ORNL-3342
UC-4 – Chemistry
TID-4500 (17th ed., Rev.)

A COMPREHENSIVE STUDY OF THE NEUTRON ACTIVATION ANALYSIS OF URANIUM BY DELAYED-NEUTRON COUNTING

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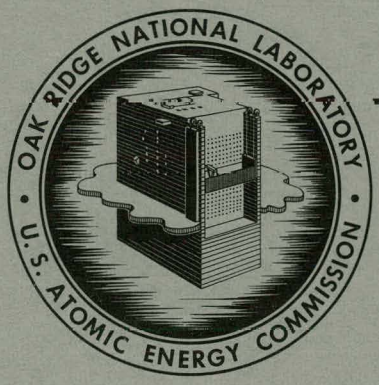

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DATE ISSUED

OCT 16 1962

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0.0. Abstract

The method of neutron activation analysis of uranium by delayed-neutron counting has been investigated in order to ascertain if the method would be suitable for routine application to such analyses. It has been shown that the method can be used extensively and routinely for the determination of uranium. Emphasis has been placed on the determination of uranium in the types of sample materials encountered in nuclear technology. Determinations of uranium have been made on such materials as ores, granite, sea sediments, biological tissue, graphite, and metal alloys.

The method is based upon the fact that delayed neutrons are emitted from fission products produced by the interaction of neutrons with U^{235}. Since the U^{235} component of uranium undergoes most of the fissions when a sample is in a neutron flux, the method is predominately one for the determination of U^{235}. The total uranium in a sample or the isotopic composition of the uranium in a sample can be determined provided one has a prior knowledge of one of these quantities. The U^{235} content of a test sample is obtained by comparing its delayed-neutron count to that obtained with a comparator sample containing a known quantity of U^{235}. Calculations are made according to the equation:

$$U^{235}_{\text{Sample}} \text{ in Test} = U^{235}_{\text{Sample}} \text{ in Comparator} \frac{\text{Net Count of Test Sample}}{\text{Net Count of Comparator Sample}}.$$

Neutron activations were made in the pneumatic tube irradiation facility of the Oak Ridge Research Reactor. A thermal neutron flux of about 6×10^{13} $n/cm^2/sec$ is obtained in this facility with the reactor

operating at 30 M.W. A neutron moderator (paraffin) and BF_3 tube detector assembly having a neutron counting efficiency of about 5 per cent was used to assay the delayed-neutron activity of the samples. Under these conditions and with the proper choice of irradiation and counting times, a sensitivity of 1000 counts per 10^{-9} grams of U^{235} is obtained. The method can readily be used to analyze samples containing 10 to 10^{-3} micrograms of U^{235}. The lower limit of analysis is determined by the sensitivity of the method whereas the upper limit is imposed by radiation safety requirements.

The precision of the method has been found to be normally about $\pm$ 3.0 per cent expressed as relative standard deviation. With proper precautions in making the irradiations, somewhat more precise determinations can be made.

1.0. Introduction

A number of analytical methods exist for the quantitative determination of microgram and submicrogram quantities of uranium. Gindler[1] lists eleven methods and reports on the range of quantity of uranium in micrograms for which each method is applicable. These methods and the lower limits of analysis are listed in Table I. For the determination of small quantities of uranium in a variety of matrix materials, almost all methods require a considerable amount of time for completion and/or suffer from extensive interferences so that chemical separations of the uranium must be made before its determination. Many of the methods reported in the literature lack the necessary sensitivity for the determination of submicrogram amounts of uranium.

The method of neutron activation with subsequent assay of the induced radionuclides makes possible the determination of very small quantities of uranium. Usually the analysis is carried out by gamma-ray counting one or more of the fission products of U^{235} or the gamma-ray counting of U^{239} (or its daughter Np^{239}) formed by neutron capture of U^{238}. A sensitivity of about 10^{-4} micrograms of U^{238} can be obtained by this method with short irradiations (about 20 minutes) in a neutron flux of 6×10^{13} $n/cm^2/sec$ if the short-lived product U^{239} ($t_{1/2}$ = 23 min.) is counted. Longer irradiations are required if the same sensitivity is desired and if the radioactivity of the daughter product Np^{239} ($t_{1/2}$ = 2.3 d) is assayed. If the Ba^{140} ($t_{1/2}$ = 12.8 d) fission product of U^{235} is isolated and its radioactivity is assayed, an irradiation time of one week or more (in a

TABLE I

SENSITIVITY OF VARIOUS METHODS
FOR THE DETERMINATION OF URANIUM

Method	Lower Analysis Limit (micrograms)
Neutron Activation	10^{-4}
Fluoroscopy	10^{-4}
Emission Spectroscopy	5×10^{-2}
Visual Chromatography on Paper	10^{-1}
Volumetric (including micro-volumetric) Methods	1
Autoradiography (α emission) Counting of Tracks	1
Colorimetry	10^{b}
Alpha Counting	50
Polarography	10^{2}
Potentiometry	2×10^{2}
Gravimetric Methods	5×10^{4}

[a] Taken from J. E. Gindler,[1] Radiochemistry of Uranium, Natl. Acad. Sci. - Natl. Research Council - Nuclear Sci. Ser. NAS-NS-3050 (1962).

[b] Lower limit obtained with dibenzoylmethane as the colorimetric reagent. Gindler[1] also lists values for thiocyanate and H_2O_2-$HClO_4$.

neutron flux of 6 x 10^{13} n/cm^2/sec) is required to approach a sensitivity of 10^{-4} micrograms for natural uranium. Analyses by neutron activation of both U^{235} and U^{238} have been used extensively and reported by a number of groups.(2-5) In most cases, however, neutron activation of elements in the matrix containing the uranium make necessary radiochemical separations before the radionuclides produced from the uranium can be assayed. Such separations make the usual neutron activation method for uranium laborious and time consuming.

An alternate approach to the neutron activation analysis of uranium is to count the delayed neutrons emitted by the fission products of U-235. Echo and Turk(6) first described the application of this technique to the determination of U^{235}. By a systematic irradiation and counting procedure, they made determinations of U^{235} in a number of liquid samples containing known quantities of U^{235} which varied from 10^{-2} to 10^{-3} micrograms. Three synthetic ore samples containing known amounts of U^{235} were also analyzed. They reported 0.05 microgram of U^{235} as a lower limit for a determination. They found the method to be rapid and accurate, to require very little sample preparation, and to be free of any interferences except from those materials which have high neutron fission cross-sections (such as Pu^{239} and U^{233}) or high-neutron capture cross-sections (such as Cd^{113} and B^{10}). Amiel(7) has made a more extensive study of delayed neutron emission for the determination of fissionable materials. He applied the method to the determination of uranium in a large number of geological samples and to samples of pure uranium reagents, as well

as the determination of the isotopic composition of a uranium sample. A limit of detection of U^{235} was found to be about 2×10^{-4} microgram with 7×10^{-3} microgram of U^{235} giving 300 delayed-neutron counts. He also used the method for the determination of thorium in a number of sample types and discussed the application of the method to the determination of U^{233} in thorium, Pu^{239} in uranium, as well as the possible use of the method for uranium-thorium prospecting. Both solid and liquid samples of uranium and thorium were analyzed.

The different sources of interference in the method were investigated and discussed. In addition to the interferences mentioned by Echo and Turk,[6] Amiel listed the interference due to the delayed neutron precursor N^{17} formed by the reaction $O^{17}(n,p)N^{17}$ with fast neutrons as well as two secondary reactions. He showed that this source of interference could be eliminated by allowing the N^{17} ($t_{1/2}$ = 4.2 sec.) to decay before counting the delayed neutrons due to uranium or thorium fission. He evaluated the effect of the "self-shadowing" of samples from the bombarding neutrons with samples containing lithium and boron and found the effect unimportant in most cases. He also discussed the possibility of interferences from (γ,n) reactions due to intense high-energy gamma-rays emitted by the sample as a result of neutron activation of sample matrices. He estimated this effect to be negligible in most cases. In agreement with Echo and Turk,[6] Amiel found the method to be sensitive, accurate, and rapid and to require little or no sample preparation.

The present study of the neutron activation analysis of uranium by delayed neutron counting was undertaken in order to ascertain if the method would be suitable for routine application. Preliminary reports of certain parts of this work have been previously presented.[8] In view of the findings of Echo and Turk,[6] it was believed that the method would be an excellent one for the routine analysis of a wide variety of uranium-containing materials encountered in nuclear technology. Though based on the fact that it is the U^{235} component of uranium which undergoes most of the fissions and thereby produces most of the delayed neutrons, the method can be used according to the following categories of analysis: (1) the determination of U^{235} in samples containing uranium of unknown isotopic composition, (2) the determination of total uranium in samples containing uranium of known isotopic composition, and (3) the determination of the isotopic composition of the uranium in samples containing known amounts of total uranium. An analysis is made by comparing the delayed neutron count obtained for a sample with the count obtained for a comparator sample containing a known quantity of U^{235}. For a determination of the total uranium in a sample (analysis category 2), it is not necessary to know the isotopic composition of the uranium in the sample provided a comparator sample is used which has the same isotopic composition as the unknown or test sample. The possibility will be discussed in a later section of determining the isotopic composition of uranium by making irradiations with and without the sample being enclosed in a cadmium container. The delayed-neutron-counting method has been used

according to each of the three analysis categories listed above, though more extensively for categories 1 and 2. The method can be used to determine uranium in ores, metals, nonmetals, biological materials, solutions, etc. The sensitivity of the method is sufficient to detect 10^{-4} micrograms of U^{235}; 10^{-3} microgram will give approximately 10^{3} delayed-neutron counts depending on the conditions of measurement.

2.0. Principles of Method

The determination of U-235 by delayed-neutron counting is based upon the fact that some of the fission products of U-235 emit neutrons over a short period of time after fission has taken place. The fission products of other fissionable elements such as Pu^{239} and U^{233} also emit neutrons and these elements can also be analyzed by this method. The delayed neutrons are emitted from nuclei which have been left in highly excited states (by an amount of energy exceeding the binding energy of a neutron) by the negatron decay of fission-produced parent nuclei. The neutrons are emitted instantaneously after the the negatron is emitted and thereby exhibit half-lives in their emission which coincide with the half-lives of the negatron-emitting parent nuclides. The term precursor has been applied to a radionuclide which decays by negatron emission to produce a neutron-emitting radionuclide. By means of radiochemical separations, at least seven radionuclides which are precursors of delayed-neutron emitters have been shown to be present in the fission product of U^{235}.(9-13) These seven precursors and their half-lives are listed in Table II.

The existence of delayed-neutron emission is highly important to the operation and control of nuclear reactors; and consequently, the decay characteristics of delayed-neutron activity have been investigated rather extensively.(9-13) Most recent investigators have been able to resolve the delayed-neutron activity resulting from the fission of U^{235}, into six groups, each group having a characteristic half-life and absolute group yield (delayed neutrons emitted per group per fission). Keepin, et al.,(9) have studied the delayed-neutron activity resulting

TABLE II

DELAYED-NEUTRON PRECURSORS RESULTING FROM FISSION OF U-235[1]

Precursor	Half-Life, sec.
Br-87	54.5
I-137	24.4
Br-88	16.3
I-138	6.3
Br-89	4.4
I-139	2.0
Br-90	1.6

[1] See references (9-13).

from the fission of U^{235}, U^{233}, and Pu^{239} by both thermal and fast neutrons and from the fission of U^{238} and Th^{232} by fast neutrons. It was found that the delayed-neutron activity resulting from the fission of each of these nuclides could be resolved into six groups with fair agreement in the half-lives of corresponding groups. Slight differences in the half-lives of corresponding groups were obtained when different nuclides were fissioned as well as when the method of fission was different, as for example, when U-235 was fissioned first with thermal neutrons and then with fast neutrons. Quite large differences between corresponding groups for absolute group yields were obtained when different nuclides were fissioned. The data obtained by Keepin, et al,[9] for thermal neutron fission of U^{235}, U^{233}, and Pu^{239} is given in Table III; Table IV lists the data obtained for the fast-neutron fission of U^{235}, U^{233}, U^{238}, Pu^{239}, and Th^{232}. Keepin, et al,[9] interpreted their results in terms of the existence of six main delayed-neutron precursors. Small differences between the half-lives of corresponding groups obtained either for different nuclides or the same nuclide for different modes of fission were believed to result from (1) perturbations of the derived half-lives by different yields of the six main delayed-neutron precursors or (2) perturbations of the derived half-lives by different yields of minor delayed neutron precursors having half-lives which are different from the six main precursors.

