DP-MS-75-37

MASTER CONF-751009--2

THE 100 mg ^{252}Cf ACTIVATION ANALYSIS FACILITY AT THE SAVANNAH RIVER LABORATORY

by

K. W. MacMurdo and W. W. Bowman

Savannah River Laboratory
E. I. du Pont de Nemours and Company
Aiken, South Carolina

This paper is proposed for presentation at the
International Nuclear and Atomic Activation Analysis Conference and 19th Annual Meeting on Analytical Chemistry in Nuclear Technology
October 14-16, 1975
Gatlinburg, Tennessee

This paper was prepared in connection with work under Contract No. AT(07-2)-1 with the U. S. Energy Research and Development Administration.

DISCLAIMER

DP-MS-75-37

THE 100 mg ^{252}Cf ACTIVATION ANALYSIS FACILITY AT THE SAVANNAH RIVER LABORATORY*

K. W. MacMurdo and W. W. Bowman

Savannah River Laboratory
E. I. du Pont de Nemours and Company
Aiken, SC 29801

ABSTRACT

The ^{252}Cf Activation Analysis Facility at the Savannah River Laboratory (SRL) is used routinely for multielement analyses of a wide variety of solid and liquid samples, e.g., metal alloys, fly ash and other airborne particles, rocks, and aqueous and nonaqueous solutions. An automated absolute activation analysis technique, developed to use neutron transport codes to calculate multienergy group neutron spectra and fluxes, converts counting data directly into elemental concentrations expressed in parts per million. The facility contains four sources of ^{252}Cf totaling slightly over 100 mg. A pneumatic "rabbit" system permits automatic irradiation/decay/counting regimes to be performed unattended on up to 100 samples. Detection sensitivities of $\leq$400 ppb natural uranium and $\leq$0.5 nCi/g for ^{239}Pu are observed. Detection limits for over 65 elements have been determined. Over 40 elements are detectable at the one part per million level or less. Overall accuracies of ±10% are observed for most elements.

---

* The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U.S. Energy Research and Development Administration.

INTRODUCTION

The basic principles of neutron activation analysis have been understood for over thirty years but generally have not been applied to routine analytical procedures. Routine analyses are usually accomplished by the comparative standard technique, in which a standard of essentially identical matrix and similar in trace constituents is analyzed simultaneously with the sample. The comparative standard technique makes it possible to ignore uncertainties associated with the basic principles of the technique and to reduce the analysis procedure to the determination of simple ratios of numbers. Because the technique requires estimates of sample composition, and preparation, packaging, irradiation, decay, and counting of the standard under identical conditions, sample throughput necessarily is reduced by at least a factor of two. The comparative standard technique has become widely used by reactor neutron activation analysts because :

1. Uncertainties in radioactive decay parameters such as half-life and gamma ray decay abundance are eliminated from further consideration.
2. Variations in effective element response to the particular irradiation conditions are eliminated regardless of matrix effects (i.e., neutron self-absorption).
3. The analyst may ignore changes in the neutron flux and energy distribution which accompany changes in reactor power level and fuel burnup.

4. The need for absolute detector efficiency calibrations is eliminated.

At the Savannah River Laboratory (SRL), the availability of large sources of ^{252}Cf on loan from the U. S. Energy Research and Development Administration (ERDA) has provided a unique opportunity to develop and test the limits of application of a technique termed "Automated Absolute Activation Analysis." Reliable neutron transport codes for light- and heavy-water moderator configurations are used to calculate multi-energy group neutron spectra and the thermal and epithermal fluxes at the sample irradiation sites. These calculated neutron spectra and flux data are combined with multi-energy (2- or 84-energy group) cross sections to compute elemental neutron capture rates within the sample. Unlike in a reactor, the neutron energy spectrum surrounding the large ^{252}Cf source is constant, and the magnitude of the flux simply changes with the ^{252}Cf half-life.

Installation of a fast pneumatic sample transfer "rabbit" system under automatic preset control permits cyclic irradiation/decay/counting sequences with the facility unattended. In many cases, more sensitive trace analyses are obtained by the counting of short half-life activation products. Applications of cyclic activation procedures has proven particularly beneficial in the delayed neutron analysis of fissile material.

Computerized data reduction converts counting data directly into elemental concentrations expressed in parts per million.

The data reduction process, using the SRL IBM 360-195 computer, is described in a companion paper.

DESCRIPTION OF FACILITY

The ^{252}Cf Activation Analysis Facility at SRL (Figure 1) is used routinely for multielement analyses of a wide variety of solid and liquid samples. The irradiation facility now contains four sources of ^{252}Cf totaling slightly over 100 mg. The sources are rotated to ensure flux equalization and are surrounded by an annulus of D_2O, which is immersed in an outer vessel containing H_2O for moderation and personnel shielding.

Two concentric rings of nine irradiation sites surround the sources (Figure 2). The inner concentric ring is located in the region moderated by H_2O; the outer ring is located in the D_2O annulus. Due to the smaller neutron absorption cross section of deuterium, the effect of the D_2O moderator is to increase the thermal neutron flux at both rings of irradiation sites. Three sites in the inner ring are connected to the pneumatic rabbit system (Figure 3), which permits automatic cyclic (repeated) irradiation/decay/counting regimes to be performed on up to 100 samples with the facility unattended. The remaining fifteen irradiation sites are for manual irradiations yielding long-lived activation products. Figure 4 shows the annular tank containing D_2O and the second ring of 9 irradiation tubes.

Timing information used in the data reduction scheme is pro-

vided by photocells along the sample paths in the rabbit system. Counting capabilities include automatic and simultaneous acquisition of both delayed neutron data (fissile material analysis) and gamma ray spectral data (Figure 5) using a multichannel analyzer (Figure 6). Counting data are automatically transferred to magnetic tape after each analysis.

AUTOMATED ABSOLUTE ACTIVATION ANALYSIS

To maximize sample throughput, a technique termed "Automated Absolute Activation Analysis" was developed to provide qualitative and semiquantitative analyses (±10%) without comparative standards or flux monitors. Automated refers to the totally computerized data reduction algorithim which converts the gamma ray spectra of irradiated samples directly into concentration (Figure 7) and to the programmed sample handling with the pneumatic rabbit system (Figure 8). Computer calculations of the thermal and epithermal neutron fluxes and the neutron energy spectrum for sample irradiation sites in both the light- and heavy-water-moderated regions were verified experimentally (Figures 9-11). The thermal flux at both rings of irradiation sites is greater than that expected for a solely light-water-moderated system. Specific neutron capture reaction rates are computed from the multi-energy group neutron spectrum and a library of cross section data tabulated in either 2- or 84-energy groups. Elemental composition is calculated from results of the gamma ray spectrum analysis combined with experimental timing information, spectrometric decay data, detector efficiencies, and the specific neutron capture reaction rates.

DETECTION LIMITS

Over forty elements are detectable at the 1 part per million level or less. Table 1 lists calculated elemental detection limits for 10-gram samples irradiated and counted under various regimes.

CYCLIC OPERATION

The advantage of cyclic activation is illustrated dramatically in the analysis of trace fissile materials such as natural uranium in rock, sediment, and soil samples. A relatively high efficiency (∿25%) delayed-neutron counter is installed in the pneumatic rabbit system for these analyses. Computer calculations based on the half-lives and group yields (Table 2) of beta-delayed neutron precursors optimize the cyclic irradiation and counting intervals for various fissile isotopes as a function of rabbit transit times (Figure 12). The calculated detector response for six delayed neutron groups assuming a 1.0 second transit time is shown in Figure 13. Detection sensitivities of ≤400 ppb natural uranium and ≤0.5 nCi/g for ^{239}Pu were observed.

