DETERMINATION OF BERYLLIUM BY THE PHOTONEUTRON METHOD

Gerald Goldstein

Analytical Chemistry Division
Oak Ridge National Laboratory*
Oak Ridge, Tennessee

(1d)

CONF-17-4

Abstract

Apparatus was designed and constructed for the determination of beryllium by the photoneutron method which can be employed in any analytical laboratory without hazard or difficulty. Because large $B^{10}F_3$ neutron counter tubes (2") are used, the neutron detection efficiency of the instrument is sufficiently great so that a γ source activity of only ~300 millicuries of Sb^{124} is necessary for most samples. With this source activity sample solutions containing as little as 60 μg of Be per ml, or 1.5 mg total beryllium, can be analyzed with a relative standard deviation of 1%. Interference caused by elements which absorb neutrons can be eliminated by the cadmium shield technique. Deuterium is an interference if present in a 25-fold excess over beryllium. Results are shown for the determination of beryllium in several types of materials.

Oak Ridge Radioisotopes Conference, Applications to Physical Science and Engineering
Gatlinburg, Tennessee
April 1-3, 1963

---

*Operated by Union Carbide Nuclear Company for the U. S. Atomic Energy Commission.

Facsimile Price $ 2.60
Microfilm Price $ .89

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

DISCLAIMER

INTRODUCTION

Since the photoneutron method for the determination of beryllium was first introduced (8,9), it has been extensively utilized to detect and measure beryllium in geological samples (1—5,17,18,20), ore processing samples (15), and even in beryllium metal (19). Portable instruments have been designed (1,2,4,5,10,12,14,17,18,20) and are commercially available which have revolutionized beryllium prospecting methods.

In most respects the photoneutron reaction provides an ideal analytical method; it is rapid, nondestructive, and virtually free of interferences; and is far more versatile and reliable than the chemical methods used for beryllium analysis. This method is, therefore, potentially of great value as a laboratory technique because it is capable of determining beryllium over a wide concentration range and in a large variety of materials without prior separation of the beryllium. Instruments for applying the photoneutron method in the laboratory have been described by British (13,15), Russian (14), French (6), and Italian (7) workers, but these have the disadvantages that large samples are required and a gamma source of high activity (1 to 1.5 curies) is necessary for adequate sensitivity. Consequently, work was undertaken to design and construct an instrument suitable for use in the average analytical laboratory. The primary objective was to devise an instrument which is simple to construct and operate, can be used for both solid and liquid samples, and provides adequate sensitivity with minimum radiation hazard. In addition, for our purposes, a certain amount of portability was desirable. That is, when the source is removed, the instrument can be transported from place to place.

Excellent discussions of the principle of the photoneutron method and the considerations involved in designing an instrument (1,6,11,12,14) are available and will not be repeated here.

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus is shown in Figure 1, and

(Figure 1)

details of the sample stage and container are presented in Figure 2.

(Figure 2)

The electrical connections to the BF_3 tubes are connected by a single concentric cable to the high-voltage supply and pre-amplifier. Associated electronic equipment consisting of a high-voltage power supply (NJE Corporation, Model S-324), linear amplifier (Atomic Instrument Co., Model 218), scaler (Atomic Instrument Co., Model 101B), and timer are placed in a 4-ft. rack. Four inches of lead shielding was stacked around the apparatus which was placed on a table in a corner of the laboratory, and the table area was roped off.

Reagents

Standard beryllium solution, 10.0 mg per ml. Prepared by dissolving 5.00 g of beryllium metal in dilute HCl, then diluting the solution to 500 ml with 10% HCl. Other solutions were prepared by appropriate dilution of the stock solution.

Procedure

Initial Adjustment. With the Sb^{124} source in place, set the band width at 0.5 megacycles, high voltage at 1600 v, amplifier coarse gain to 16, fine gain to 1, pulse height selector at maximum, and count one minute backgrounds at decreasing pulse height discriminator settings. Stop when the counting rate becomes greater than 100 cpm. Then increase the high voltage by 100 volts and repeat, until 2000 volts is reached. Insert a sample in position (2 mg Be/ml in 5 ml cell) by loading the sample on the sample stage and slipping the stage over the source rod by means of 2' tongs, and obtain counting rates at the same settings as the backgrounds. From this data, instrument settings can be chosen at which the net sample counting rate is at a maximum and is independent, or almost independent, of high voltage and pulse height discriminator settings.

