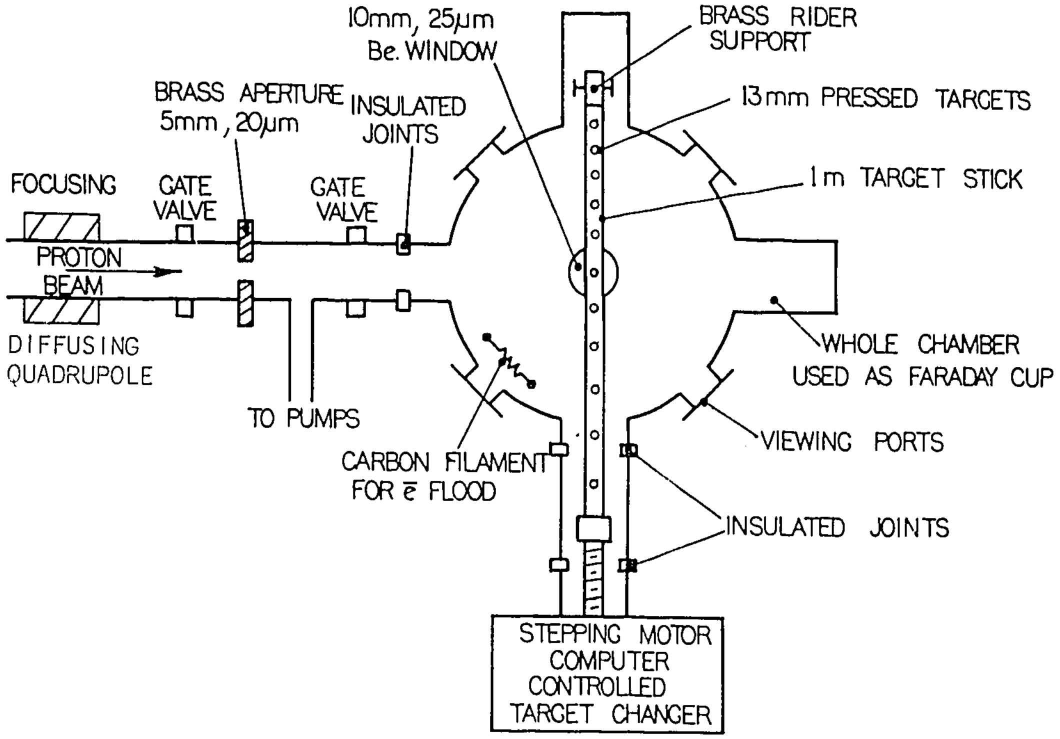
Sample	Matrix	Nominal Th	PIXE Th	NAA Th	Nominal U	PIXE U	DNA U
1	C	10	13±4	-			
2	C	25	*	25±24			
3	C	100	*	97±36			
4	C	50	*	51±24			
5	C	75	72±8	61±30			
6	C	150	207±21	173±33			
7	C	250	408±30	400±50			
8	C				10	12±3	10.2±0.6
9	C				25	25±6	31±6
10	C				50	43±6	47±6
11	C				75	82±10	66±6
12	C				100	75±8	79±6
13	C				150	121±11	135±9
14	C				250	248±15	229±9
15	C	447	409±30	464±60			
16	C	809	804±40	806±70			
17	C				431	276±16	407±15
18	C				492	698±42	716±30
19	C				998	888±44	996±30
20	C	25	30±8	28±21	25	35±6	38±6

TABLE 1 (cont'd)