MATRIX EFFECTS

Because of the absence of sample matrix effects, the reported analyses of known aqueous solutions by the absolute technique contain only the statistical errors of the cross sections, neutron fluxes, and radioactive decay parameters. Overall accuracies of ±10% are observed for most elements (Table 3). Some solid samples, such as gold wire, distort the neutron flux and energy distribution because of the higher density of absorbing nuclii.

To test the extent of matrix effects of other solids, NBS low alloy steel (Table 4), coal and fly ash standards (Table 5), USGS rock (Table 6), and other solid samples of known composition have been analyzed. Results indicate that flux depression and/or spectrum modification effects are not serious except for sample matrices with high densities of nuclii with large cross sections. For such matrices, simple dissolution into an aqueous medium minimizes flux depression effects.

TABLE 1

Elemental Detection Limits[a] of 100 mg ^{252}Cf Facility

Detection Limit, ppm	*Element*
<0.001	Eu, Dy
0.001 - 0.01	Mn, In, ^{129}I, Ir, Au, Lu, Ho, Sm, Re, ^{239}Pu[b]
0.01 - 0.1	Na, Sc, Co, Ga, Br, Ag, Sb, I, Cs, La, Pr, Tm, Yb, Ta, W, Pt, As, Se
0.1 - 1.0	Ar, K, Cr, V, Cu, Cd, Ce, Nd, Gd, Tb, Er, Hf, Hg, Ge, Sr, Nat. U[b]
1.0 - 10	Cl, Zn, Mo, Ru, Rh, Pd, Te, Ba, Os
10 - 100	F, Mg, Al, Ti, Ni, Sn, Rb, Y
100 - 1000	Ca, Fe, Zr
>1000	Pb, O, S

---

a. Based on 100 counts in photopeak from 15% efficient Ge(Li) detector. 10^{2} gram sample is assumed. The lowest detection limit for each element was selected from one of the listed regimes:

No.	*Irradiation Time*	*Decay Time*	*Count Time*	*Cycles*
1	6 sec	1 sec	6 sec	50
2	1 hr	5 min	30 min	1
3	1 day	1 hr	30 min	1
4	7 days	1 hr	30 min	1

b. Based on the 25% efficiency of the delayed neutron detector.

TABLE 2

Delayed Neutron Group Half-Lives and Yields

Group	*Half-Life, sec*	*^{235}U Yield, $n/10^3$ fissions*	*^{239}Pu Yield, $n/10^3$ fissions*
1	56	0.52	0.21
2	23	3.46	1.82
3	6.2	3.10	1.29
4	2.1	6.24	1.99
5	0.62	1.82	0.52
6	0.25	0.66	0.27
	Sum:	15.80	6.10

TABLE 3. Absolute Activation Results of ^{252}Cf Measurement Program

Element	*Concentration, ppm*		*% Deviation*
	Reported	*Found*	
Al	370	338	-8.6
Na	690	667	-3.3
Mn	5	5.15	+3.0
V	20	18.4	+8.0
Co	140	131	-6.4
Cu	95	95	0.0
Zn	930	940	+1.1
Se	840	895	+6.5
As	70	79	+12.9
Mo	2910	3420	+17.5
Hg	930	1030	+10.8
Cd	2330	1850	+20.6
Eu	0.9	1-7	-
Sc	*a*	2.04	-
Br	*a*	4.1	-
Au	*a*	0.009	-

a. Not reported.

TABLE 4. Analysis of NBS Low Alloy Steels

(Data not available at time report was prepared.)

TABLE 5. Analysis of NBS Coal Standard SRM-1632

Element[a]	*Concentration*		
	NBS	*INNA*[b]	*AAAA*[c]
Al, wt %		1.85 ±0.13	1.6 ±0.1
Fe, wt %	0.87 ±0.03	0.84 ±0.04	0.89 ±0.03
K, wt %		0.28 ±0.03	0.30 ±0.02
Mg, wt %		0.20 ±0.05	0.95 ±0.20
Na		414 ±20	380 ±3
Cl		890 ±125	800 ±50
Sc		3.7 ±0.3	3.6 ±0.2
Ti	800	1040 ±110	1200 ±400
V	35 ±3	36 ±3	35 ±5
Cr	20.2 ±0.5	19.7 ±0.9	29 ±5
Mn	40 ±3	43 ±4	43 ±1
Co	6	5.7 ±0.4	5 ±1
Zn	37 ±4	30 ±10	43 ±16
As	5.9 ±0.6	6.5 ±1.4	4.7 ±0.5
Br		19.3 ±1.9	15 ±1
Sr		161 ±16	170 ±20
Ba		350 ±30	300 ±30
Sb		3.9 ±1.3	3.8 ±0.2
Cs		1.4 ±0.1	3.5 ±1.3
La		10.7 ±1.2	8.3 ±0.2
Ce		19.5 ±1.0	26 ±5
Sm		1.7 ±0.2	1.4 ±0.10
Yb		0.7 ±0.1	1.0
U		1.41 ±0.07	1.34 ±0.50
Eu		0.33 ±0.03	0.41 ±0.02
Ga			5 ±1
Dy			1.0 ±0.1

---

a. Concentration in ppm, unless otherwise indicated.

b. Value reported by Instrumental Neutron Activation Analysis Round Robin, J. M. Ondov, et al., *Anal. Chem. 47*, 1102 (1975).

c. Value found by absolute activation analysis at SRL. Uncertainties based on counting statistics only.

TABLE 6. Analysis of NBS Fly Ash Standard SRM-1633

Element[a]	*Concentration* *NBS*	*INAA*	*AAAA*
Fe, wt %		6.2 ±0.3	6.3 ±0.1
Mg, wt %		1.8 ±0.4	1.7 ±0.2
Al, wt %		12.7 ±0.5	12.1 ±0.2
Si, wt %		21 ±2	
Ca, wt %		4.7 ±0.6	
K, wt %		1.61 ±0.15	1.51 ±0.05
Na		3200 ±400	2650 ±50
Sc		27 ±1	24 ±1
Mn	493 ±7	496 ±19	400 ±20
Co	38	42 ±1	38 ±2
As	61 ±6	58 ±4	54 ±3
Sr	1380	1700 ±300	1200 ±400
Sb		6.9 ±0.6	7.4 ±0.3
Ba		2700 ±200	3200 ±400
La		82 ±2	68 ±2
Sm		12.4 ±0.9	11 ±1
Dy			9 ±2
Hf		7.9 ±0.4	6.6 ±0.8
W		4.6 ±1.6	6 ±1
Cr	131 ±2	127 ±6	100 ±11
Br		12 ±4	6 ±1
Ce		146 ±15	200 ±30
Yb		7 ±3	6 ±2
Lu		1 ±0.1	4 ±1
Zn	210 ±20	216 ±25	270 ±30
Se	9.4 ±0.5	10.2 ±1.4	50 ±12
Cs		8.6 ±1.1	7.5 ±1.1
Tb		1.9 ±0.3	1.2 ±0.2
Ta		1.8 ±0.3	2.0 ±0.1
Cl		42 ±10	40 ±8

a. Concentration in ppm, unless otherwise indicated.

