URANIUM ANALYSIS BY NEUTRON ACTIVATION DELAYED NEUTRON COUNTING

by

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Uranium analysis by neutron activation/delayed neutron counting has been examined extensively by Echo and Turk[1] (1957) Amiel[2] (1962), Dyer, Emery and Leddicotte[3] (1962) and Gale[4] (1967). Delayed neutron counting has been used by many groups in analyzing the uranium content of lunar samples[5], meteorites[6,7] and geochemical materials[8,9] It has clearly been established as a rapid, precise, relatively accurate, low cost, high volume method of uranium analysis and hence is particularly applicable to geochemical assay of all types of samples - waters, soils, lake and stream sediments, rocks and ores.

As an alytical technique it is not subject to matrix effects, has few interferences, can be automated, is non-destructive and does not require highly skilled personnel. Its only major drawback is that it does require access to a reactor facility.

With the increased emphasis currently being placed on uranium exploration, Atomic Energy of Canada Ltd., Commercial Products, became interested in this technique as it represented an extension of existing neutron activation analysis capability based upon the Slowpoke reactor. The system developed and currently employed by Commercial Products has a sensitivity of 205 ± 4 counts per µg of natural uranium with a limit of detection of 0.1 µg uranium i.e. 0.1 ppm for a 1g sample.

Apart from a number of short-lived light nuclides, fission is the only nuclear reaction which produces nuclides emitting delayed neutrons. The number of delayed neutrons emitted following irradiation is a linear function of the amount of fissile material present in the sample. Because neutrons can be detected and selectively counted, the technique is highly specific for fissile material irrespective of the nature of the sample. The only naturally occurring fissile nuclides are U^{235}, U^{238} and Th^{232}. However, as only U^{235} is fissioned by thermal neutrons, neutron activation/delayed neutron counting is specific for the determination of U^{235} or in fact, uranium, assuming of course the normal isotopic abundance of 0.72% U^{235} in natural uránium.

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The technique of neutron activation/delayed neutron counting involves irradiating an unknown sample for a given period of time, transferring the sample to a counting facility and after some suitable delay period, counting the sample for a given length of time. By comparing the delayed neutron count to that obtained from a standard or reference material, the uranium content of the unknown can be determined.

By applying standard radioactivation equations the optimum irradiation parameters can be theoretically determined[2/3]. With an operating flux of 1×10^{12} n cm^{-2} sec^{-1} and 60/10/60 sec irradiation history, 40% of the total available delayed neutrons can be counted.

A block diagram of the delayed neutron counting system and electronic circuitry is shown in Figure 1. Up to 50 samples may be stacked into the rabbit loader at one time. The rabbit dimensions are 1.9 inches inside height by 0.54 inches inside diameter. Samples are pneumatically transferred to the reactor and back to a counting facility which consists of six BF_3 detector tubes embedded in paraffin. After counting, samples are ejected to a shielded storage container. The system is controlled by 5 timers - the irradiation timer, a cycle timer, a delay timer, a counter timer and a sample eject timer. The BF_3 counters are connected in parallel and operated from a common high voltage power supply. The neutron signal is taken through a preamp, amp, SCA to a dual counter timer and a hard copy produced on a printer.

The various components of the actual system are shown in Figure 2. The system was calibrated using three IAEA reference low grade uranium ores. Varying amounts of each reference sample were analyzed, each result being the average of at least five measurements. The calibration curve is shown in Figure 3. From the curve the sensitivity is 205 ± 4 counts per µg of natural uranium. A blank background determination consisting of an empty rabbit irradiated under the same conditions produces 27 ± 5 counts.

The rather high sensitivity of the technique can be attributed to the following factors:

1. The large U^{235} thermal neutron fission cross section of 577 barns.

2. Delayed neutrons are produced in 1.58% of the U^{235} fissions caused by thermal neutrons[10].

3. The short half-lives of the delayed neutron precursors, <55 sec, allows a definite fraction of the delayed neutrons to be counted[10].