If there is any doubt that the initial gain settings are the best, repeat the adjustment procedure at other settings.

This adjustment should be repeated once a month.

Calibration. Obtain net counting rates for standard beryllium solution as follows. In the 5-ml cells count standards ranging from 1.0 to 3.0 mg/ml; in the 25-ml cells 0.3 to 1.0 mg/ml standards; and in the 50-ml cells 0.1 to 0.5 mg/ml standards. Collect at least 10,000 counts in each case. Calculate an average calibration factor for each cell (cpm per mg/ml).

Sample Analysis. Pipet a 5-, 25-, or 50-ml portion of a sample solution containing between 0.1 and 3 mg of beryllium per ml into the appropriate cell. Load the sample in the apparatus and count until at least 10,000 counts are collected. Calculate counts per minute and with the calibration factor determine mg Be/ml.

RESULTS AND DISCUSSION

Evaluation of Apparatus

Although this apparatus, as well as other instruments designed for use in the laboratory, is fundamentally the same as Gaudin and Pannell's original (9), several improvements have been incorporated.

The use of enriched Sb^{123} as the source, as suggested by Milner, Edwards, and Henry (16), rather than natural antimony has several advantages. Thermal neutron activation of natural antimony produces high activities of Sb^{122} (Table I) which takes no part in photoneutron

(Table I)

generation. Besides increasing the radiation hazard, the additional gamma flux can cause instrumental difficulties. Only a small weight of enriched Sb^{123} is necessary to produce sufficient Sb^{124} activity; 40 mg of 98% enriched Sb^{123} irradiated for 14 days in the Oak Ridge Research Reactor produced about 400 millicuries of Sb^{124}.

Polyethylene is used as the moderator rather than paraffin because of its better physical properties.

Increased sensitivity was achieved by the use of 2" BF_3 tubes instead of the 1" tubes normally employed. The larger tubes are about 5 times more efficient than the smaller. In tests with a calibrated

Am^{241}-Be neutron source (4.5-Mev average energy), the efficiency of the apparatus was 5.1%. However, the background is also greater, 40 cpm compared to ~20 cpm for 1" tubes, and the 2" tubes are somewhat more sensitive to gamma radiation. Because of the effect of gamma radiation on the tubes, a high voltage plateau may not be found when the instrumental operating conditions are evaluated (11,14). Figure 3

(Figure 3)

shows typical data which were obtained in the initial adjustment procedure with a beryllium solution in place. Most regulated high voltage supplies are sufficiently stable so that there is no drift in the period of time required for calibration and sample analysis.

Radiation Hazard

Table II shows survey meter readings at various points around the

(Table II)

installation. It is apparent that some hazard is associated with the beamed gamma flux from the top of the source holder, but this is easily remedied with a 6" piece of lead rod. The operator is exposed to 100 mr on the hands and 50 mr at head level in changing samples, but the total exposure time is small, certainly less than one hour per week. In transferring a fresh source from the carrier to the source holder, precautions must be taken since the source activity is about 20 r at one foot. The transfer can usually be made in a few seconds with 3' tongs.

Sensitivity and Precision

The data in Table III were calculated from calibration data obtained (Table III) with a source activity of 315 mc and a background of 40 cpm. Sensitivity and precision depend only on counting statistics and can be recalculated for other source activities by using the K value. A minimum of about 1.5 mg of beryllium is necessary under these conditions, but this can be decreased by using a source of higher activity, accepting a larger standard deviation, counting for a longer time, or using a smaller capacity cell.

The most sensitive instrument previously designed used 12-1" BF_3 tubes and gave a count rate of 400 cpm per mg of Be per curie (11). The same factor for this instrument is 544 cpm using the 5-ml sample cell and should be about 700 cpm for a 1-ml cell.

