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NEUTRON ACTIVATION ANALYSIS METHODS FOR THE GROUP VIII ELEMENTS

C. E. Miller

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ANALYTICAL CHEMISTRY DIVISION

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C. E. Miller

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Oak Ridge, Tennessee
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Figures 1-4, 6, and 20 have been adapted from gamma-ray spectra published by R. L. Heath. Figure 15 has been adapted from one published by P. R. Bell.

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INTRODUCTION

Nuclear activation was used as a method of analysis as early as 1935 when Hevesy and Levi[1] developed a method for the determination of dysprosium in yttrium. In this method a sample was irradiated with neutrons, and the radioactivity induced into the sample was characterized and measured. The amount of radioactivity induced into the dysprosium was a measure of the amount of dysprosium in the sample. Other examples of the use of nuclear activation as a method of analysis are given elsewhere.[2]

It was not until 1951 that the method was used on a routine scale by Leddicotte and Reynolds[3] at the Oak Ridge National Laboratory. At that time the Oak Ridge National Laboratory was the only installation having irradiation space in a nuclear reactor available for routine use. Since 1951 the availability of irradiation space has increased and with it the applications of activation analysis. Through this increase in application, the analytical chemist has come to recognize nuclear activation as an important and sensitive method of analysis.

The primary distinction between activation analysis and other methods of analysis is in the exploitation of nuclear properties rather than atomic or chemical properties. Elements which are "normally" similar in atomic or chemical properties may now be determined by analysis methods utilizing their nuclear properties.

The results of an investigation of the application of neutron activation analysis to a group of chemically similar elements, that is, Group VIII of the Periodic Table, is reported in this paper. The problems involved in inducing radioactivity in these elements, as well as the measurement of this radioactivity are discussed. In addition, the use of different types of nuclear reactions and the interferences produced by some of these reactions in certain elemental analyses by activation analysis are described. The use of short-lived radionuclides for analysis is also described. Gamma-ray spectra of the radionuclides used in the investigation are presented, and the use of these spectra in particular analyses is discussed.

CHAPTER I

PRINCIPLES OF ACTIVATION ANALYSIS

The fact that nuclei undergo nuclear reactions when bombarded by neutrons from a nuclear reactor or by charged particles from an accelerator is the basis for the activation analysis method. As chemical reactions involving color development permit colorimetric analyses, or as atomic excitation makes possible spectrographic analysis, so nuclear reactions producing radioactive nuclides make possible activation analysis. The radionuclide produced in a nuclear reaction can be characterized by its half-life and its radiations. A quantitative measure of these radiations can be a quantitative measure of the nuclide present.

To understand the factors which affect this method it is necessary to look at the mathematical equations which describe the "activation" of a nucleus. These equations are based upon the general equation for growth of radioactivity and are presented by Friedlander and Kennedy.[4]

The general case is that of a radionuclide decaying to produce another radionuclide, where

N_1 = the number of nuclei of the parent nuclide,

N_2 = the number of nuclei of the daughter nuclide,

λ_1 = the decay constant of the parent nuclide,

λ_2 = the decay constant of the daughter nuclide.

The rate of change of N_1 is given by Equation 1:

$$-\frac{dN_1}{dt} = \lambda_1 N_1 \tag{1}$$

Integration of Equation 1 gives

$$N_1 = N_1^o \exp(-\lambda_1 t) \tag{2}$$

where $N_1^o = N_1$ at $t = 0$.

The rate of change of N_2 is given by the equation

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \tag{3}$$

so that N_2 is being produced at a rate $\lambda_1 N_1$ and at the same time decaying at a rate $\lambda_2 N_2$.

To integrate Equation 3, it is necessary to solve a first-order, linear differential equation in which

$$N_2 = uv \tag{4}$$

where u and v are functions of time. Thus,

$$\frac{dN_2}{dt} = u(\frac{dv}{dt}) + v(\frac{du}{dt}) \tag{5}$$

The substitution of Equations 4 and 5 into Equation 3 and the rearranging of terms gives

$$u(\frac{dv}{dt}) + v(\frac{du}{dt}) + \lambda_2 uv - \lambda_1 N_1^o \exp(-\lambda_1 t) = 0 \tag{6}$$

The rearranging of Equation 6 gives

$$u(\frac{dv}{dt} + \lambda_2 v) + v(\frac{du}{dt}) - \lambda_1 N_1^o \exp(-\lambda_1 t) = 0 \tag{7}$$

Setting $\frac{dv}{dt} + \lambda_2 v = 0$ and integrating this gives Equation 8:

$$v = \exp(-\lambda_2 t) \tag{8}$$

The substitution of this solution into Equation 7 gives

$$\exp(-\lambda_2 t)\left(\frac{du}{dt}\right) - \lambda_1 N_1^o \exp(-\lambda_1 t) = 0 \tag{9}$$

and solving for du:

$$du = \lambda_1 N_1^o \exp\left[(\lambda_2 - \lambda_1)t\right] dt \tag{10}$$

then,

$$u = \frac{\lambda_1 N_1^o}{\lambda_2 - \lambda_1} \exp\left[(\lambda_2 - \lambda_1)t\right] + C \tag{11}$$

where C = a constant of integration. The substitution of Equations 11 and 8 into Equation 4 results in Equation 12.

$$N_2 = uv = \frac{\lambda_1 N_1^o}{\lambda_2 - \lambda_1} \exp(-\lambda_1 t) + C \exp(-\lambda_2 t) \tag{12}$$

The constant, C, is evaluated from the condition that $N_2 = N_2^o$ at T = 0:

$$C = \frac{-\lambda_1 N_1^o}{\lambda_2 - \lambda_1} + N_2^o \tag{13}$$

The substitution of Equation 13 into Equation 12 and rearranging results in the general equation for the growth of a radioactive product:

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^o \left[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\right] + N_2^o \exp(-\lambda_2 t) \tag{14}$$

If this growth of a radioactive product is taking place in a nuclear reactor, Equation 14 can be used to calculate the number of radioactive nuclei, N_2, present at any time, t, that were produced from N_1^o stable nuclei. Since in this application of Equation 14, the parent nuclide will be stable, λ_1 will not be a decay constant, but rather a constant denoting the dependence of the rate of change of the parent nuclide on the neutron flux, f, and on the activation cross section, σ_{ac}, of the parent nuclide.[5]

Thus
$$\lambda_1 = f\sigma_{ac} \tag{15}$$

By setting $N_2^o = 0$ at $t = 0$, $\lambda_1 \ll \lambda_2$, and $\exp(-\lambda_1 t) = 1$, Equation 14 results in the growth formula for N_2 as a function of time in a neutron flux, f:

$$N_2 = \frac{f\sigma_{ac}}{\lambda_2} N_1^o \left[1 - \exp(-\lambda_2 t)\right] \tag{16}$$

The activity, A_2, of the radioactive nuclide produced is given by

$$A_2 = \lambda_2 N_2 = f\sigma_{ac} N_1^o \left[1 - \exp(-\lambda_2 t)\right] \tag{17}$$

To convert N_1^o nuclei to the weight of element represented by N_1^o nuclei Equation 18 is used:

$$N_1^o = \frac{\text{Avogadro's Number} \times W\theta}{M} \tag{18}$$

where Avagadro's Number = 6.02×10^{23} nuclei per gram-atomic weight

W = weight of the element represented by N_1^o nuclei

θ = natural abundance of the stable nuclide undergoing reaction

M = atomic weight of the element represented by N_1^o nuclei

Equation 17 then becomes:

$$A = \frac{6.02 \times 10^{23}\, f\sigma_{ac} W\theta \left[1 - \exp(-\lambda t)\right]}{M} \tag{19}$$

for $A = A_2$ and $\lambda = \lambda_2$.

The term $\left[1 - \exp(-\lambda t)\right]$ can be called the "saturation factor"; and it expresses the fraction of the maximum radioactivity produced in time, t. In 10.00 half-lives, a fraction equal to 0.999 of the maximum radioactivity is obtained.

The basic equation used in any activation analysis is the rearrangement of Equation 19:

$$W = \frac{AM}{6.02 \times 10^{23} f\sigma_{ac} \theta\left[1 - \exp(-\lambda t)\right]} \tag{20}$$

The limits of measurement for the weight of the element which can be determined, then, is dependent upon three factors: the bombarding particle flux, f; the activation cross section, σ_{ac}, for the particular nuclear reaction occurring; and the length of irradiation time expressed as the "saturation factor." The activation cross section is a fixed quantity for any particular nuclide and nuclear reaction. The flux and length of irradiation time can be varied and, therefore, the analyst has some control over the amount of activity that will represent a certain weight of element.

In actual practice a comparator method[6] is generally used since the measurment of the flux is somewhat difficult, and activation cross section data are not reliable. In the comparator method, a standard material that contains a known amount of the element to be determined is irradiated simultaneously with the material to be analyzed. A comparison is then made between the radioactivity induced in the element to be determined in the sample with that induced in the element to be determined in the comparator. This method reduces Equation 20 to

$$\frac{W_s}{W_c} = \frac{A_{ts}}{A_{tc}} \tag{21}$$

where W_s = weight of element to be determined in the sample

W_c = weight of element to be determined in the comparator

A_{ts} = radioactivity induced in the element to be determined in the sample

A_{tc} = radioactivity induced in the element to be determined in the comparator.

The fact is emphasized in Equation 21 that a certain amount of radioactivity represents a certain weight of element. Thus, it is most important that the radioactivity being measured emanate from the radionuclides of the element to be determined.

If the radioactivity induced in other components of the sample does not interfere with the measurement of radioactivity induced in the element to be determined, a nondestructive analysis can be made. In a nondestructive analysis, chemical separations are not made; the sample is irradiated and then the radioactivity is measured directly.

If the radioactivity induced in other components of the sample does interfere with the measurement of radioactivity induced in the element to be determined, a destructive analysis must be made. In a destructive analysis the sample is dissolved after being irradiated, and the various constituents are separated by precipitation, ion exchange, solvent extraction, or other methods. In quantitative analyses, especially analyses for trace elements, "carriers" are added to the solution of the irradiated sample, and a chemical separation is made. The use of carriers makes possible ordinary analytical manipulations on a milligram scale.

The separation of a radionuclide and its carrier element from the other components of a sample need not be quantitative. The yield of the separation is determined by comparing the weight of the element, which theoretically could be obtained from the amount of carrier added, to the actual weight of element obtained by the separation.

Mathematically this is expressed as

$$Y = \frac{W}{W_o} \tag{22}$$

where Y = a yield factor

W = weight of element obtained from separation

W_o = theoretical weight of element based on amount of carrier added.

The yield of the carrier represents the yield of the radionuclide provided there has been complete exchange between the radionuclides of the sample and the stable nuclides of the carrier. A correction for carrier yield, Y, is then made to the radioactivity measurement, A, so that the measurement represents the total radioactivity in the sample, A_{ts}, and in the comparator, A_{tc}:

$$A_{ts} = \frac{A_s}{Y_s}, \text{ and } A_{tc} = \frac{A_c}{Y_c} \tag{23}$$

where A_s = radioactivity in the precipitate separated from the sample

A_c = radioactivity in the precipitate separated from the comparator

Y_s = yield factor for the sample

Y_c = yield factor for the comparator.

When Equation 23 is substituted into Equation 21, Equation 24 is obtained:

$$\frac{W_s}{W_c} = \frac{A_s Y_c}{A_c Y_s} \tag{24}$$

where W_s = weight of element obtained by separation of the element to be determined in the sample

W_c = weight of element obtained by separation of the element to be determined in the comparator.

In destructive analyses irradiations are generally made at the highest flux possible for the longest period of time practical. This insures a maximum amount of radioactivity being produced. Nuclides having sufficiently long half lives (>10 m) are used in order to provide adequate time for chemical separation.

Thus, in the method of activation analysis, there are several conditions that may be varied. These include the neutron flux, the length of irradiation time, and the choice of which radionuclide is to represent a certain element. Elements that have similar chemistry may have different nuclear properties; by varying the conditions mentioned above, the differences in nuclear properties may be magnified.

CHAPTER II

NUCLEAR PROPERTIES OF THE GROUP VIII ELEMENTS

The Group VIII elements are iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum. Because of chemical dissimilarities within the group, these elements are generally treated in two subgroups; namely, iron, cobalt, and nickel; and the "Platinum-group metals". The general analytical chemistry of these elements will not be discussed here. Selected methods for the determination of iron, cobalt, and nickel are listed by Walton.[8] Methods for the determination of the "Platinum-group metals" are given in detail by Schoeller and Powell.[9]

The problem of analysis for an element is generally complicated when the element is present in micro- and submicrogram quantities, and the problem becomes more complicated when a chemical separation from elements within the same group is required. The elements of Group VIII are not exceptions. Iron, cobalt, and nickel are easily determined; however, the "Platinum-group metals" are noted for their difficult chemistry. The chemistries of rhodium and iridium are probably the most difficult because of the insolubilities of these elements and because of their similar chemical properties. In a review of gravimetric methods for the determination of the "Platinum-group metals," Beamish[10] reports that analytical methods for the determination of rhodium are few in number

and that no gravimetric reagent is specific for a practical separation.[11] The same difficulties apply to iridium.[12]

The nuclear properties of the Group VIII elements, however, do not show this similarity. Except for iron and cobalt, the radionuclides produced by neutron reactions upon the stable nuclei of these elements can be readily distinguished from one another. Thus, the quantitative determination by activation analysis is greatly simplified over determinations by the usual chemical methods.

When destructive analyses are made, carrier techniques described earlier (p. 8) provide quantitative results without the use of quantitative separations. When nondestructive analyses are made, conditions described earlier (p. 7) may be established so that in favorable cases a particular nuclide is activated and quantitative results are obtained without any chemical separations.

In Table 1, a list is given of the stable nuclides of the Group VIII elements that will produce radionuclides through an (n,γ) reaction in a neutron source. The most practical radionuclide to be used as a means of analysis for that element is indicated by an asterisk beside the radionuclide produced in the reaction. The other radionuclides listed in the table have either particularly long or short half lives or radiations which cannot be detected in the usual manner. Data presented in Table 1 were taken from Strominger, Hollander, and Seaborg.[13] Activation cross sections are tabulated as barns (1 barn = 10^{-24} $cm.^2$) in this and succeeding tables. Similarly, half lives are denoted as y = years, d = days, h = hours, m = minutes, and s = seconds.

TABLE 1

PRINCIPAL STABLE NUCLIDES OF THE GROUP VIII ELEMENTS WHICH PRODUCE RADIONUCLIDES BY AN (n,γ) REACTION

Stable Nuclide	Natural Abundance, %	Activation Cross Section, barn	Radionuclide Produced	Half Life of Radionuclide
Fe^{54}	5.84	2.3	Fe^{55}	2.94 y
Fe^{58}	0.31	0.98	Fe^{59}*	45.1 d
Co^{59}	100	16	Co^{60m}*	10.5 m
		36	Co^{60}*	5.3 y
Ni^{58}	67.8	4.2	Ni^{59}	8×10^4 y
Ni^{62}	3.66	15	Ni^{63}	80 y
Ni^{64}	1.16	1.5	Ni^{65}*	2.56 h
Ru^{96}	5.5	0.01	Ru^{97}	2.8 d
Ru^{102}	31.5	1.2	Ru^{103}*	41.0 d
Ru^{104}	18.7	0.7	Ru^{105}*	4.5 h
Rh^{103}	100	12	Rh^{104m}*	4.4 m
		140	Rh^{104}	42 s
Pd^{102}	0.96	4.8	Pd^{103}	17 d
Pd^{106}	27.33	--	Pd^{107}	21.3 s
Pd^{108}	26.71	0.07	Pd^{109m}*	4.8 m
		11	Pd^{109}*	13.6 h
Pd^{110}	11.81	--	Pd^{111m}	5.5 h
		0.3	Pd^{111}	22.0 m
Os^{184}	0.018	200	Os^{185}	95.0 d

TABLE 1--Continued

Stable Nuclide	Natural Abundance, %	Activation Cross Section, barn	Radionuclide Produced	Half Life of Radionuclide
Os^{189}	16.1	--	Os^{190m}	10 m
Os^{190}	26.4	--	Os^{191m}	14 h
		8	Os^{191}*	16.0 d
Os^{192}	41.0	1.6	Os^{193}*	31.5 h
Ir^{191}	38.5	260	Ir^{192m}	1.45 m
		700	Ir^{192}*	74.5 d
Ir^{193}	61.5	130	Ir^{194}*	19.0 h
Pt^{192}	0.78	~8	Pt^{193}	3.5 d
Pt^{194}	32.8	1.2	Pt^{195}*	~6 d
Pt^{196}	25.4	--	Pt^{197m}	80 m
		0.80	Pt^{197}*	18 m
Pt^{198}	7.2	4.0	Pt^{199}*	31 m

Figures 1 - 6 show the gamma-ray spectra of those nuclides which can be used for analysis. Gamma-ray spectra of the short-lived radionuclides are shown in Figures 22 - 27 in Chapter VIII.