An analysis for uranium is made by irradiating a test sample in a nuclear reactor for a period of time ranging from seconds to minutes, rapidly removing the sample to a neutron counting facility, allowing

TABLE III

DELAYED-NEUTRON GROUPS FROM THERMAL-NEUTRON FISSION[a]

Nuclide	Number of Delayed Neutrons per Fission	Group Index (i)	Half-life (Sec.)	Absolute Group Yield (%)[b]
U-235	0.0158 ± 0.0005	1	55.72 ± 1.28	0.052 ± 0.005
		2	22.72 ± 0.71	0.346 ± 0.018
		3	6.22 ± 0.23	0.310 ± 0.036
		4	2.30 ± 0.09	0.624 ± 0.026
		5	0.610 ± 0.083	0.182 ± 0.015
		6	0.230 ± 0.025	0.066 ± 0.008
U-233	0.0066 ± 0.0003	1	55.00 ± 0.54	0.057 ± 0.003
		2	20.57 ± 0.38	0.197 ± 0.009
		3	5.00 ± 0.21	0.166 ± 0.027
		4	2.13 ± 0.20	0.184 ± 0.016
		5	0.615 ± 0.240	0.034 ± 0.016
		6	0.277 ± 0.047	0.022 ± 0.009
Pu-239	0.0061 ± 0.0003	1	55.28 ± 2.34	0.021 ± 0.006
		2	23.04 ± 1.67	0.182 ± 0.023
		3	5.66 ± 0.40	0.129 ± 0.030
		4	2.13 ± 0.24	0.199 ± 0.022
		5	0.618 ± 0.213	0.052 ± 0.018
		6	0.257 ± 0.045	0.027 ± 0.010

[a] Data taken from Keepin, G. R., Wimitt, T. F., and Ziegler, R. K., "Delayed Neutrons from Fissionable Isotopes of Uranium, Plutonium, and Thorium," Phys. Rev. 107, 1044-1049 (1957), J. Nuc. Energy 6, 1-21 (1957-58).

[b] Absolute group yield (%) means the number of delayed neutrons per 100 fissions.

TABLE IV

DELAYED-NEUTRON GROUPS FROM FAST NEUTRON FISSION[a]

Nuclide	Number of Delayed Neutrons per Fission	Group Index (i)	Half-life (sec.)	Absolute Group Yield (%)[b]
U-235	0.0165 ± 0.0005	1	54.5 ± 0.94	0.063 ± 0.005
		2	21.84 ± 0.54	0.351 ± 0.011
		3	6.00 ± 0.17	0.310 ± 0.028
		4	2.23 ± 0.06	0.672 ± 0.023
		5	.496 ± 0.029	0.211 ± 0.015
		6	.179 ± 0.017	0.043 ± 0.005
U-233	0.0070 ± 0.0004	1	55.11 ± 1.86	0.060 ± 0.003
		2	20.74 ± 0.86	0.192 ± 0.009
		3	5.30 ± 0.19	0.159 ± 0.025
		4	2.29 ± 0.01	0.222 ± 0.012
		5	.546 ± 0.108	0.051 ± 0.010
		6	.221 ± 0.042	0.016 ± 0.005
U-238	0.0412 ± 0.0017	1	52.38 ± 0.29	0.054 ± 0.005
		2	21.58 ± 0.39	0.564 ± 0.025
		3	5.00 ± 0.19	0.667 ± 0.087
		4	1.93 ± 0.07	1.599 ± 0.081
		5	0.490 ± 0.023	0.927 ± 0.060
		6	0.172 ± 0.009	0.309 ± 0.024
Th-232	0.0496 ± 0.00020	1	56.03 ± 0.95	0.169 ± 0.012
		2	20.75 ± 0.66	0.744 ± 0.037
		3	5.74 ± 0.24	0.769 ± 0.108
		4	2.16 ± 0.08	2.212 ± 0.110
		5	0.571 ± 0.042	0.853 ± 0.073
		6	0.211 ± 0.019	0.213 ± 0.031
Pu-239	0.0063 ± 0.0003	1	53.75 ± 0.95	0.024 ± 0.002
		2	22.29 ± 0.36	0.176 ± 0.009
		3	5.19 ± 0.12	0.136 ± 0.013
		4	2.09 ± 0.08	0.207 ± 0.012
		5	0.549 ± 0.049	0.065 ± 0.007
		6	0.216 ± 0.017	0.022 ± 0.003

[a] Data taken from Keepin, G. R., Wimitt, T. F., and Ziegler, R. K., "Delayed Neutrons from Fissionable Isotopes of Uranium, Plutonium, and Thorium," Phys. Rev. 107, 1044-1049 (1957), J. Nuc. Energy 6, 1-21 (1957-58).

[b] Absolute group yield (%) means the number of delayed neutrons per 100 fissions.

the counter to collect counts for a period of time and recording the collected count. A blank sample and a comparator sample are then treated precisely as was the test sample. The blank sample usually consists of an empty rabbit. In those cases in which a uranium analysis is desired on a material to which uranium has been added, the original matrix material to which no uranium has been added can serve as the blank along with the rabbit containing the material. The comparator sample should contain a known quantity of U^{235} and/or total uranium. The U^{235} content of the test sample is obtained by the following equation:

$$U^{235}\ \underset{\text{Sample}}{\text{Content of Test}} = U^{235}\ \underset{\text{Sample}}{\text{Content of Comparator}} \frac{C_t - BG}{C_c - BG} \qquad (1)$$

where C_t is the total delayed-neutron count of the test sample,

C_c is the total delayed-neutron count of the comparator sample, and

BG is the background count which is obtained as explained above. To obtain total uranium in a sample when the comparator contains uranium of the same isotopic composition as the uranium in the test sample, "total uranium" can be inserted in equation 1 in place of U^{235}. If the isotopic compositions are different for the uranium in the test and comparator samples, the total uranium in the test sample can be obtained by the equation:

$$\text{Total U in Test Sample} = \frac{U^{235} \text{ in Comparator}}{P} \times \frac{C_t - BG}{C_c - BG} \qquad (2)$$

where P is the per cent of the uranium in the test sample which is U^{235}, other terms being the same as in equation 1.

Equation 2 can be used to solve for P when a determination is made of the per cent U^{235} in a sample containing a known quantity of total uranium.

The rather high sensitivity attainable with the method is due to the following factors: (1) the relatively high fission cross-section of U^{235} for thermal neutrons (577 barns),[14] (2) the fact that approximately 1.58 per cent of the fissions of U^{235} caused by thermal neutrons result in the emission of delayed neutrons,[9] (3) the relatively short half-lives of the delayed-neutrons precursors which allow the counting of a definite fraction of the total delayed neutrons emitted,[9] (4) the fact that neutron detectors can be constructed which have neutron counting efficiencies of 5 - 10 per cent or greater, and (5) the fact that neutron sources with a thermal neutron flux of 10^{13} $n/cm^2/sec$ or higher can be obtained in nuclear reactor irradiation facilities.

By treating the delayed-neutron activity resulting from the fission of U^{235} as distinct groups each having definite half-lives and absolute group yields, one can write an equation which gives the rate of delayed neutron emission of a sample at any time during or after an irradiation of the sample in a neutron flux. If a sample of U^{235} containing N atoms of U^{235} is irradiated in a neutron flux, ϕ, for a period of time, t_b, and allowed to decay for a time, t_d, the rate of delayed-neutron emission, A_d, of the sample at the end of the decay time, as given by the conventional radioactivation equation, is

$$A_d = \phi\sigma N \sum A_i (1-e^{-\lambda_i t_b})e^{-\lambda_i t_d} \qquad (1)$$

where σ is the thermal neutron fission cross-section of U^{235} for the neutron flux to which the sample is exposed,

A_i is the absolute group yield of delayed neutron precursors in the i th delayed-neutron group, and

λ_i is the decay constant of the i th delayed-neutron group.

The summation term indicates that a summation is taken over all of the delayed neutron groups since the rate of total delayed-neutron emission is equal to the sum of the rates of delayed-neutron emission of each individual delayed-neutron group. Equation 1 can be modified to give the number of delayed, neutrons, N_d, which are emitted over a time interval, t_c, measured from the end of t_d.

$$N_d = \phi N \sum \frac{a_i}{\lambda_i} (1-e^{-\lambda_i t_b})e^{-\lambda_i t_d}(1-e^{-\lambda_i t_c}) \qquad (2)$$

Equation 2 can be used to estimate the optimum or best values of t_b, t_d, and t_c to be used for analyses of samples containing any particular quantity of U^{235}. In equations 1 and 2, the fission of the U^{235} which is caused by epithermal neutrons is neglected.

Determinations of U^{235} on which this report is based were carried out using a thermal neutron flux of about 6×10^{13} $n/cm^2/sec$. Using this neutron flux value, a thermal neutron fission cross-section of 577 barns for U^{235} and the half-lives and absolute group yields of the delayed-neutron groups of U^{235} given by Keepin, et al,[9] calculations have been made for the delayed neutron activity, A_d, and the number of delayed-neutron precursors contained in the sample as functions of time, following the irradiation of a 1-microgram sample

of U^{235}. For purposes of calculation, values of the irradiation time, t_b, were chosen to be 20, 60, and 126 seconds and a time sufficient to saturate all of the delayed neutron groups. The results are presented graphically in Figures 1 and 2. The abscissas of Figures 1 and 2 indicate the elapsed time in seconds from the end of the irradiation. The ordinates of Figures 1 and 2 indicate (as a function of time measured from the end of the irradiation) the rate of delayed neutron emission and the number of delayed neutron precursors contained in the sample, respectively. The number of delayed neutron precursors contained in the sample is equal to the number of delayed neutrons which are emitted by the sample if all of the delayed-neutron precursors are allowed to decay completely. Since the half-lives of delayed-neutron groups 5 and 6 are so small, calculations were made only for groups 1 through 4, and the curves shown in Figures 1 and 2 show only the decay of these four groups.

From the curves in Figure 2, one can obtain the approximate number of delayed neutrons, N_d, emitted by a sample of U^{235} over any period of time following an irradiation of either 20, 60, or 120 seconds or a time sufficiently long to produce saturation activity of all the delayed neutron groups. As an example, suppose a 1 μg sample of U^{235} is irradiated for 60 seconds (t_b = 60 sec.) at a thermal neutron flux of 6×10^{13} $n/cm^2/sec$. The sample is allowed to decay for 10 seconds (t_d = 10 seconds). If one wishes to know the number of delayed neutrons, N_d, which will be emitted by the sample over a 60-second interval following the 10-second decay period, one obtains the value of N_d as follows: First, the curve in Figure 2 is

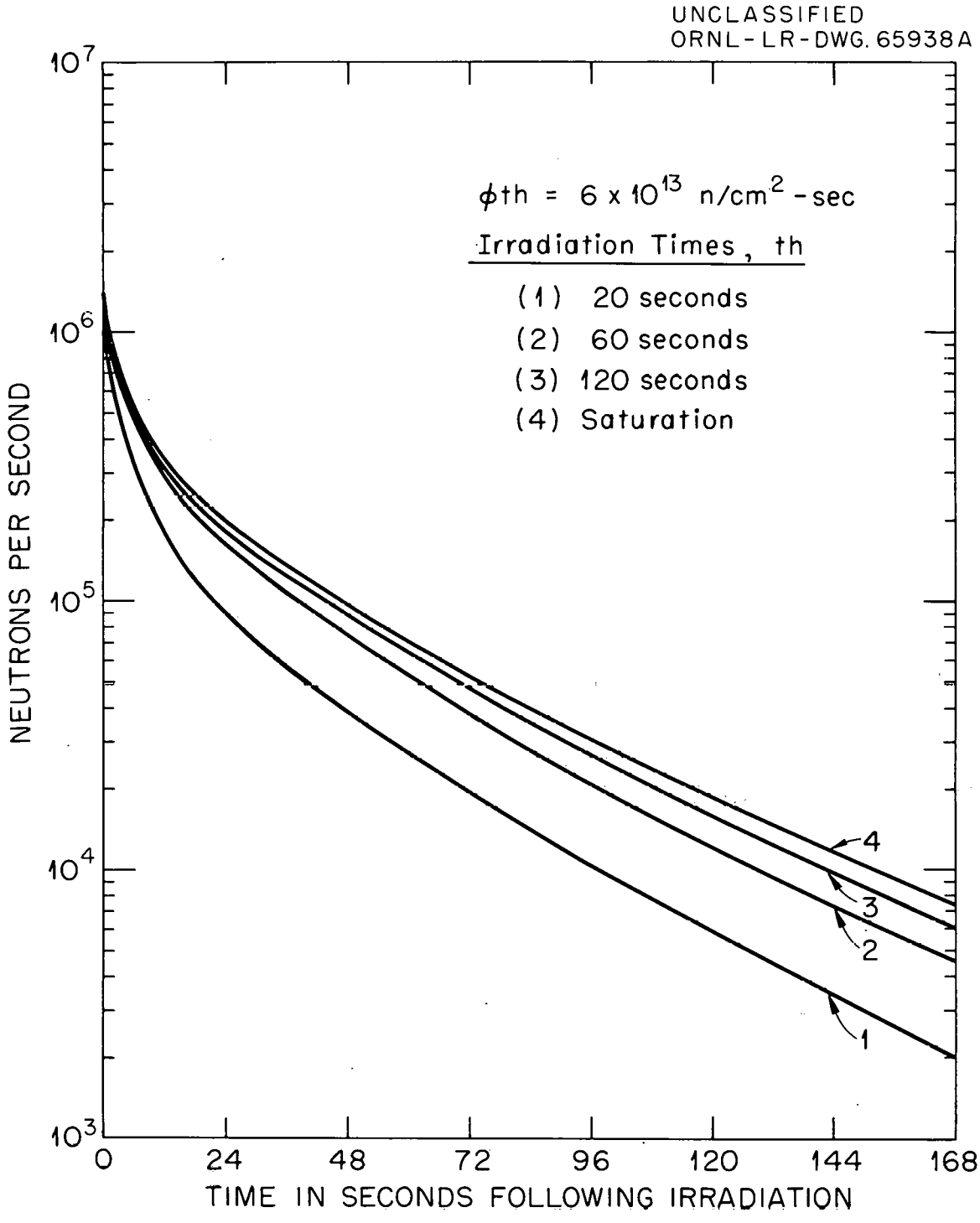

Fig. 1. Rate of Delayed-Neutron Emission Following Irradiation of 1 μg of U^{235}.