4. Counting efficiencies of better than 10% can be achieved.

5. Thermal neutron fluxes of 1 x 10^{12}n cm^{-2} sec^{-1} or greater are readily available.

6. Interfering reactions are not of significant importance.

In general the accuracy and precision of this technique are dominated by the statistics of radioactive counting, particularly at low uranium levels - below 5 µg. From Table 1 which contains results for internal standards and samples that have been analyzed a number of times it can be seen that the limit of precision is slightly greater than ±1%. In all cases the experimental precision closely approximated the theoretical standard deviation calculated from the statistics of radioactive counting.

Some of the factors affecting the precision of the delayed neutron counting method of uranium analysis are as follows:

1. The reproducibility of the sample position in the reactor and the stability of the neutron flux to which the sample is exposed. Neither of these factors pose a problem with the Slowpoke Reactor.

2. The vertical thermal flux variation over one capsule length is ±2.6% from the average[11]. This represents a source of error for samples of varying volume.

3. Errors due to variations in the irradiation time, delay time and counting time can be estimated. A variance of ±1 sec in the irradiation time introduces an error of less than ±1%. A variance of ±0.1 sec in the delay time introduces an error of ±0.5% and a similar variance in the counting time produces a negible error in the net signal.

4. Coincidence counting losses become significant when the net signal exceeds 350K counts as shown in Figure 4. This effect can be eliminated by irradiating at a lower power, by using a smaller sample or corrected for from the curve. In fact Figure 4 represents a calibration curve for the range 0.1µg to 5 mg of natural uranium.

5. Weighing errors are at most a few tenths of one percent.

As mentioned previously the method is subject to very few interferences when used to analyze natural materials[2,3,4]. As in most reactors, Slowpoke contains a significant fast neutron flux, (approximately 3 x 10^{11}n cm^{-2} sec^{-1}@ 20 kW for neutrons >1 MeV) which can cause fission of Th^{232} producing similar delayed neutron emitting products to U^{235} [10]. However, the sensitivity for thorium using Slowpoke is only 2.4±0.1 counts per µg or approximately 1% of the sensitivity for uranium. The

lower sensitivity is due to a much smaller fast neutron fission cross section and a lower fast neutron flux.

Some light nuclides also decay by neutron emission. These are Li^9 produced by Be^9 (n,p) Li^9 and N^{17} produced primarily by O^{17} (n,p)N^{17} . With a half-life of 0.17 sec and a 10 sec delay period, Li^9 will not cause any interference. However, N^{17} has a 4.17 sec half-life and could pose a problem. It can be shown theoretically that for an aqueous sample of 1 ml, the N^{17} formed by this reaction would be too small to measure. This was confirmed experimentally. The oxygen content of rock or sediment samples therefore should not create any interference.

Pulse build-up effects due to gamma activity is probably the most important source of interference in the analysis of geochemical samples. The counting system is electronically biased to reject up to 15 mCi of gamma activity from Al (Figure 5). This level of activity is produced from 450 mg of aluminum under normal irradiation conditions. Aluminum-28 represents the most severe gamma interference to be found in typical geochemical samples.

Certain other nuclides such as B^{10}, Li^6, Cd^{113}, and Gd^{157} which have very large thermal neutron capture cross sections could cause interference due to severe flux depressions. This effect was in fact measured by Amiel[2] and Gale[4] both of whom found an interference of about 4% per 10mg B and 1.5% per 10m of Li. The same authors found no self-shielding effects for uranium and thorium up to 500mg and 100mg respectively. In any event such effects could be minimized or eliminated by taking smaller samples.

Cost and sample turnaround time are always important factors in routine analysis. The price depends on the number of samples submitted and generally is in the range of $2.50 to $5.00 per sample. Sample turnaround time is limited by the system capacity. With our current operating regime the present maximum is 200-250 samples per day. To date over 8000 samples have been analyzed since mid July.

So in summary, the advantages of this technique in analyzing geochemical samples are its reliability, speed of throughput, lack of interference and low cost.

We are currently examining the possibility of extending this technique to water samples with a better sensitivity, to larger drill core samples, to thorium analysis and possibly to U^{235}/U^{238} isotopic ratio determinations.