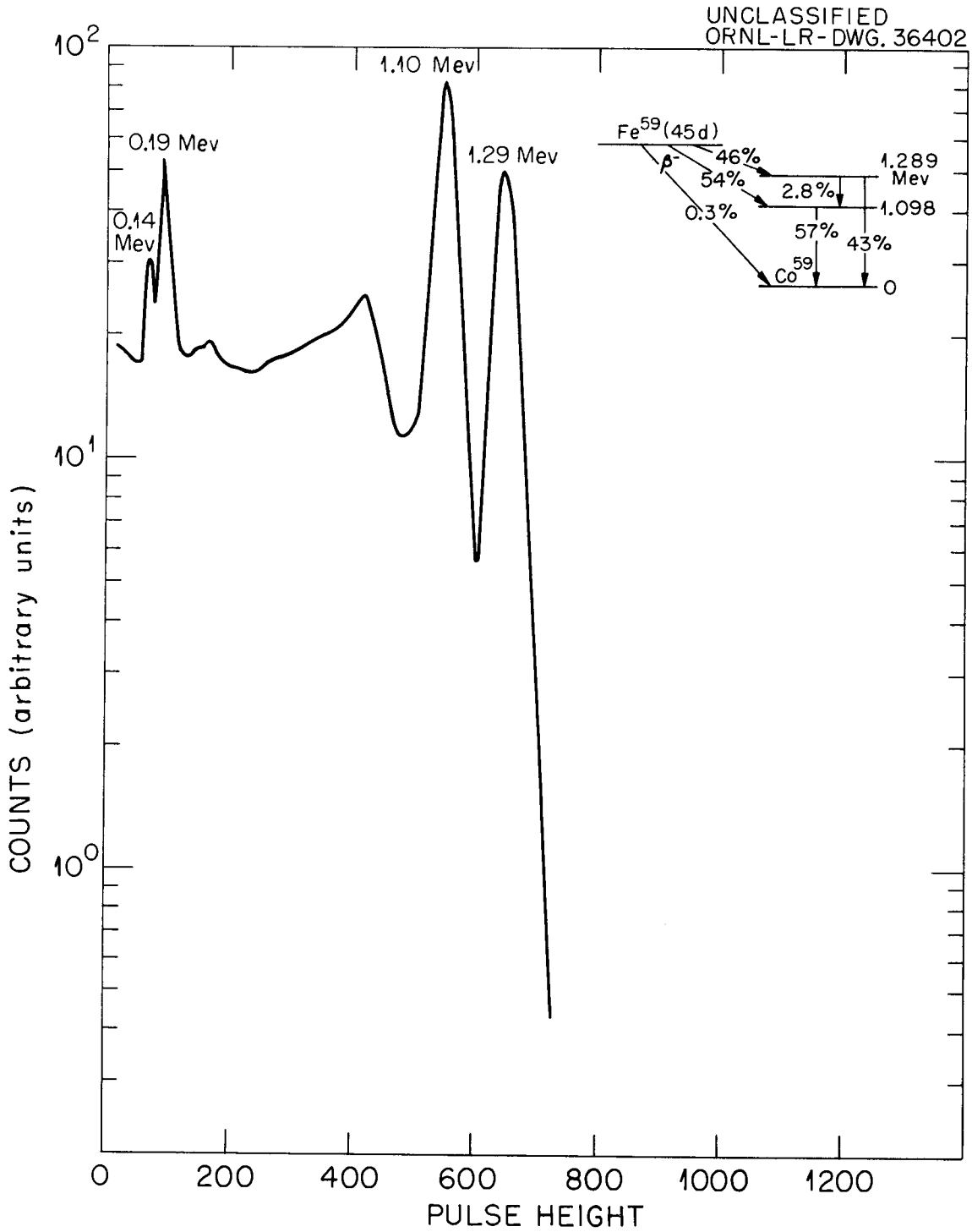

Fig. 1.--Gamma-Ray Spectrum of Iron-59

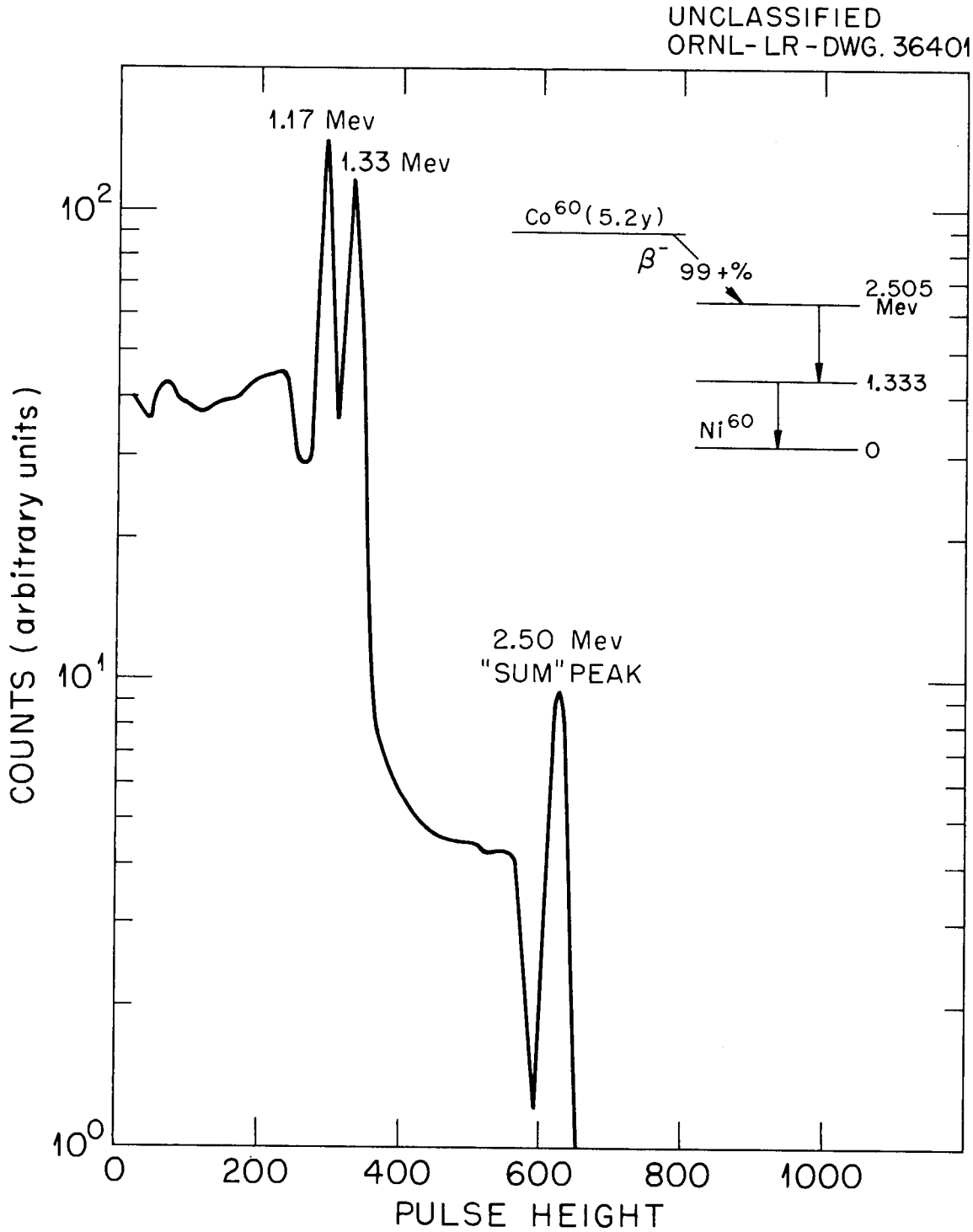

Fig. 2.--Gamma-Ray Spectrum of Cobalt-60

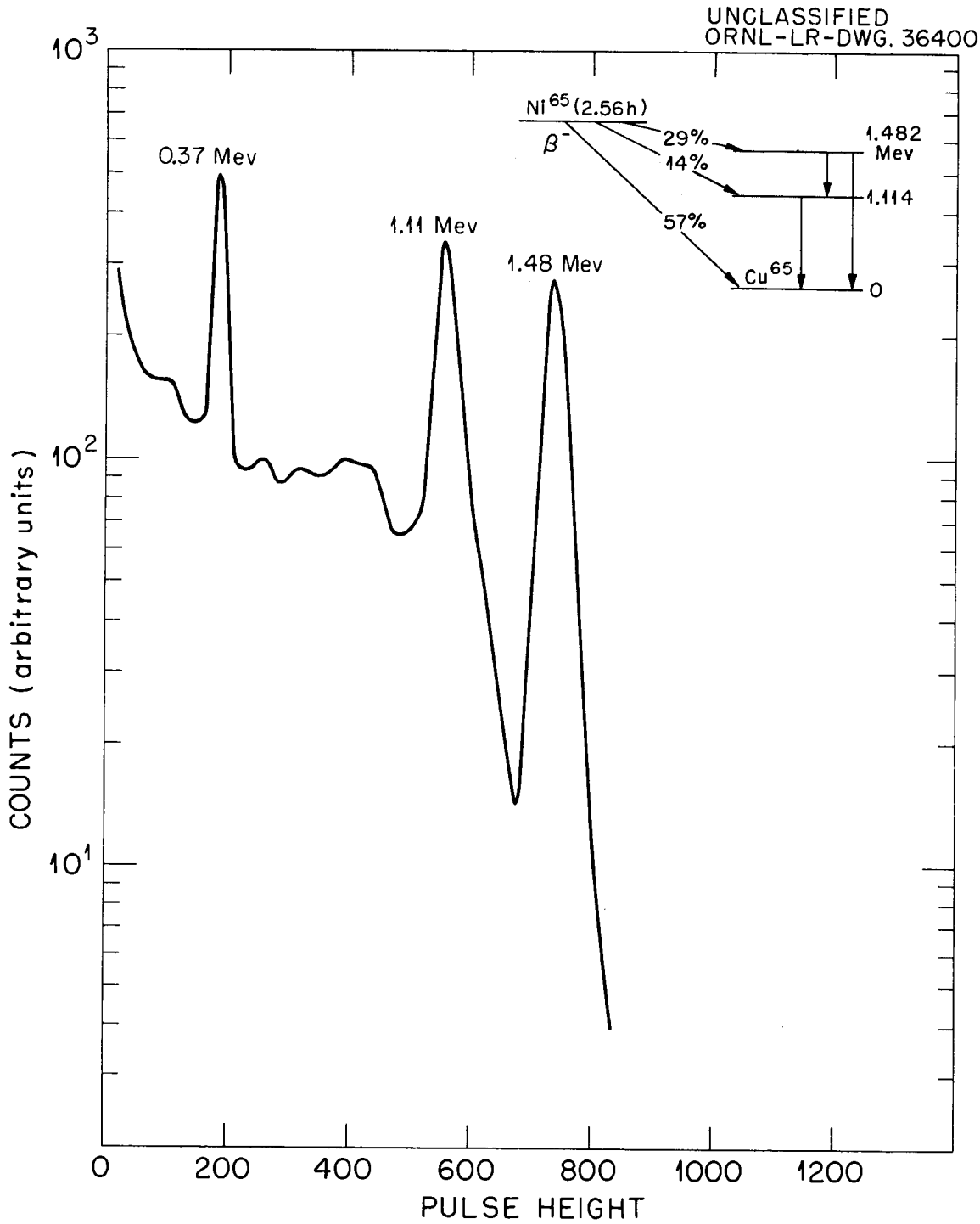

Fig. 3.--Gamma-Ray Spectrum of Nickel-65

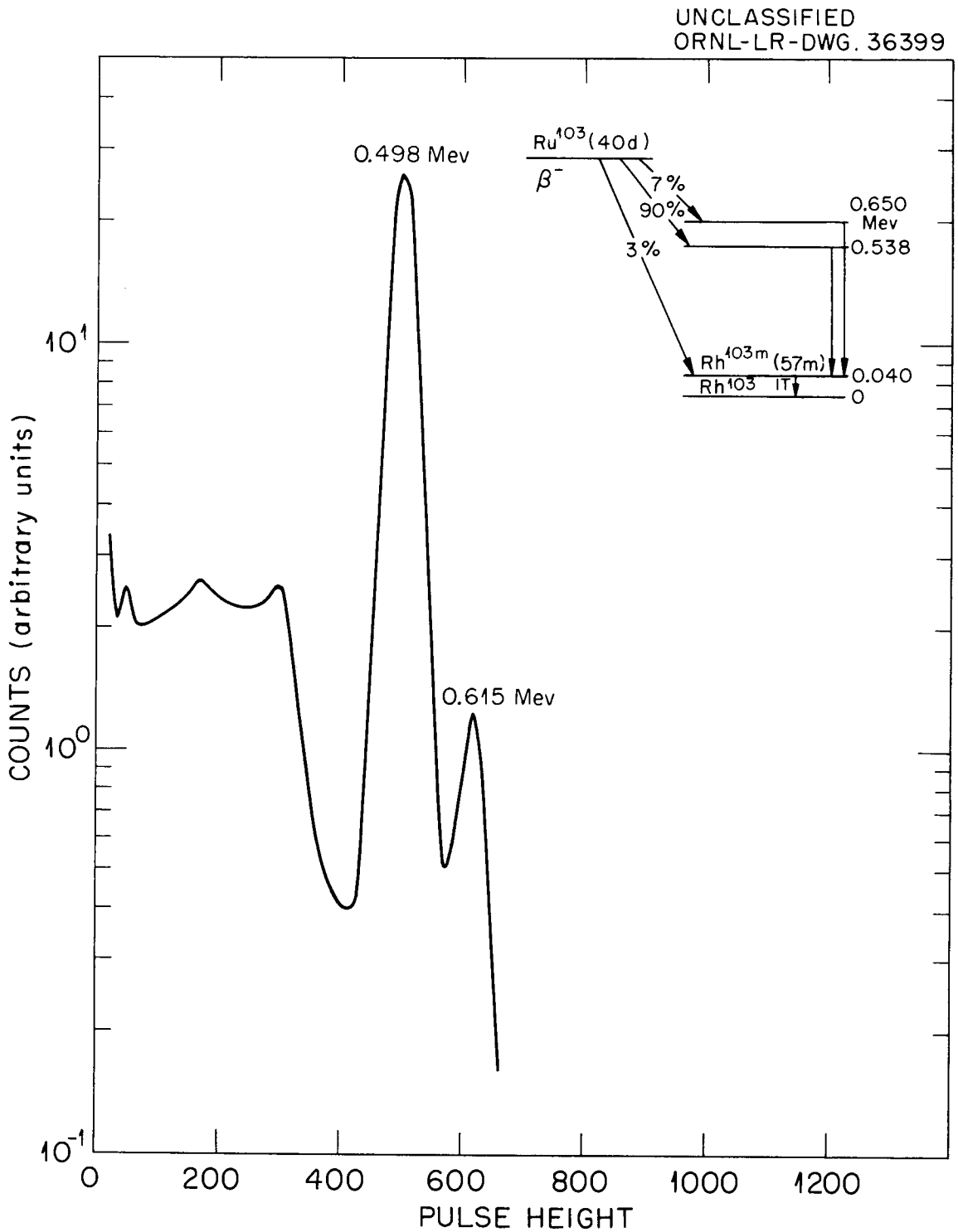

Fig. 4.--Gamma-Ray Spectrum of Ruthenium-103

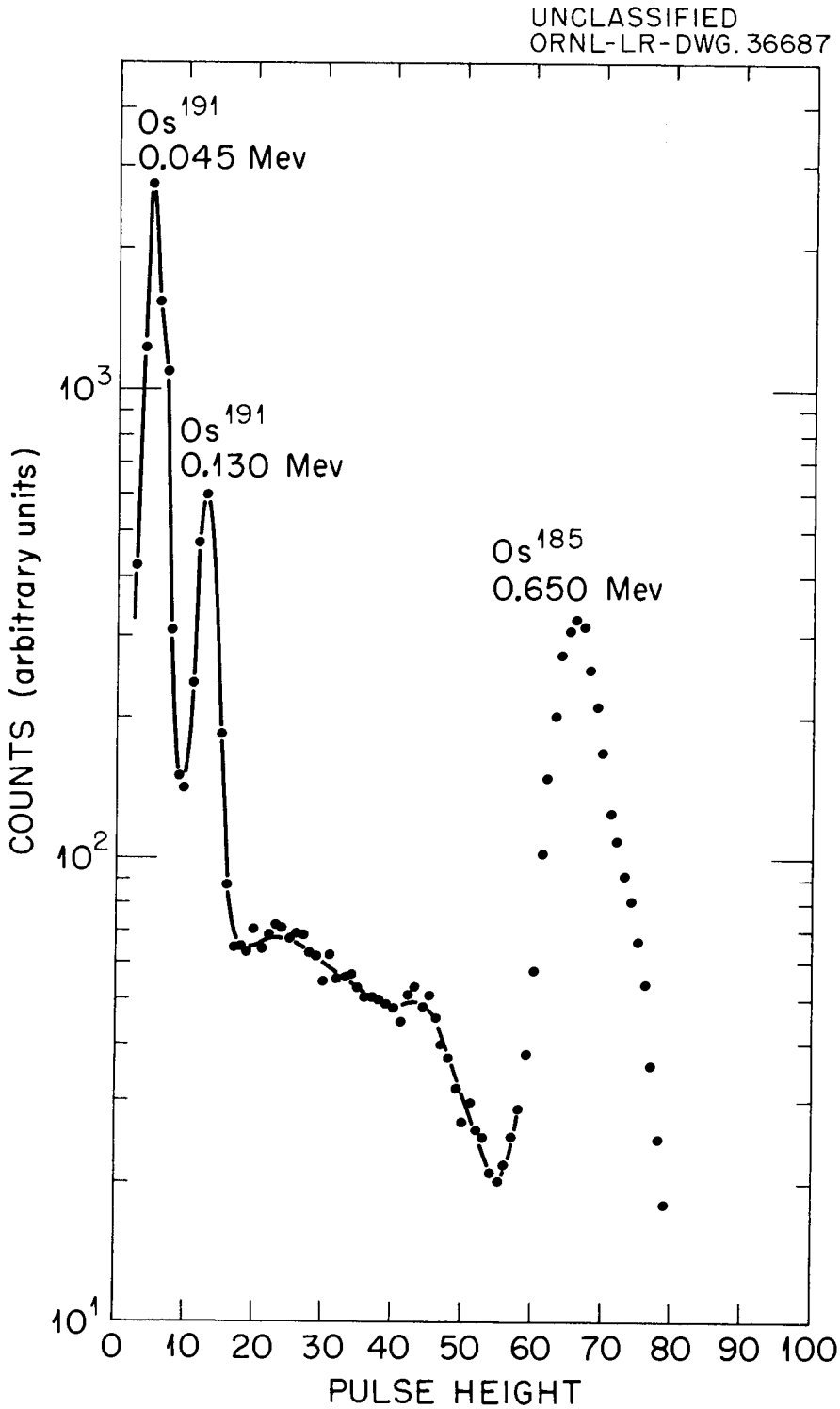

Fig. 5.--Gamma-Ray Spectrum of Osmium-191

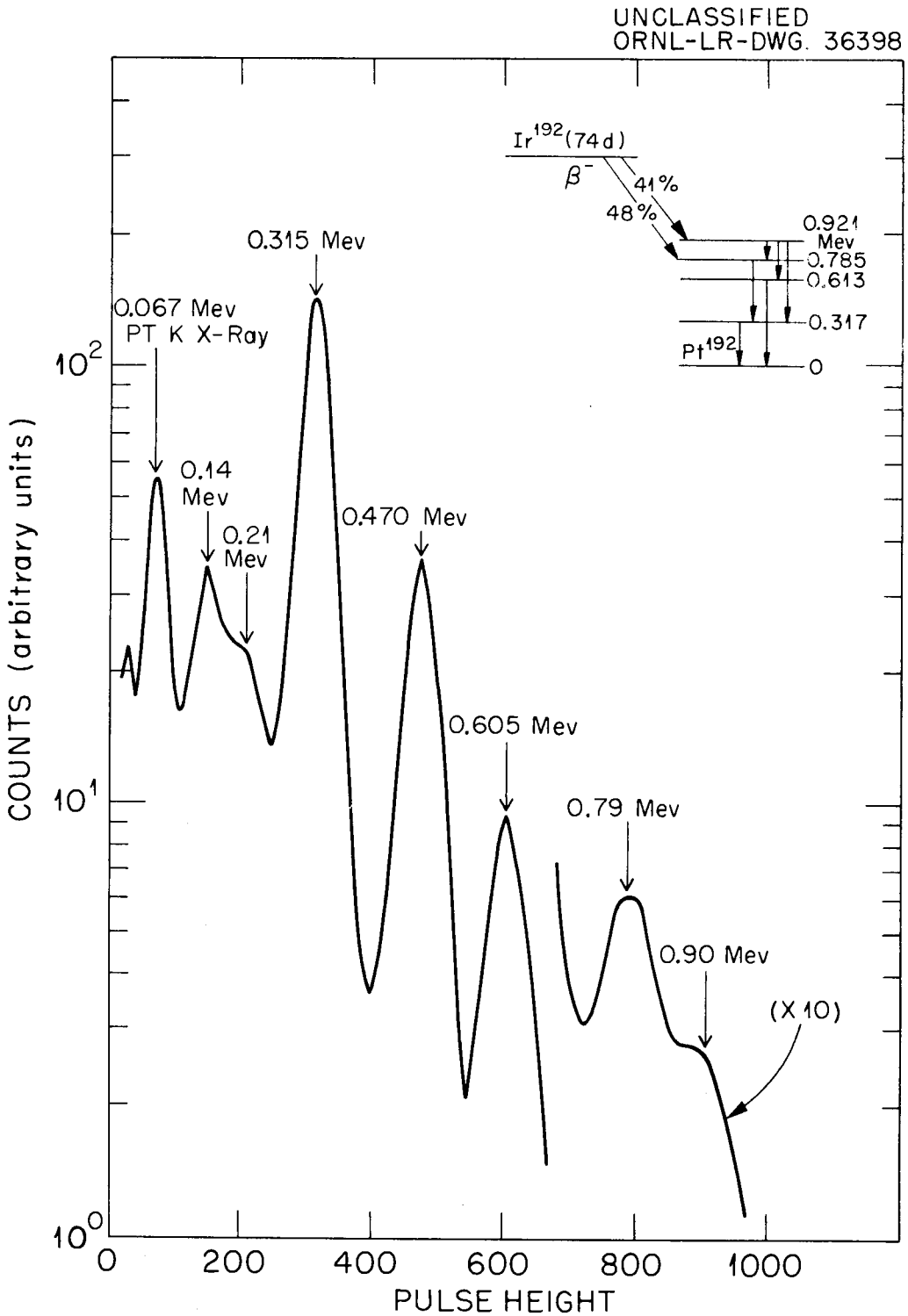

Fig. 6.--Gamma-Ray Spectrum of Iridium-192

CHAPTER III

MEASUREMENT OF RADIOACTIVITY

It can be seen from Equations 20 and 21 that the measurement of radioactivity is the basic measurement in activation analysis.

In 1951 when Leddicotte and Reynolds[14] published a table of sensitivities for elements determined by activation analysis, the radioactivity measurements on which the sensitivities were based were obtained by means of a Geiger-Mueller counter. Today several types of instruments are available which can be used to measure radioactivity and many ways to make this measurement selective.

The following methods of radioactivity measurement have been used in the work described herein: beta counting, gross gamma counting, and differential gamma counting.

Beta Counting

Method

In this investigation, beta counting was carried out by use of a Geiger-Mueller counter. Price[15] describes the use of this type counter; thus, no further description will be given herein. When this method is used destructive analyses are generally made so that the radioactivity that is measured emanates only from the element being determined. In favorable cases in which a short-lived radioactivity is to be measured

in the presence of a long-lived radioactivity, or vice versa, measurements may be made by decay studies.[16]

Instruments

The instrument used in beta counting was a thin-mica-window Geiger-Mueller tube, type T6C-2, manufactured by Tracerlab, Inc. A scaler manufactured by Nuclear Instrument and Chemical Corporation was used to record the counts detected. The detector was mounted in a 2-in. thick, cylindrical lead shield, which reduced the counter background from spurious radiations to approximately 25 counts/min. Coincidence loss in this system was approximately 0.5%/1000 counts/min.[17]

Gross Gamma Counting

Method

The development of scintillation crystals has greatly influenced the method of gamma counting. Prior to 1951, gamma rays were counted by use of a Geiger-Mueller counter. This usually was the same counter setup used for beta counting. Today, however, scintillators are used in which the interaction of the gamma ray and the scintillator produces a light photon. This light photon is received at the photocathode of a photomultiplier tube. The result is a pulse whose height is dependent upon the energy of the incident gamma ray. For a complete description of the interactions of gamma rays and scintillators, see Davisson.[18]

In gross gamma counting, energy discrimination on the basis of the pulse height is not made. Each pulse, regardless of its height, is counted by a scaler that is adjusted to accept all pulses above the noise level of the electronic system. In this method, as in beta counting,

destructive analyses are generally made so that the radioactivity that is measured emanates only from the element to be determined. Nondestructive analyses by means of radioactivity decay studies may be made in those favorable cases in which a short-lived radioactivity is to be measured in the presence of a long-lived radioactivity or vice versa.

Instruments

A gross-gamma scintillation counter was used for the measurement of radioactivity. This counter consisted of a detector and a scaler. The detector was a cylindrical "thallium activated" sodium iodide crystal 2 in. in length by 2 in. in diameter with a center well 1.5 in. deep and 0.86 in. in diameter. This crystal was optically coupled[19] to an RCA 5819 photomultiplier tube. The scaler was an Atomic Instrument Company Model No. 101B Research Scaler. The detector was enclosed in a lead-brick shield 8 x 8 x 16 in. and 4 in. thick. The background of this counter at the time of these measurements was 350 counts/min.

Differential Gamma Counting

Method

Differential gamma counting is the process of counting gamma rays of particular energies. The energy discrimination is made on the basis of the height of the pulse produced by the interaction of the gamma ray and the scintillator.

If a plot is made of the number of pulses per pulse-height interval (ordinate) versus the pulse height (abscissa), a distribution known as a gamma-ray spectrum is obtained. A typical spectrum of a radionuclide