Effect of Other Elements

Potential interferences fall into two classes: elements having high thermal or epithermal neutron cross sections which would tend to absorb the photoneutrons, and elements having a high cross section for the (γ,n) reaction and might also release photoneutrons. Table IV shows the effect of an element with a high thermal neutron cross section, cadmium (σ = 2500 barns), on the determination of beryllium. In these tests 20,000 counts were collected for both standard and sample, and so the relative standard deviation of the difference is 1.0%, and therefore, an error of $\pm$ 2.0% is significant at the 95% confidence level. The larger the volume of solution, the greater the interference because water moderates the photoneutrons which are originally 20-Kev average energy. Results in

parentheses were obtained with a 0.1" cadmium shield in place between the sample and the BF_3 tubes to screen out thermal neutrons (9,13,16). There is a loss in counting rate of about 15% with the shield in place, but the error caused by neutron absorbers is completely eliminated. Actually, only a few elements (Cd, Sm, Eu, Gd) have sufficiently high cross sections to interfere. Elements which were tested in a 20:1 ratio to Be and did not interfere are Li, K, Cu, Zn, Ba, Al, Zr, Sn, Pb, Bi, Fe, Co, Ni, Th, U, and B to the limit of solubility of H_3BO_3 in acid solution.

Only one isotope besides Be^9 is capable of undergoing a (γ,n) reaction with Sb^{124} gamma irradiation and that is deuterium. Samples of D_2O were placed in the apparatus, and the results are presented in Table V. A 24:1 weight ratio of D_2O to Be would only cause a 1% error

(Table V)

in the determination of Be. These results do indicate, however, that the photoneutron method may be used to determine deuterium. With this apparatus, the sensitivity for D_2O in H_2O, for example, (60-min. count, 1% standard deviation, 50-ml cell) is ~10% v/v, and by using a gamma source which has a greater flux at >2.2 Mev (Co^{56}, for example), sensitivity could probably be increased by two orders of magnitude.

Application to Samples

The apparatus described has been used to determine beryllium in various types of samples as shown in Table VI, compared with results

(Table VI)

obtained by colorimetric methods after appropriate separations. In all cases the sample was first put into solution by the most convenient method and a portion of the solution analyzed directly without any separations by the recommended procedure. Counting times required were not greater than 10 minutes with a 300-millicurie source. The standard deviation of duplicates was 1.1%, slightly smaller than the theoretical value based on counting statistics.

Some mention should be made of the cost of this apparatus. Materials, including electronics and enriched Sb^{123}, are about $3,000. Irradiation charges are $150 for 14 days, and for most purposes this 400-millicurie source is useful for about 2 half-lives (120 days).

LITERATURE CITED

1. Bisby, H., U. K. At. Energy Authority Rept: AERE-R-3021 (1959).
2. Bisby, H., Nucl. Power 5, (3), 100 (1960).
3. Bowie, S. H. U., Bisby, H., Burke, K. C., and Hale, F. H., Trans. Inst. Mining Met. 69, 345 (1960).
4. Brownell, G. M., Econ. Geol. 54, 1103 (1959).
5. Dibbs, H. P., Can., Dep. Mines Tech. Surv., Mines Branch, Tech. Bull. TB-33 (March, 1962).
6. Dumesnil, P., Ind. At. 5 (11/12), 61 (1961).
7. Fauci, A., and Meloni, S., Chim. Ind. (Milan) 44, 972 (1962).
8. Gaudin, M. A., Dasher, J., Pannell, J. H., and Freyberger, W. L., Trans. AIME 187, 495 (1950).
9. Gaudin, M. A., and Pannell, J. H., Anal. Chem. 23, 1261 (1951).
10. Hale, F. H., and Bisby, H., "Radioisotopes in the Physical Sciences and Industry," Vol. II, p. 291, International Atomic Energy Agency, Vienna, 1962.
11. Iredale, P., U. K. At. Energy Authority Report AERE-EL/M-108 (1960).
12. Metcalfe, J., and Ryan, J. A., (ed.), U. K. At. Energy Authority Report PG 171 (1961), p. 43.
13. Ibid., p. 55.
14. Mezhiborskaya, Kh. B., "Photoneutron Method of Determining Beryllium," Consultants Bureau Enterprises, Inc., New York, 1961.
15. Milner, G. W. C., and Edwards, J. W., U. K. At. Energy Authority Rept. AERE-R-2965 (1959).
16. Milner, G. W. C., Edwards, J. W., and Henry, W. M., U. K. At. Energy Authority Rept. AERE-R-3212 (1960).

17. Mountjoy, W., and Lipp, H. H., U. S. Geol. Survey, Professional Papers No. 424-C, C-379-80 (1961).

18. Moyd, L., and Moyd, P., Trans. AIME 217, 372 (1960).

19. Postma, Jr., F. W., and McMurray, Jr., C. S., Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tennessee, October 9—11, 1962.