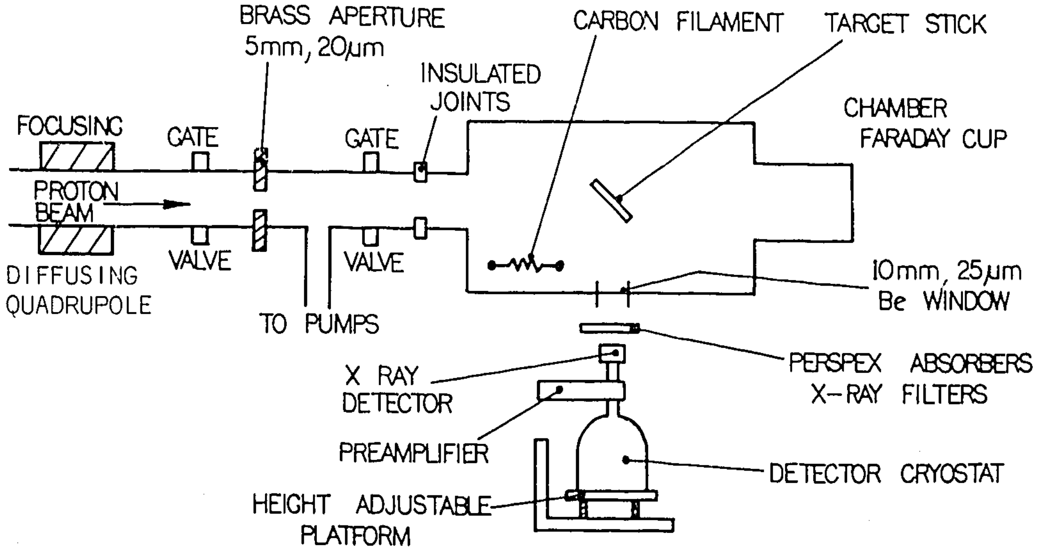
Sample	Matrix	Nominal Th	PIXE Th	NAA Th	Nominal U	PIXE U	DNA U
21	C	75	92±9	93±33	75	111±11	108±6
22	C	150	209±21	147±42	150	235±15	181±12
23	C	1833	1841±55	1832±110			
24	C	2207	2282±68	2186±120			
25	C	7.8	8±2	-	4.3	3±1	5.3±1.2
26	C	104	99±10	109±36	174	201±16	184±9
27	C	1.4	-	-	169	272±18	174±6
28	C	1.6	-	-	450	419±30	465±12
29	DL-1(1)	83	56±7	93±30	41	43±8	43±6
30	DL-1(2)	83	67±8	68±27	41	47±8	41±6
31	BL-4	13.6	22±5	-	1730	1718±80	1767±150
32	DH-1	1043	1246±60	1052±31	1770	1817±80	1784±150
33	BL-2	16	19±6	-	4530	4511±150	4648±120
34	SY-2	370	404±30	381±48	290	281±18	298±18
35	GSP-1	104	98±10	95±12	2.0	-	3.2±1.5
36	C	3928	3739±113	3938±160			
37	C				1680	1248±60	1224±36
38	C				3584	3323±100	3400±90

Errors are quoted for the 3σ confidence level throughout this table.

Key : * Not analysed using this technique. - Not detected by this technique.