emitting monoenergetic gamma rays is shown in Figure 7. The basic features of this spectrum are the "full-energy peak" (photopeak) which represents the total energy of the incident gamma rays; the Compton electron distribution, which arises from gamma-ray collisions in the scintillator and the subsequent escape of the degraded photon; and the backscatter peak, which results when large-angle Compton scattering from the environment reflects degraded photons into the scintillator. In certain instances, pair production[20] in the scintillator resulting from gamma-ray energies above about 1.5 Mev, adds to the complexity of the spectrum.

The radioactivity of a radionuclide can be measured from a gamma-ray spectrum. A differential pulse-height analyzer[21] is used to measure the pulse-height distribution. It can be controlled to select a certain pulse-height range and to count the number of pulses (counts) having pulse heights (energies) within that range. Thus, the range of pulse heights corresponding to the full-energy peak may be selected and only that portion of the spectrum recorded. The area under the full-energy peak is then compared with the area under the full-energy peak of a comparator sample.

The radioactivity from the spectrum may also be measured on an "absolute" basis. In the absolute measurement of radioactivity, the major problem is to convert the observed counting rate into a disintegration rate that relates the amount of radioactivity to the actual number of nuclei present in the sample.

The total area of the spectrum is proportional to the photon emission rate, N_o, and this is related to the disintegration rate, A, by the branching ratio, b, the number of photons/disintegration, as follows:

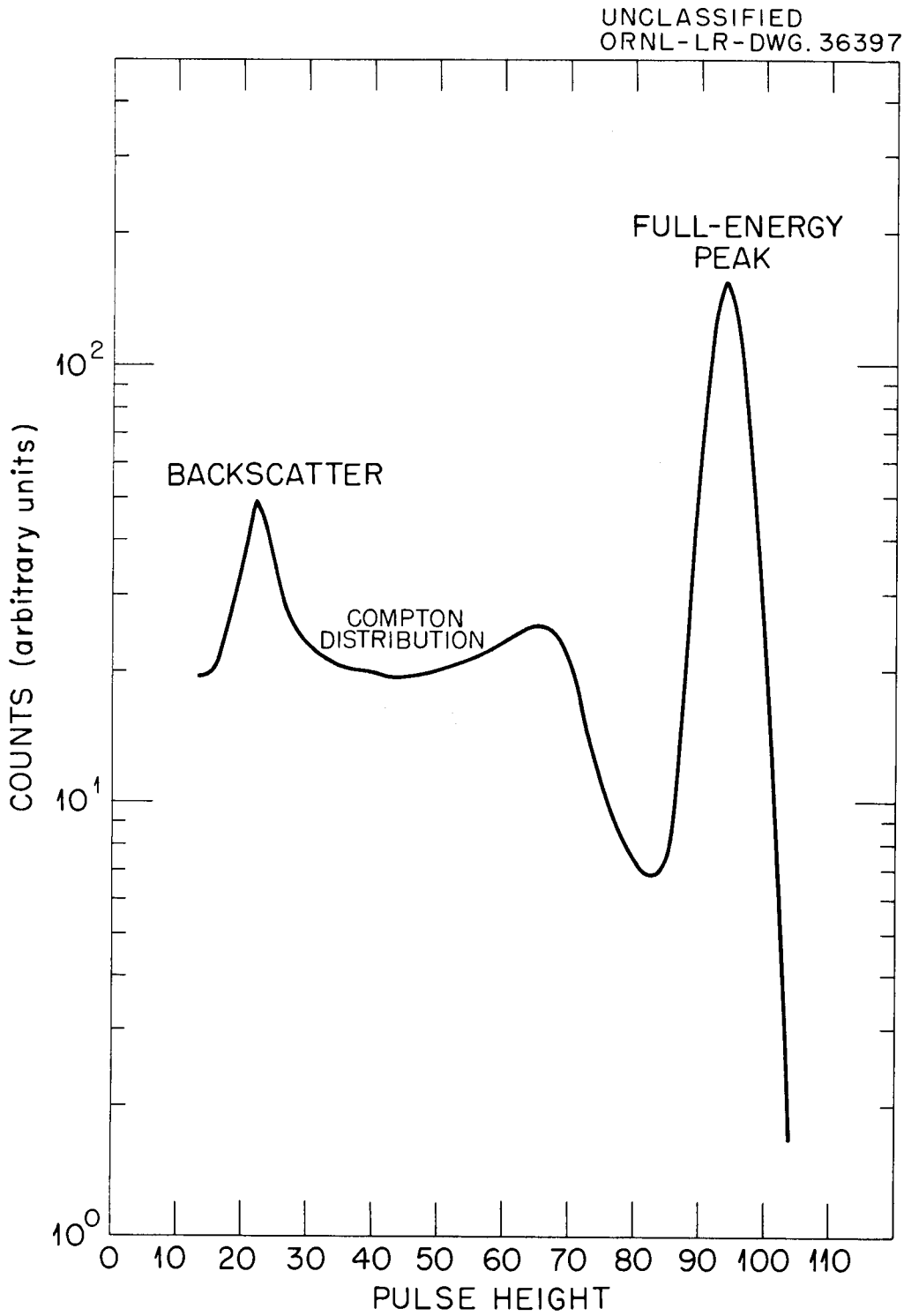

Fig. 7.--Typical Gamma-Ray Spectrum of a Monoenergetic Gamma Ray

$$b = \frac{N_o}{A} \tag{25}$$

The branching ratio, b, can generally be obtained from the literature.[22] The photon emission rate, N_o, presented by Heath[23] is obtained from Equation 26.

$$N_o = \frac{N_p}{\epsilon_T PZ} \tag{26}$$

where N_o = the photon emission rate in units of photons/sec

N_p = the counting rate in units of counts/sec under the full-energy peak

ϵ_T = the absolute total detection efficiency for the source-detector geometry used

P = the appropriate peak-to-total ratio (ratio of area of the full-energy peak to the total area of the spectrum)

Z = a correction factor for absorption in the source and in any absorber used.

A description of the absolute total detector efficiency, as well as its value and the values of the peak-to-total ratios for gamma rays of various energies, are given by Heath.[24]

In both the comparator and the absolute methods of measurement of radioactivity from a spectrum, the area of the spectrum under the full-energy peak must be found. Since a gamma-ray full-energy peak has a Gaussian shape,[25] its counting rate, N_p, may be found by fitting a Gaussian curve to the full-energy peak. The variation in the shape of a full-energy peak from that of a Gaussian curve is discussed below. The Gaussian curve must have a width corresponding to the resolution width of the instrument at the energy of the full-energy peak. Gaussian curves having these widths were prepared.

Gaussian Curves

The first step in the preparation of these Gaussian curves was to determine a resolution curve for the gamma-ray scintillation spectrometer used. The resolution of a spectrometer is defined as the full width at a point on the full-energy peak which is one-half the maximum height of the peak divided by the energy of the peak. In Table 2 are listed the radionuclides with known gamma-ray energies used to obtain the resolution function in Figure 8. Cesium-137 and scandium-46 each have two full-energy peaks at different energies which were convenient for making the necessary measurements.

TABLE 2

RADIONUCLIDES USED TO DETERMINE RESOLUTION FUNCTION

Radionuclide	Half Life	Gamma-ray Energy, Mev	Resolution, %
Cs^{137}	30 y	0.032	30.0
Am^{241}	462 y	0.0598	17.7
Hg^{203}	48 d	0.279	10.5
Cs^{137}	30 y	0.663	7.9
Mn^{54}	312 d	0.835	7.2
Sc^{46}	85 d	1.12	6.5
Na^{22}	2.6 y	1.28	6.5
Sc^{46}	85 d	2.01	5.4

The experimentally determined resolution function was used to determine the widths from which Gaussian curves could be constructed.

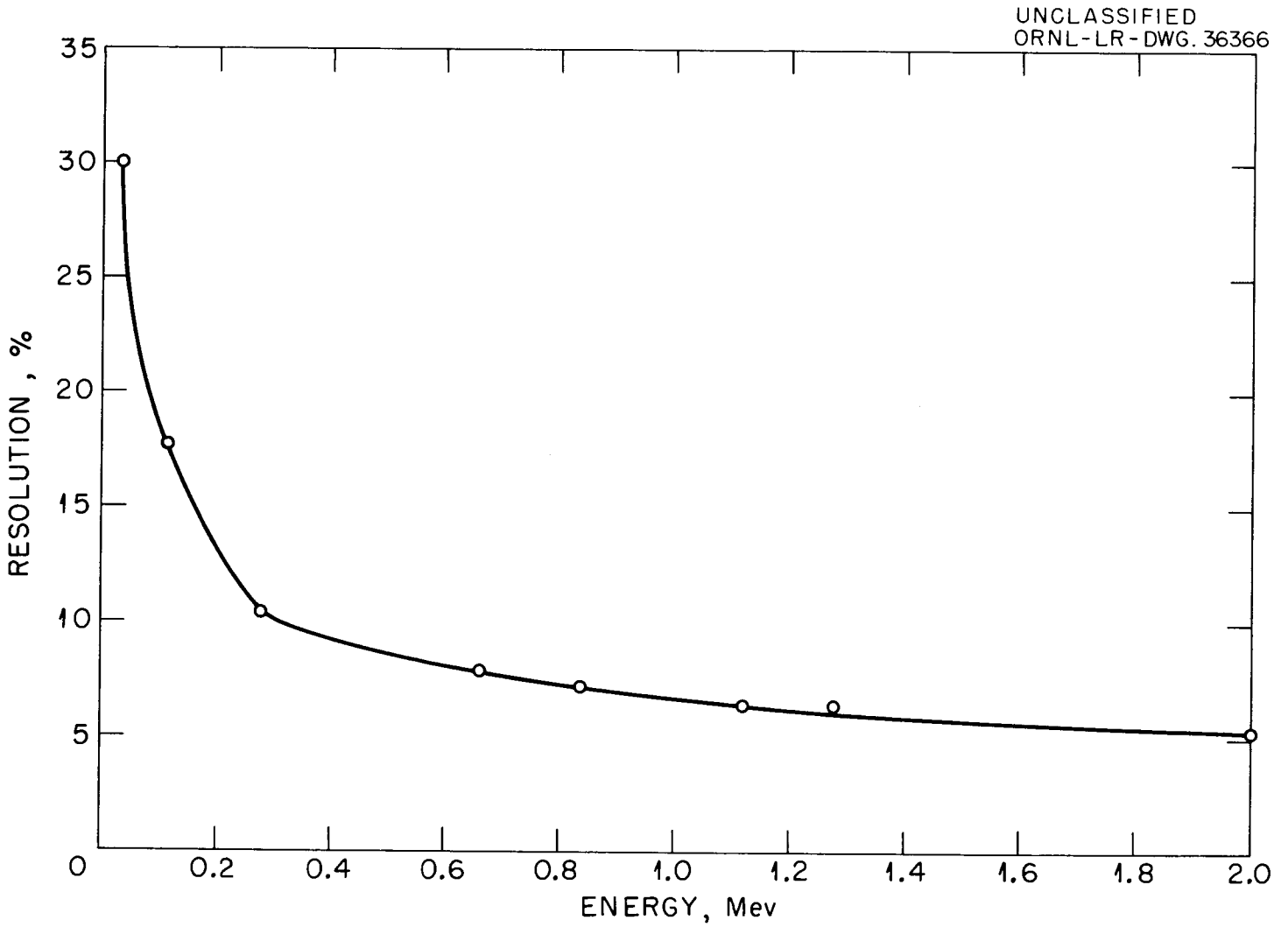

Fig. 8.--Resolution Function of a 3 by 3 in. Sodium Iodide (Thallium Activated) Crystal