TABLE 7. Analysis of USGS Rock Standards

Element	*Concentration Found*	*USGS Range*
A. Sample DTS-1		
a. Major, wt %		
Na	0.062 ±0.006	0.007-0.05
Fe	6.8 ±0.9	6.0-7.7
Mg	28 ±8	28-33
Al	0.36 ±0.02	0.08-0.97
Cr	0.36 ±0.01	0.28-0.56
b. Minor constituents, ppm		
Sc	3.3 ±0.9	2-4.5
Co	137 ±10	96-160
Zn	180 ±70	23-140
Mn	860 ±10	450-1460
B. Sample GSP-1		
a. Major, wt %		
Na	1.9 ±0.1	1.97-2.20
K	5.0 ±1.0	4.41-4.64
Fe	3.0 ±0.2	2.78-3.40
Al	7.3 ±1.4	7.31-7.70
F	0.32 ±0.10	0.37-0.48
b. Minor, ppm		
Sc	5.2 ±0.9	2.3-22
Co	7.6 ±2.5	3-22
Sb	3.3 ±0.9	1.38-3.09
La	160 ±10	160-450
Ce	380 ±150	350-800
Eu	2.6 ±1.1	2.0-3.5
Hf	12 ±4	9.7-15
Zn	220 ±70	54-340
Mn	280 ±6	260-450