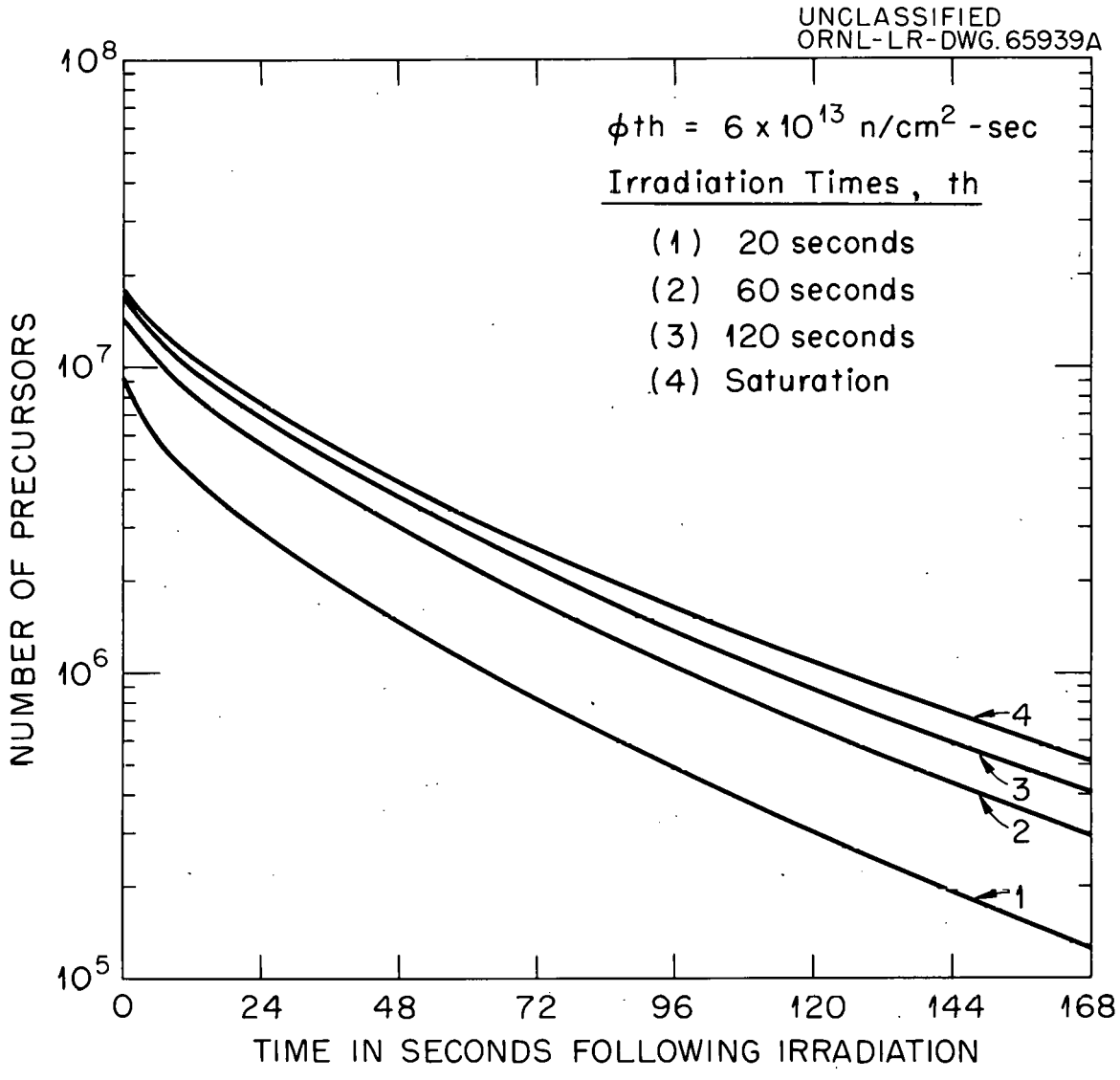

Fig. 2. Number of Delayed-Neutron Precursors Produced from 1 μg of U^{235}.

selected for which t_b is equal to 60 seconds. A value of N_d at t equal to 10 seconds is seen to be 8.8×10^6 neutrons; at t equal to 70 seconds, N_d is seen to be 1.8×10^6. The difference in these numbers, 7.0×10^6, is the approximate number of neutrons emitted by the sample over the time interval of interest.

As in other neutron activation methods of analysis, higher sensitivities are favored by irradiations of relatively longer times, allowing relatively little time to elapse before counting, and counting for relatively longer times. Table V lists some values taken from the curves in Figure 2 for the number of neutrons emitted by a 1-μg sample of U^{235} for various values of t_b, t_d, and t_c when the sample is irradiated in a thermal neutron flux of 6×10^{13} $n/cm^2/sec$. It is seen in Table V that if a 1-μg sample of U^{235} is irradiated in a neutron flux of 6×10^{13} until all of the delayed neutron groups are saturated, approximately 1.8×10^7 delayed neutrons will be emitted by the sample. Thus, if a neutron counter having a neutron counting efficiency of 5 per cent is used to assay the neutron activity of the sample, a collected count of 9×10^5 c/μg of U^{235} or 900 counts per 10^{-9} grams of U^{235} will be obtained if counting is begun immediately after the irradiation. Normally, samples can be transferred from the irradiation position in a reactor through a pneumatic tube to a neutron counter in a time of about 2 seconds, so that the sample neutron activity can be assayed almost during its entire decay. Shorter times of irradiation, longer times of delay before counting, and shorter times of counting reduces the sensitivity of the method. However, as can be seen in Table V, if

TABLE V

NUMBER OF DELAYED NEUTRONS EMITTED FOLLOWING IRRADIATION OF 1 MICROGRAM OF U^{235}

Time Values, seconds*			Neutrons Emitted By 1 μg of U^{235}
t_b	t_d	t_c	
S	0	C	1.8×10^7
120	0	60	1.4×10^7
60	0	60	1.3×10^7
60	10	60	7.0×10^6
20	10	60	4.0×10^6

*S = saturation, C = time for all neutrons to be emitted.

a microgram of U^{235} is irradiated for only 20 seconds, alloyed to decay 10 seconds before counting, and counts are collected for 60 seconds, the total neutrons emitted during the 60-second count time is still 4.0×10^{6}. With a neutron counting efficiency of 5 per cent, the neutron count is 2000 counts per 10^{-8} gram of U^{235}. Therefore, it is seen that relatively short irradiation times can be used to analyze samples for U^{235} if the samples contain as much as 10^{-8} grams of U^{235}.

3.0. Experimental

3.1. Apparatus

All irradiations were carried out in the pneumatic tube in Hole HN-3 in the Oak Ridge Research Reactor (ORR). The pneumatic tube irradiation facility in Hole HN-3 of the ORR consists of the pneumatic tube, the control panel for the pneumatic tube, and two sample loading stations. The design and operation of this irradiation facility has been previously described.[15] At the time of the previous description, only sample loading station 1 was in use. Station 2 is now being used for delayed-neutron counting. The additions and modifications which have been made to the system are described below.

Pneumatic Tube: Figure 3 shows the design of the pneumatic tube and how Sample Loading Station 2 (Figure 5) is connected into the system. Station 2 also consists of a neutron moderator and detector assembly for counting delayed neutrons. At this station, rabbits are loaded into the bottom of the assembly, sent into the reactor through the pneumatic tube, irradiated for a preselected time, and automatically removed from the reactor to the assembly for delayed-neutron counting. Station 2 can be operated when air supply valve S1 is closed, air supply valve S2 is open, and the hood selector valve is in the Hood 2 position (see Figure 4).

Neutron Moderator and Detector Assembly and Counting Equipment: The neutron moderator and detector assembly, shown in detail in Figure 5, consists of a paraffin cylinder having a diameter of 19 1/4 inches and a height of 24 inches. A teflon tube with an internal diameter of 0.620 inches and an external diameter of 3 inches traverses

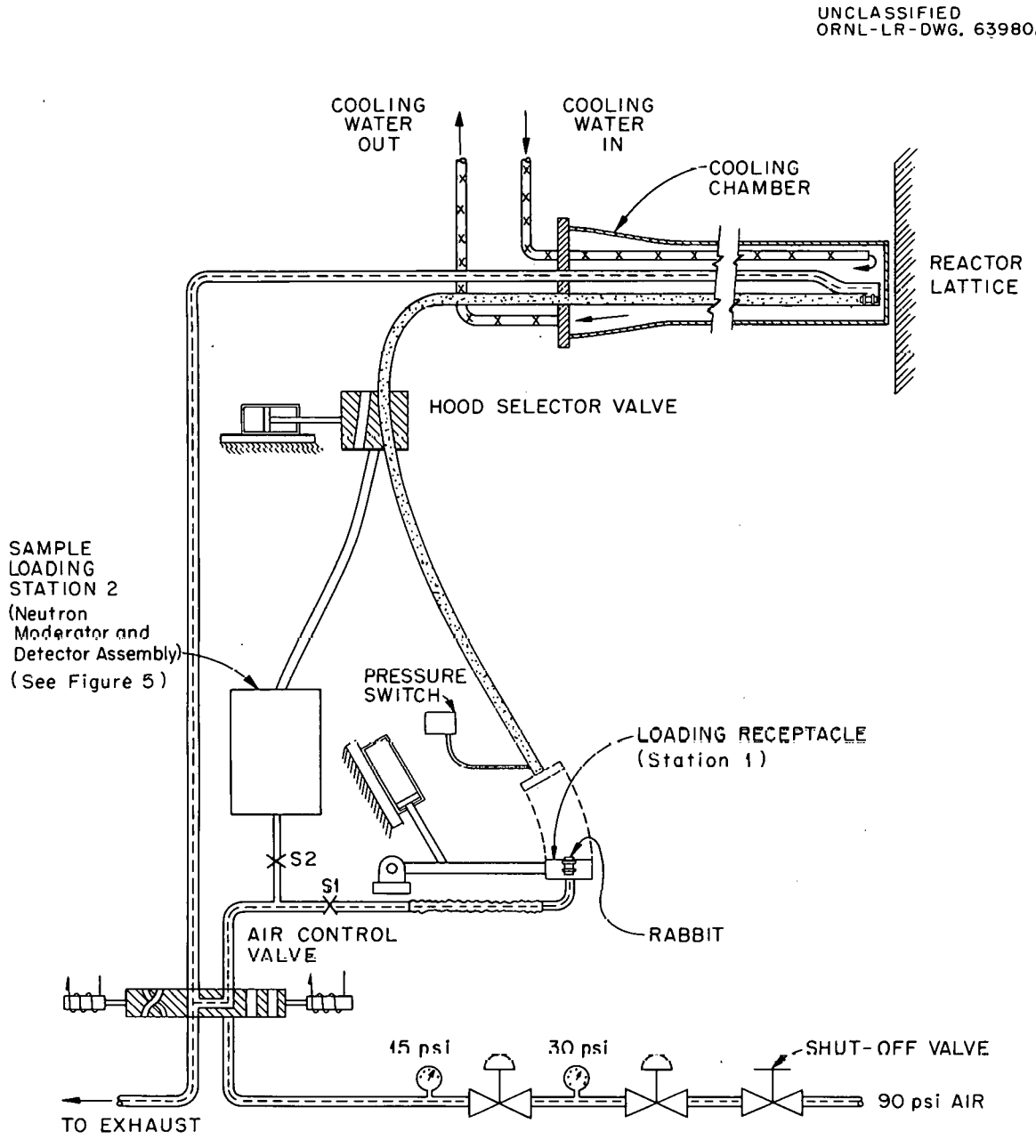

Fig. 3. Pneumatic Tube System — ORR.