The following equations[26] in which y is the dependent variable were used to determine the shape of the Gaussian curves in Figures 9 and 10:

$$y = k \exp(-h^2x^2) \tag{27}$$

and

$$k = \frac{h\Delta x}{\sqrt{\pi}}$$

where x = independent variable, in this instance, distance from origin

Δx = increment in which x is measured

h = a normalization constant chosen so that the area under the curve is equal to 1.000

The width, $w_{\frac{1}{2}}$, is taken as the full width at one-half the maximum value of y. The value of y is y = k at a value of x = 0. The width, $w_{\frac{1}{2}}$, shown in Equation 33 is then calculated at a value $y = \frac{k}{2}$. The value of x for the value $y = \frac{k}{2}$ is calculated from Equation 27. For these conditions, the following equations can be derived:

$$\frac{k}{2} = k \exp(-h^2x^2) \tag{28}$$

$$x = \frac{1}{h}(\ln 2)^{\frac{1}{2}} \tag{29}$$

Since a Gaussian curve is symmetrical about the x value at which y is a maximum, the width, $w_{\frac{1}{2}}$, is given by the equation

$$w_{\frac{1}{2}} = 2x = \frac{2}{h}(\ln 2)^{\frac{1}{2}} \tag{30}$$

$$w_{\frac{1}{2}} = \frac{1.665}{h} \tag{31}$$

The width, $w_{\frac{1}{2}}$, in terms of the height, k, is given by the substitution of Equation 27 into Equation 31:

$$w_{\frac{1}{2}} = \frac{1.665\ \Delta x}{k\sqrt{\pi}} = \frac{0.9396\ \Delta x}{k} \tag{32}$$

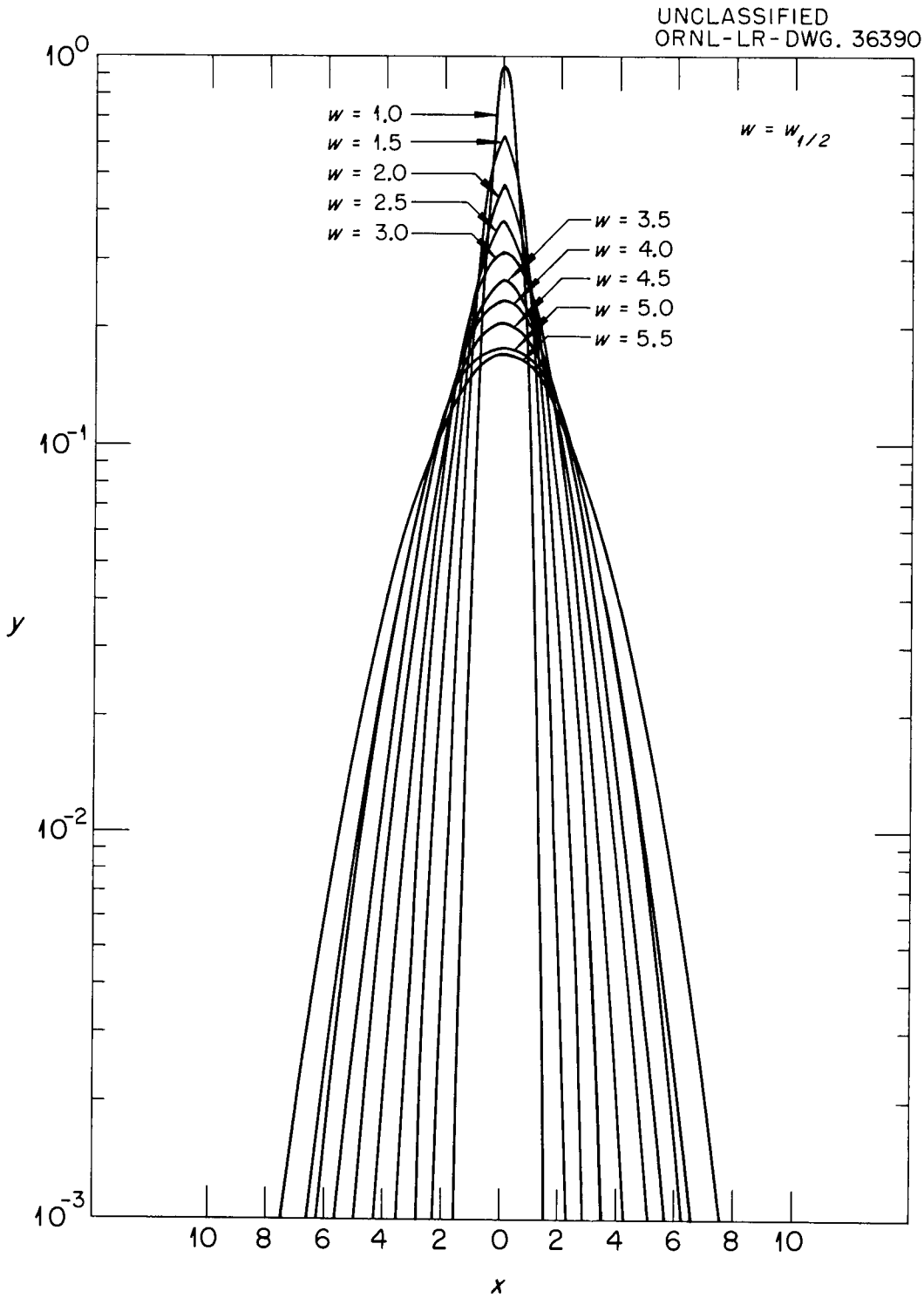

Fig. 9.--Gaussian Curves Having Widths of 1 to 5 Pulse Height Units

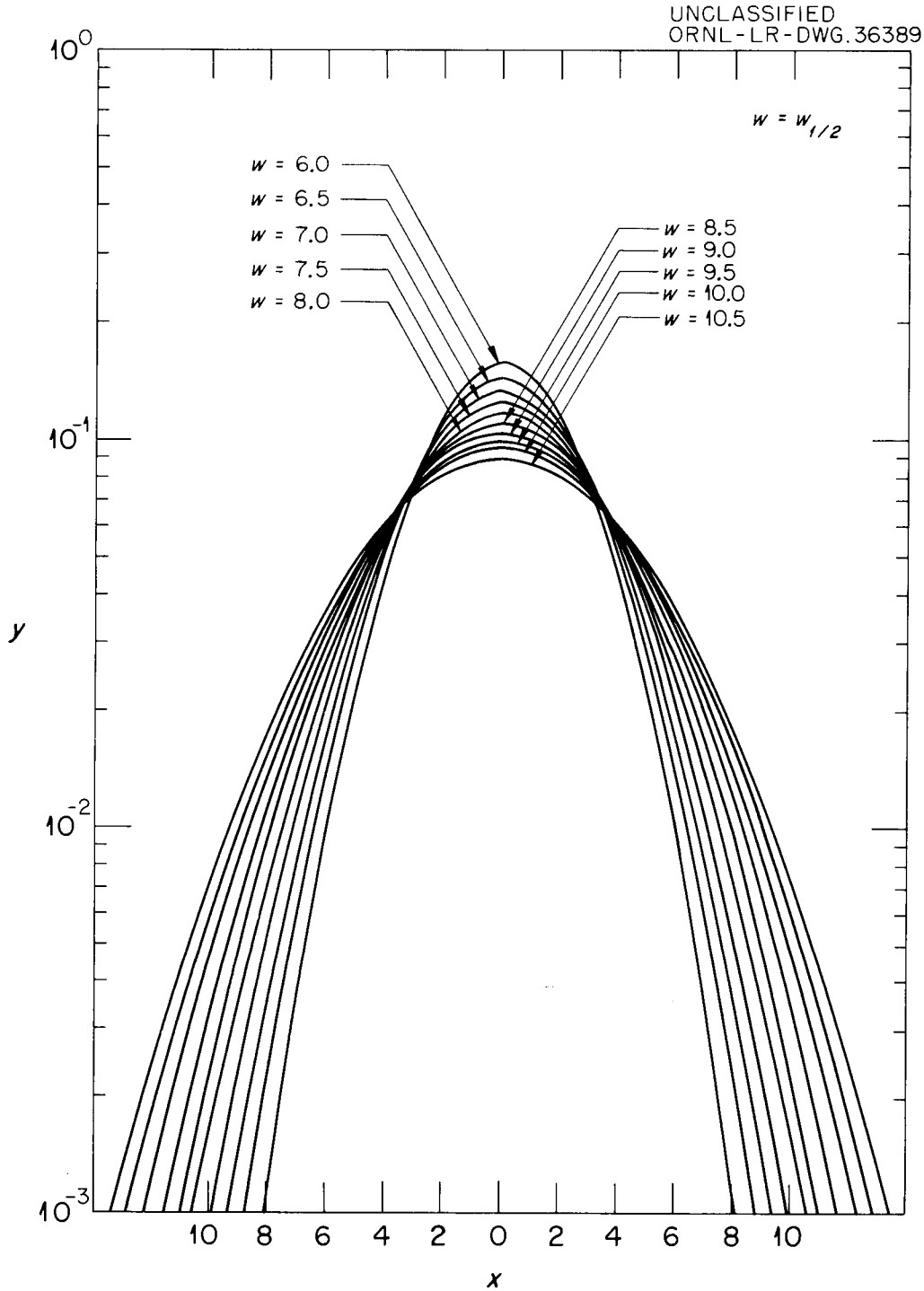

Fig. 10.--Gaussian Curves Having Widths of 5.5 to 10.5 Pulse Height Units.

If x is measured in terms of energy, then Δx is the increment of energy per unit of x. If, however, x is measured in units of x (channels on a multichannel gamma-ray spectrometer), then $\Delta x = 1$ since a value of y is obtained for each unit of x measured.

In terms of units of x (channels) then, the width, $w_{\frac{1}{2}}$, and the height, k, are related by a constant as follows:

$$w_{\frac{1}{2}} = \frac{0.9396}{k} \tag{33}$$

This equation indicates that a curve having a maximum $y_1 = k_1$ at some value, x_1, and a second curve having a maximum $y_2 = k_2$ at some value, x_2, will have the same shape if the width $(w_{\frac{1}{2}})_1 = (w_{\frac{1}{2}})_2$.

From the resolution function in Figure 8, then, the width of a full-energy peak may be determined if its energy is known. This width is used to select the proper Gaussian curve to fit the peak. It will be found that when the sides of the peaks are matched, the top portions of the peaks do not match, and vice versa. It is best, however to fit the peak portions of the curves to each other. It is shown by Equation 34 that most reliable data appears on the peak portion of the curve. If the observation is X counts, the standard deviation,[27] σ, in X counts is:

$$\sigma = X^{\frac{1}{2}} \tag{34}$$

It is obvious that X will be largest at the counting peak. This is shown in Figure 11 in which the vertical lines through each point represent the standard deviation of that point. The relative standard deviation σ/R is smallest at the peak; thus, data taken from the peak are more reliable than the data taken from low portions of the curve.

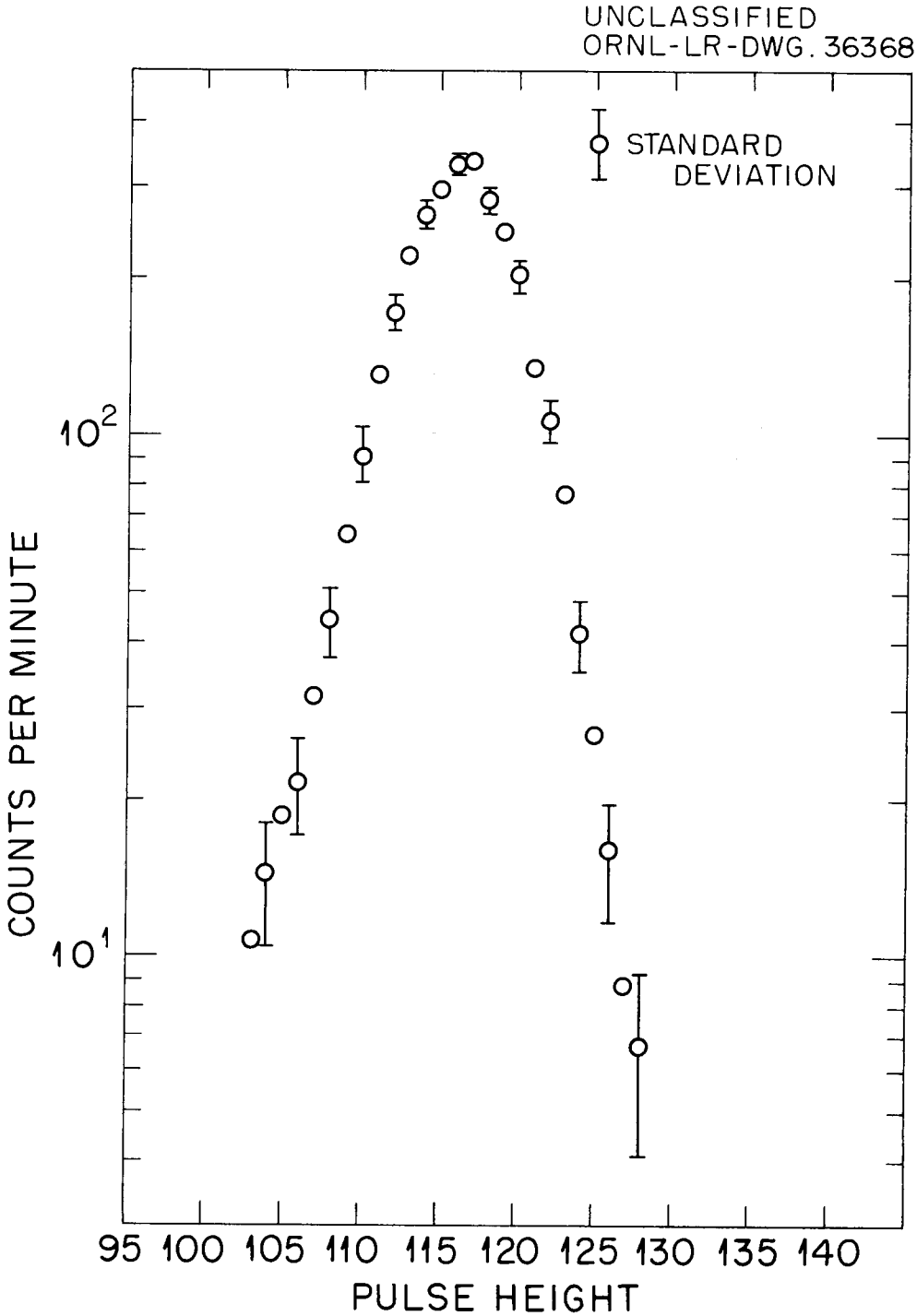

Fig. 11.--Standard Deviation of Experimental Data Describing a Full-Energy Peak.

It can be shown further that the experimental full-energy peak and the calculated Gaussian curve should be matched at the peaks by plotting the logarithmic form of Equation 27:

$$\ln y = \ln k - h^2x^2 \tag{35}$$

where y = counting rate in units of counts/min

k = counting rate at the peak point

x = distance from the origin in units of pulse height, (the origin taken to be the peak point).

The full-energy peak shown in Figure 11 has been replotted by the use of Equation 35 and is shown in Figure 12. The points in the figure represent the experimental full-energy peak, and the straight line represents the Equation 35 plotted for the calculated Gaussian curve having the same full width as the experimental full-energy peak at half the maximum height. The best match between the line and the experimental points is at the higher counting rates.