PIXE CHAMBER TOP VIEW



PIXE CHAMBER SIDE VIEW

FIGURE 1. EXPERIMENTAL ARRANGEMENT - SCHEMATIC

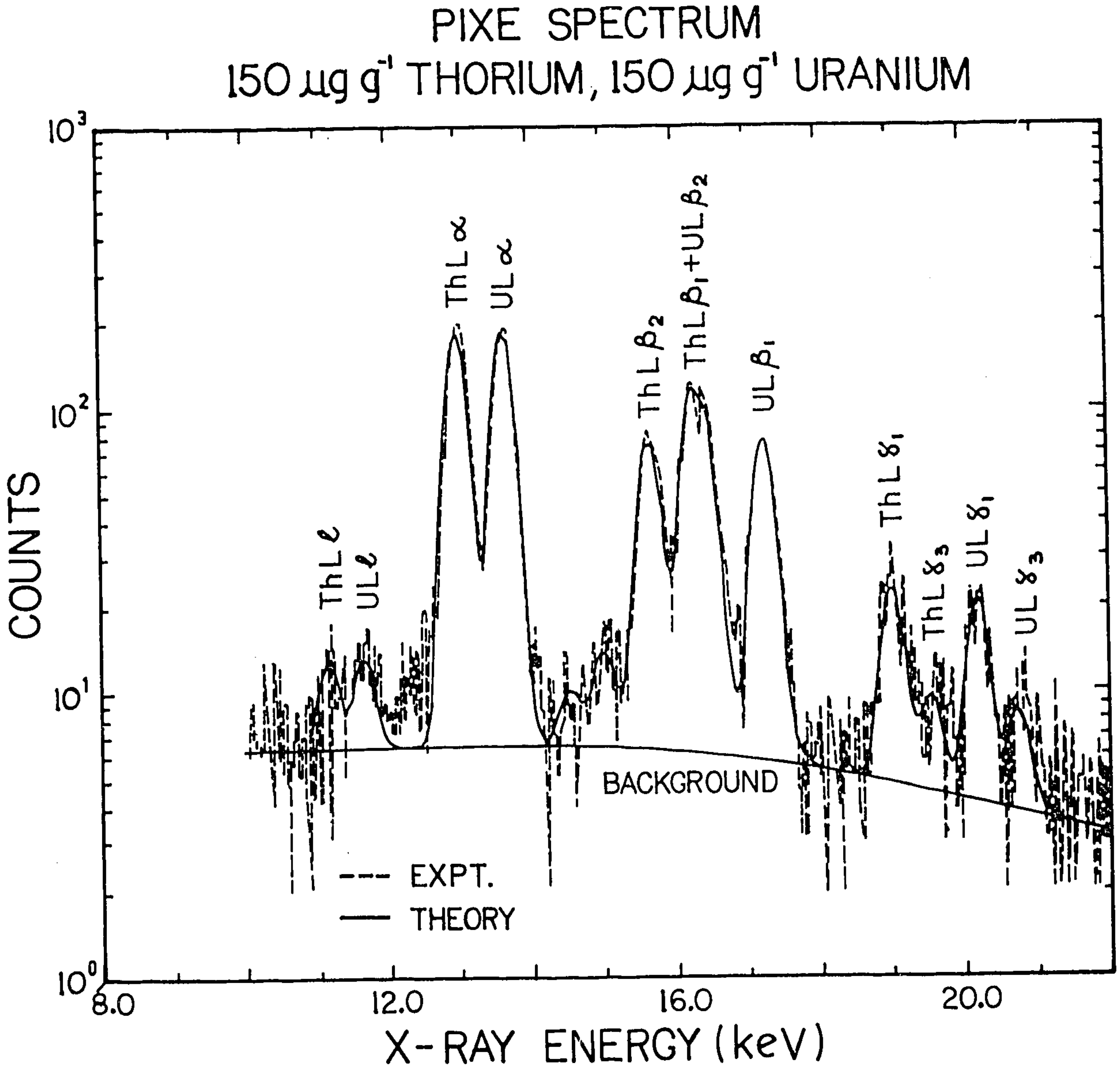