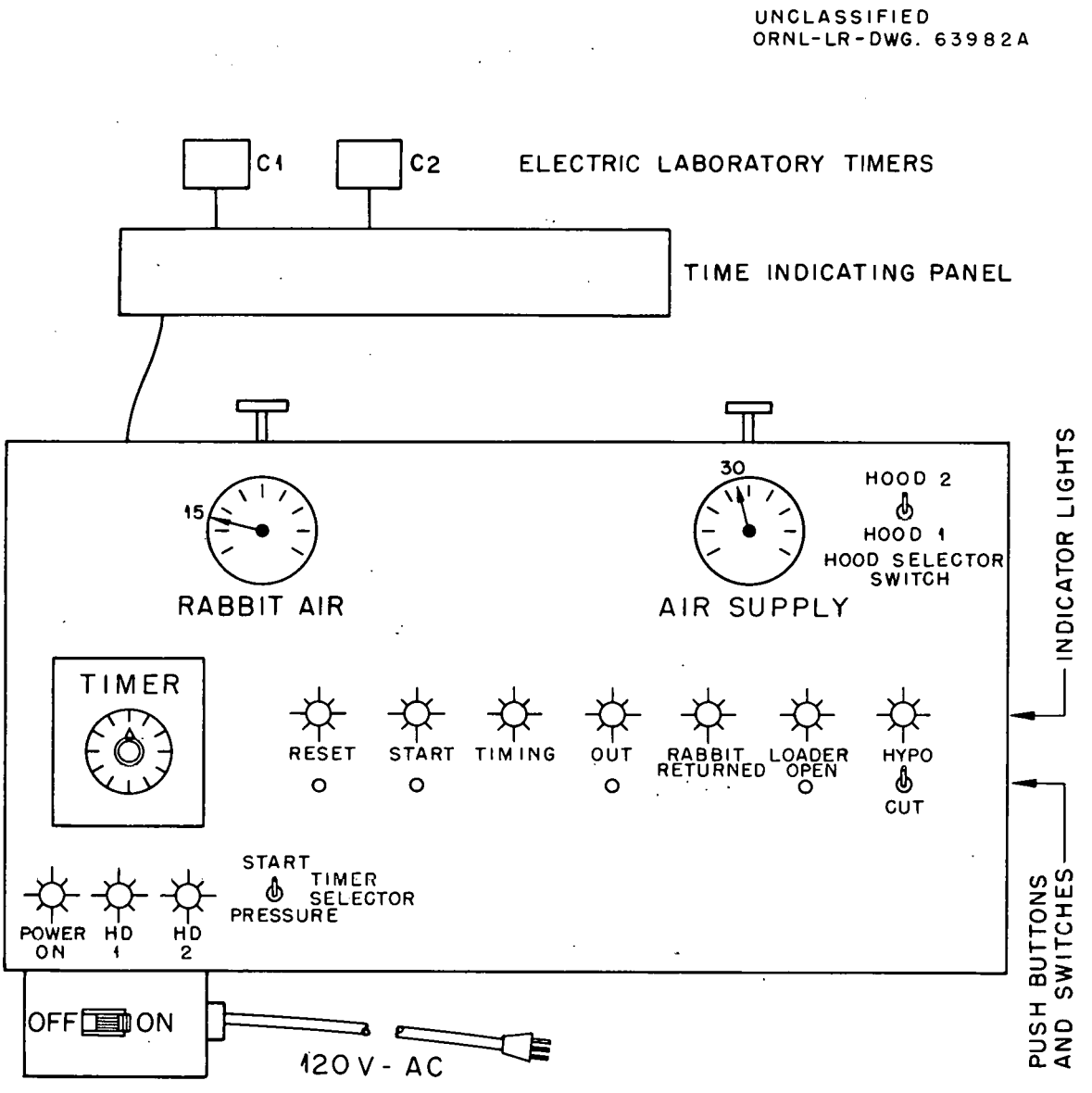

Fig. 4. Pneumatic Tube Control Panel.

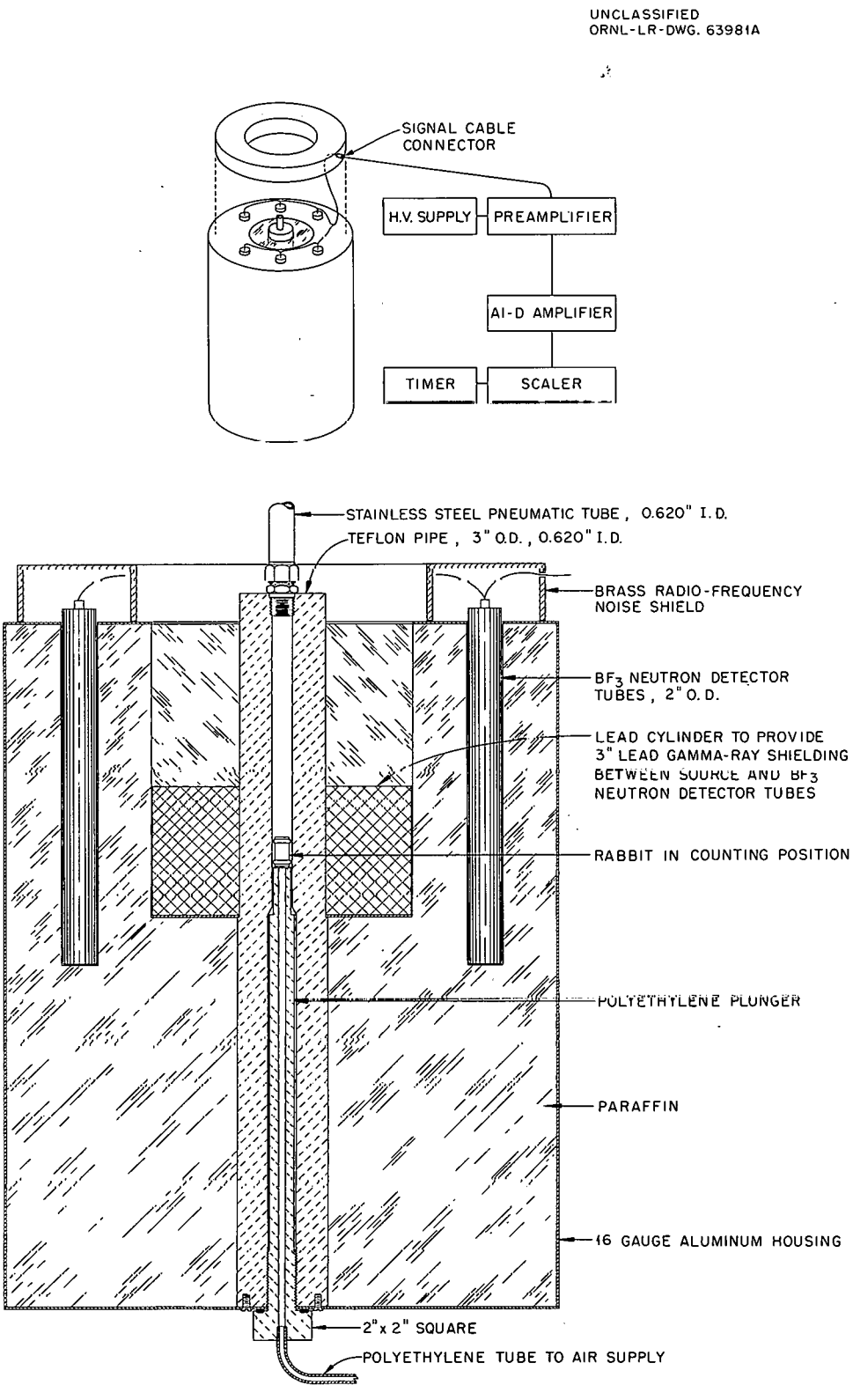

Fig. 5. Delayed-Neutron Moderator and Detector Assembly and Electronic Components.

the axis of the paraffin cylinder. The teflon tube is connected to the stainless steel pneumatic tube, both of which have the same internal diameter to allow rabbits to travel from one to the other. Six BF_3 neutron detector tubes are embedded in the paraffin parallel to and symmetrically around the teflon tube. A rabbit (shown in Figure 6) containing a uranium-bearing sample is loaded into the bottom of the assembly and pushed into place with the plunger shown in Figure 5. The plunger has the functions of holding a sample in the counting position (see Figure 5) and providing an inlet and outlet for the air necessary to operate the pneumatic tube. Air enters the pneumatic tube through the plunger to push the rabbit through the pneumatic tube into the reactor and escapes through the plunger when the rabbit is returned to the assembly.

The counting equipment used to count delayed neutrons consists of the BF_3 neutron detector tubes, preamplifier, amplifier, high speed scaler and high voltage supply and an electric timer for measuring the interval of time, t_c, during which the scaler is allowed to collect counts. A schematic diagram of this equipment is shown as part of Figure 5. The BF_3 tubes are connected in parallel to the preamplifier. The circuit which connects the BF_3 tubes is enclosed in a brass shield to reduce noise due to stray radiofrequency radiation.

Pneumatic Tube Control Panel: The control panel which controls the operation of the pneumatic tube is shown in block diagram in Figure 4. The operation of the control panel has been previously described by Cristy.[15] Two modifications have been made to the panel to assist in its operation and to permit the use of Sample Loading

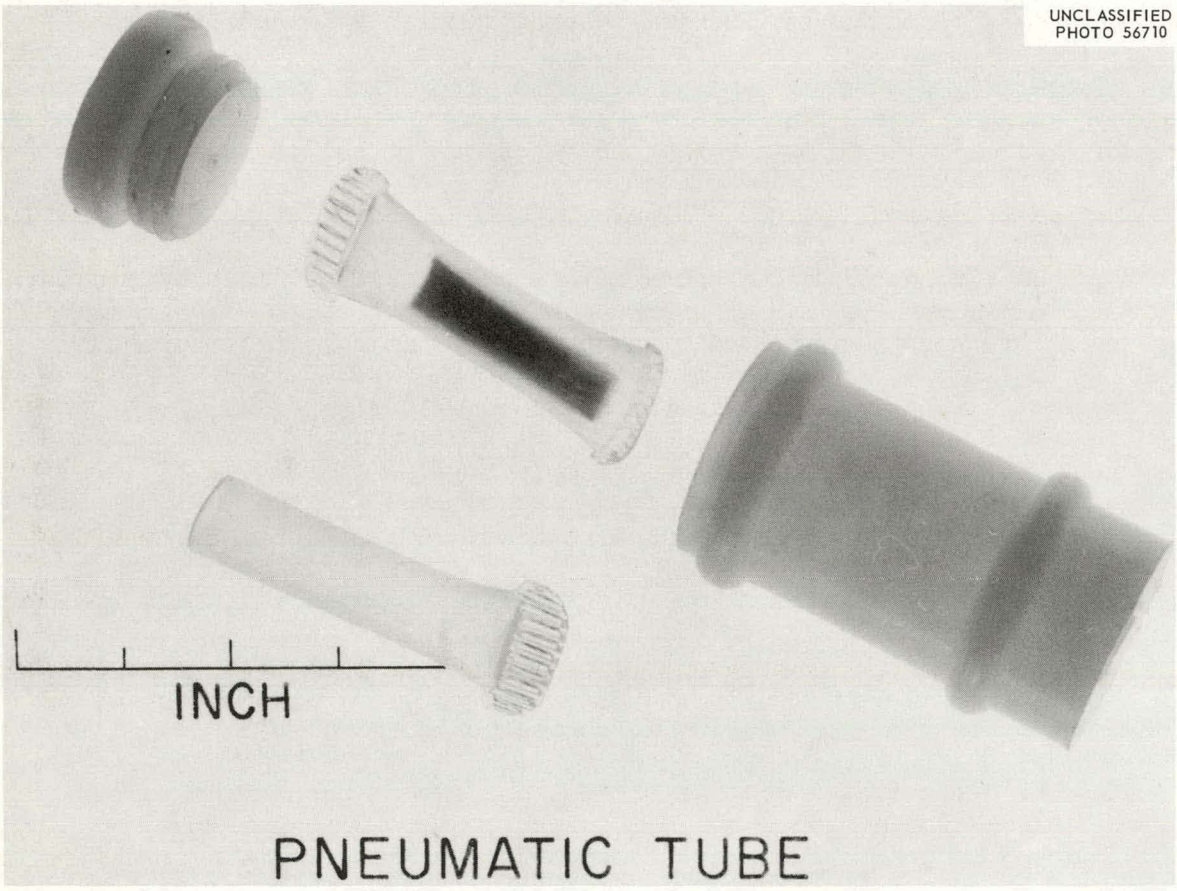

Fig. 6. Rabbit and Method of Sealing Samples in Polyethylene Tubes.