The Gaussian curves have been normalized so that the area under the curve equals 1.000. By use of these curves, the proper shape of an experimental full-energy peak can be obtained and with it the "best" value for the differential peak height, k. Since the shape of the experimental curve and that of the Gaussian curve are the same, the areas under the curves are proportional to the heights, and thus:

$$\frac{k_G}{S_G} = \frac{k_E}{S_E} \text{ for } (w_{\frac{1}{2}})_E = (w_{\frac{1}{2}})_G \tag{36}$$

k_E = value of y_E at $X_E = 0$ (peak height)

k_G = value of y_G at $X_E = 0$ (peak height)

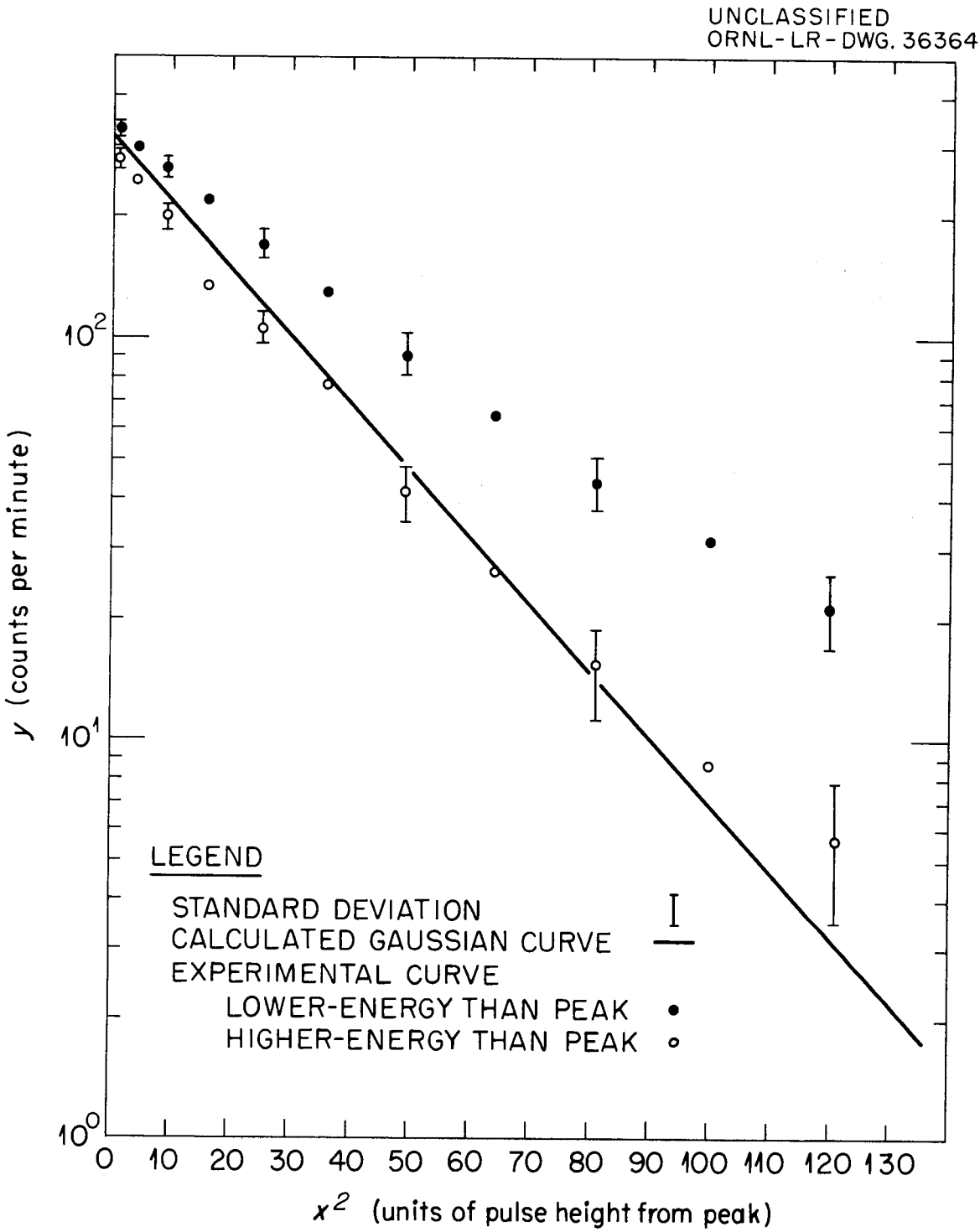

Fig. 12.--Gaussian Representation of Data

S_G = area under Gaussian curve and equal to 1.000 since curve was normalized to this area

S_E = area under experimental curve

$(w_{\frac{1}{2}})_G$ = full width of Gaussian curve at one-half the maximum height

$(w_{\frac{1}{2}})_E$ = full width of experimental curve at one-half the maximum height

From Equation 36

$$S_E = \frac{k_E}{k_G} \text{ for } (w_{\frac{1}{2}})_E = (w_{\frac{1}{2}})_G \tag{37}$$

In Table 3 are given the values of k_G for the value of $(w_{\frac{1}{2}})_G$ plotted in Figures 9 and 10. It can be seen that from Equation 33, values of k for $w_{\frac{1}{2}}$ other than those found in Table 3 can be calculated.

TABLE 3

HEIGHT, k_G, FOR GAUSSIAN CURVES OF WIDTH, $(w_{\frac{1}{2}})_G$

$(w_{\frac{1}{2}})_G$	k_G	$(w_{\frac{1}{2}})_G$	k_G
1.0	0.9396	6.0	0.1566
1.5	0.6264	6.5	0.1446
2.0	0.4698	7.0	0.1342
2.5	0.3758	7.5	0.1253
3.0	0.3132	8.0	0.1174
3.5	0.2684	8.5	0.1105
4.0	0.2349	9.0	0.1044
4.5	0.2088	9.5	0.09890
5.0	0.1879	10.0	0.09396
5.5	0.1708	10.5	0.08949

The monoenergetic gamma-ray spectrum shown in Figure 7 represents an ideal case. If there is more than one full-energy peak in the spectrum, it is necessary to correct for the influence one full-energy peak

may have on any other in the spectrum. The counts which describe a full-energy peak when they are recorded by a spectrometer are the sum of all counts having that particular energy range selected on the differential pulse-height analyzer. If the Compton distribution of one full-energy peak lies under another full-energy peak of lesser energy, the two counting rates are counted together and thus the lower-energy peak is distorted. The higher-energy peak is not affected. If it is necessary to determine a disintegration rate from a lower-energy peak, corrections must be made by subtracting the contribution from the higher-energy peak from that of the lower-energy peak. The effect of a higher-energy peak on a lower-energy peak is shown in Figure 13.

It is this method of subtracting spectra that provides a means of nondestructive analysis. A composite spectrum may be obtained in which the gamma radiations from several different radionuclides in the sample are being counted. Qualitative identification of the radionuclides can be made by observing the full-energy peak energy positions and their decay rates. Once the radionuclides in the composite spectrum are identified, it is necessary to obtain a pure spectrum of each radionuclide so that the composite spectrum may be resolved by the successive subtraction of each pure spectrum. The pure spectrum of a radionuclide may be obtained in some instances from a gamma-ray spectrum catalog such as that authored by Heath[28] or by experiment. If a catalog is used, the spectrum of the mixture must be measured under the same conditions as was the spectrum given in the catalog. Putman and Taylor[29] have described a method of subtracting spectra by instrumental means. The final step is to determine the radioactivity from one of the resolved full-energy peaks as described above.

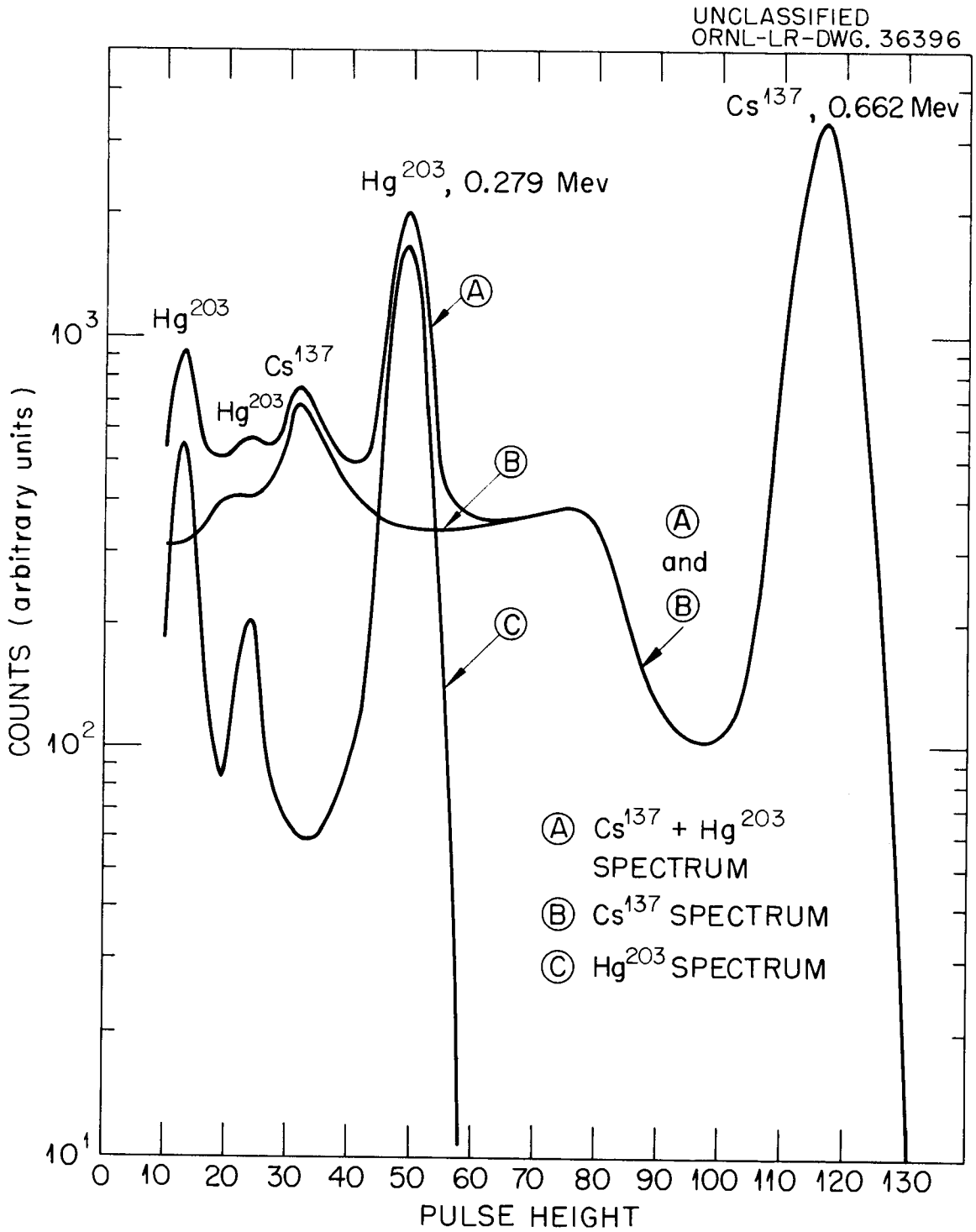

Fig. 13.--Effects of High-Energy Peaks on Low-Energy Peaks

Figure 14 shows the composite spectrum of a mixture of rhodium and platinum and the resulting spectra obtained after subtracting out the platinum spectrum.

Instruments

The following instruments were used to measure the radioactivity by differential gamma counting.

Single-Channel Gamma Spectrometer.--A single-channel, automatic-recording, scanning spectrometer was used. This instrument was designed at the Oak Ridge National Laboratory but is similar to the Technical Measurement Corporation[30] S-11 spectrometer.

Multichannel Gamma Spectrometer.--A 20-channel differential pulse-height analyzer, namely, Atomic Instrument Company[31] model 520, was used in the work described herein. A 256-channel analyzer, built by Radiation Counter Laboratories[32] from a design by Schuman and McMahon,[33] was also used.

Detectors

Three detector crystals were used with both the 20-channel and 256-channel instruments. These include a $1\frac{1}{2}$ in. dia by 3/32 in. sodium iodide (thallium activated) crystal, 3 in. dia by 3 in. sodium iodide (thallium activated) crystal, and a 4 in. dia by 4 in. sodium iodide (thallium activated) crystal.

The detector used is dependent somewhat on what portion of the spectrum is of interest. It has been stated earlier (p. 37) that a higher-energy peak affects a lower-energy peak by adding substantial

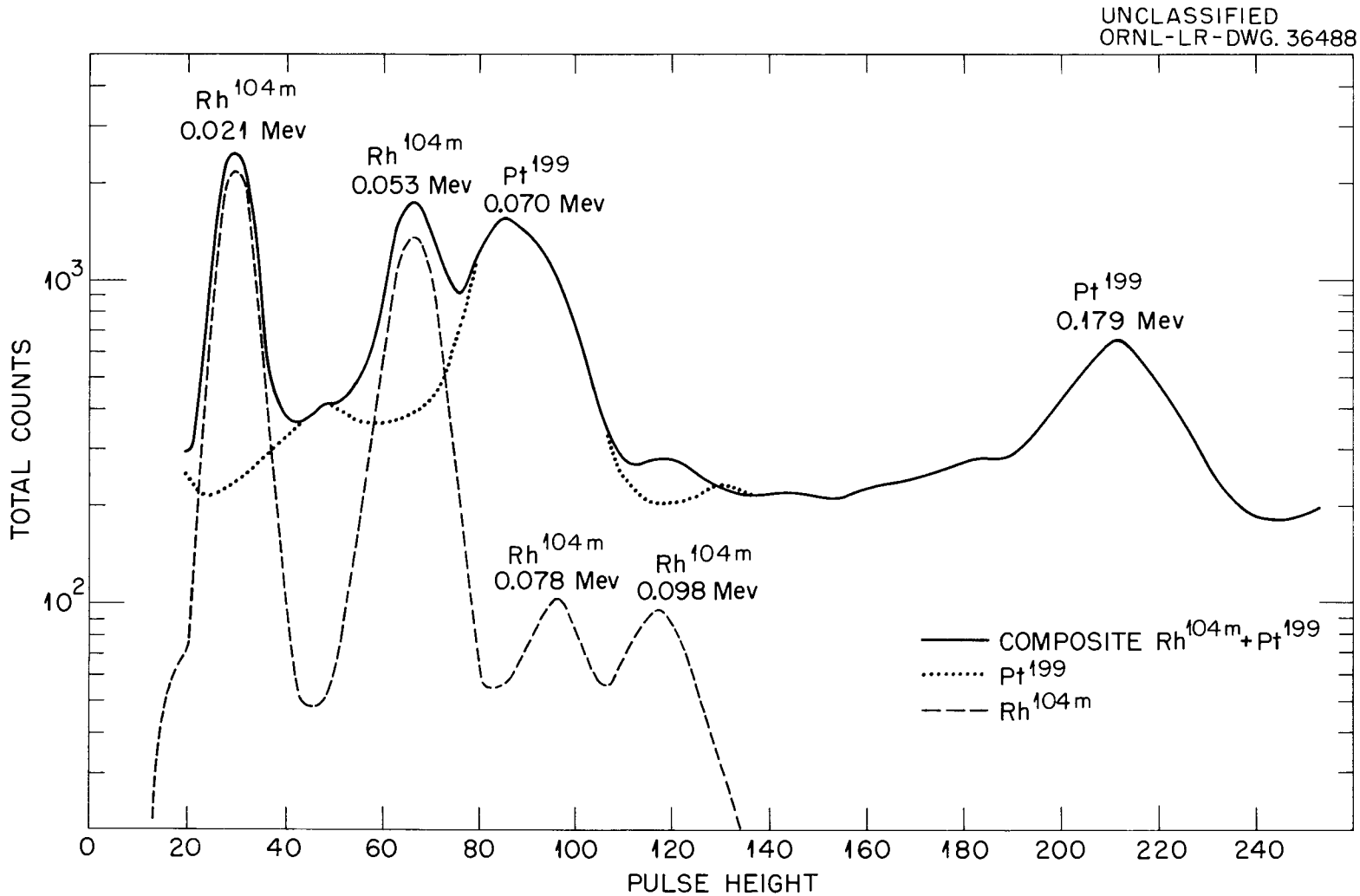

Fig. 14.--Composite Gamma-Ray Spectrum of Rhodium and Platinum Mixtures

counts to the lower-energy peak. These counts result from the degradation of higher-energy gamma rays by Compton collisions where only a portion of the gamma-ray energy is lost to the scintillator. This small amount of energy results in pulses at lower energy and thus adds to the low-energy range of the spectrum. Thus, the $1\frac{1}{2}$ in. dia by 3/32 in. sodium iodide (thallium activated) crystal was employed to facilitate the use of the low energy spectrum. The 3 in. dia by 3 in. crystal and the 4 in. dia by 4 in. crystal were used to record the high energy spectra.

The efficiency with which a crystal detects gamma rays is a measure of the fraction of gamma rays absorbed by the crystal in passage through it. For maximum efficiency, ϵ_o, the assumption is made that all absorption processes result in a count. The absorption of gamma rays in the crystal depends upon the gamma absorption coefficient, μ, the thickness, d, of the crystal, and the source-to-crystal distance, D. Their relation to the efficiency is expressed in the following equation if the source is collimated or if D is large

$$\epsilon_o = 1 - \exp(-\mu d) \tag{38}$$

Figure 15 shows the dependence of the gamma absorption coefficient for sodium iodide on the gamma-ray energy. In Table 4 are given the values of the maximum efficiency, ϵ_o, for various gamma-ray energies and crystal thicknesses. It can be seen from this table that a thin crystal greatly decreases the effect of higher-energy gamma rays because the efficiencies for detecting these gamma rays are reduced. This effect can also be seen in the spectrum of mercury-203 in Figure 16; the spectrum was taken on a 3-in. crystal and on a 3/32-in. crystal.

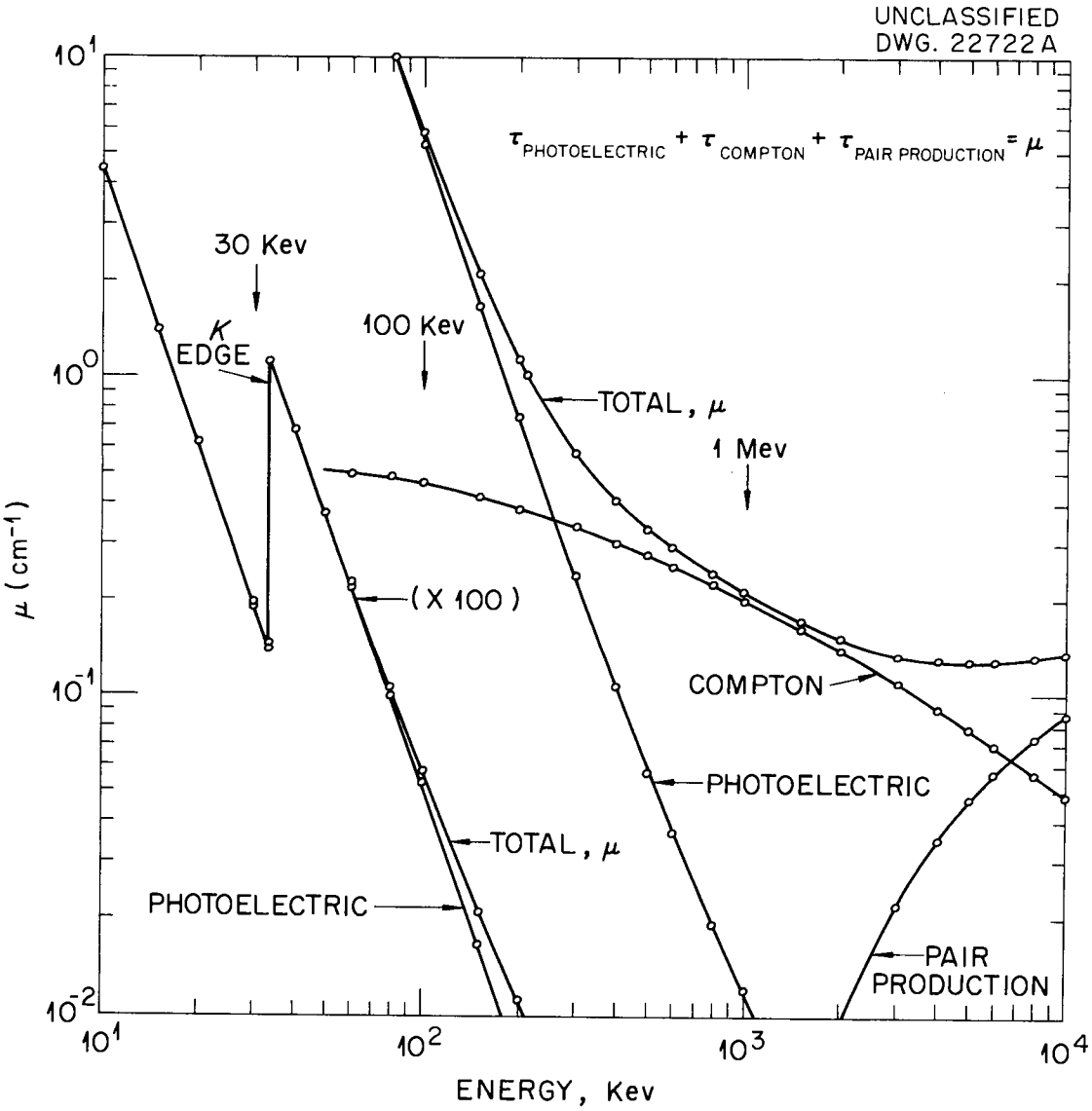

Fig. 15.--Absorption Coefficients of Sodium Iodide Crystals for Various Gamma-Ray Energies.