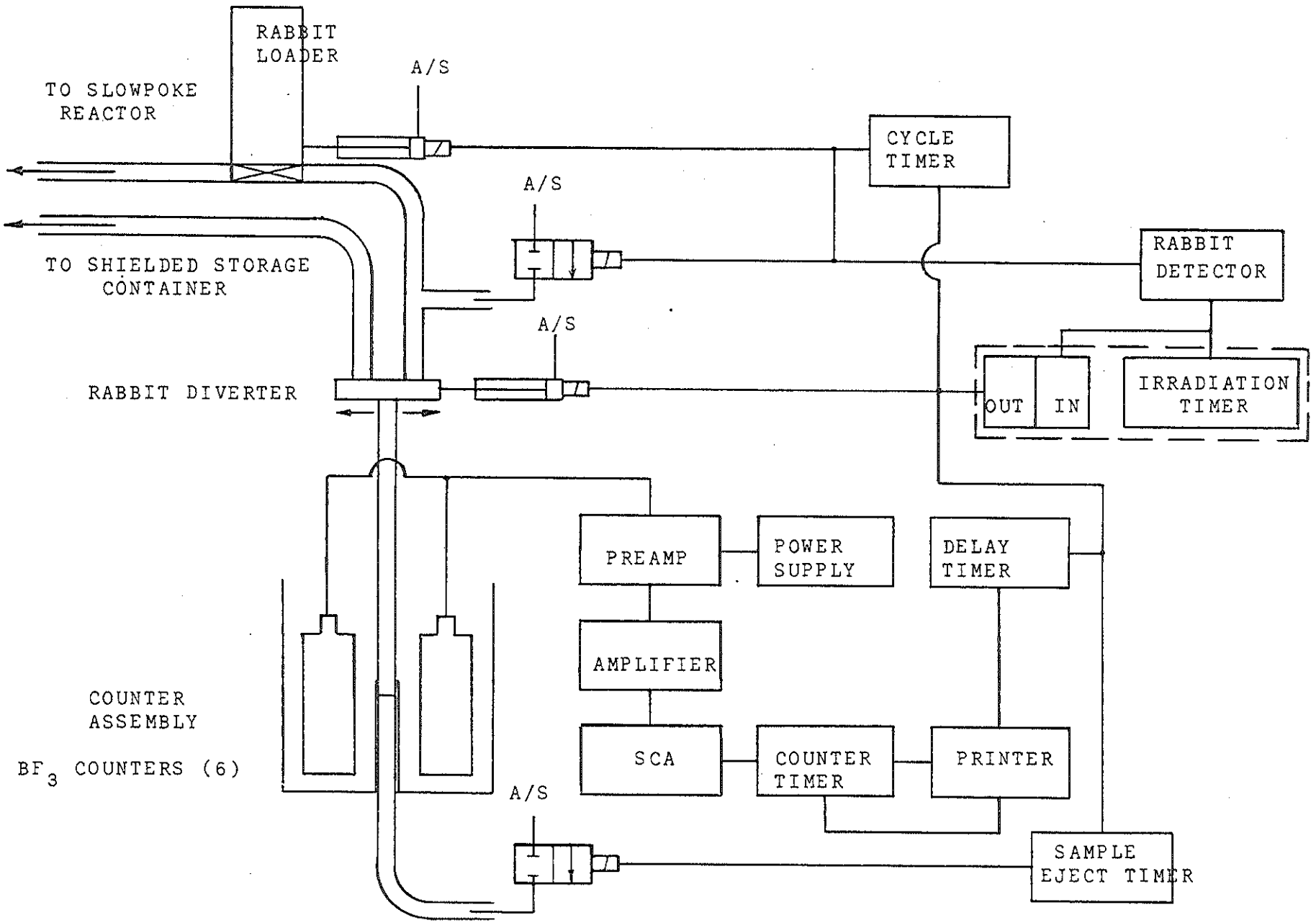
TABLE 1

TABLE 1

ERROR ESTIMATES FOR URANIUM ASSAY

Sample Designation	# Times Analyzed	Mean Total Signal	Standard Deviation	% Standard Deviation	Theoretical Standard Deviation	(µg) Uranium
Woden 11	19	154	12	7.8	12	0.6
Sample # 4	20	373	24	6.4	19	1.7
Sample # 44	20	511	27	5.3	23	2.4
Sample # 24	20	816	28	3.4	29	3.8
Sample # 29	20	1182	42	3.6	34	5.6
BL3-5	11	355	23	6.5	19	1.6
DGH-1-1	21	973	27	2.8	31	4.6
DGH-1-2	20	3671	63	1.7	61	18
BL3-6	18	7105	86	1.2	84	35
BL3-9	18	20310	226	1.1	143	99