Station 2. A hood selector switch in the upper right corner of the panel permits either station 1 or 2 to be selected as desired by controlling the position of the hood selector valve (shown in Figure 4) of the pneumatic tube. A time indicating panel has also been added to the control panel. The function of the time indicating panel is to facilitate the measurement of various time intervals of interest whenever samples are irradiated and counted. Electric laboratory timing clocks are plugged into the time indicating panel to make the time interval measurements. The time indicating panel is shown in Figure 4 with two electric laboratory timing clocks, C1 and C2, connected. Clock C1 begins timing whenever the irradiation start switch on the control panel is depressed and stops timing when the irradiation ends. Since the counter is manually operated, the function of clock C1 is to show the time which remains for an irradiation which is in progress, and therefore, indicates when one should prepare to turn the counter on. Clock C2 begins timing when an irradiation is started and continues to time after the irradiation ends. The time interval which one allows to elapse between the end of an irradiation and the time the counter is turned on (the delay time, t_d) can be judged to within $\pm$ 0.1 seconds by observing clock C2.

3.2. Irradiation and Counting Procedure

To make an irradiation of a sample for delayed neutron counting, one first selects the time interval of irradiation, t_b, and the delay time, t_d. The hood selector switch on the control panel is placed in the Hood 2 position and the time t_b is set on the microflex preset

timer on the control panel. The air selector valves S1 and S2 are turned so that S1 is closed and S2 is open. The plunger in the neutron moderator and detector assembly (Loading Station 2) is removed, a rabbit containing the sample is inserted and the plunger reinserted and locked into place. The clocks C1 and C2 are set to zero, the reset switch and irradiation start switch on the control panel are depressed respectively in succession. After the irradiation, the time t_d is allowed to elapse by observing clock C2; the counter is turned on, and allowed to collect counts for a preselected counting time t_c.

3.3. Sample Containers and Sample Preparation

Samples are transferred through the pneumatic tube in small cylindrical boxes called rabbits. The rabbits are made of high-density polyethylene. A picture of a rabbit is shown in Figure 6. The rabbits are sealed with screw-cap lids. The dimensions of the rabbit are as follows:

Dimension	Length	Diameter
Outer	2.78 cm	1.48 cm
Inner	1.95 cm	0.90 cm

Samples can be sealed tightly in the rabbits by means of the screw-cap lids with little chance of any portion of a sample being lost to contaminate the pneumatic tube. However, it has become routine practice to seal samples in polyethylene tubes before placing them in the rabbits. The polyethylene tubes are (see Figure 6) cut from low density polyethylene tubing. The ends of the polyethylene

tubes are sealed by holding them with forceps in a low flame until they melt. The polyethylene tubes, being of a low density type of polyethylene, melt and seal easily in this manner. By using this procedure an additional measure of safety is taken against loss of samples from a rabbit and pneumatic tube contamination.[a]

Essentially all the effort required to prepare a sample for an activation is to weigh a portion of a solid sample or to take an aliquot of a liquid. If a solid sample is dissolved, the resulting solution is diluted to a known volume before an aliquot is taken for analysis. Usually, the volume of an aliquot of liquid is not more than a few hundred microliters. At first it was found to be difficult to use micropipettes to place a known volume of liquid in one of the polyethylene tubes accurately. However, two techniques are now used for this procedure. If the volume of the aliquot is about 50 μl or less, a piece of absorbent tissue (uranium free) can be placed in a polyethylene tube and the end of the micropipette touched to the tissue so that the solution is absorbed in the tissue. A rinse can be treated in the same manner. If the volume of the aliquot is too large to be absorbed on the tissue, the tissue can be omitted, a polyethylene tube sealed on one end, and weighed, an aliquot of unknown volume can be added and the tube sealed and then

[a]Sealing a sample in a polyethylene tube also helps serve the function of keeping the sample in a known fixed position within the rabbit. As will be discussed later, there is a neutron flux gradient of about 2% per millimeter along the axis of a rabbit when the rabbit is in the irradiation position. Thus, it is important to maintain a test sample and a comparator sample in the same positions within their respective rabbits in order to make analyses with maximum precision.

weighed again. The difference in the two weights is the weight of the aliquot of liquid. The volume of the aliquot can be obtained by measuring the density of the liquid and then calculating the volume. It has been found that the polyethylene tubes can be sealed with negligible loss of weight.

3.4. Experimental Results

Background Count Measurements: The background count of the neutron detector with no freshly irradiated rabbit in the detector normally runs about 40 - 50 counts per minute. However, during the course of this study, the determination of very low level amounts of uranium was hampered by a slight uranium contamination in the pneumatic tube. The count obtained for an empty rabbit is approximately that obtained for 10^{-3} micrograms (1 nanogram) of U^{235} or about 1000 counts when a rabbit is irradiated for one minute and counted for one minute immediately upon discharge of the rabbit from the reactor. Since samples are normally counted in the rabbits in which they are irradiated, this background of about 1000 counts is that applied to most sample analyses. The background count obtained in this manner, however, is quite variable and values having the range of 900 to 1400 counts have been obtained. This background count was shown to be due to U^{235} (or other fissionable nuclides) contamination in the pneumatic tube by making decay measurements on the activity and by making an independent activation analysis of some of the rabbits in another reactor irradiation facility in which the rabbit did not come into contact with the walls of the facility. The decay measurements

corresponded quite closely to a decay measurement of an irradiated sample of U^{235}. For the independent activation analysis of the rabbits, an activation was made for one week in a flux of 7×10^{11} $n/cm^2/sec$. A decay study by gamma-ray spectrometry of the radionuclides induced in the rabbits revealed no fission products of U^{235}. Such an analysis is sensitive enough to reveal easily 1 nanogram of U^{235}.

Samples which are sealed in polyethylene tubes can be irradiated in one rabbit and after discharge from the reactor removed from this rabbit and placed in another rabbit or suitable container for delayed-neutron counting. By this procedure the contamination picked up by the rabbit from the pneumatic tube is eliminated and the only background is then the normal 40 - 50 counts per minute mentioned above. This procedure has been used for a number of samples containing from 10^{-3} to 10^{-4} micrograms of U^{235}. The time required to make such a change in the sample container is about 20 seconds. It can be seen from Figure 2 that a delay of 20 seconds in the time before counting is begun results in a loss of sensitivity due to decay of delayed-neutron activity amounting to about 40 per cent when the irradiation time is 1 minute. Even with this loss in sensitivity, determinations can be made more precisely by this technique on samples containing 10^{-3} micrograms or less of U^{235}.

Neutron Flux and Neutron Flux Gradient in the HN-3 Irradiation Facility: The neutron flux in the HN-3 irradiation facility has been measured using cobalt-aluminum, gold-aluminum, and thin gold leaf activation monitors.[16] By loading a rabbit with disks of cobalt-aluminum alloy spaced every 1.59 mm along the rabbit, the neutron flux

in the rabbit irradiation position was found to have a gradient of about 1.9% per mm along the axis of the rabbit. The value of the thermal neutron flux in the end of the rabbit facing the reactor core was found to have the value 7.1×10^{13} n/cm^2/sec; and in the opposite end of the rabbit a value of 4.5×10^{13} n/cm^2/sec was found. The effect of this gradient on the fission of U^{235} was determined by irradiating and assaying the delayed neutron activity of a 0.100 μg sample of U^{235} placed at different positions within a rabbit. The gradient of the delayed neutron count was found to be 1.5% per mm along the axis of the rabbit. Thus, in carrying out analyses by delayed-neutron counting in this facility, it is imperative that the positions of test samples and comparator samples in their respective rabbits be as nearly the same as possible if the desired precision is to be obtained. Techniques which can be used to insure that the positions of a test sample and a comparator sample are as nearly identical as possible are to make the sizes or volumes of the two samples nearly the same, place the two samples in the bottom of the rabbits and pack absorbent tissue or polyethylene film on top of them to hold them in place. If the samples are sealed in polyethylene tubes, the above principles should be adhered to as well as having any void space in the polyethylene tube as small as possible.

The fission neutron flux in this irradiation facility was obtained by making irradiations of very pure aluminum.[17] Two samples of this aluminum (as turnings) were placed in the bottom of a rabbit and polyethylene film was packed in the rabbit and the screw-cap lid was tightened on the rabbit. The rabbit was irradiated so that the sample end of the rabbit was toward the reactor core. The threshold reaction

$Al^{27}(n,\alpha)Na^{24}$ was employed to measure the fission neutron flux. According to Hughes[18] the average cross-section for this reaction for a fission neutron flux is 0.60 millibarns. The absolute disintegration rate of the Na^{24} was assayed using a gamma-ray spectrometer and a Na^{24} standard of known disintegration rate. A fission neutron flux of 1.6×10^{13} $n/cm^2/sec$ was obtained for both samples of aluminum.

Detection of N^{17}: An attempt was made to detect the delayed-neutron precursor, N^{17}, so that an estimate could be made of its interference to the determination of uranium in water solutions. An empty rabbit was irradiated several times for 20 seconds and counted for 20 seconds immediately upon discharge from the reactor. The range of counts obtained for the several irradiations fell between 900 - 1100 counts. The rabbit was then filled with distilled water and again irradiated and counted several times as before. Again the count fell in the range of 900 - 1100 counts. No attempt was made to seal small volumes of water in plastic tube, make an irradiation, transfer the sample to another rabbit, and take a count in order to eliminate the background due to the pneumatic tube contamination which is picked up by the rabbit. The time necessary to make the sample transfer is so long that most of the N^{17} ($t_{1/2}$ = 4.2 seconds) decays before the transfer can be made.

The N^{17} formed by the reaction $O^{17}(n,p)N^{17}$ might represent a possible interference to the determination of U^{235}. However, as shown above, the interference is very small if it occurs at all. Usually the volume of an aqueous solution which is analyzed for U^{235} does not

exceed 100 μl so that any interference from N^{17} would be extremely small. In any case, the N^{17} could be allowed to decay before counting the delayed neutrons due to U^{235} fission if an interference from N^{17} were observed.

It is a matter of interest to calculate the saturation equilibrium value for the number of atoms of N^{17} when 1 gram of natural water is irradiated in a neutron flux such as exists in the HN-3 facility. This number of atoms, N, of N^{17} is given by the equation:[18]

$$N = \frac{N'\phi\sigma}{\lambda} \qquad (3)$$

where N' is the number of atoms of O^{17} in 1 gram of natural water,

ϕ is the fission neutron flux,

σ is the cross-section for the reaction $O^{17}(n,p)N^{17}$, and

λ is the decay constant ($0.6931\ t_{1/2}$) for N^{17}.

Values for N' and σ of 1.24×10^{19} atoms per gram and 5.2 microbarns, respectively, were given by Roys and Shure.[19] Inserting these values, a value of 1.6×10^{13} $n/cm^2/sec$ for ϕ, and a value of 0.24 sec^{-1} for λ into equation 3 given for N a value equal to about 4000 atoms. If all of these atoms are allowed to decay in a counter with a 0.05 neutron counting efficiency, the expected count would be about 200. Thus, it is seen that if the background for a rabbit was sufficiently constant it should be possible to detect the N^{17} formed in 1 gram of water. Since the background is so high and quite variable, the detection appears to be highly improbable. For an aqueous sample volume of 100 μl or less, the count due to N^{17} formed according to this reaction would be much to small to measure.

Sensitivity of Detection for U^{238} and Th^{232}: The sensitivity for the detection and/or determination of U^{238} and Th^{232} has been determined. Measurements were made with a 1.6 milligram sample of U^{238} as U_3O_8 which was believed to contain less than 1 μg of U^{235} per gram of U^{238} or total uranium. The sample was irradiated and counted with and without a cadmium shield with a 40 mil wall thickness. The purpose of the cadmium was to shield the sample from thermal neutrons and thereby reduce the fission rate of the U^{235} in the sample. The rate of fission of U^{238} should not be affected since it is fissioned by fast neutrons which should not be absorbed significantly in the cadmium shield. In each irradiation the sample was placed in the end of the rabbit next to the reactor core. Irradiations were made for 20 seconds and delayed-neutron counts were taken for 60 seconds after a 20-second delay. Similar measurements were also made on samples of uranium which were 0.164 per cent U^{235}, natural uranium, and 93.1 per cent U^{235}. The results obtained for these measurements are given in Table VI. From the measurements with the uranium which contained less than 1 μg U^{235} per gram of U^{238}, the sensitivity for U^{238} appears to lie in the range 0.87 - 1.4 x 10^4 counts per mg of U^{238}. The lower limit is the cadmium covered valve and the upper limit was obtained without a cadmium cover. Although the cadmium cover reduced the count somewhat, it is not known if this reduction is due to a lowering of the rate of fission (and, therefore, the delayed-neutron count) of the U^{235} contained in the sample or if the cover reduces the rate of fission of U^{238}. In any event, it is believed that the values obtained represent a fair approximation of

TABLE VI

SENSITIVITY VALUES AND CADMIUM RATIOS FOR URANIUM OF VARIOUS ISOTOPIC COMPOSITIONS AND FOR THORIUM[a]

Sample Material	Sample Weight, mg.	U^{235}, %	CCB[b]		Cadmium Ratio	Sensitivity, c/mg
			Bare	Cd Covered		
U	1.6	$\sim 10^{-4}$	2.19×10^{4}	1.37×10^{4}	1.6	$(0.87 - 1.4) \times 10^{4}$
U	0.576	0.164	1.45×10^{5}	1.98×10^{4}	7.33	2.52×10^{5}
U	0.221	0.715	2.63×10^{5}	1.01×10^{4}	26.0	1.19×10^{6}
U	7.99×10^{-3}	93.1	1.37×10^{6}	3.27×10^{4}	41.8	1.66×10^{8}[c]
Th	27.1		2.27×10^{5}	2.16×10^{5}	1.05	8.38×10^{3}

[a] All samples were irradiated 20 seconds and counted 1 minute after a 20-second delay.