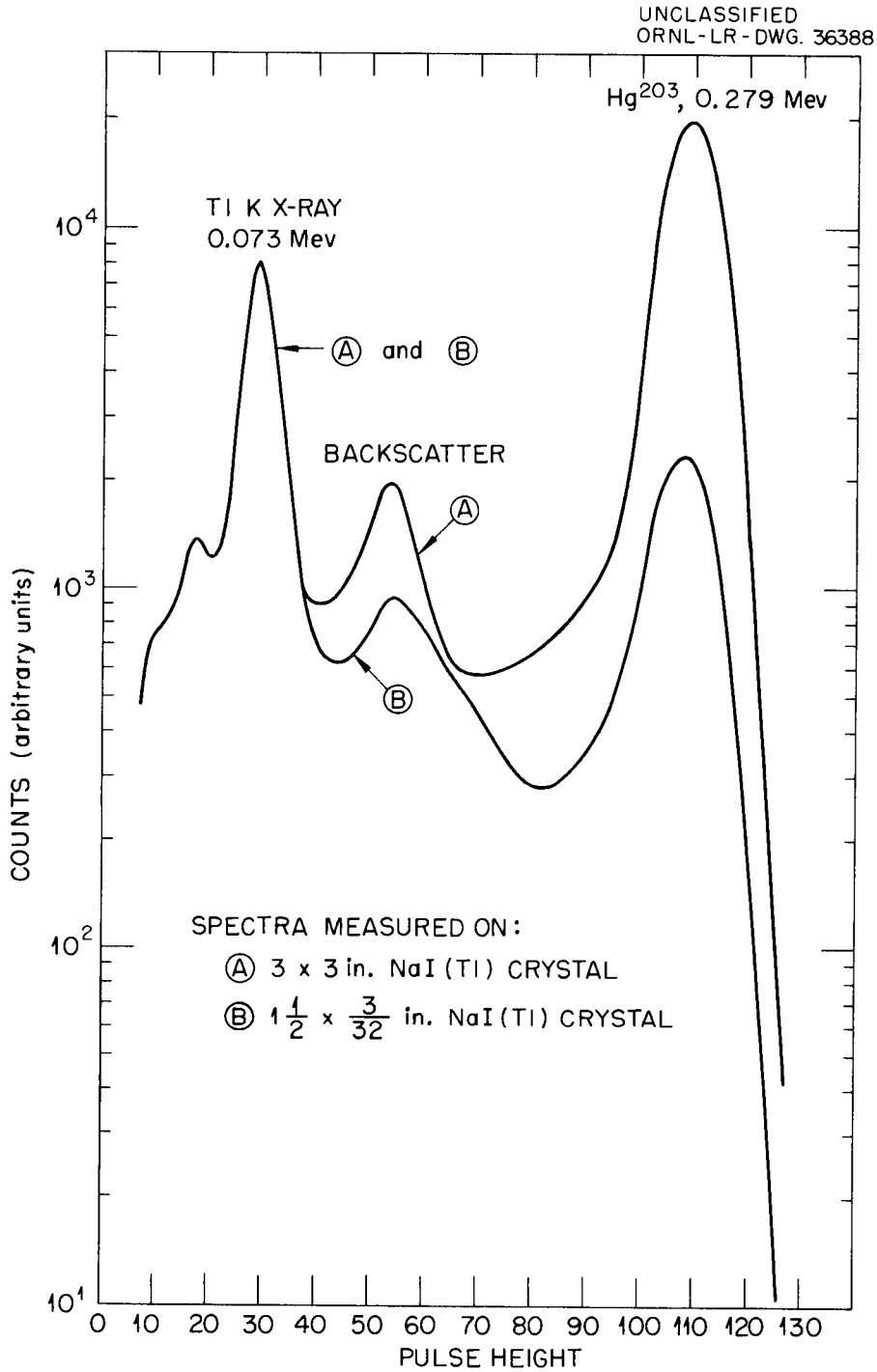

Fig. 16.--Comparison of Gamma-Ray Spectra Taken with a 3-in. Thick and a 3/32-in. Thick Sodium Iodide (Thallium-Activated) Crystal.

TABLE 4

MAXIMUM EFFICIENCIES FOR ABSORPTION OF GAMMA RAYS IN SODIUM IODIDE CRYSTALS

Gamma-Ray Energy, Mev	Maximum Efficiencies for Crystal Thickness Indicated		
	3/32 inches	3 inches	4 inches
0.032	0.976	1.000	1.000
0.060	0.995	1.000	1.000
0.087	0.850	1.000	1.000
0.130	0.508	1.000	1.000
0.160	0.350	1.000	1.000
0.206	0.302	1.000	1.000
0.279	0.165	0.997	1.000
0.468	0.077	0.931	0.971
0.663	0.058	0.871	0.935
0.835	0.049	0.826	0.903
1.12	0.047	0.781	0.869
1.27	0.045	0.766	0.855
2.01	0.030	0.680	0.781

Miller, Reynolds, and Snow[34] also calculated the efficiencies and photofractions of monoenergetic gamma rays from a broad parallel beam incident on sodium iodide crystals of various sizes. They define their efficiency as the ratio of the number of gamma rays which experience an interaction with the crystal to the number incident on the crystal face. In addition, they define photofraction as the fraction of those gamma rays that do interact and which are totally absorbed within the crystal.

The information on efficiencies and photofractions clearly demonstrates that it is possible to obtain discrimination between high- and low-energy gamma rays by a judicious choice of crystal thickness. This

technique should prove helpful in the nondestructive analysis of mixtures because the gamma-ray spectra in such cases are very complex.

CHAPTER IV

COMPARISON OF COUNTING METHODS

Method of Comparison

In Chapter III three methods of measuring radioactivity were discussed: beta counting, gross gamma counting, and differential gamma counting. If it is assumed that a nuclide disintegrates with the emission of both beta particles and gamma rays, then it is necessary to find a method of counting that will give a maximum counting rate with the greatest precision. This method of counting can be determined by setting the relative standard deviation of any two methods equal and making a calculation, whereby it can be determined which is the better method if the sample contains a certain number of counts.[35] Thus, in the case of gross gamma counting versus gross beta counting:

$$\sigma_1 = \left(\frac{R_{S1} + 2R_{B1}}{t_1}\right)^{\frac{1}{2}} \tag{39}$$

$$\sigma_2 = \left(\frac{R_{S2} + 2R_{B2}}{t_2}\right)^{\frac{1}{2}} \tag{40}$$

where σ_1 = standard deviation in the gross gamma counting rate

σ_2 = standard deviation in the gross beta counting rate

R_{S1} = net gross gamma counting rate

R_{S2} = net gross beta counting rate

R_{B1} = gross gamma background

R_{B2} = gross beta background

t_1 = the counting time required to count the sample by gross gamma counting

t_2 = the counting time required to count the sample by gross beta counting.

For the purpose of these comparisons, the time interval used in counting the sample is taken to be the same as that used in counting the background.

To compare the gross gamma counting with gross beta counting let

$$\frac{\sigma_1}{R_{S1}} = \frac{\sigma_2}{R_{S2}} \tag{41}$$

then

$$\frac{\left(\frac{R_{S1} + 2R_{B1}}{t_1}\right)^{\frac{1}{2}}}{R_{S1}} = \frac{\left(\frac{R_{S2} + 2R_{B2}}{t_2}\right)^{\frac{1}{2}}}{R_{S2}} \tag{42}$$

Let $T = \frac{t_1}{t_2}$ and solve for T, the ratio of the length of time required to count the sample by one method to that required by another method.

$$T = \frac{t_1}{t_2} = \left(\frac{R_{S1} + 2R_{B1}}{R_{S2} + 2R_{B2}}\right)\left(\frac{R_{S2}}{R_{S1}}\right)^2 \tag{43}$$

A net counting rate at which two counting methods yield the radioactivity with the same degree of precision in the same length of time will occur when T = 1.

Thus, by means of Equation 43, a comparison can also be made of differential gamma counting with gross beta counting, and of differential gamma counting with gross gamma counting. In these comparisons, it is important to know the limits of the ratio of the net counting rates and of the ratio of the background counting rates for all cases in which T = 1.

To illustrate this let $T = 1$

$$R_{S1} = aR_{S2}$$

$R_{B1} = bR_{B2}$ and substitute these into Equation 43

$$1 = \left(\frac{aR_{S2} + 2bR_{B2}}{R_{S2} + 2R_{B2}}\right)\left(\frac{1}{a}\right)^2 \tag{44}$$

Equation 45 is obtained by rearranging Equation 44

$$(a^2 - a)R_{S2} = (b - a^2)2R_{B2} \tag{45}$$

Equation 45 can be applied to these cases:

1.	$a > 1$	$a^2 - a = +$	$\therefore b > a^2 > 1$
2.	$a = 1$	$a^2 - a = 0$	$\therefore b = a^2 = 1$
3.	$a < 1$	$a^2 - a = -$	$\therefore b < a^2 < 1$

As an example of the conclusions reached from the applications of Equations 43 and 45 let $R_{S1}/R_{S2} = a = 1.66$

$$R_{N1} = 250 \text{ counts/min.}$$

$$R_{B2} = 25 \text{ counts / min.}$$

Since a is greater than one, then b must be greater than a^2, and so it is since $a^2 = (1.66)^2 = 2.78$ and $b = 250/25 = 10$. The fact that the ratios a and b fit case 1 indicates that there is a gross gamma counting rate, R_{S1}, and a gross beta counting rate, R_{S2}, for which $T = 1$. To find these counting rates, these values are substituted into Equation 43

$$1 = \left(\frac{1.66\ R_{S2} + 2(250)}{R_{S2} + 2(25)}\right)\left(\frac{1}{1.66}\right)^2$$

$$2.76\ R_{S2} + 138 = 1.66\ R_{S2} + 500$$

$$1.10\ R_{S2} = 362$$

$$R_{S2} = 329$$

Since $\frac{R_{S1}}{R_{S2}} = 1.66$, $R_{S1} = 546$.

The relative standard deviation, σ/R, in each of these counting rates is 5.9%. A comparison of the relative standard deviations of gross gamma counting and gross beta counting at other counting rates is given in Table 5.

TABLE 5

COMPARISON OF RELATIVE STANDARD DEVIATIONS OF GROSS GAMMA COUNTING RATES (R_{S1}) WITH BETA COUNTING RATES (R_{S2}) WHEN $R_{S1}/R_{S2} = 1.66$

Type of Counting	Gross Counting Rate, Counts/min.	Background Counting Rate, Counts/min.	Net Counting Rate, Counts/min.	Standard Deviation, Counts/min.	Relative Standard Deviation, %
γ	318	250	68	23.8	35.0
β	66	25	41	9.5	23.2
γ	386	250	136	25.2	18.5
β	107	25	82	11.5	14.0
γ	523	250	273	27.5	10.2
β	189	25	164	14.6	8.9
γ	796	250	546	32.3	5.9
β	354	25	329	19.5	5.9
γ	1,342	250	1,092	39.9	3.6
β	683	25	658	26.6	4.0
γ	2,434	250	2,184	51.8	2.4
β	1,341	25	1,316	37.0	2.8

In Table 6 are listed the types of radiation and their energies for the radionuclides that are most likely to be formed by the neutron

irradiation of the Group VIII elements. For certain radionuclides that emit both beta and gamma radiations, the following experiments were performed to determine which counting method should be used in measuring the radioactivity of the respective radionuclide. Counting rates and background rates are, of course, dependent on the instrument and shielding used.

Irradiation Facility

All neutron irradiations made relative to experiments described herein were made in the pneumatic tube (Hole No. 22) of the Oak Ridge Graphite Reactor.[36]

Nickel-65

Experimental Procedure

Three weighed samples of nickel powder were irradiated at a flux of 5×10^{11} neutrons/cm^2/sec for a period of 4 hours. After the irradiation, each of the samples was dissolved in concentrated nitric acid, and the solution was diluted to a volume of 25 ml. Four 3-ml aliquots were taken from each solution. Cobalt holdback carrier[37] was added to each aliquot, and the resulting solution was made basic with 6 M ammonium hydroxide. Nickel dimethylglyoxime was then precipitated by adding 0.1 M solution of dimethylglyoxime in 95% ethanol. The precipitate was washed with ethanol, then dissolved in 6 M hydrochloric acid, and reprecipitated as nickel dimethylglyoxime.[38] Each of the twelve precipitates was filtered onto a tared Whatman 41H filter paper, dried, and weighed. In a gamma-ray spectrum observed by means of an automatic recording single-

TABLE 6

RADIATIONS OF RADIONUCLIDES OF GROUP VIII ELEMENTS

Radionuclide	Half Life	Beta Radiations, Mev	Gamma Radiations, Mev
Fe^{59}	45.1 d	0.271, 0.462, 1.560	0.191, 1.098, 1.289
Co^{60}	5.2 y	0.312, 1.478	1.17, 1.333
Ni^{65}	2.56 h	0.60, 1.01, 2.10	0.37, 1.12, 1.49
Ru^{97}	2.8 d	None	0.109, 0.216, 0.325, 0.570
Ru^{103}	41.0 d	0.119, 0.227	0.498, 0.610
Ru^{105}	4.5 h	1.15	Complex
Rh^{104m}	4.4 m	None	0.0511, 0.0772
Rh^{104}	42 s	0.7, 1.9, 2.5	0.556, 1.24
Pd^{109}	13.6 h	1.02	None
Pd^{111m}	5.5 h	2.15	None
Os^{185}	94 d	None	Complex
Os^{193}	31.5 h	0.68, 0.86, 1.00, 1.06, 1.14	Complex
Ir^{192}	74.5 d	0.67	Complex
Ir^{194}	19.0 h	0.43, 0.98, 1.91, 2.24	Complex
Pt^{197}	18 h	0.468, 0.479, 0.670	0.27, 0.191, 0.279
Pt^{199}	31 m	0.8, 1.1, 1.3, 1.7, 1.8	0.074, 0.197, 0.246, and others

channel gamma-ray spectrometer, no radiochemical impurities were found in the precipitates.

The precipitates were prepared for beta counting by mounting on a 3-1/4 by 2-1/2 in. heavy card which has a 1-in. diameter hole in its center; the hole was covered with cellophane. Beta counting was done with an end-window Geiger-Mueller counter.

The beta mount was taken apart and the precipitate and the filter paper placed into a 10 by 75 mm culture tube for gross gamma counting. The count was made in a well-type 2 by 2 in. crystal of sodium iodide (thallium activated).

A differential gamma count was taken on each precipitate in the same culture tube. A single-channel gamma-ray scintillation spectrometer with a well-type 2 by 2 in. crystal of sodium iodide (thallium activated) was used. The region of the spectrum corresponding to the 1.49-Mev full-energy peak of nickel was selected since, at this energy, the background of the spectrometer would have the least effect. The background gamma-ray intensity versus gamma-ray energy is shown in Figure 17.

Data

A comparison of the counting rates obtained by the three methods of counting is given in Table 7. Counting rates are reported in counts per minute per milligram of nickel at the time the sample was taken from the reactor.