20. Vaughn, W. W., Wilson, E. E., and Ohm, J. M., U. S. Geol. Survey. Circ. 427 (1960).

LIST OF TABLES

Table I. Calculated Activities[a] of Sb^{122} and Sb^{124} in Natural Antimony and 98% Enriched Sb^{123} After 14-Day Irradiation

Cooling Time, days	Sb^{124}, millicuries	Sb^{122}, millicuries	
		Natural Sb	98% Sb^{123}
0	315	4220	61
7	290	747	11
14	268	131	1.9

[a]Does not include resonance activation.

Table II. Approximate Radiation Level at Various Positions With a 300—400 mc Source

Position	mr/hr
Under table	20
Surface of Pb barrier	< 10
Top of Pb barrier	100
Top of instrument	400
Top of source holder	2000

Table III. Sensitivity of Photoneutron Apparatus

Sample Cell, ml	K[a]	Sensitivity, mg Be/ml[b]		
		30 min.	60 min.	Equiv. to Bkgd.
5	2.72	0.58	0.35	0.05
25	10.2	.16	.09	.01
50	16.6	.10	.06	.008

[a] cpm per mg Be/ml per millicurie.

[b] Minimum amount which can be determined with a standard deviation of 1% in the counting time indicated.

Table IV. Effect of Cadmium on the Determination of Beryllium

Ratio, Cd/Be	Error, %		
	5 ml	25 ml	50 ml cell
60	+0.5	-2.3 (-0.9)[a]	-4.1 (-0.8)
120	+0.7	-3.7 (+0.6)	-5.2 (-0.6)
190	-2.0	-4.1 (+0.4)	-5.4 (-2.1)

[a]Values in parentheses obtained with cadmium shield in place.

Table V. Photoneutrons From Deuterium

Sample Cell, ml	cpm per ml of D_2O	g D_2O equiv. 1 mg Be
5	75.8	2.4
25	57.8	2.3
50	46.0	2.4

Table VI. Application to Samples

Sample Composition	Be, %	
	Photoneutron	Other Method
$LiF-BeF_2-ZrF_4$	6.94, 6.90	6.91
$LiF-BeF_2-ZrF_4-Th_4$	6.66, 6.63	6.87
BeO-MgO	19.2, 19.4	19.4, 19.5
$BeO-MgO-ThO_2$	30.4, 30.0	30.1
Be-Cu alloy	2.04, 2.06	--

LIST OF FIGURES

Number	Caption	ORNL-LR-Dwg. (or Photo) No.
2	d. Sample.	
3	Count rate as a function of high voltage and pulse height discriminator settings.	77650