FIGURE 1



NEUTRON COUNTING ASSEMBLY AND BLOCK DIAGRAM

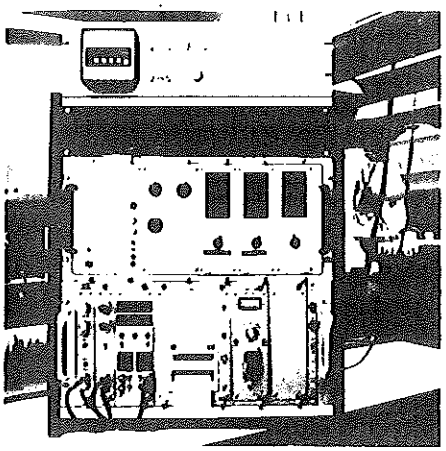


FIGURE 2.1
ELECTRONIC COMPONENTS

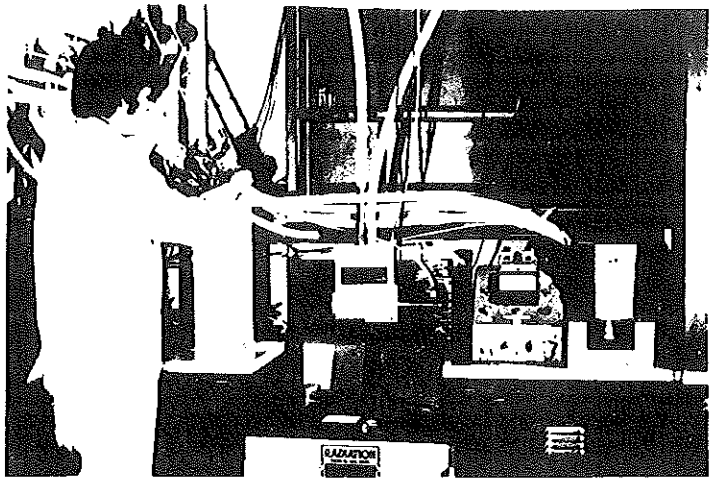


FIGURE 2.2