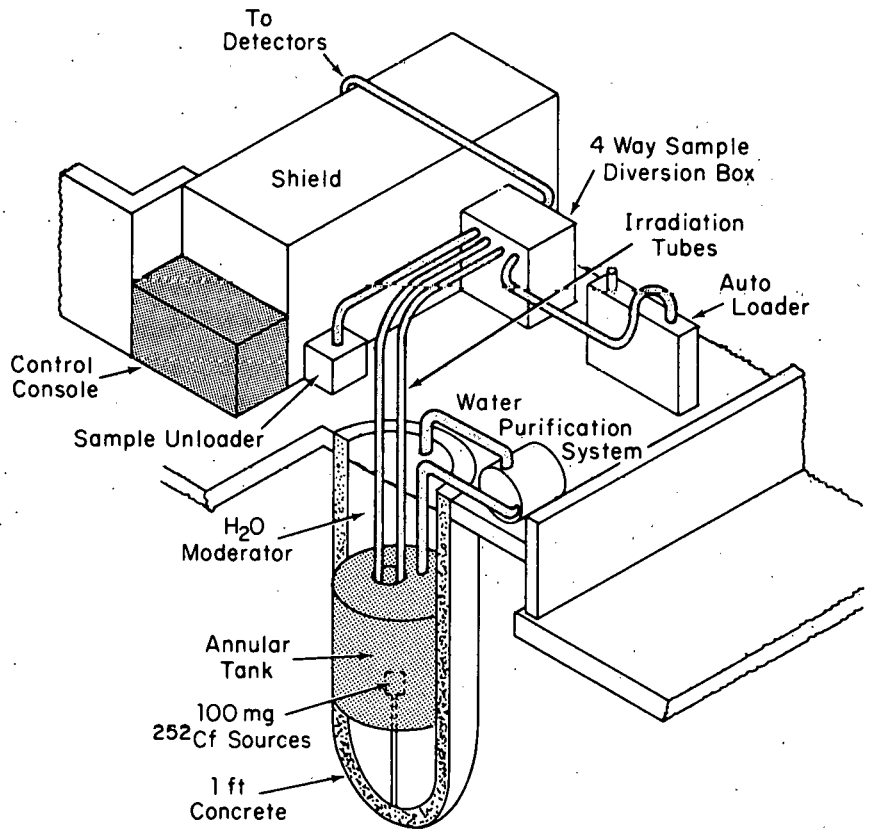

FIGURE 1. Schematic of the 100 Milligram ^{252}Cf Activation Facility at SRL

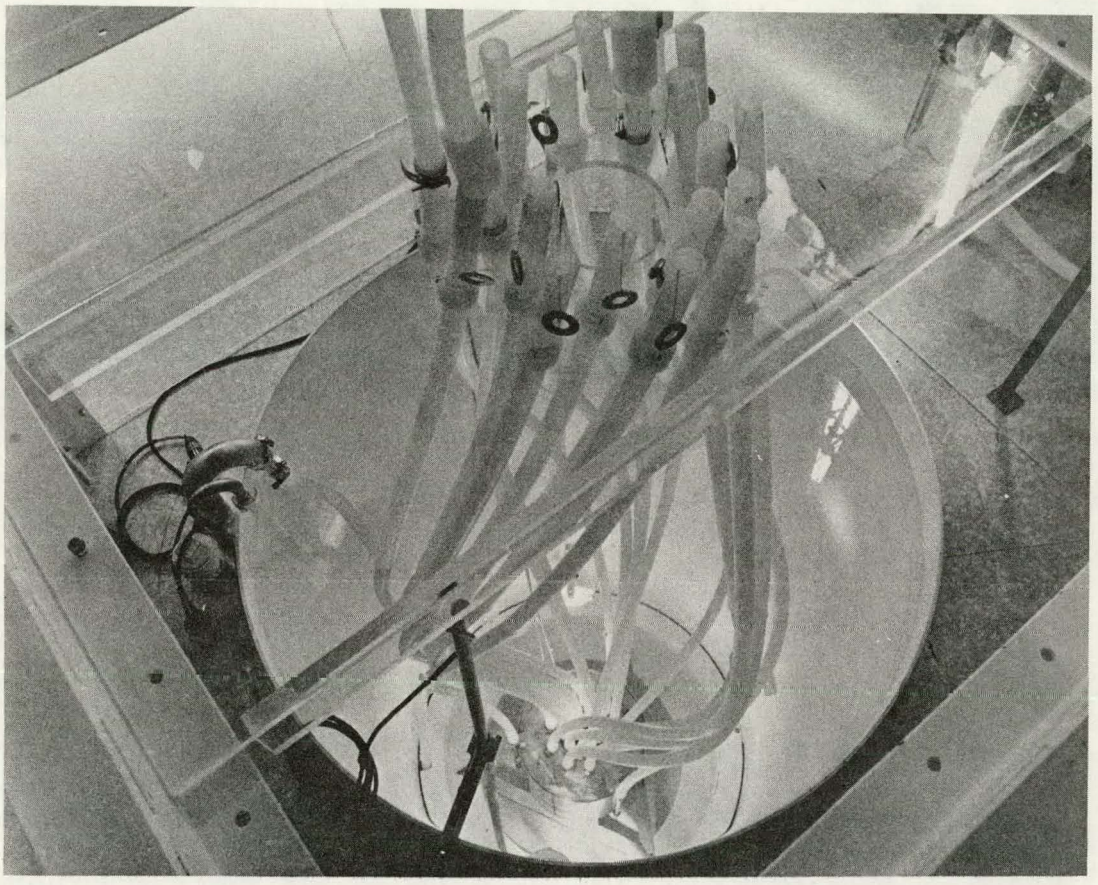

FIGURE 2. ^{252}Cf Source Tank

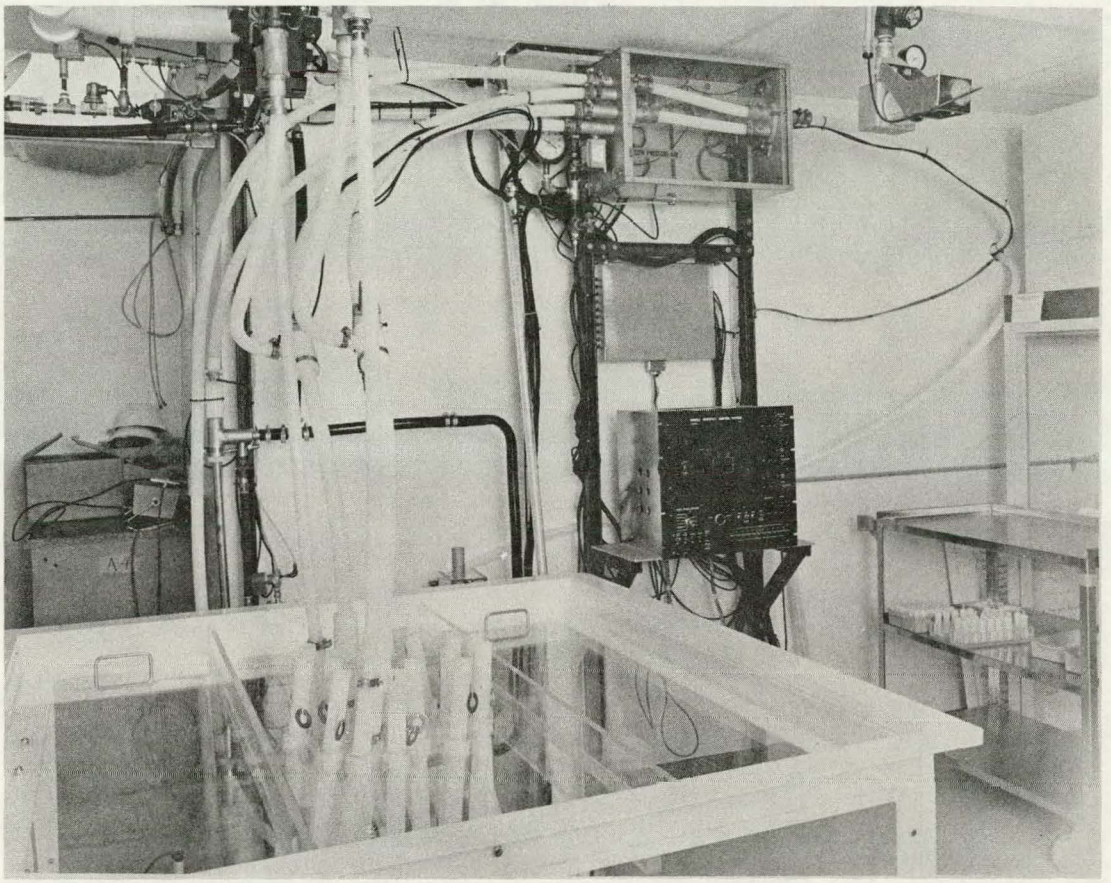

FIGURE 3. Source Tank Room and Pneumatic Components

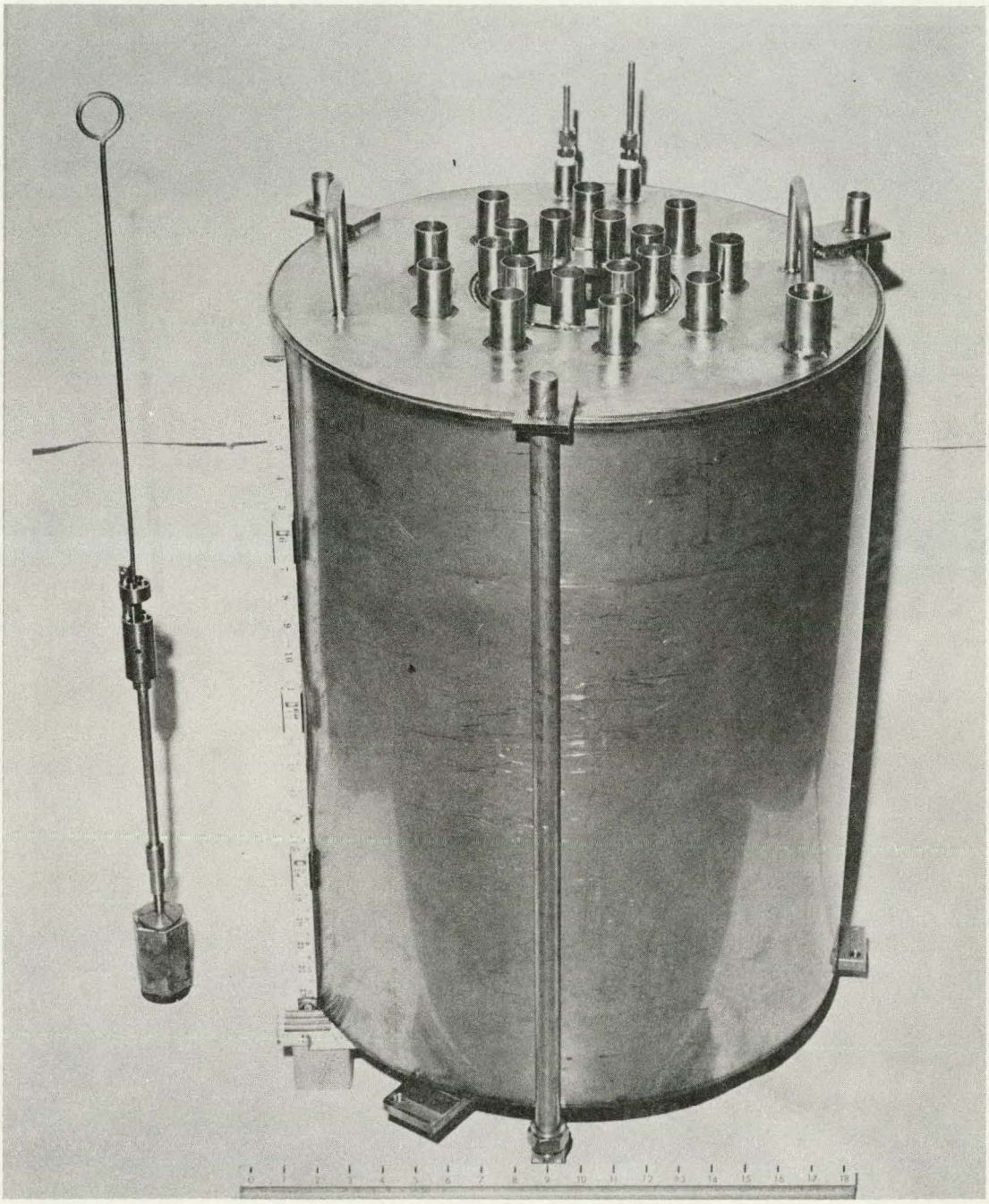

FIGURE 4. H_2O/D_2O Annulus