UNCLASSIFIED
ORNL-LR-DWG. 77040

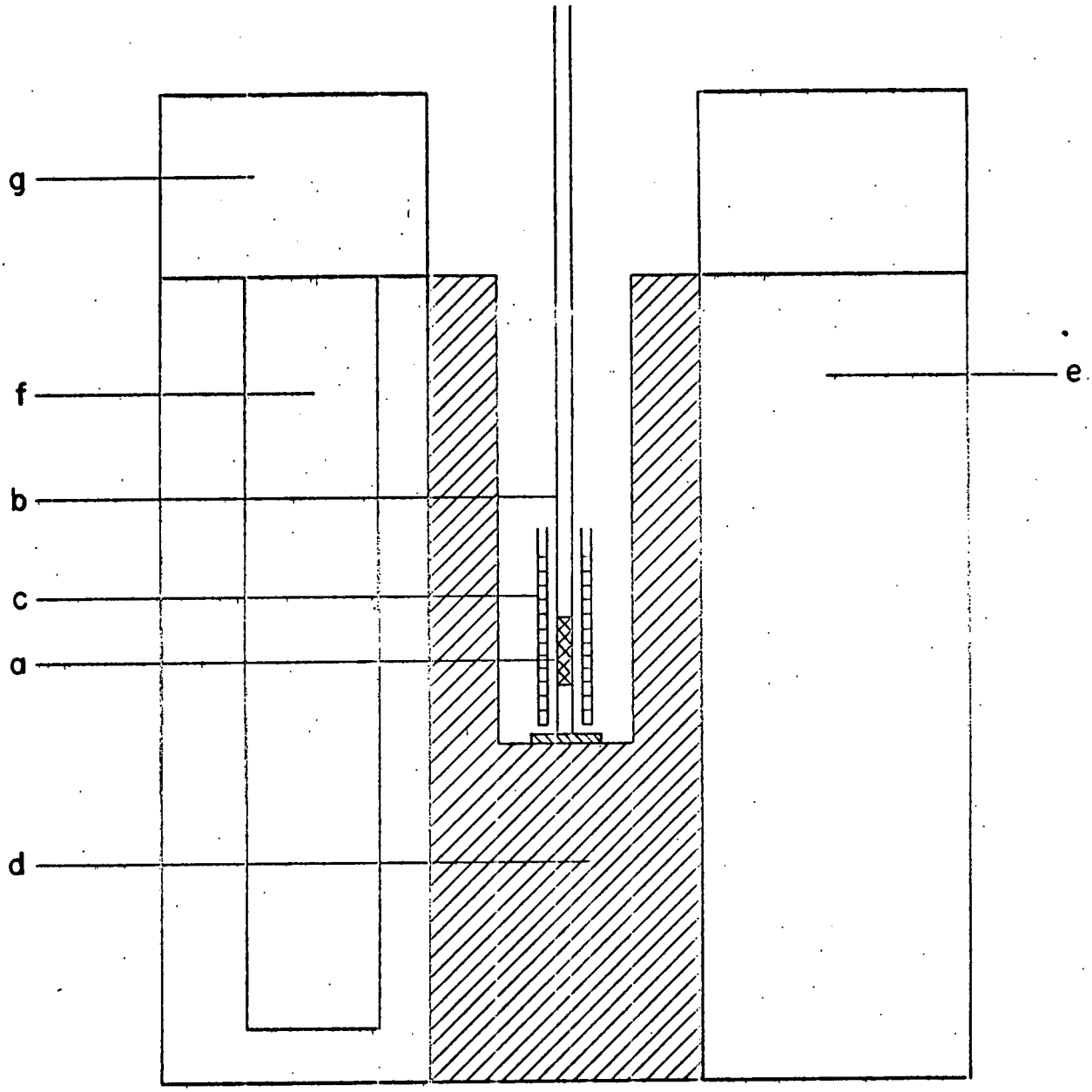

Figure 1. Schematic diagram of apparatus.