SAMPLE LOADER
AND PNEUMATIC TRANSFER LINES

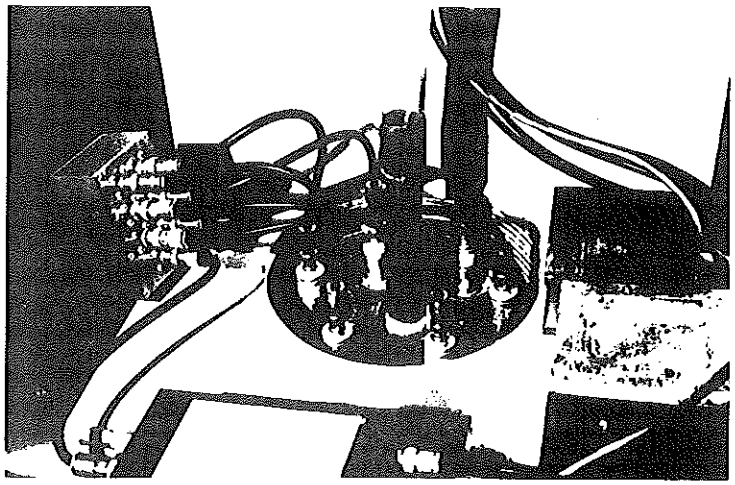


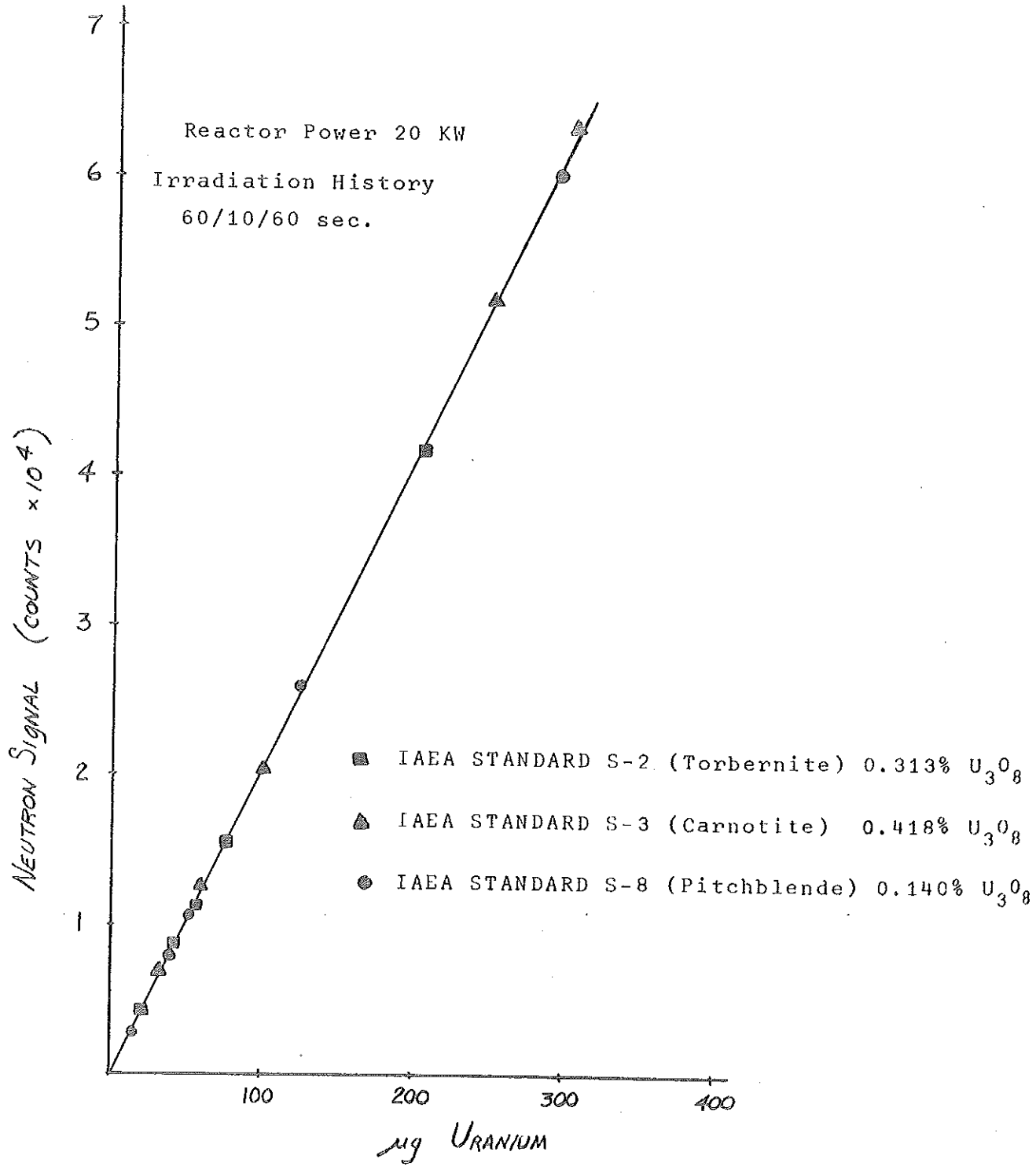
FIGURE 2.3

BF_3 TUBES IN THE COUNTING FACILITY