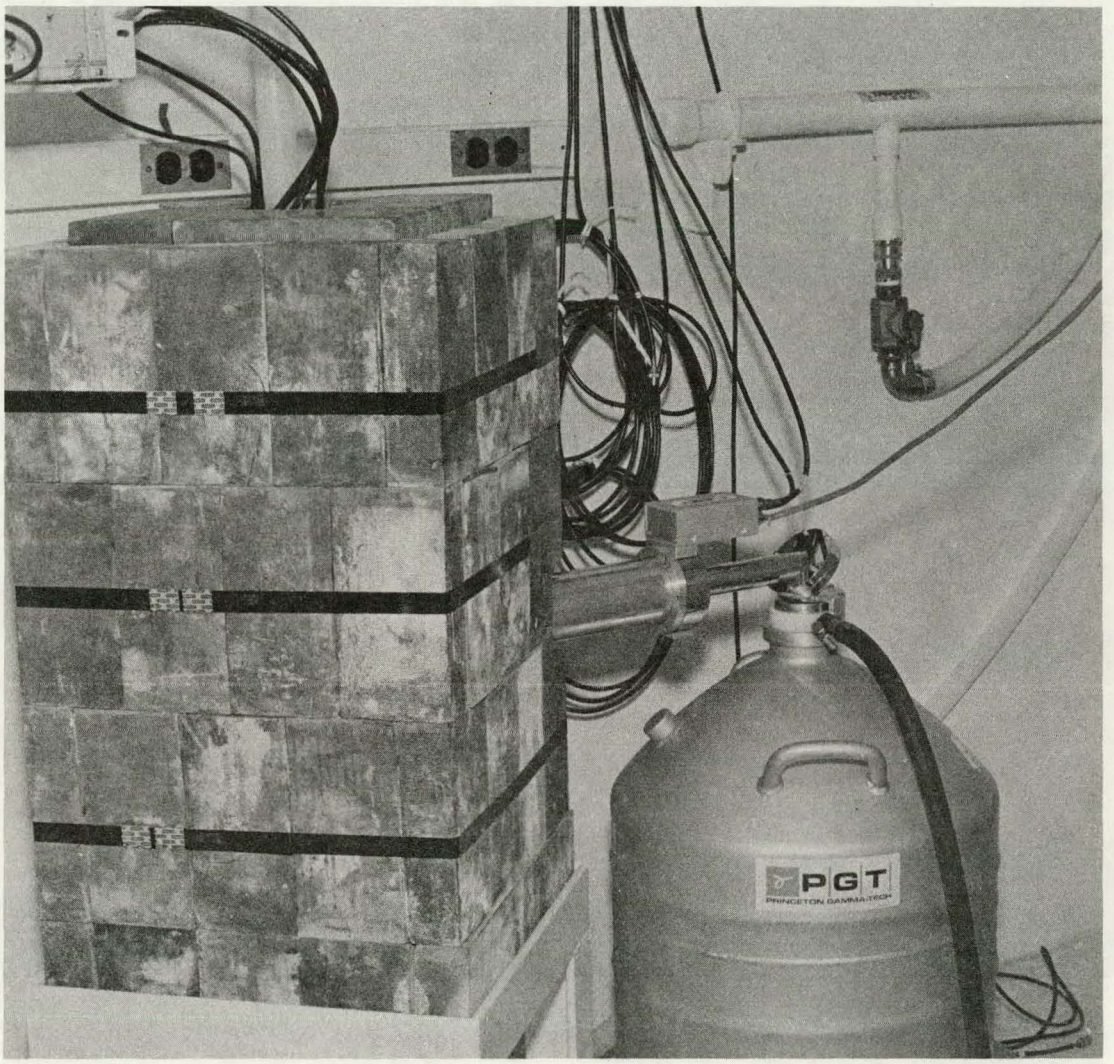

FIGURE 5. Shielded Dual Gamma-Ray, Delayed-Neutron Detector

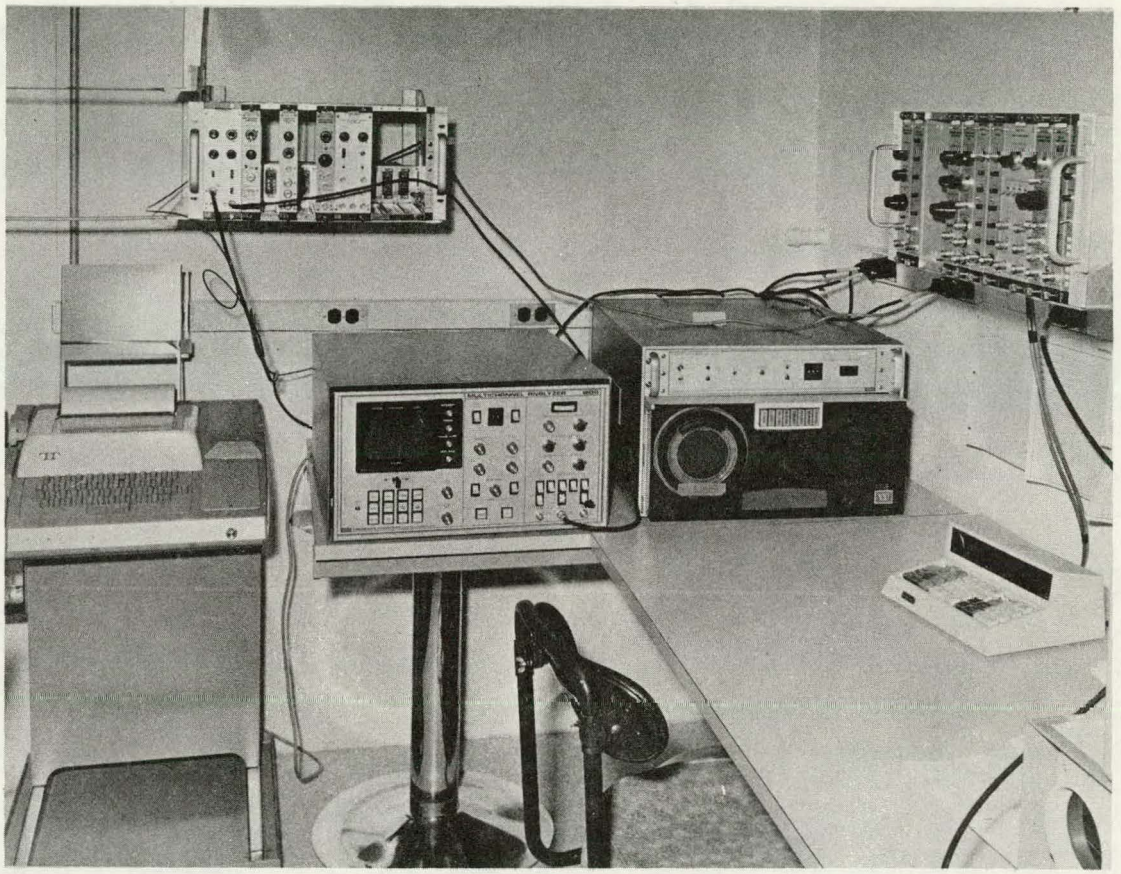

FIGURE 6. Data Acquisition Equipment

$$ppm = \frac{A\lambda(At.\ Wt.)}{W(Iso.Ab.)\ (6.023 \times 10^{17})E_\gamma I_\gamma (Prod.\ Rate)SCD\left[\frac{M}{1-Q} - \frac{Q(1-Q^M)}{(1-Q)^2}\right]} \quad (1)$$