[b] CCB means count corrected for background.

[c] This value is in terms of c/mg U-235 and not total uranium.

the sensitivity for U^{238}. From these data one can calculate the contribution from U^{238} fission to the delayed neutron count obtained when natural uranium is irradiated and counted. For the conditions of irradiation and counting given, the per cent of the counts obtained for natural uranium due to U^{238} fission is given by:

$$\frac{\text{Count/mg } U^{238}}{\text{Count/mg Nat. U}} \times 10^2 = \frac{1.4 \times 10^4}{1.19 \times 10^6} \times 10^2 = 1.2\%$$

An attempt was made to obtain a value for the U^{238} contribution to the count in natural uranium by subtracting the contribution of U^{235} from the count obtained for natural uranium. However, since such a large per cent of the count obtained for natural uranium is due to U^{235}, the difference in the values obtained did not appear to be large enough to be significant. The same situation was found to apply to the uranium containing 0.164% U^{235}. However, with a number of measurements on this uranium and U^{235}, it should be possible to obtain the U^{238} count contribution. Other measurements with uranium more depleted than 0.164% U^{235} would certainly allow more accurate values for the sensitivity for U^{238} to be determined.

The sensitivity for Th^{232} was measured using enough highly pure thorium oxide to give 27.1 mg of thorium. The sample was sealed in a polyethylene tube and irradiated and counted under the same conditions as was the uranium. A value of 8.38×10^3 counts per milligram of thorium was obtained for the sensitivity.

It was of interest to calculate the sensitivity for the determination of U^{238} according to equation 2, using the value 1.6×10^{13} $n/cm^2/sec$ for the fission neutron flux, the values for the delayed-

neutron group yields for U^{238} are given in Table II, and a cross-section for the fission of U^{238} by a fission neutron flux of 310 millibarns.[20] The calculation was somewhat simplified due to the fact that only delayed neutron group 2, for purposes of approximation, need be considered. Delayed neutron group 1 can be omitted since its yield is small compared to group 2 especially since the irradiation is short. Groups 3 - 6 can be neglected because of their short half-lives since a delay period of 20 seconds was employed. Neglecting these groups, therefore, and calculating a value for N_d in equation 2 for delayed-neutron group 2 gives a value of 4.7×10^5 delayed neutrons emitted per milligram of U^{238} under the irradiation and counting conditions used. When this value is multiplied by the neutron counting efficiency (0.05) of the counter, a value of 2.3×10^4 delayed-neutrons counted per milligram of U^{238} is obtained. This value is about a factor of two larger than the experimental value. A similar calculation of the sensitivity for Th^{232} using data from Table III for the yield and half-life of delayed-neutron group 2 of Th^{232} and a cross-section of 59 millibarns for the fission of Th^{232} by a fission neutron flux[21] gives 1.2×10^5 delayed neutrons emitted per milligram of Th^{232}. Multiplying this value by 0.05 gives 6.0×10^3 delayed neutrons counted per milligram of Th^{232} which is irradiated and counted under the conditions specified. This value is slightly lower than the value measured experimentally.

Comparison of Uranium Standard: Most comparator samples used in the analyses were taken from one of four solutions containing known amounts of U^{235}. Three standard uranium solutions were prepared from U_3O_8 in which the uranium was 93.1% U^{235}. Designated as standards A, B, and C, standard A was prepared by dissolving 12.69 mg of the U_3O_8 enriched in U^{235} in nitric acid and diluting to 100 ml to give a solution containing 100.0 μg of U^{235} per ml. Standards B and C were prepared by making 10 to 1 and 100 to 1 dilutions of aliquots of standard A to give solutions containing 10.00 and 1.00 μg of U^{235} per ml, respectively. A standard uranium solution (Standard D) was prepared from National Bureau of Standards U_3O_8 in which the uranium was presumed to be of natural composition by dissolving 148.5 mg of the U_3O_8 in nitric acid and diluting to 100 ml to give a solution containing 1.00 mg of natural uranium per ml. Standards A, B, and D were intercompared by delayed-neutron counting. The results of these comparisons are shown in Table VII and expressed in terms of the net delayed-neutron count per μg of U^{235} (hereafter designated the sensitivity). It is seen that standard D gave a sensitivity about 3.7 per cent higher than the average sensitivity of U^{235} for standards A and B. It has been shown that for natural uranium the fission of U^{238} in this irradiation facility contributes about 1.2 per cent to the count obtained. Thus, if the counts obtained for standard D is lowered by this amount to compensate for the U^{238} fission, the difference between the averaged sensitivities for standards A and B and Standard D becomes less than 3 per cent.

TABLE VII

COMPARISON OF SENSITIVITY OBTAINED WITH THREE URANIUM COMPARATOR STANDARDS[a]

Standard[b]	Volume of Aliquot, µl	Wt. of U-235 in Aliquct, µg	Net Delayed-Neutron Count	Sensitivity	Average Values of Sensitivity
A	10.0	1.00	2.30×10^5 2.29×10^5	2.30×10^5 2.29×10^5	
	10.0	1.00	2.32×10^5 2.32×10^5	2.32×10^5 2.32×10^5	
	10.0	1.00	2.29×10^5 2.29×10^5	2.29×10^5 2.29×10^5	For A 2.30×10^5
B	10.0	0.100	2.33×10^4 2.32×10^4	2.33×10^5 2.32×10^5	
	10.0	0.100	2.25×10^4 2.35×10^4	2.25×10^5 2.35×10^5	
	9.8	0.098	2.26×10^4 2.27×10^4	2.31×10^5 2.32×10^5	For B 2.31×10^5
D	30.4	0.217	2.41×10^5 2.40×10^5	2.41×10^5 2.40×10^5	
	20.0	0.143	2.39×10^5 2.38×10^5	2.39×10^5 2.38×10^5	For D 2.39×10^5

[a] All samples were irradiated 60 seconds and counted 60 seconds after a 20-second delay time.

[b] The solution designated as standard A was prepared to contain 100.0 µg U-235 per ml; standard B to contain 10 µg U-235 per ml, and standard D to contain 1.00 mg of total uranium (natural composition) per ml.

Neutron Flux Stability and Precision of Measurements: After finding that a rather large neutron flux gradient exists across the length of a rabbit in the HN-3 irradiation facility, an experiment was made to test the stability of the neutron flux over a period of a few hours. A piece of uranium metal foil weighing 0.398 mg (0.164% U^{235}) was sealed tightly in a small piece of polyethylene tubing so that it could not move inside the tubing. The sample was then placed in a rabbit and polyethylene film was packed tightly on top of the sample to prevent it from shifting position within the rabbit. The lid of the rabbit was screwed into place and the rabbit was irradiated and the delayed-neutron activity was assayed at 30-minute intervals to obtain a total of nine measurements over a period of 4 1/2 hours. The results are shown in Table VIII. The average of the counts obtained is 125,430. The relative standard deviation and mean deviation are 0.45 and 0.41 per cent, respectively. The standard deviation expected from counting statistics alone is 0.28 per cent. Even though the precision in these measurements is high, they still do not show unambiguously the short time variations of neutron flux for there is the possibility that the sample did move within the rabbit from one irradiation to another (a movement of about 0.3 mm would account for the variation observed) or that the rabbit does not return each time to exactly the same position near the reactor core. The measurements do show, however, that when a sample position can be fixed very accurately within a rabbit, rather highly precise measurements can be made.

TABLE VIII

DELAYED NEUTRON COUNTS FOR A SAMPLE WITH THE POSITION OF THE SAMPLE FIXED ACCURATELY WITHIN THE RABBIT*

Delayed Neutron Count
124,430
125,040
126,220
125,650
125,340
126,260
125,330
125,510
125,080

Mean = 125,430; Mean Deviation = 428 or 0.34%; Standard Deviation = 580 or 0.46%

*The sample, a piece of uranium foil, was sealed in a polyethylene tube, packed in a rabbit with polyethylene film, irradiated for 1 minute and counted for 1 minute with a 30-second delay. Measurements were made every half-hour.

Another series of measurements were made with liquid samples containing different amounts of U^{235} to show what variations are obtained for samples which might be typical of samples in which uranium is to be determined. The samples were sealed in polyethylene tubes, placed in rabbits, irradiated for two minutes and counted for three minutes after a 10-second delay. Five consecutive measurements were taken on each sample. The results are shown in Table IX along with the calculated standard deviation of the counts obtained. These measurements were made in the early phases of this study, i.e., before the large effect of the neutron flux gradient along the rabbit was fully realized. Some paper absorbent tissue was used to pack the samples in the rabbits, but no special effort was made to insure that the samples did not move slightly within the rabbits. Also, there was enough empty space in the polyethylene tubes so that it was possible for the liquid to move 3 - 5 mm within the tubes. The rather large variations obtained for the measurements are believed to reflect the instability of sample position within the rabbit.

Calibration Measurements: Samples have been analyzed for uranium using a number of time combinations of t_b, t_d, and t_c. For this reason, it was felt that it would not be of much use to prepare calibration curves with uranium standards in order to allow the analysis of a group of samples for uranium by comparing the counts obtained to values on the calibration curves. For such a technique, a calibration curve would need to be prepared for each set of timing conditions. Any modification which changed the efficiency of the counter would change the curves and they might need to be prepared again. Instead,

TABLE IX

PRECISION MEASUREMENTS ON LIQUID SAMPLES
CONTAINING VARIOUS QUANTITIES OF U-235

Weight of U-235, μg	Net Delayed Neutron Count	Standard Deviation (Per Cent)
0.0058	1,115	
	1,209	
	1,500	14
	1,198	
	1,049	
0.058	11,417	
	12,929	
	11,801	4.8
	11,801	
	11,920	
0.178	35,000	
	35,960	
	34,840	1.8
	34,770	
	34,800	
0.145	30,590	
	29,310	
	30,080	2.9
	30,000	
	28,420	
1.78	17,400	
	19,200	
	17,400	4.5
	17,530	
	17,280	

it is believed to be more desirable to irradiate and count suitable standards at the time a group of samples are being analyzed. Nevertheless, some calibration measurements have been made, and it is instructive to look at the results. The calibration measurements were taken over a wide weight range of U^{235} for three different values of delay time using an irradiation time and a count time of 1 minute each. The delay times chosen were 70 seconds, 20 seconds, and 2 seconds, i.e., the time which is required for the rabbit to travel from the reactor core to the detector and moderator assembly. In the latter measurements, the counter was turned on when the rabbit left the reactor core and before it arrived at the detector and moderator assembly. The results of these measurements are shown in Table X in terms of net delayed neutron count obtained for each sample of U^{235}. In addition, the net delayed neutron count obtained for each sample was divided by the weight of U^{235} contained in the sample in order to obtain the sensitivity and thus show any variations of the sensitivity with increasing weight of U^{235}.