FIGURE 2. PIXE SPECTRUM FOR 'STANDARD' SAMPLE #22

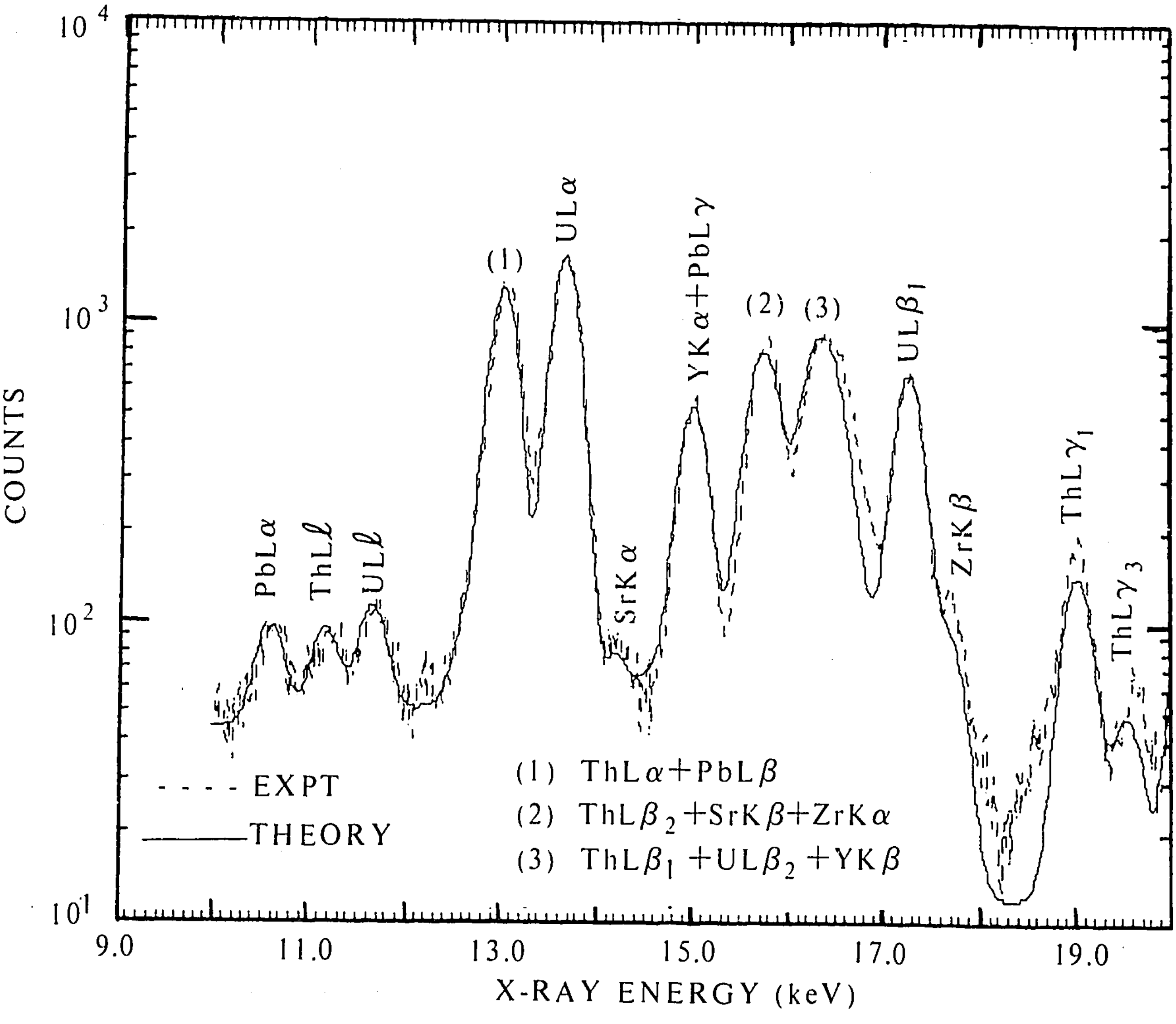