where λ = decay constant

At.Wt. = atomic weight of target isotope

W = sample weight

Iso.Ab. = isotopic abundance of target isotope

E_γ = detection efficiency

I_γ = gamma ray intensity, photons/decay

Prod. Rate = neutron captures/second for the target isotope

S = saturation factor $[1 - \exp(-\lambda t_{irr})]$

C = counting factor $[1 - \exp(-\lambda t_{count})]$

D = decay factor $[\exp(-\lambda t_D)]$

$Q = \exp(-\lambda t_{cycle})$

M = number of irradiations and counting cycles

FIGURE 7. Basic Equation of Automated Absolute Activation Analysis

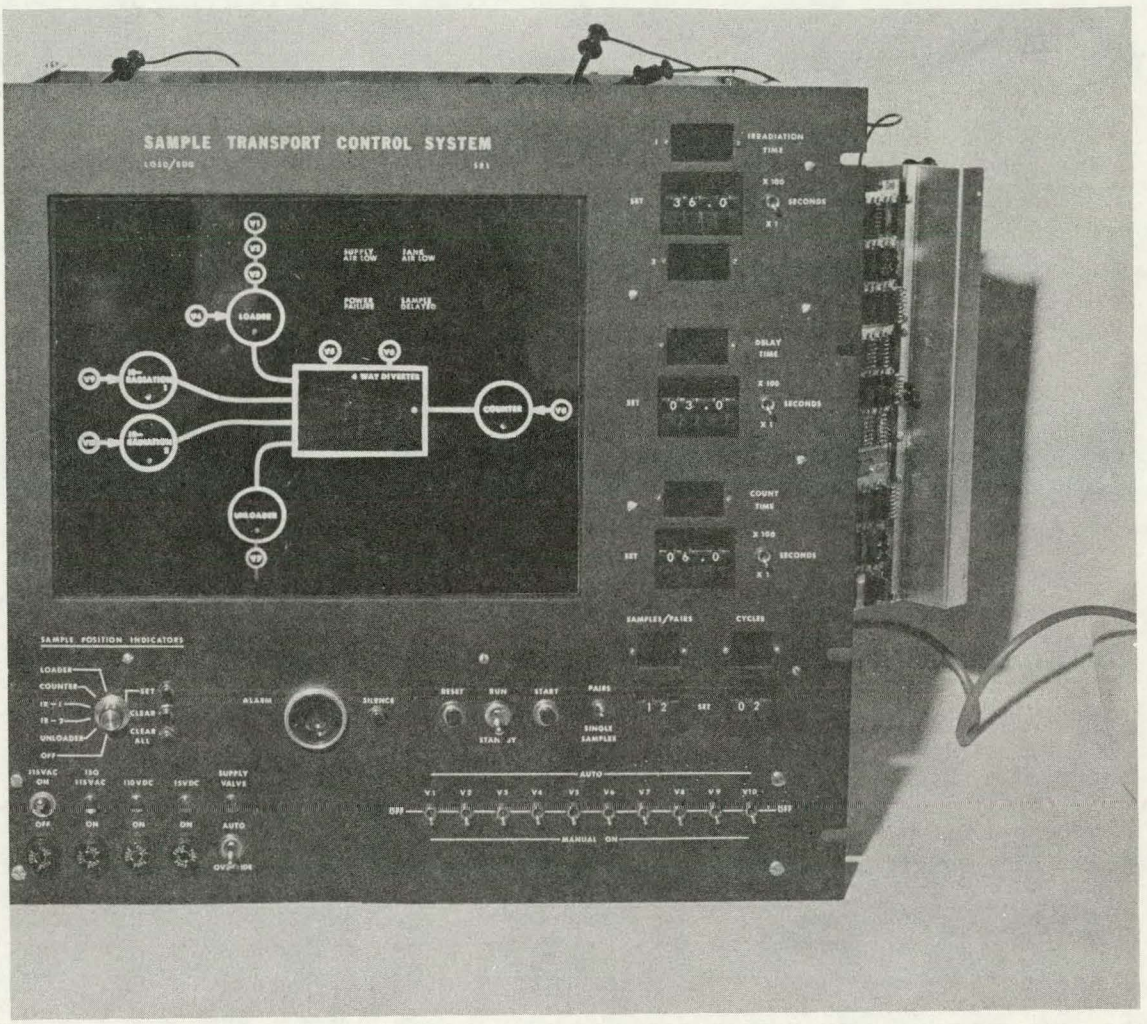

FIGURE 8. Automatic Control Unit

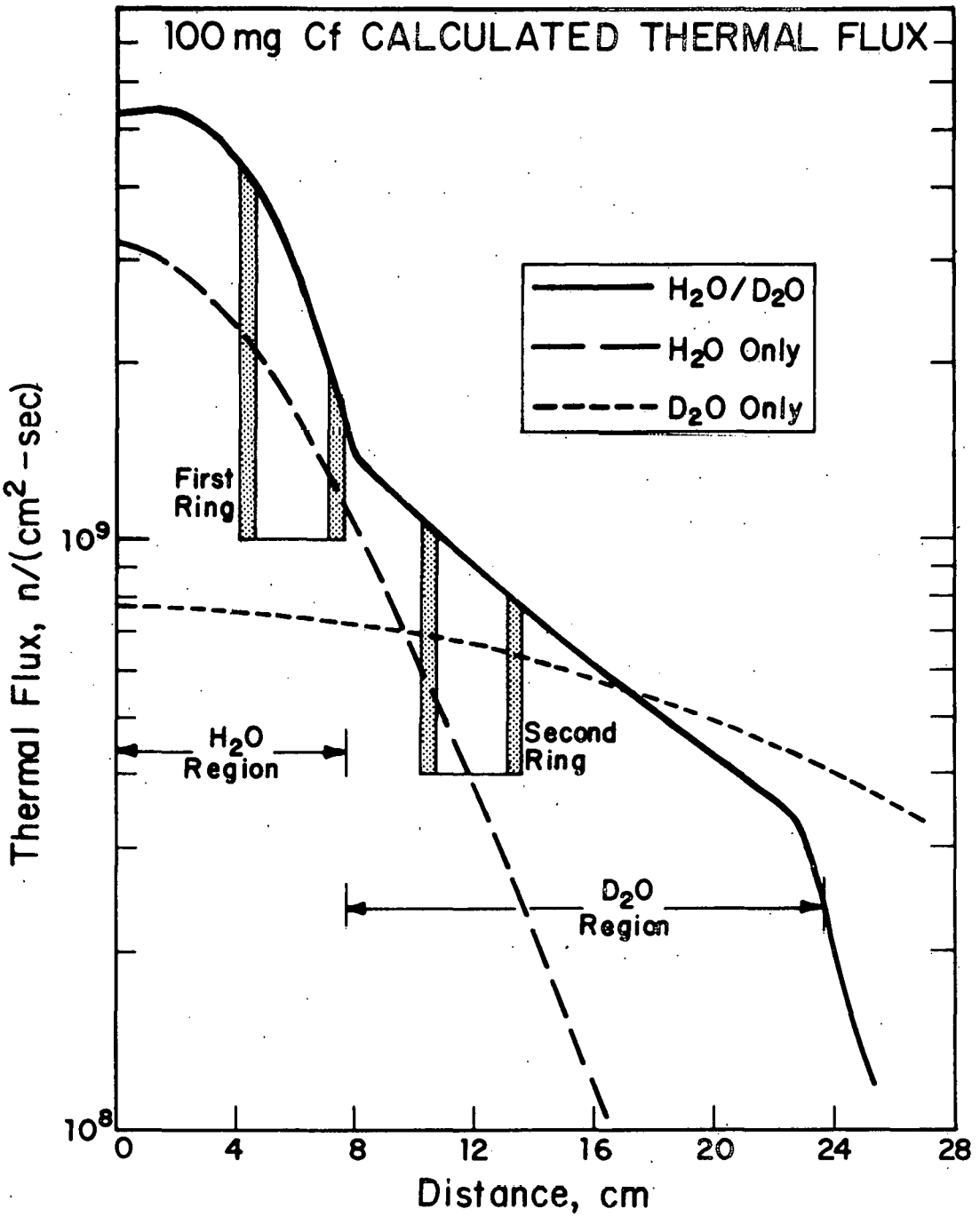

FIGURE 9. Thermal Flux *vs* Distance

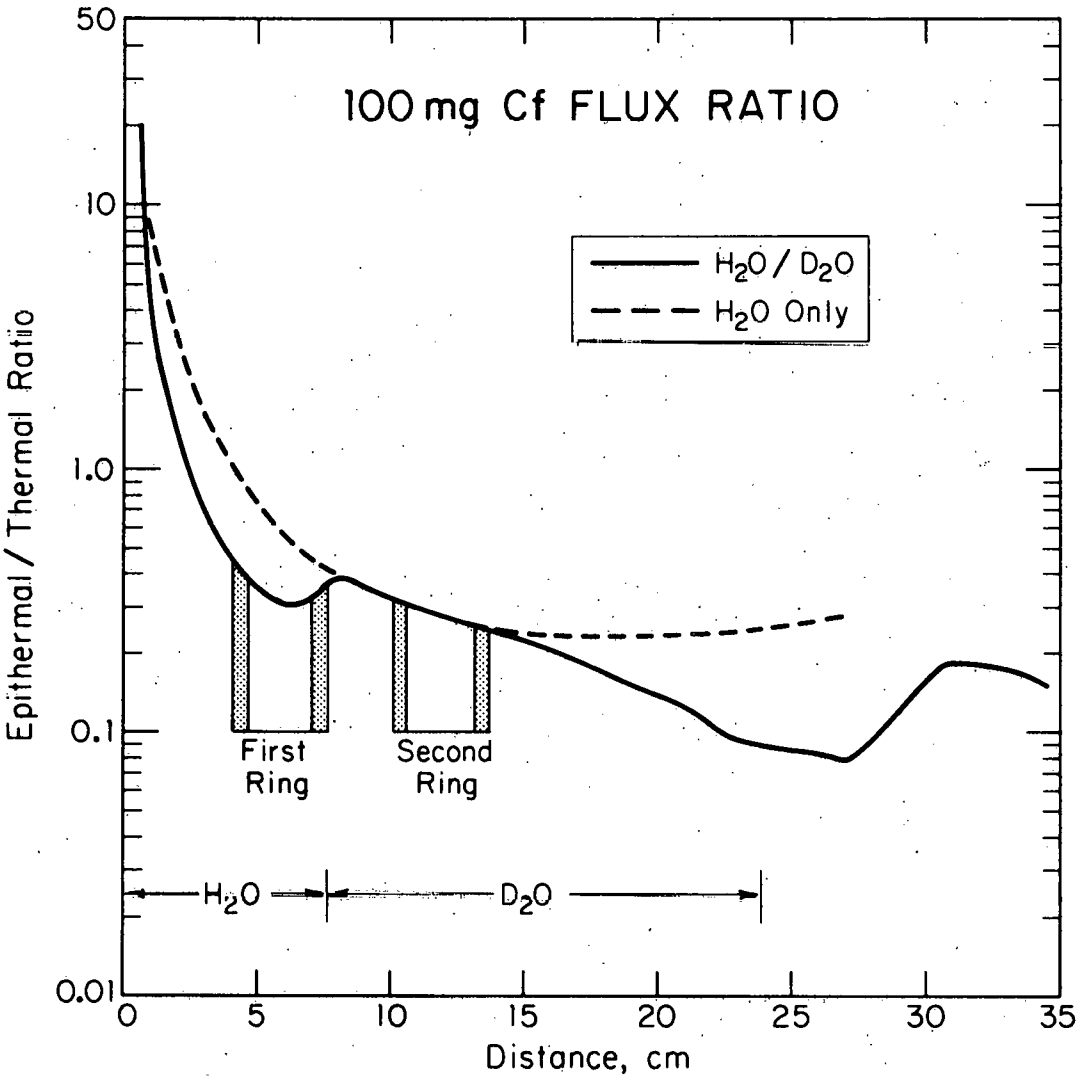