With delay times of 20 and 70 seconds, the sensitivity begins to drop rather rapidly when the count obtained exceeds 200,000 in a 1-minute counting period. With a delay time of 2 seconds the sensitivity begins to become lower with recorded counts of much less than 200,000. Most of this decrease in sensitivity with increased count-rate is undoubtedly due to coincidence loss in the detector and counting system. The loss is more pronounced with a delay time of only 2 seconds due to the fact that the shorter-lived delayed neutron groups are still present when the counter is turned on and the initial

TABLE X

CALIBRATION MEASUREMENTS[a]

Delayed Neutron Count Versus Sample Weight

t_d = 2 sec.			t_d = 20 sec.			t_d = 70 sec.		
Wt. U-235, µg	Net Count	Sensitivity[b] x 10^{-5}	Wt. U-235, µg	Net Count	Sensitivity[b] x 10^{-5}	Wt. U-235, µg	Net Count	Sensitivity[b] x 10^{-4}
0.0134	8,990	6.71	0.0134	4,068	3.03	0.264	15,877	6.02
0.0200	12,870	6.45	0.0200	5,992	3.00	0.668	43,157	6.46
0.0500	30,080	6.02	0.0500	14,800	2.96	0.986	59,170	6.12
0.100	59,600	5.96	0.126	34,000	2.70	2.10	138,000	6.58
0.126	73,000	5.80	0.210	56,400	2.68	3.83	238,000	6.12
0.210	131,000	6.24	1.05	274,000	2.61	7.58	456,000	6.03
0.585	340,000	5.81	1.15	291,000	2.53	11.6	677,000	5.83
1.05	514,000	4.90				16.5	939,000	5.69
1.15	621,000	5.30				31.9	1,480,000	4.67
2.17	911,000	4.20						
3.10	1,136,000	3.86						
5.12	1,485,000	2.91						

[a] All samples were irradiated 1 min. and counted for 1 min.

[b] Sensitivity equals the net count divided by the sample weight in micrograms.

count rate is very high even though the total recorded count is relatively low. The counts of 200,000 which were obtained during one minute of count time do not represent a constant count rate; however, if one assumes that they do as a first approximation, it is seen that at a count rate of about 3,000 counts per second the counter begins to loose counts. If this number is divided by 0.05 (the approximate efficiency of the counter), a value of 60,000 neutrons per second is obtained for the rate of neutron emission of the sample at which coincidence loss becomes significant. It can be shown from the curves in Figure 1, that if 0.06 μg of U^{235} is irradiated 1 minute in a neutron flux of 6×10^{13}, the sample will have a neutron emission rate of about 6×10^{4} n/sec at the time of discharge from the reactor. Thus, it is advisable to make t_d larger than 2 seconds for samples which contain 0.06 μg or more of U^{235} in order to minimize counting losses.

Some Typical Uranium Analyses: Uranium determinations have been made on a number of different types of sample materials including ores, granite, sea sediments, graphite, biological tissue, and zirconium-uranium alloys. Determinations have also been made of the uranium isotopic composition of uranium oxides and uranium metal. Table XI shows the results of some of these analyses. For those analyses in which the total uranium was determined, the isotopic composition was known or a comparator sample was used which had the same isotopic composition as the uranium in the test samples. In most of the isotopic composition determinations the uranium assayed had a U^{235} content which was high enough so that the neutron counts

due to U^{238} fission could be neglected. One sample which was uranium metal foil containing 0.164 per cent U^{235} according to mass spectrometric measurements was determined to be 0.168 per cent U^{235} before counts due to U^{238} fission were taken into account. After subtracting the contribution due to U^{238} from the measured count, a value of 0.164 per cent U^{235} was obtained. Most of the analyses given in Table XI were made before the large effect of the neutron flux gradient was realized. Consequently, the precision indication given for some of the determinations is considerably larger than can now be obtained with the method by an accurate stable placement of the sample within the rabbit.

TABLE XI

SOME TYPICAL URANIUM DETERMINATIONS BY DELAYED NEUTRON COUNTING

Sample Material	Sample Weight, mg	Analyzed For	Portions Analyzed	Time Measurements[a] t_b	t_d	t_c	ccb[b] for Sample	Standard	ccb for[b] Standard	Results, %	Error, %	Other Methods Type	Results
U Ore	99 - 100[c]	Total U (Natural)	3	30	140	200	3.82×10^4/100 mg	0.818 mg U	1.02×10^4	3.05	2.8	γ-ray spectrometry	2.84%
U Ore	75 - 103	Total U (Natural)	3	120	60	130	3.39×10^4/100 mg	0.0251 mg U	8.70×10^3	0.098	7.9	β counting	0.098%
U Ore	63 - 147	Total U (Natural)	3	120	60	130	6.46×10^4/100 mg	0.0251 mg U	8.70×10^3	0.186	11	γ-ray spectrometry	0.15%
Granite	977.2	Total U (Natural)	1	10	2	60	7.08×10^3	0.126 μg U-235	2.93×10^4	4.2×10^{-4}	2		$2.7 - 3.7 \times 10^{-4}$%
Sea Sediment	107.4	Total U (Natural)	1	10	2	60	6.09×10^2	0.126 μg U-235	2.93×10^4	3.4×10^{-4}		Neutron activation analysis	
U Ore	0.025 - 0.103	Total U (Natural)	2	120	20	150	3.17×10^5 mg	0.100 mg U	1.04×10^5	30.8	5.8	γ-ray spectrometry	
U Metal Foil	0.157	% U-235	1	60	70	60	1.66×10^4	1.05 γg U-235	6.60×10^4	0.168		Mass spectrometry	0.164
Graphite	112.3	Total U (Depleted)	1	20	100	60	4.82×10^5	19 mg U foil	5.15×10^5	16.0		Calculated	16.1
Graphite	90.5	Total U	1	20	100	60	3.91×10^5	19 mg U foil	5.15×10^5	16.0		None	
Graphite	49.2	U-235	1	160	10	180	2.45×10^3	1.00 μg U-235	6.63×10^4	0.75×10^{-4}	4.4	None	
Graphite	49.5	U-235	1	140	10	180	3.71×10^3	1.00 μg U-235	6.63×10^4	1.13×10^{-4}	3.9	None	
Zr-U Alloy	13 - 36	U-235	3	120	90	70	233 c/mg	0.178 μg U-235	3.03×10^3	4.38×10^{-3}	9.5	None	
U_3O_8	2.42×10^{-4}	U-235	1	20	20	60	1.22×10^5	1.00 μg U-235	1.67×10^5	30.2		Mass spectrometry	30.0

[a] Time Measurements: t_b = irradiation time; t_d = delay time; t_c = count time.

[b] ccb means count corrected for background or blank count.

[c] A range of weight indicates the weight range for a number of replicate samples.

4.0. Discussion

4.1. Precision

No rigorous statistical evaluation of this method for uranium determination with the HN-3 irradiation facility has been made. It has been observed that when duplicate or triplicate samples of the same sample material are analyzed the results usually show a range 1 - 5 per cent variation irrespective of the magnitude of the count obtained (see Table IX). Of course, if a very low count is obtained, then statistical variations due to the random nature of radioactive decay can make the error larger than 5 per cent. Some of the factors which govern the precision of these measurements have been evaluated.

The precision obtained for a series of measurements of U^{235} is believed to be determined by the following factors: (1) the precision with which samples can be prepared, (2) the precision with which samples can be placed in a fixed reproducible position in the rabbits, (3) the stability of the neutron flux to which the samples are exposed, (4) the precision with which the times of irradiation, delay before counting, and counting can be controlled or measured, (5) coincident counting losses due to counting rates which are too high, and (6) statistical variations due to the random nature of radioactive decay.

The precision with which samples can be prepared for analysis by this method is the same as that which can be obtained for other methods of analysis. All samples taken for delayed-neutron measurements in this study were either weighed on an analytical balance or measured with a micropipet. It is to be expected that errors introduced in

measuring weights or volumes in this manner would at most be only a few tenths of one per cent.

The effects on the precision of the instability of the neutron flux and the instability of sample position within a rabbit are rather difficult to separate and evaluate. However, it has been been shown (see Table VIII) that any variation of neutron flux over a period of a few hours is less than 1 per cent. The neutron flux may change more than that amount over a period of a few days as the fuel in the reactor is being "burned up" or from one fuel loading to another. However, these effects are not of much interest in connection with the use of this method since standard comparator samples are always measured at the time uranium determinations are made. The largest contributing factor to variations in results of analyses is believed to be the neutron flux gradient along a rabbit. The magnitude of this effect has been shown to be 1.5 to 2.0 per cent per millimeter. However, it has been shown that by fixing the position of a sample in a rabbit so that little if any movement of the sample within the rabbit is permitted, measurements can be made which approach the precision dictated by counting statistics. Many of the determinations reported in Table XII were made before the effect of the neutron flux gradient was fully realized. It is, therefore, thought that for those analyses reported in Table XI for which an estimate of the precision is given most of the estimated error is due to instability of sample position within the rabbits or the inability to reproducibly place replicate samples exactly in the same position in the rabbits. It is relatively easy to place two samples of the same size

successively in one of the rabbits so that their centers of mass coincide within 1 - 2 millimeters. The positioning of the samples becomes slightly more difficult if the two samples are slightly different in size. The rabbits travel through the pneumatic tube at a fairly high speed (70 feet in 2 seconds) and receive a sizable jolt when they reach the end of the pneumatic tube. It would appear that this jolt would be enough to displace by a few millimeters a sample within the rabbit unless the sample is very tightly packed in the rabbit. In the initial phases of this study, liquid samples were sealed in polyethylene tubes with a void in the tubes in some cases as large as the sample volume itself (25 - 100 μl). The tubes were placed in the rabbits nearly parallel to the axis of the rabbit and absorbent paper tissue was packed in around the sample. In some cases it was possible for the sample tube to move about 3 to 5 millimeters when the rabbit hit the end of the pneumatic tube. For such measurements one might expect variations of 4 - 9 per cent in the recorded count which is approximately the variations which were obtained.

The electric clocks and timers used with the HN-3 irradiation facility permit the time interval of irradiation of a sample, t_b, the delayed time before counting is initiated, t_c, and the interval of time that counts are collected, t_c, to be controlled or measured to within $\pm$ 0.1 second or better. By the use of equations 1 and 2, using the decay parameters of delayed neutron decay given by Keepin, et al,[9] one can estimate the error to be expected from variations of the times t_b, t_d, and t_c. In all but two measurements reported

in Table XII, irradiation times of 20 seconds or longer were used. A variation in the timing of an irradiation interval would have the largest effect on the saturation of the delayed neutron groups having the larger half-lives. Assuming a value of 20 seconds for t_b and a variation or uncertainty in t_b of 0.2 seconds, it can be shown that the variations of the saturation of the delayed neutron groups with half-lives 55.72 seconds and 22.72 seconds is about 1 per cent and 0.5 per cent, respectively. The effect on the shorter-lived delayed neutron groups would be much less. Since the absolute group yield for group 2 is much larger than for group 1, the expected variation would be less than 1 per cent. If an irradiation time of 1 minute is employed, the effect of a variation of 0.2 seconds in t_b is very sharply reduced.

The most critical of all the timing measurements is the delay time. The error introduced by a $\pm$ 0.1 second in the measurement of t_d can also be estimated. Since the rate of delayed neutron emission is largest when the sample is first discharged from the reactor, the largest error due to an error in the measurement of t_d would occur if the delay time was made equal to the time taken for the rabbit to be discharged to the counter. The time required for a rabbit to be discharged has been measured and found to be 2.0 $\pm$ 0.1 seconds. If an irradiation time of 20 seconds, a delay time of 2.0 $\pm$ 0.1 seconds, and a count time of 60 seconds are assumed, then the expected error in the observed count should be given approximately by

$$\frac{A_d' \times (\text{Time uncertainty}) \times 100}{N_d'} = \text{per cent error in observed count}$$

where A_d' is the rate of delayed neutron emission in neutrons per second, two seconds after a 20-second irradiation.

N_d' is the number of neutrons emitted by the sample over a 60-second interval with t_b equal to 20 seconds and t_d equal to 2 seconds.

Values for these quantities can be obtained for a 1-μg sample of U^{235} from Figures 1 and 2. From Figure 1, A_d is seen to be approximately 6.2×10^5 n/sec. From Figure 2, N_d is found to be 6.7×10^6 n. Solving the equation above with the proper numbers gives a value of 1.9 per cent error in the observed count.

Longer delay times should result in much smaller errors in the observed count.

Usually a counting time of 1 - 2 minutes is employed. It can be similarly shown that an error of $\pm$ 0.1 second in a count time of 60 seconds should result in errors in the observed count which are negligible. Therefore, in all measurements thus far made, errors in timing intervals should have caused variations in the observed counts of not more than 2 - 3 per cent and in most cases less than 1 per cent.

The error introduced into a uranium determination due to coincident counting losses can be minimized by two techniques: (1) having the counting rate small enough so that there is negligible loss of counts and (2) having the counting rate of the comparator sample nearly equal to test sample so that the counting losses for one are nearly compensated by the counting losses of the other. These two principles have been adhered to in this study. It was found that for the counter used in this study counting rates of 5 - 6 thousand counts per second resulted in counting loss of the order of 1 - 3 per cent.

For an assay of radioactivity taken over a period of time which is equal to or longer than the half-life of the radionuclide, Friedlander and Kennedy[22] give for the standard deviation, σ, the expression

$$\sigma = \sqrt{N_o E(1-e^{-\lambda t})(1-E+Ee^{-\lambda t})} \qquad (4)$$

where N_o is the number of atoms of the radionuclide which are present when the assay is begun,

λ is the decay constant of the radionuclide,

t is the time interval of the assay, and

E is the detector efficiency.