Gross Gamma Counting versus Gross Beta Counting.--From Table 7 it can be seen that the average ratio, a, of the gross gamma counting rate, R_{S1}, to the gross beta counting rate, R_{S2}, is 1.66. As shown in

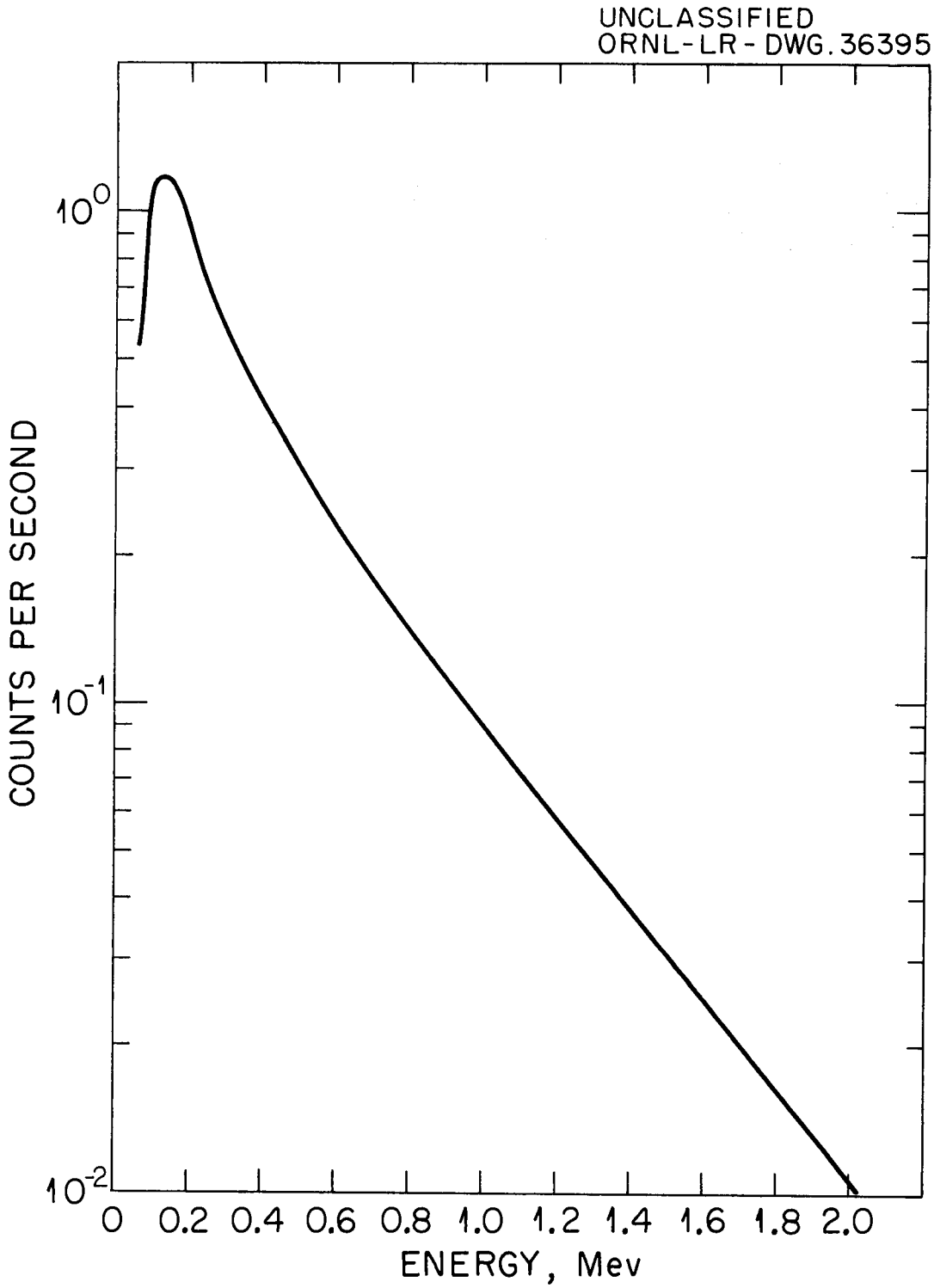

Fig. 17.--Typical Gamma-Ray Background Spectrum

TABLE 7

COUNTING RATE RATIOS OF NICKEL-65

Sample	Counting Rate in Counts/min			Ratios of Counting Rates		
	Gross Beta	Gross Gamma	Differential Gamma	Gross Gamma / Gross Beta	Differential Gamma / Gross Beta	Differential Gamma / Gross Gamma
A-1	245,944	400,641	18,854	1.63	0.0766	0.0470
A-2	252,180	411,673	18,576	1.63	0.0737	0.0451
A-3	250,984	421,085	20,023	1.68	0.0798	0.0476
A-4	261,938	418,054	18,393	1.60	0.0702	0.0440
B-1	243,761	416,645	19,685	1.71	0.0808	0.0472
B-2	249,152	397,577	18,619	1.60	0.0747	0.0468
B-3	245,756	404,913	19,928	1.65	0.0811	0.0492
B-4	243,987	413,144	20,759	1.69	0.0851	0.0502
C-1	244,273	401,547	18,775	1.64	0.0769	0.0468
C-2	248,889	415,778	20,246	1.67	0.0813	0.0487
C-3	248,185	.....	.....	....	.....	.....
Average	.....	.....	.....	1.66	0.0784	0.0473

Table 5, in which the ratio $R_{S1}/R_{S2} = 1.66$ was used as an example, the gross gamma counting rate, R_{S1}, and the gross beta counting rate, R_{S2}, at which the two counting methods give equal precision of measurement ($T = 1$) are 546 and 329 counts/min, respectively, at background counting rates of 250 and 25 counts/min, respectively.

Differential Gamma Counting versus Gross Beta Counting.--The average ratio, a, of the differential gamma counting rate, R_{S1}, to the gross beta counting rate, R_{S2}, is 0.0784 as given in Table 7 and falls into case 3 of Equation 45. The ratio, b, of differential gamma background counting rate to the gross beta background counting rate must be less than a^2, that is, $(0.0284)^2$. It is, however, $10/25 = 0.4$. Thus, there is no differential gamma counting rate whose precision of measurement equals that of the gross beta counting rate for the same period of counting time.

Differential Gamma Counting versus Gross Gamma Counting.--The average ratio, a, of the differential counting rate, R_{S1}, to gross gamma counting rate, R_{S2}, is 0.0473 as given in Table 7 and also falls into case 3 of Equation 45. The ratio, b, of the differential gamma background counting rate to the gross gamma background counting rate must be less than a^2, that is, $(0.0473)^2$. It is, however, $10/250 = 0.04$. Thus, there is no differential gamma counting rate whose precision of measurement equals that of the gross gamma counting rate for the same period of counting time.

Iron-59, Cobalt-60, and Iridium-192

The counting rate ratio data for iron-59, cobalt-60 and iridium-192 are given in Tables 8, 9, and 10, respectively. The experimental

TABLE 8

COUNTING RATE RATIO FOR IRON-59

Sample	Counting Rate in Counts/min			Ratios of Counting Rates		
	Gross Beta	Gross Gamma	Differential Gamma	Gross Gamma / Gross Beta	Differential Gamma / Gross Beta	Differential Gamma / Gross Gamma
1	13,222	84,066	8,207	6.36	0.621	0.0976
2	12,661	84,246	8,052	6.65	0.636	0.0956
3	13,524	84,587	8,082	6.25	0.598	0.0955
4	13,430	82,001	7,689	6.10	0.572	0.0938
5	13,406	88,878	8,547	6.63	0.638	0.0962
6	13,056	84,670	8,107	6.48	0.621	0.0957
7	12,936	86,874	8,254	6.72	0.638	0.0950
8	12,752	84,326	8,099	6.61	0.635	0.0960
Average	.....	.....	.....	6.48	0.620	0.095

TABLE 9

COUNTING RATE RATIO FOR COBALT-60

Sample	Counting Rate in Counts/min			Ratios of Counting Rates		
	Gross Beta	Gross Gamma	Differential Gamma	Gross Gamma / Gross Beta	Differential Gamma / Gross Beta	Differential Gamma / Gross Gamma
1	8,173	130,382	9,950	15.95	1.217	0.0748
2	9,450	141,107	10,737	14.93	1.136	0.0762
3	8,662	128,211	9,792	14.80	1.130	0.0764
4	8,962	128,393	9,988	14.33	1.114	0.0778
5	8,997	128,218	10,005	14.25	1.112	0.0780
6	8,710	129,783	10,114	14.73	1.161	0.0779
7	8,706	125,775	9,694	14.45	1.113	0.0771
8	8,502	132,715	10,430	15.61	1.227	0.0786
9	8,573	129,930	10,432	15.15	1.217	0.0803
10	8,746	132,569	10,305	15.16	1.178	0.0777
Average	.....	.....	.....	14.94	1.160	0.0775

TABLE 10

COUNTING RATE RATIO FOR IRIDIUM-192

Sample	Counting Rate in Counts/min			Ratios of Counting Rates		
	Gross Beta	Gross Gamma	Differential Gamma	Gross Gamma / Gross Beta	Differential Gamma / Gross Beta	Differential Gamma / Gross Gamma
1	8,868	99,014	20,712	11.16	2.34	0.2092
2	9,636	97,439	20,820	10.11	2.16	0.2137
3	9,276	94,520	20,289	10.19	2.19	0.2146
4	9,556	91,977	20,049	9.62	2.10	0.2180
5	9,632	96,984	20,581	10.07	2.14	0.2122
6	9,728	99,466	20,863	10.22	2.14	0.2097
7	9,461	95,570	20,266	10.10	2.14	0.2120
8	9,789	97,797	20,750	9.99	2.12	0.2122
Average	.....	.....	.....	10.18	2.17	0.2127

procedures used with these radionuclides were essentially the same as that used for nickel-65 except that instead of the precipitates being counted, the individual solutions obtained were pipetted onto filter papers, which were then dried and counted in the same manner as nickel-65 was counted.

Summary

A summary of the results of the comparisons of counting methods is given in Table 11. The method of counting that will provide the greatest precision of measurement for a specified period of counting time is indicated in the last column. The recommended method of counting is suitable only if the element is determined by destructive analysis and the radionuclide counted in radiochemically pure form.

TABLE 11

SUMMARY OF COMPARISON OF COUNTING METHODS

Radionuclide	Average Ratio of Counting Rates			Recommended Counting Method
	Gross Gamma / Gross Beta	Differential Gamma / Gross Beta	Differential Gamma / Gross Gamma	
Fe^{59}	6.48	0.620	0.0957	Gross gamma
Ni^{65}	1.66	0.0784	0.0473	Gross gamma above 796 gross gamma counts/min. Beta count below this.
Co^{60}	14.94	1.160	0.0775	Gross gamma
Ir^{192}	10.18	2.17	0.2127	Gross gamma

CHAPTER V

OPTIMUM COUNTING RATE

Theory

Loevinger and Berman[39] have presented a method for determining the number of sample counts and background counts necessary to insure an acceptable per cent error in a minimum total time. This error (relative standard error) at the 68% confidence level for the determination of one count can be considered to be the same as the relative standard deviation of the count. They show that there is an optimum ratio of total-to-background counting time such that the combined counting time can be a minimum. Thus, if there are many samples to be counted, the total counting time required to count these samples will be minimized.

In general practice, counting the sample and background for different periods of time is inconvenient when many samples must be counted. It is simpler to decide what per cent error in the net count is acceptable; then knowing the approximate background, to count the sample and background for equal periods of time such that the acceptable per cent error in the net sample count will be obtained. To assist in doing this, Equation 54 which expresses the relationship between the sample counting rate, the sample counting time, the error in the background counting rate, and the fractional error in the net sample counting rate, was derived in

the following manner:

let R_T = total counting rate of sample,

R_B = background counting rate,

R_n = net counting rate of sample,

t_T = sample counting time,

t_B = background counting time,

σ_T = standard deviation of the sample counting rate,

σ_B = standard deviation of the background counting rate,

σ_n = standard deviation of the net counting rate.

Equations 46-49 are given to relate the above quantities to each other:[40]

$$\sigma_T = \left(\frac{R_T}{t_T}\right)^{\frac{1}{2}} \tag{46}$$

$$\sigma_B = \left(\frac{R_B}{t_B}\right)^{\frac{1}{2}} \tag{47}$$

$$\sigma_n = (\sigma_T^2 + \sigma_B^2)^{\frac{1}{2}} = \left(\frac{R_T}{t_T} + \frac{R_B}{t_B}\right)^{\frac{1}{2}} \tag{48}$$

$$R_T = R_n + R_B \tag{49}$$

Equation 50 is obtained by substituting Equation 49 into Equation 48

$$\sigma_n = \left(\frac{R_n + 2R_B}{t}\right)^{\frac{1}{2}} \tag{50}$$

where $t = t_T = t_B$. Let

$$R_n = X\sigma_B \tag{51}$$

where X = a proportionality factor. Then Equation 52 is obtained by substituting Equations 47 and 51 into Equation 50

$$\sigma_n = \left(\frac{X\sigma_B + 2\sigma_B^2}{t}\right)^{\frac{1}{2}} \tag{52}$$

The relative standard deviation, σ_n/R_n, of the net counting rate, R_n, of the sample is then given by

$$\frac{\sigma_n}{R_n} = \left(\frac{1}{tX\sigma_B} + \frac{2}{X^2}\right)^{\frac{1}{2}} \tag{53}$$

and

$$\left(\frac{\sigma_n}{R_n}\right) X^2 t\sigma_B - X - 2t\sigma_B = 0 \tag{54}$$

A plot of X, the proportionality factor, versus σ_B, the standard deviation of the background counting rate, is given in Figure 18 for various values of σ_n/R_n x 100 per cent error of the net sample count, and t, the counting time.

Discussion

The following examples illustrate the value of Figure 18 in the determination of the net sample necessary for a preset error.

Example 1.--If a maximum error of 5 per cent is acceptable for a particular count, the first step in determining the net counting rate of the sample that will be required under a particular set of conditions is to find the standard deviation in the background for the desired period of counting time. Let

$$R_B = 6 \text{ counts/sec}$$

$$t = 160 \text{ sec}$$

$$\frac{100\ \sigma_n}{R_n} = 5\%$$

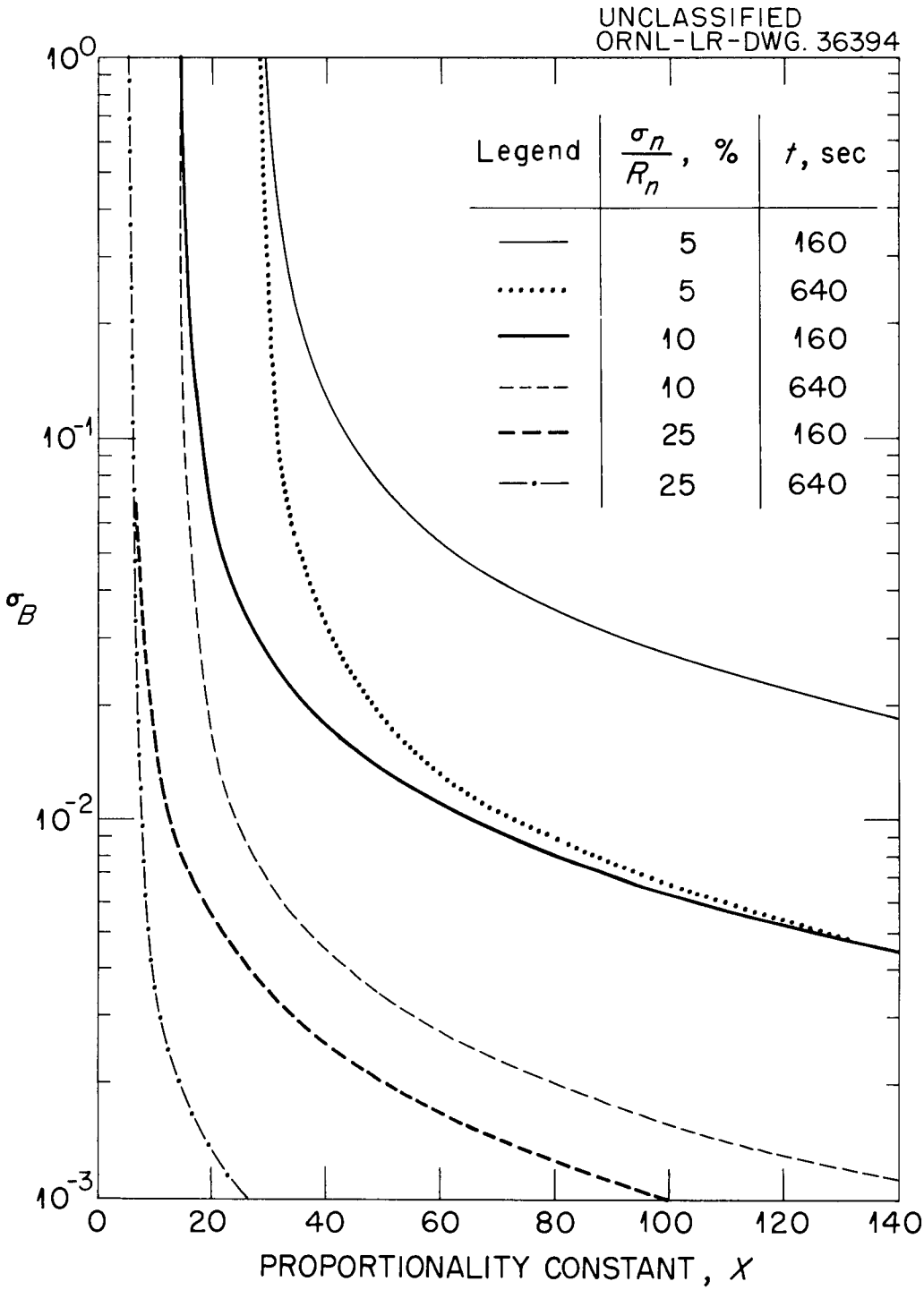

Fig. 18.--Relationship of Net Counting Rate to Standard Deviation of Background.

Then

$$\sigma_B = \left(\frac{R_B}{t}\right)^{\frac{1}{2}} = \left(\frac{6}{160}\right)^{\frac{1}{2}}$$

$$\sigma_B = 0.2 \text{ counts/sec}$$

Then from Figure 18 the value of X is found that corresponds to the following limitation: 5% error in the net counting rate of the sample; t, 160 sec; and σ_B equal to 0.19. This value of X is 35. From Equation 51, the net counting rate of the sample, R_n, is calculated.

$$R_n = (35)(0.2)$$

$$R_n = 7 \text{ counts/sec}$$

The total counting rate must be $R_n + R_B$.

$$7 + 6 = 13 \text{ counts/sec}$$

To check these results, from Equation 50

$$\sigma_n = \left(\frac{7 + 12}{160}\right)^{\frac{1}{2}} = \left(\frac{19}{160}\right)^{\frac{1}{2}}$$

$$\sigma_n = 0.35$$

$$\frac{100\ \sigma_n}{R_n} = \frac{(100)(0.35)}{7} = 5\%$$

If the sample does not have a sufficiently high counting rate to meet the restriction for a 5% error in the net counting rate of the sample longer counting times must be used.