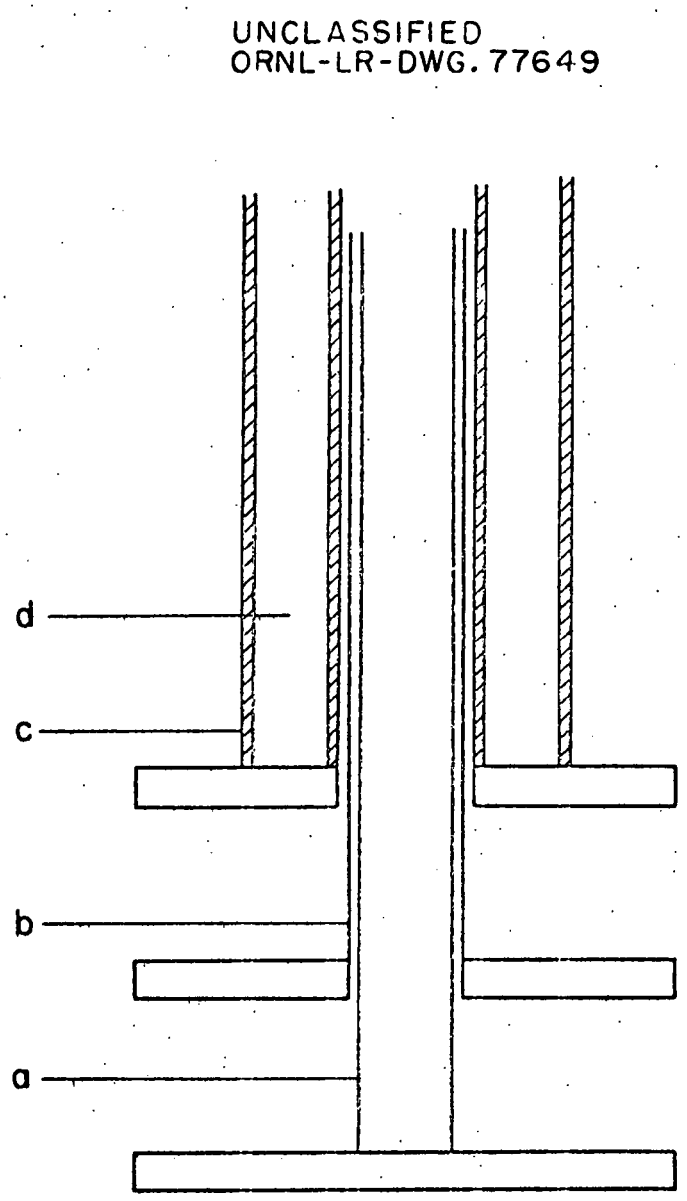

Figure 2. Sample stage and sample container.

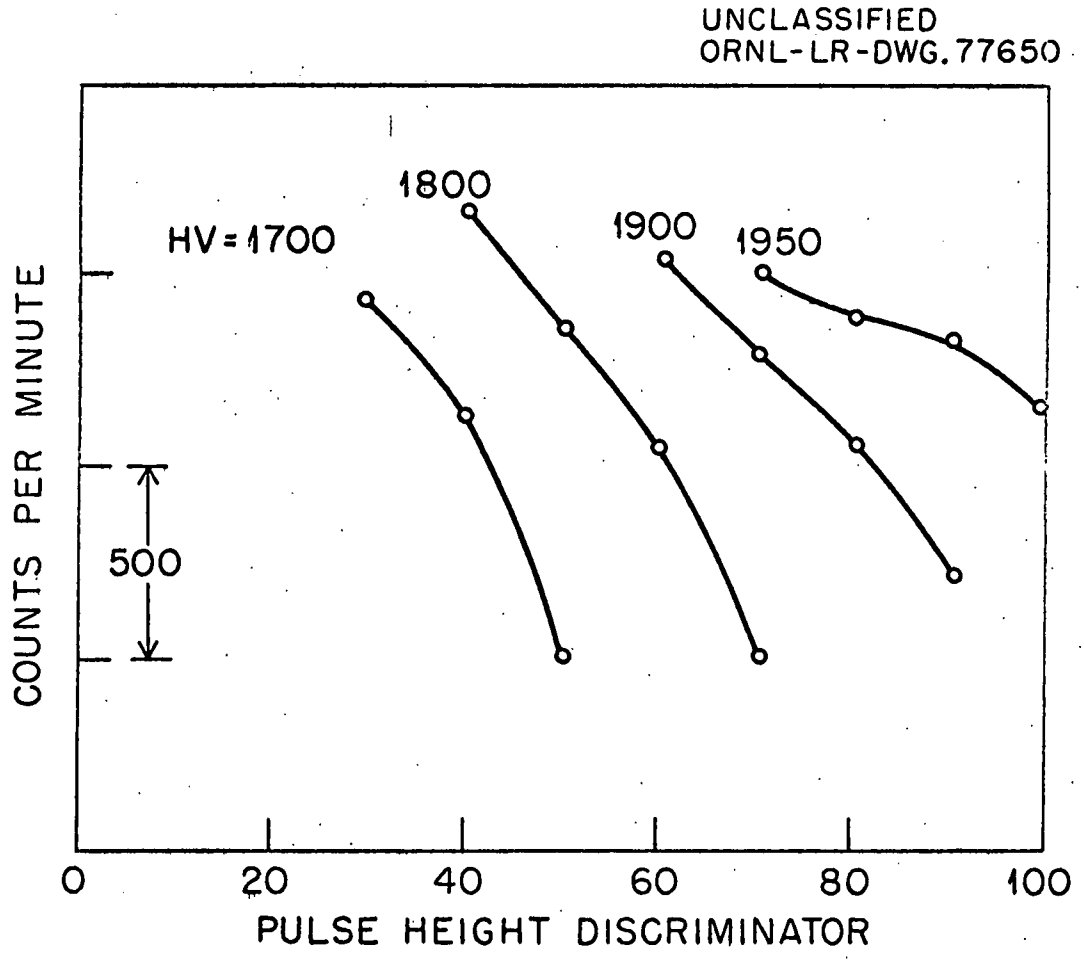

Figure 3. Count rate as a function of high voltage and pulse height discriminator settings.