FIGURE 3. EXPERIMENTAL AND CALCULATED PIXE SPECTRA FOR DH-1 ORE

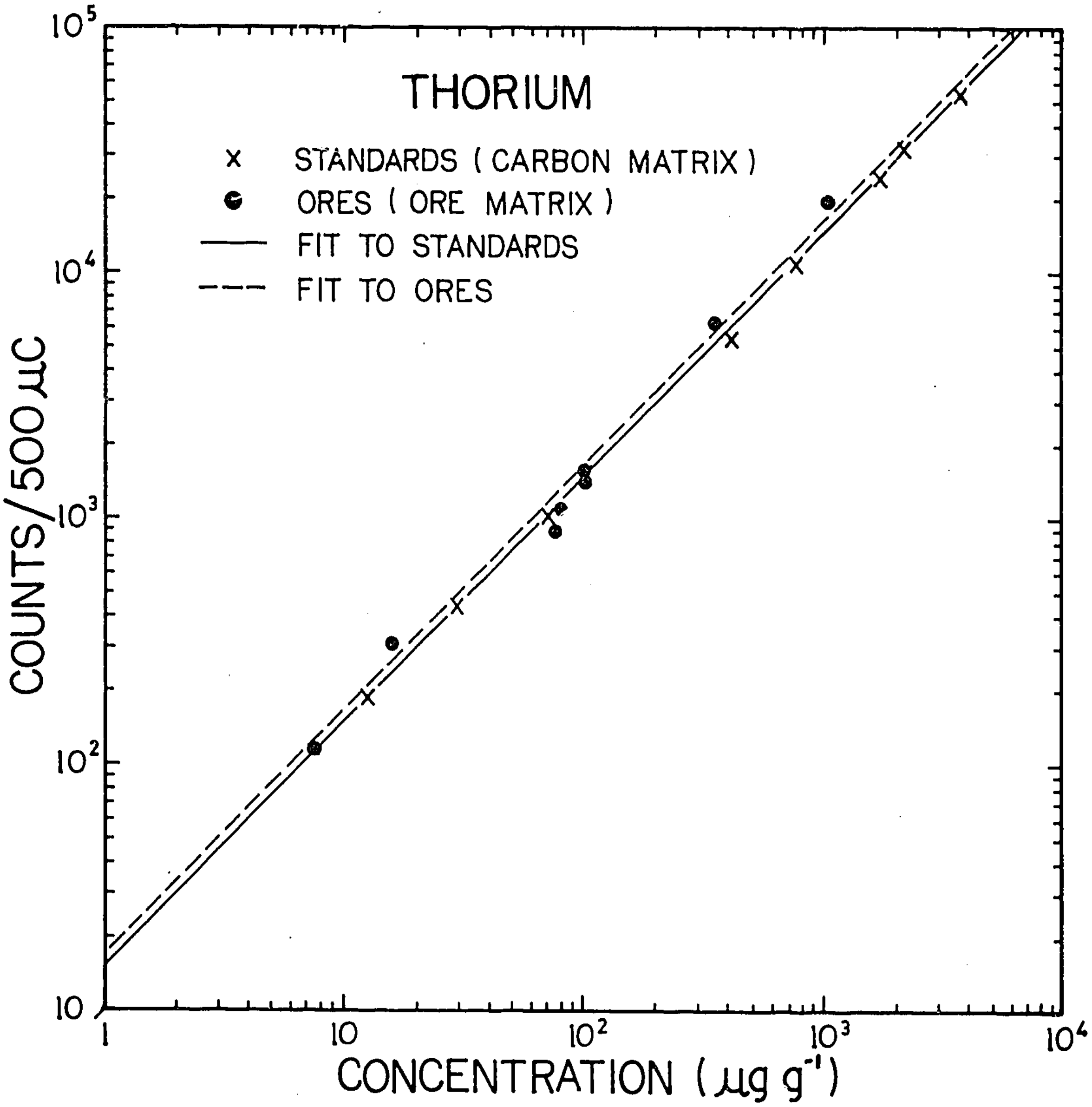


FIGURE 4. X-RAY PEAK COUNTS v. Th CONCENTRATION