DELAYED NEUTRON COUNTING SYSTEM

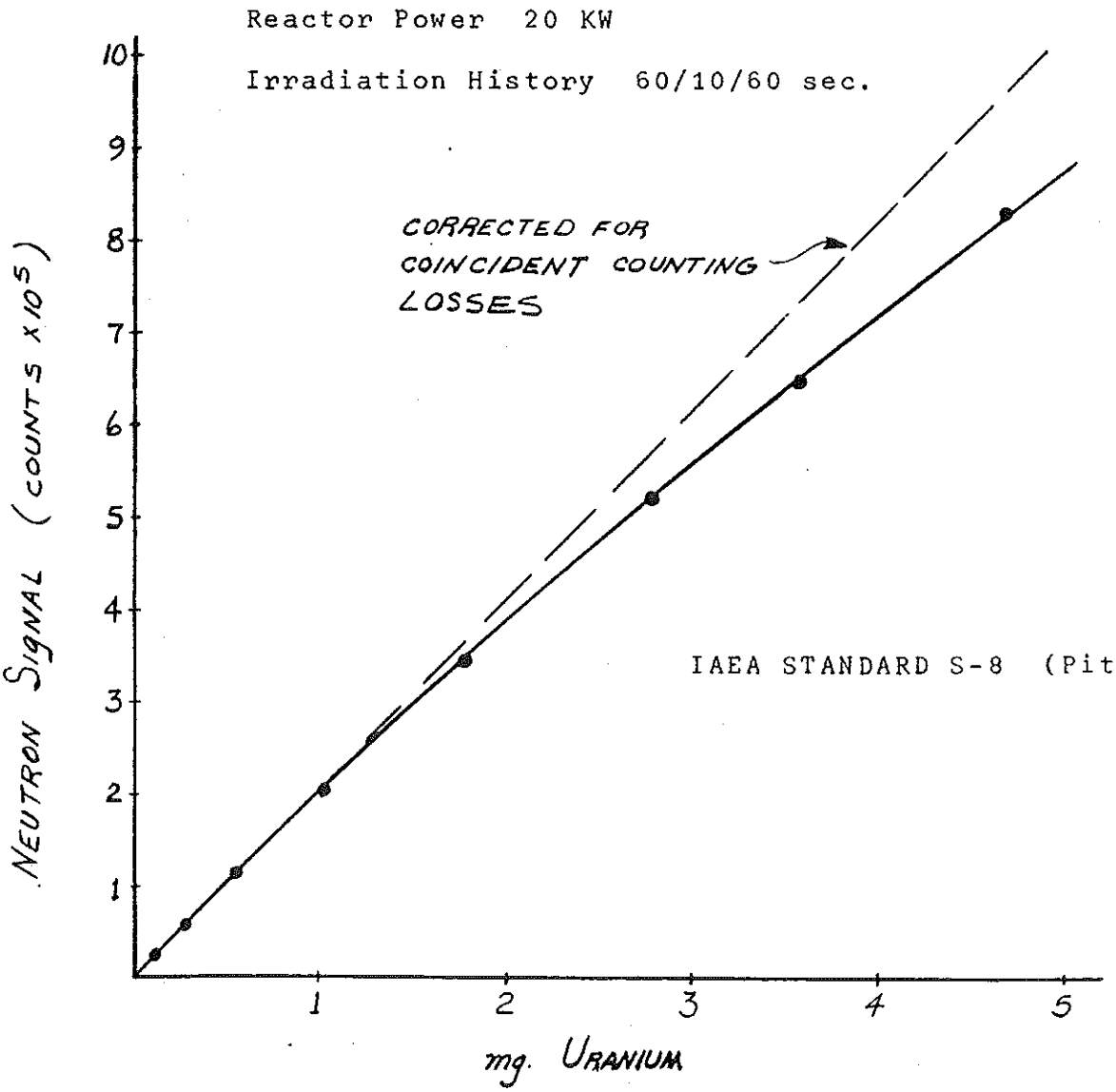
FIGURE 2

FIGURE 3



CALIBRATION CURVE FOR URANIUM

FIGURE 4



U_3O_8

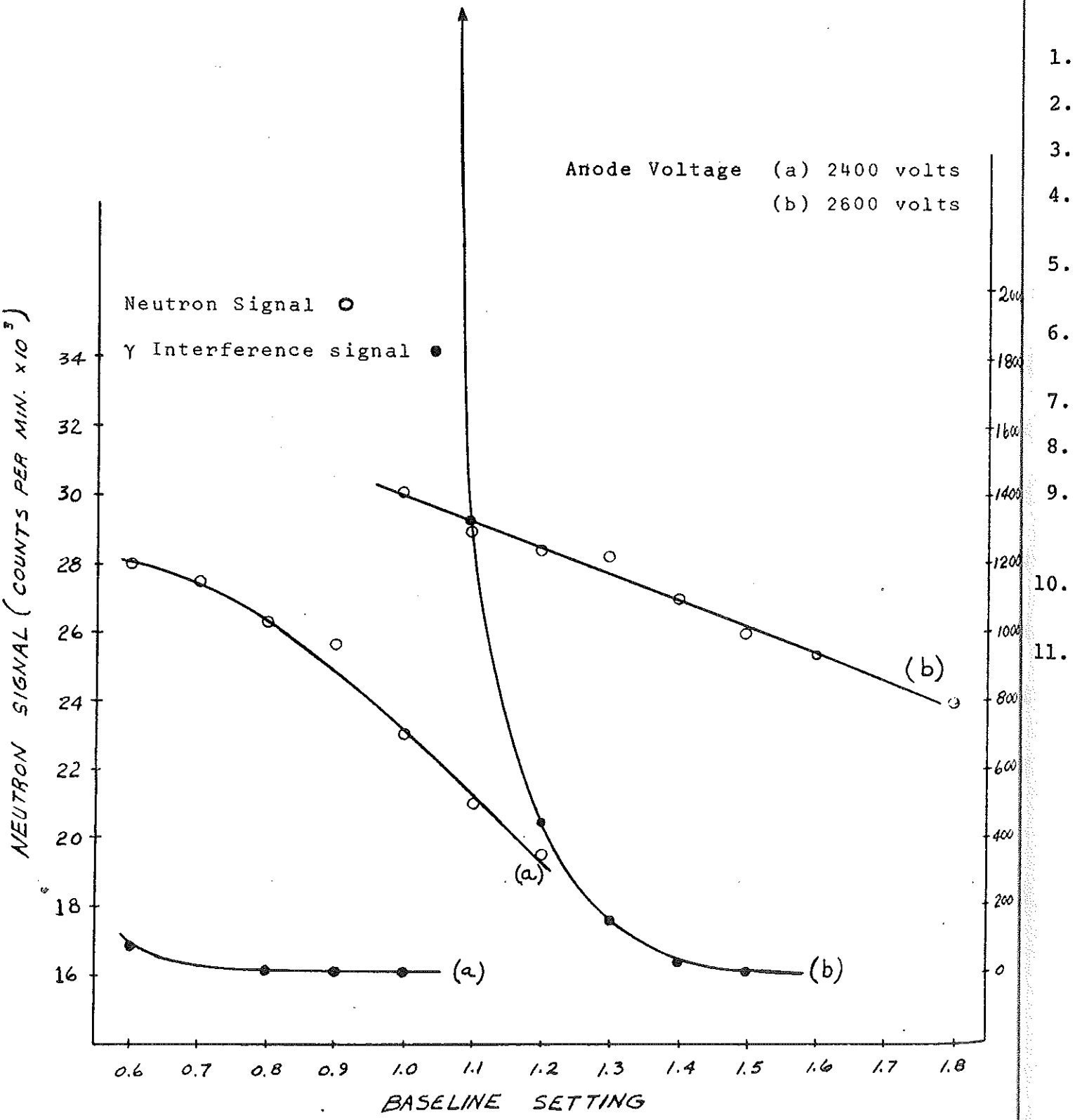
U_3O_8

U_3O_8

CALIBRATION CURVE FOR URANIUM OVER THE RANGE

0.1μg to 5mg of URANIUM

FIGURE 5



DETERMINATION OF γ INTERFERENCE THRESHOLD

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