In the case of delayed-neutron measurements made in this study, the detector efficiency was about 0.05 so that the last term under the radical in equation 4 is near enough to unity it can be neglected. Thus, the equation can be modified to give:

$$\sigma = \sqrt{N_o(1-e^{-\lambda t})\ E} = \sqrt{\text{recorded count}} \qquad (5)$$

which is the usual expression for the standard deviation which one encounters for radioactivity measurements.

It has been shown that delayed neutron measurements can be made in the HN-3 Irradiation Facility with variations which closely approach the expected standard deviation as calculated from the statistics of radioactive decay if steps are taken to minimize all the non-random effects mentioned above which contribute to variations in the method.

4.2. Optimum Conditions for Analyses

From the discussion above and from equation 1, a set of optimum conditions for uranium determination can be formulated. If the amount of U^{235} in the sample is very low (near 10^{-9} grams), a relatively long irradiation time and a short delay time is indicated in order to obtain as large a count as possible so that the statistical variation is minimized. However, due to the fact that the absolute group yield of delayed-neutron group 2 is much larger than that of group 1, not much is gained in having the irradiation time last longer than 1 minute. It is possible to control quite accurately the delay time for measurements in the HN-3 Irradiation Facility so that very short delay times can be employed for samples containing small amounts of U^{235}. However, if delay times of 5 seconds or less are used for samples containing more than 0.05 micrograms of U^{235}, significant coincident counting losses can be obtained during the first few seconds of counting. These losses are due to the fact that delayed-neutron groups 3 and 4 are decaying rapidly during these first few seconds.

These losses can be quite large for large amounts of U^{235}, and it is difficult to compensate for these losses by having a comparator containing nearly the same quantity of U^{235}. For samples containing a quantity of U^{235} in the range of 0.05 to 1 μg, an irradiation time of 20 seconds is adequate for purposes of sensitivity. The error associated with the uncertainty in the irradiation should be less than 1 per cent. A delay time of 10 - 20 seconds is indicated to minimize the error due to uncertainties in the measurement of the

delay time and the coincident counting losses. For samples containing 1 - 20 micrograms of U^{235}, longer delay times of the order of 60 - 70 seconds would be needed to minimize counting losses. Samples containing more than 10 - 20 μg of U^{235} become too radioactive to process easily with the HN-3 Irradiation Facility. A preliminary short irradiation of a sample will give an indication of the quantity of U^{235} in a sample. It would appear that a counting time of 1 minute is adequate for most analyses.

4.3. Interferences

There are four possible types of interferences in the delayed-neutron counting method to the determination of any nuclide which emits delayed neutrons. These types of interferences are: (1) other nuclides which fission and thereby result in the formation of delayed-neutron-emitting nuclides, (2) delayed-neutron emitters which are formed by primary or secondary (n,p) or (n,α) reactions, (3) neutron emission of a sample which emits high-energy gamma radiation capable of producing neutrons by (γ,n) reaction, and (4) self-shadowing effect of a sample containing nuclides with high capture cross-sections which shadow the interior of a sample from the thermal neutrons in a reactor during the irradiation of the sample.

Examples of nuclides which give the first type of interference are U^{235}, U^{233}, U^{238}, Pu^{239}, and Th^{232}. U^{235}, U^{233}, and Pu^{239} are fissioned by thermal neutrons and would present serious interference to the determination of one of these nuclides if the others are present to any appreciable extent. Th^{232} and U^{238} are fissioned by fast

neutrons and would present an interference to the determination of small amounts of U^{235} if they were present in large amounts. These effects could be reduced very greatly by making irradiations in an irradiation facility which has a high ratio of thermal to fast neutrons.

These are only a few known examples of nuclides which present an interference of the second type. Nitrogen-17 decays by negatron emission to an excited state of oxygen-17 which is a delayed neutron emitter. Nitrogen-17 has a half-life of 4.14 seconds. Nitrogen-17 can be produced by the reactions $O^{17}(n,p)N^{17}$, $O^{18}(t,\alpha)N^{17}$, and $N^{15}(t,p)N^{17}$. The first reaction can result from the reaction of the fast neutrons in a reactor with any oxygen in a sample. Tritons can be formed from the thermal neutrons in a reactor by the reaction $Li^{6}(n,\alpha)t$. The reaction $Be^{9}(n,p)Li^{9}$ can result from the reaction of fast neutrons on beryllium. The Li^{9} has a half-life of 0.17 seconds and is a precursor of a delayed-neutron emitter. Interferences from these short-lived radionuclides can be eliminated by having a delay time before counting which is long enough to allow them to decay.

Radionuclides, such as 15-h Na^{24} and 60-d Sb^{124}, which emit high energy radiation could possibly result in an interference by the reaction $H^{2}(\gamma,n)p$ and $Be(\gamma,2\alpha)n$. Interference of this sort should be very low in most cases especially since any sodium or antimony will not become intense γ-ray sources during a short irradiation for delayed-neutron measurements. Amiel[7] made experimental tests to determine if the gamma radiation emitted by the fission products of

uranium would produce an interference in samples containing beryllium, and found no interference.

There is the possibility of nuclides, such as B^{10}, Li^{6}, Cd^{113}, and Gd^{157}, which have high capture cross-sections for thermal neutrons, shadowing the interior of a sample from thermal neutrons during an irradiation to produce a negative bias interference. Making the sample smaller would reduce or eliminate this source of interference. Amiel[7] made tests of this effect on the determination of uranium by measurements on 10-ml volume samples containing various amounts of boron and lithium and found an interference of about 40% per 100 mg of B and about 16% per 100 mg of lithium.

One additional source of interference is possible from the fact that BF_3 detectors are slightly sensitive to very high fields of gamma-radiation. Most, if not all, of this interference can be eliminated by proper electronic discrimination of the γ-ray pulses from the α pulses produced in the BF_3 detectors. If this source of interference cannot be eliminated completely by electronic means, the BF_3 tubes can be shielded from the γ-radiation by placing lead around the sample. In the presently used neutron detector and moderator assembly, provision is made for the use of three inches of lead shield around the sample position. The effect of the lead on the neutrons is to reduce the neutron count by about 3 per cent. For most samples the lead is unnecessary. By removing the lead, the detectors could be moved closer to the sample, increasing the solid angle between neutron source and detectors, and thereby increasing the neutron detection efficiency of the system to possibly as much as 15 per cent or more.

In any case, it is believed that 1 - 2 inches of lead would suffice for any type of sample.

To the knowledge of the authors, in all of the measurements made in this study, the only nuclide present in the sample fissioned by thermal neutrons was U^{235} and, thus, no interfering elements were present. It was shown that nitrogen-17 (a precursor of oxygen-17, a delayed-neutron emitter) did not represent a significant interference even for the samples contained in water. For a mixture of fissionable nuclides, it might be of use for certain purposes to obtain analysis data in terms of an equivalent amount of U^{235}. In the case of the determination of uranium in low-level ores, soils, or granite, the presence of thorium might present an interference in the uranium assay. It can be shown from the data in Table VI that if the quantities of uranium and thorium in an ore are equal, the contribution of the delayed neutron count due to thorium is of the order of about 1 per cent. Amiel[4] found a similar value for the contribution of thorium. Enclosing the sample in cadmium decreases the count due to U^{235} by a factor of about 42 and allows an estimation of the thorium content of the sample. This technique was used by Amiel for thorium analyses.[7]

4.4. Further Uses of Method

Amiel[7] has shown how the method of delayed-neutron counting can be applied to the determination of thorium and uranium in mixtures of these elements by making irradiations of a sample with and without a cadmium shield. He also suggested a similar procedure for the

determination of the isotopic composition of uranium. From the results in Table VI, it appears that by making cadmium ratio measurements it should be possible to determine the isotopic composition of uranium between the limits of 1 to about 10^4 μg of U^{235} per gram of uranium without a knowledge of the total amount of uranium in the sample. For samples containing more than 10^4 μg of U^{235} per gram of uranium, a knowledge of the total amount of uranium is necessary since the fission of U^{235} is predominant even in the cadmium-shielded samples.

The sensitivity of the method for thorium determinations could be improved by the use of reactor facilities having a fast neutron flux higher than the one used in this study. The sensitivity for thorium in the present irradiation facility is about 10^4 counts per milligram of thorium. This value could be improved by making longer irradiations and increasing the efficiency of the counter. It should be possible to obtain irradiation facilities in the ORR which have a fast neutron flux of at least an order of magnitude greater than that of the present facility. Thus, it is believed that the sensitivity for thorium could be made as large as 10^6 counts per mg of thorium. Under these conditions, a gram of granite containing 50 μg of thorium would give a count possibly as large as 5×10^4.

Amiel[7] has also suggested the use of this method for the determination of U^{233} and Pu^{239} produced in reactor breeding experiments. In connection with this type of study, it should be possible to determine both nuclides in such systems as U^{238}-U^{235}, Th^{232}-Th^{233}, U^{235} (or natural U) - Th^{232}, U^{238}-Pu^{239}, etc. A general technique could

easily be worked out for determining each nuclide in such system pairs. To make such analyses, the sensitivities for each individual nuclide would be determined. Cadmium ratio values would then be determined as a function of the ratio of the nuclides and a plot of cadmium ratio versus nuclide ratio made. By determining the cadmium ratio of a test sample, the nuclide ratio of the sample could then be read from the graph. One would then assume a value for the quantity of one of the nuclides and thus calculate a "test value" for the quantity of the other nuclide. These two derived values for the quantities of the two nuclides could be tested for validity by calculating what the total count for the sample should have been by using the sensitivities determined for the two nuclides. If the calculated count and the experimental count (the count obtained without cadmium cover) do not agree closely, a more nearly correct value could be assumed for the quantity of one of the nuclides and these calculations made again. Additional successive approximations would yield values for each nuclide as accurate and precise as the detemined sensitivities. Of course, this procedure would not work for the determination of both nuclides in systems in which the nuclide ratio is so large (or small) that the fission rate of one nuclide is extremely large compared to the fission rate of the other. In this case, only one of the nuclides could be determined.

In addition to the studies suggested above, the authors plan to extend the present applications of the method by obtaining reactor irradiation facilities having values of neutron flux lower than the presently used facility so that samples which contain uranium in the

range of 10 micrograms to a few milligrams can be assayed. Also, the authors plan to study the use of a neutron generator having a fast neutron flux of about 10^{10} $n/cm^2/sec$ for uranium and thorium determinations.

The authors plan to attempt to apply this method to the determination of some of the transplutonium elements which are currently being produced in relatively large amounts. Americium-242 has interesting possibilities as a candidate for analysis by this method. The thermal neutron fission cross-section of 152-y Am^{242} has an approximate value of 6400 barns which is larger than that for U^{235} by at least a factor of 10.[14] The sensitivity of Am^{242} should, therefore, be large enough so that as little as 10^{-11} grams of Am^{242} could be detected.

5.0. Summary and Conclusions

The method of delayed-neutron counting has been shown to be an excellent one for the determination of uranium. Uranium has been determined in a wide variety of sample matrix materials. Quantities of U^{235} slightly lower than 10^{-9} grams can be determined by the method. A limit of measurement for natural uranium is about 7×10^{-7} grams.

The precision of measurements can be made to closely approach that which is prescribed by radioactivity counting statistics. The factors which control the precision of the method and the possible sources of interference in the method are discussed.

The sensitivities for the determination of U^{238} and Th^{232} have been determined to be about 10^4 counts per milligram of each nuclide for an irradiation time of 20 seconds and a 60-second count time following a delay time of 20 seconds. Longer irradiations would extend these sensitivities almost by a factor of 10. Irradiations made in a facility with a higher fast neutron flux would also extend these sensitivities.

It should be possible to extend the method to the determination of thorium in many types of materials even if the materials contain considerable amounts of uranium. Indeed, it would seem that a general approach to the determination of both nuclides in systems containing one nuclide which is fissioned by thermal neutrons, e.g., U^{235}, Pu^{239}, and one nuclide which is fissioned by fast neutrons. Such systems would be represented by the combinations U^{238} - Pu^{239} and Th^{232} - U^{233} in a reactor breeder experiment. The delayed-neutron counting method

might have some especially useful applications in the analysis of products obtained in the production of the transplutonium elements, viz. Am, Cm, Br, Cf, E, Fm, Mv, and No. Many isotopes of these elements have been shown to have relatively large (and some very large) thermal neutron fission cross-sections.

As the delayed-neutron-counting method is presently used, a sample can be analyzed for uranium in 10 to 15 minutes including the time necessary to prepare the sample, make the irradiation, take the count, and make the required calculation. For what appears to be otherwise a relatively complex and time-consuming procedure, a uranium determination by delayed-neutron counting is simple and especially free of all but a very few interferences. The special simplicity of the method makes it possible to train a technician easily and rapidly in its use.

6.0. References

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