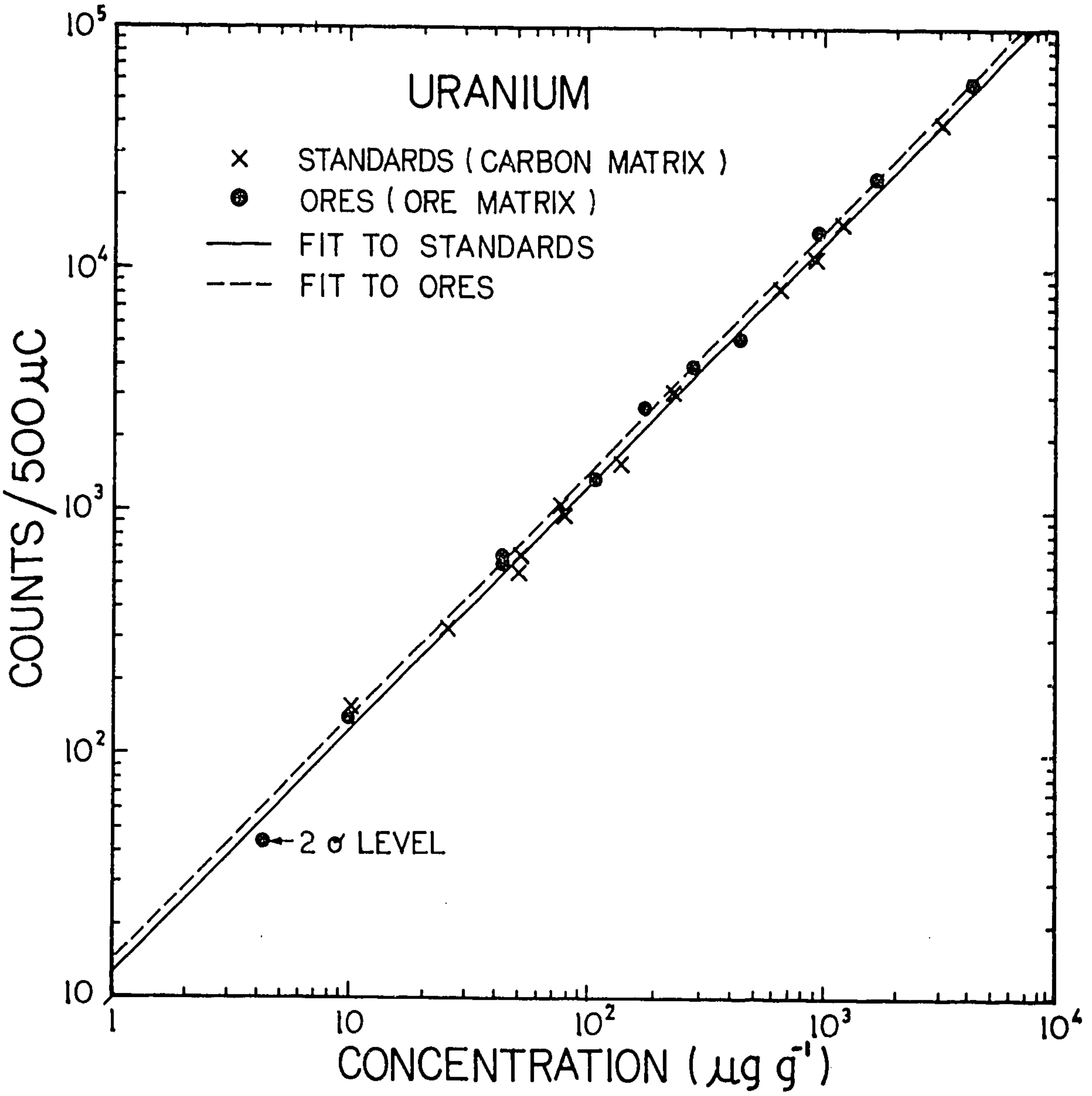


FIGURE 5. X-RAY PEAK COUNTS v. U CONCENTRATION

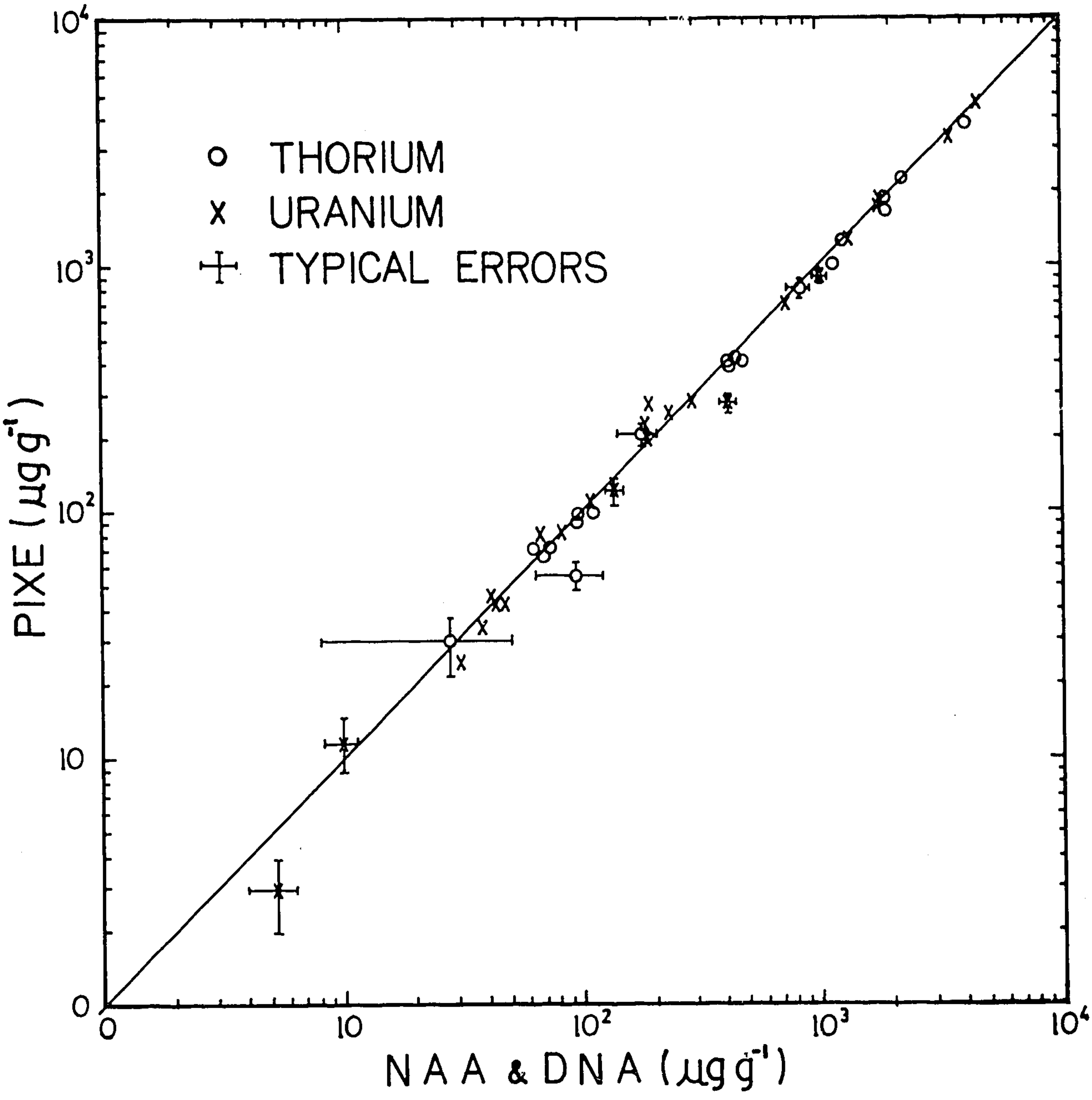


FIGURE 6. COMPARISON OF PIXE AND NEUTRON ACTIVATION

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