FIGURE 10. Epithermal/Thermal Flux Ratio *vs* Distance

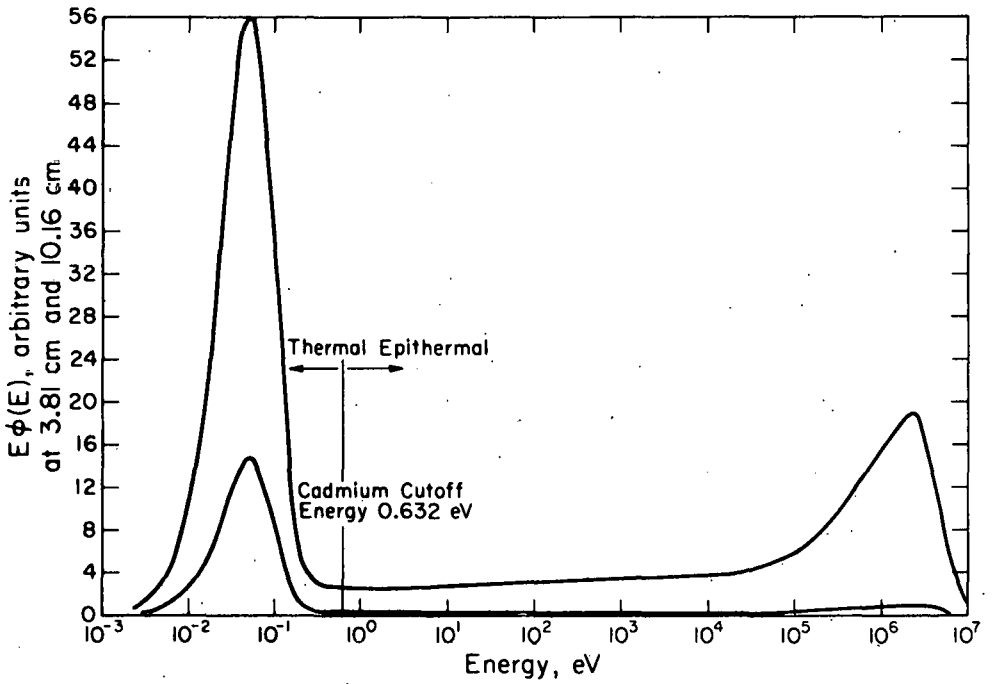

FIGURE 11. Neutron Energy Spectrum for Light Water Region

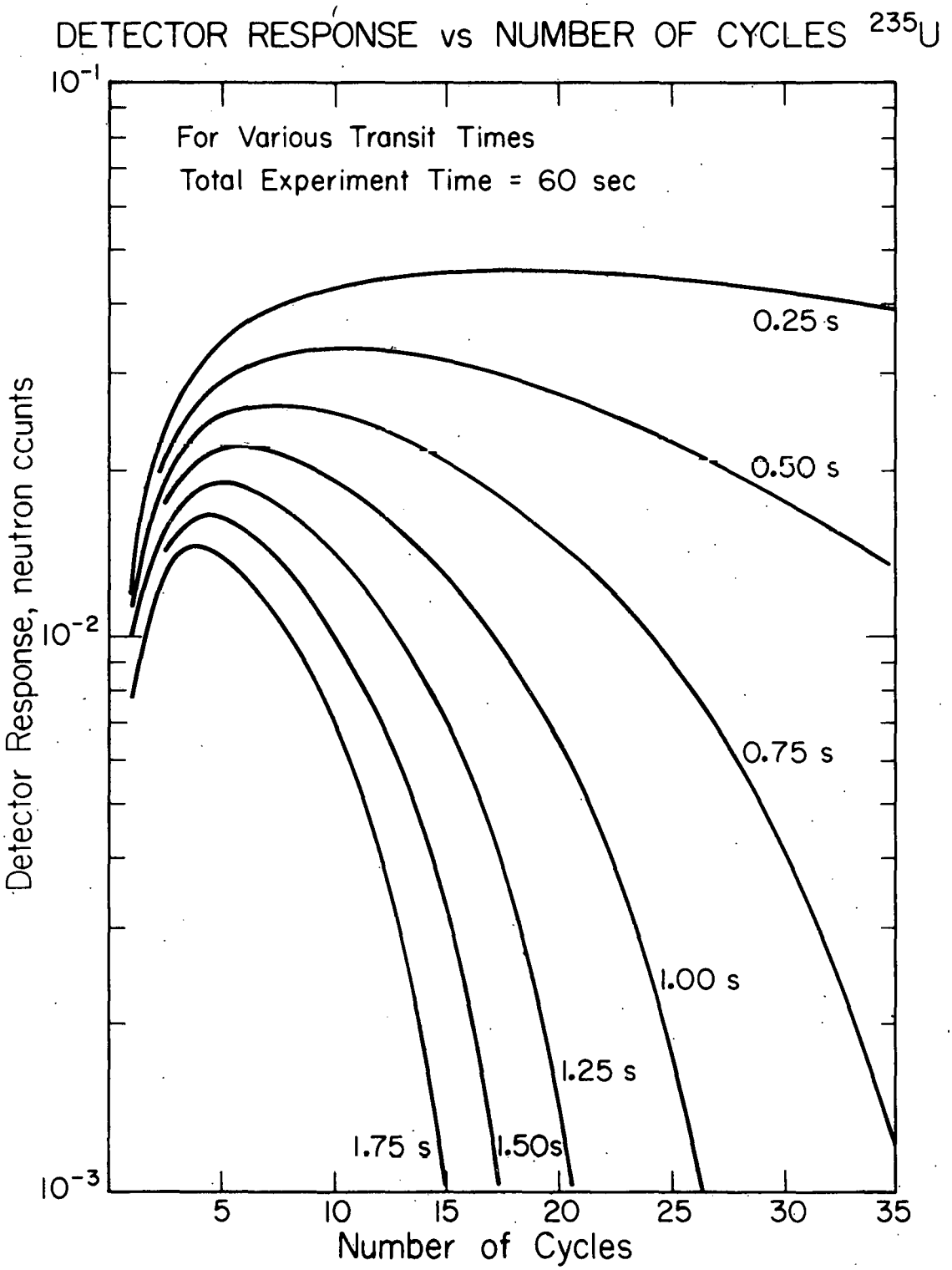

FIGURE 12. Delayed Neutron Group Response *vs* Number of Cycles for 1.0 Second Transit Time

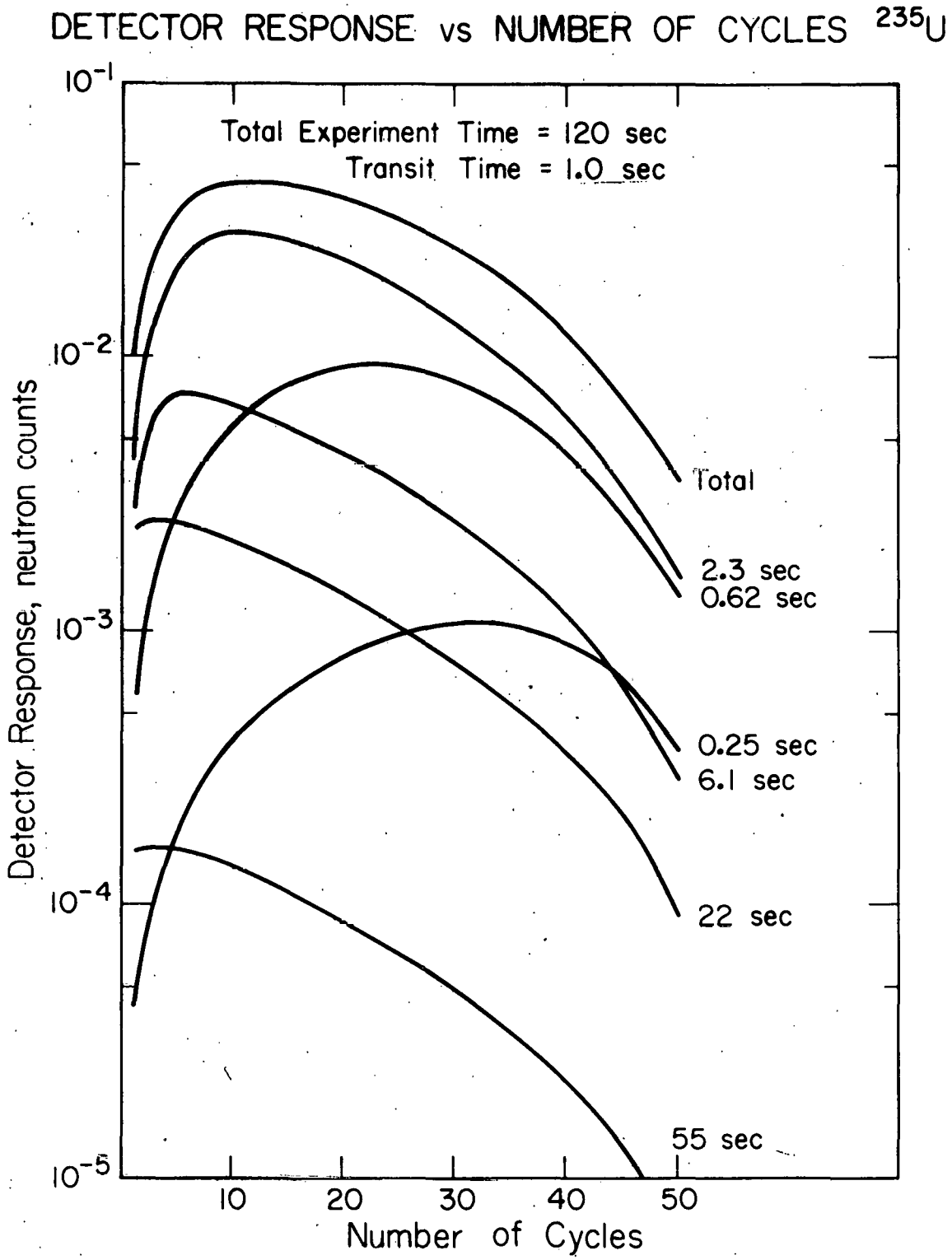

FIGURE 13. Total Detector Response for Various Transit Times