Example 2.--The following example shows the reduced counting rate necessary with the same counter background as example 1 counted for t = 640 seconds. Let

$$R_B = 6 \text{ counts/sec}$$

$$t = 640 \text{ sec}$$

$$\frac{\sigma_n}{R_n} = 5\%$$

Then

$$\sigma_B = \left(\frac{R_B}{t}\right)^{\frac{1}{2}} = \left(\frac{6}{640}\right)^{\frac{1}{2}}$$

$$\sigma_B = 0.097 \text{ counts/sec}$$

From Figure 18, the value of X corresponding to a 5% error, t, 160 sec; and σ_B equal to 0.097, this value of X is 32. Again from Equation 51, the net counting rate of the sample, R_n, is calculated.

$$R_n = (31.7)(0.097)$$

$$R_n = 3 \text{ counts/sec}$$

The total count must be 9 counts/sec (sample count plus background counts). To check these results, from Equation 50,

$$\sigma_n = \left(\frac{3 + 12}{640}\right)^{\frac{1}{2}} = \left(\frac{15}{640}\right)^{\frac{1}{2}}$$

$$\sigma_n = 0.15$$

$$\frac{100\ \sigma_n}{R_n} = \frac{(100)(0.15)}{3} = 5\%$$

Summary

An equation (54) was derived herein which makes possible the determination of the minimum counting rate a sample must have in order to be counted with an acceptable error, σ_n/R_n, in the net counting rate of the sample, in counting time, t. Further use may be made of this equation by determining the weight of sample required to produce this minimum counting rate under certain conditions of irradiation. Thus, a method of calculating the limits of quantitative measurement for the determination of elements by activation analysis has been developed.

CHAPTER VI

LIMITS OF QUANTITATIVE MEASUREMENT OF THE GROUP VIII ELEMENTS

The limit of quantitative measurement is defined as the minimum weight of an element that produces a measurable amount of radioactivity after the element has been exposed to a neutron flux for a given period of time. By the determination of the minimum number of counts that can be counted with a preset error using the procedure described in Chapter V and converting these counts into disintegrations, it is possible to calculate the minimum weight of element that will produce these counts during a specified irradiation.

To demonstrate the method of calculating these limits of quantitative measurement, ruthenium-103, 41.0 d, is used as an example. In Chapter V, it was shown that the net counting rate necessary to obtain a 5% error with a 6 counts/sec background counted for 640 sec is 3 counts/sec. This counting rate must now be converted to a disintegration rate. The ratio of counts per second to disintegrations per second, of course, varies with each radionuclide. For a gross gamma counter, this ratio, ϵ, is termed the photon efficiency and for the calculations that follow ϵ values were obtained from Figure 19.[41]

The decay scheme of ruthenium-103 (Figure 4) indicates that this radionuclide has a 0.498-Mev gamma ray and a 0.615-Mev gamma ray whose

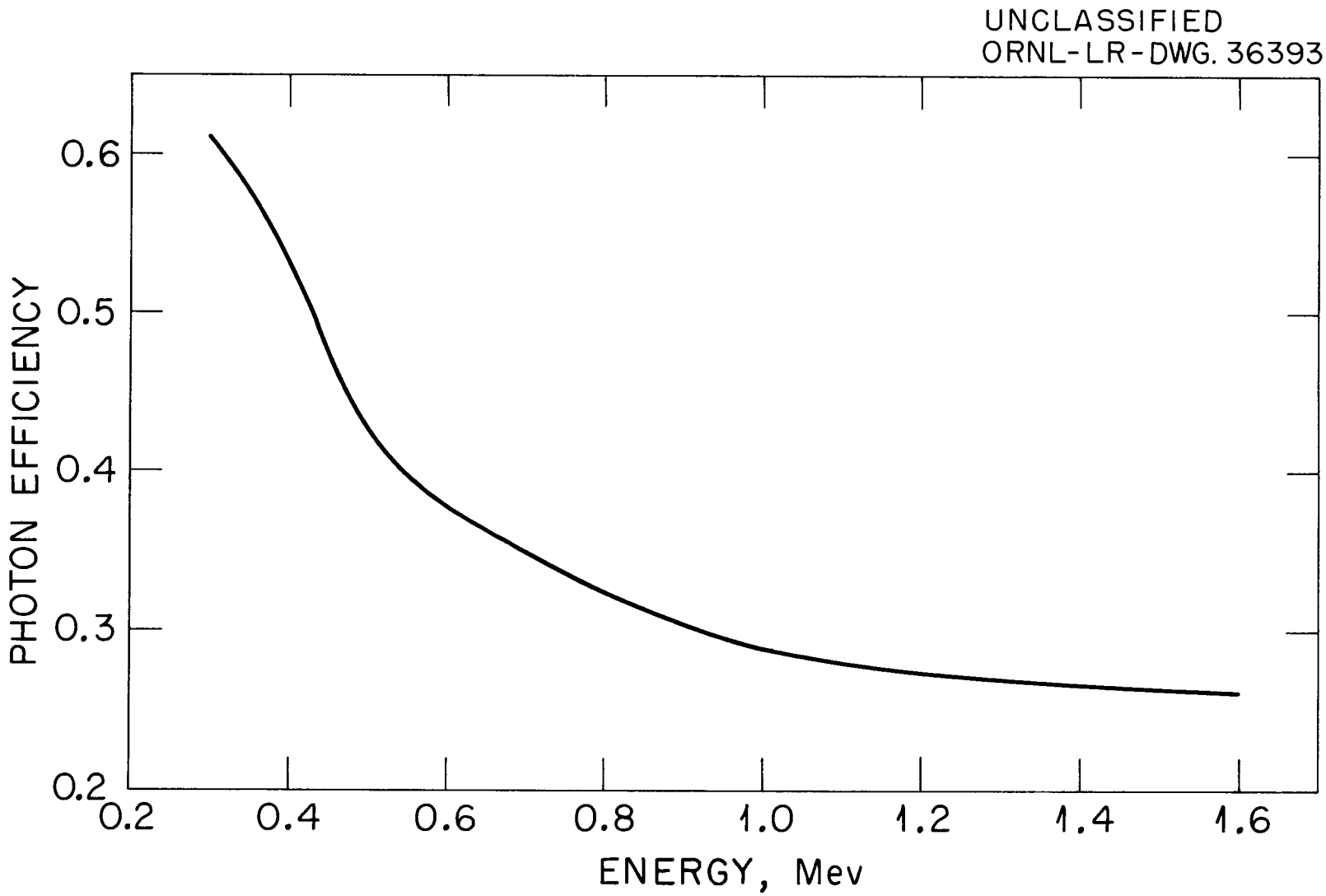

Fig. 19.--Approximate Photon Efficiencies of Scintillation Counters

branching ratios, b, are 90 per cent and 6 per cent respectively. The photon efficiencies determined from Figure 19 for these gamma rays are: 0.498 Mev, $\epsilon = 0.42$; 0.615 Mev, $\epsilon = 0.37$. An estimate of the total photon efficiency, ϵ_c, of a gross gamma counter is given by the equation:

$$\epsilon_c = \sum_i b_i \epsilon_i \tag{55}$$

Then for ruthenium-103

$$\epsilon_c = (0.9)(0.42) + (0.06)(0.37) = 0.41 \text{ c/d}$$

The disintegration rate of ruthenium-103 at a counting rate of 3 counts/sec is

$$\frac{3 \text{ c/s}}{0.41 \text{ c/d}} = 7 \text{ d/s}$$

The weight of ruthenium represented by 7 disintegrations/sec can be determined by substituting the following values into Equation 20:

$$A = 7 \text{ disintegrations/sec}$$

$$M = 101 \text{ grams}$$

$$f = 5 \times 10^{11} \text{ neutrons/cm}^2\text{/sec}$$

$$\sigma_{ac} = 1.2 \times 10^{-24} \text{ cm}^2$$

$$\theta = 0.3$$

$$1 - \exp(-\lambda t) = 0.1 \text{ (irradiation for one week)}$$

W = weight of ruthenium required to produce 3 counts/sec of ruthenium-103 radioactivity in this gross gamma counter

This substitution gives the following equation:

$$W = \frac{(7)(101)}{(5 \times 10^{11})(6 \times 10^{23})(1.2 \times 10^{-24})(0.3)(0.1)}$$

$$W = 0.06 \ \mu g$$

The limits of quantitative measurement of the Group VIII elements calculated in this manner are given in Table 12. The length of irradiation time was taken to be one week, or the length of time required for saturation, whichever was the shorter.

TABLE 12

LIMITS OF QUANTITATIVE MEASUREMENT OF GROUP VIII ELEMENTS BY (n,γ) REACTIONS

Element	Radionuclide Produced	Half Life	Irradiation Time	Limits of Quantitative Measurement, μg
Iron	Fe^{59}	45.1 d	1 week	6
Cobalt	Co^{60}	5.3 y	1 week	0.02
Nickel	Ni^{65}	2.56 h	Saturation	0.2
Ruthenium	Ru^{103}	40 d	1 week	0.06
Rhodium	Rh^{104m}	4.4 m	Saturation	0.0002
Palladium	Pd^{109}	4.8 m	Saturation	0.09
Osmium	Os^{193}	31.5 h	1 week	0.01[a]
Iridium	Ir^{194}	19 h	1 week	0.003
Platinum	Pt^{199}	31 m	Saturation	0.02[a]

[a]Branching ratios are not available. Ten disintegrations/sec were taken as the minimum detectable amount of radioactivity.

CHAPTER VII

USE OF (n,p) REACTIONS IN THE DETERMINATION OF GROUP VIII ELEMENTS

Although the (n,γ) reaction is the predominant nuclear reaction taking place in a nuclear reactor, other reactions such as the (n,p) and the (n,α) reaction do occur.[42] Of these the (n,p) reaction was investigated both from the standpoint of providing a method of determining the Group VIII elements and of providing information regarding possible interferences produced by this reaction when other types of nuclear reactions are used to determine the element of interest.

In Table 13 are listed the (n,p) reactions that could possibly be used for the determination of the Group VIII elements; these reactions are the favorable abundance of the stable nuclide and the favorable half life of the product radionuclide. The energy change and the potential barrier for proton emission, V, for each reaction[43] were calculated and are also given in Table 13.

The Q of the reaction was calculated as follows:

$$Q = \left[(m_s + m_n) - (m_r + m_p)\right] 931 \qquad (56)$$

where m_s = mass of stable nuclide in mass units

m_n = mass of neutron in mass units

m_r = mass of radionuclide in mass units

m_p = mass of proton in mass units

Mass values used in the calculations were obtained from Cameron.[44]

TABLE 13

PRINCIPAL (n,p) REACTIONS OF THE GROUP VIII ELEMENTS

Stable Nuclide	Natural Abundance %	Nuclear Reaction	Half Life of Produced Radionuclides	Q, Mev	V, Mev
Fe^{54}	5.84	$Fe^{54}(n,p)Mn^{54}$	312 d	- 0.344	5.02
Fe^{56}	91.68	$Fe^{56}(n,p)Mn^{56}$	2.58 h	- 3.45	4.97
Co^{59}	100	$Co^{59}(n,p)Fe^{59}$	45.1 d	- 1.52	5.10
Ni^{58}	67.8	$Ni^{58}(n,p)Co^{58}$	72 d	+ 0.518	5.32
Ni^{60}	26.2	$Ni^{60}(n,p)Co^{60}$	5.3 y	- 2.33	5.27
Ru^{96}	5.5	$Ru^{96}(n,p)Te^{96}$	4.3 d	+ 1.87	7.40
Ru^{99}	12.7	$Ru^{99}(n,p)Te^{99}$	6.04 h	+ 0.929	7.34
Rh^{103}	100	$Rh^{103}(n,p)Ru^{103}$	41.0 d	+ 0.026	7.43
Pd^{105}	22.23	$Pd^{105}(n,p)Rh^{105}$	36.5 h	+ 0.464	7.56
Pd^{106}	27.33	$Pd^{106}(n,p)Rh^{106}$	2 h	- 3.07	7.54
Os^{188}	13.3	$Os^{188}(n,p)Re^{188}$	17.0 h	+ 1.50	10.7
Ir^{191}	38.5	$Ir^{191}(n,p)Os^{191}$	14 h	- 0.095	10.8
Ir^{193}	61.5	$Ir^{193}(n,p)Os^{193}$	31.5 h	+ 0.745	10.8
Pt^{194}	32.8	$Pt^{194}(n,p)Ir^{194}$	19.0 h	+ 1.88	10.9
Pt^{195}	33.7	$Pt^{195}(n,p)Ir^{195}$	2.3 h	+ 1.03	10.9

The potential barrier was calculated as follows:

$$V = \frac{Z_1 Z_2 e^2}{R_1 + R_2} \tag{57}$$

where Z_1 = charge on nucleus 1

Z_2 = charge on nucleus 2

R_1 = radius of nucleus 1

R_2 = radius of nucleus 2

e = electronic charge in electrostatic units.

A negative Q value indicates that the nuclear reaction is ~~exo~~endo-ergic and may be carried out with thermal neutrons (average energy, 0.025 ev). A positive Q value indicates that the nuclear reaction is ~~endo~~exo-ergic and thus requires high-energy neutrons. In those cases in which there are more than one nuclear reaction that is endoergic, for instance, for iron, the reaction with which the more negative Q value is associated requires the higher-energy neutrons.

In order to determine the feasibility of the use of a particular nuclear reaction in a method of activation analysis, it is necessary to know the activation cross section for that reaction. This value may be calculated from Equation 20. The radioactivity produced in a specific weight of element is measured. At the same time the flux of the neutrons inducing the reaction is measured. The values thus obtained are used in Equation 20 to calculate the cross section. Even though some of the reactions listed in Table 13 are exoergic, neutrons having energies greater than the energy of thermal neutrons are needed to supply sufficient energy for the proton to overcome the potential barrier. Thus, the proper flux value to be used in Equation 20 is the number of these high-energy neutron/cm^2/sec. Flux measurements of neutrons having energies greater than the energy of thermal neutrons are difficult to make because of the inadequacy of high-energy flux monitoring date. It is more convenient to measure the thermal flux. Since the ratio of the thermal-neutron flux to the fast-neutron flux remains constant in Hole

No. 22 of the ORNL Graphite Reactor,[45] the thermal-neutron flux may be used as a convenient measure of the fast-neutron flux.

In the calculation of an activation cross section in this manner, that is, using the thermal neutron flux rather than the fast neutron flux, a relative cross section is obtained which represents a practical value that can be used with a readily measurable neutron flux. The cross section thus obtained is valid only for Hole No. 22 of the ORNL Graphite Reactor.

The (n,p) Reactions of Iron, Cobalt, and Nickel

When the values of Q and V presented in Table 13 are considered, iron, cobalt, and nickel are seen to have approximately the same potential barrier. Of the five possible (n,p) reactions for iron, cobalt, and nickel given in Table 13 the $Fe^{54}(n,p)Mn^{54}$ reaction and the $Ni^{58}(n,p)Co^{58}$ reaction are expected to have the highest activation cross sections because of their more positive Q values. The activation cross sections for both these reactions were determined and compared with those of the $Fe^{56}(n,p)Mn^{56}$ and the $Ni^{60}(n,p)Co^{60}$ reactions, respectively, in the following manner.

Activation Cross Section of the $Fe^{54}(n,p)Mn^{54}$ Reaction

Preparation of Ferric Oxide.--Iron wire was dissolved in concentrated hydrochloric acid and the solution was passed through a column of Dowex-1 anion-exchange resin.[46] The iron was adsorbed on the column. The column was then washed with 6 M hydrochloric acid and finally with 3 M hydrochloric acid in order to elute ferric chloride. The iron (III)

in the eluate was reduced with potassium iodide and the eluate boiled to remove all free iodine. The solution was made 1 M in hydrochloric acid and again put on the anion-exchange column. Antimony, the principal impurity observed in a gamma-ray spectrum of an irradiated iron sample, remained on the column and iron (II) passed through. The iron (II) in the effluent was oxidized with sodium bromate and precipitated with ammonium hydroxide. The ferric hydroxide precipitate was washed with water and centrifuged two times. After a final washing, the precipitate was filtered through Whatman 41H filter paper and ignited in a muffle furnace at 500° for one-half hour. The product was ferric oxide.[47]

Irradiation of Ferric Oxide.--Samples of ferric oxide were weighed into quartz tubes, which were sealed at one end and stoppered with a cork. Some of these tubes were placed in a irradiation container and were irradiated in Hole No. 22 of the ORNL Graphite Reactor for a 16-hr period. The other tubes were irradiated in the same manner for a 60.5-hr period.

Determination of Manganese-54.--Since iron-59, with its 1.1- and 1.29-Mev gamma rays, is formed in much higher yield than is manganese-54, a chemical separation was necessary before the 0.835-Mev gamma ray of manganese-54 could be measured with the required sensitivity.

The irradiated ferric oxide was allowed to decay for one week in order to remove any 2.58 h manganese-56 radioactivity. The sample was then dissolved in concentrated hydrochloric acid, and manganese carrier was added. This solution was passed through a column of Dowex-1 anion exchange resin which had been washed with 12 M hydrochloric acid. The iron was adsorbed on the column and the manganese passed through. The

manganese solution was collected and made basic with ammonium hydroxide. Hydrogen sulfide was bubbled through the solution to precipitate manganese sulfide.[48] The manganese sulfide was then centrifuged and washed once with water. It was then dissolved in concentrated nitric acid, and any free sulfur that was formed was removed with a stirring rod. Small portions of potassium chlorate were added to the nitric acid solution of manganese, and the solution was boiled. Manganese dioxide[49] was precipitated, centrifuged, washed with water, and finally with ethyl alcohol. The precipitate was collected on tared Munktell #00 filter paper and dried in an oven at 110° for 10 min. The filter paper and manganese dioxide were then weighed and placed in a 10 by 75 mm pyrex culture tube to be counted by differential gamma counting on a 20-channel gamma-ray scintillation spectrometer.

The radioactivity of manganese-54 was determined from the area under the 0.835-Mev full-energy peak. From this radioactivity the cross section was calculated by use of Equation 20.

Data.--The results of these determinations of the activation cross section of the $Fe^{54}(n,p)Mn^{54}$ reaction are given in Table 14.

* Activation Cross Section of the $Ni^{58}(n,p)Co^{58}$ Reaction

Preparation of Nickel Oxide.--Nickel powder was dissolved in concentrated hydrochloric acid. The solution was filtered and passed onto a column of Dowex-1 anion-exchange resin that had been previously washed with 12 M hydrochloric acid. Any cobalt impurity in the nickel was adsorbed on the column, whereas the nickel was washed through. Nickel hydroxide was precipitated by adding a solution of lithium hydroxide.

The precipitate was washed with several portions of water and filtered onto Whatman 41H filter paper. This was ignited in a muffle furnace at 800° to nickel oxide.[50]

TABLE 14

THE (n,p) CROSS SECTION OF IRON-54

Experiment	Weight of Iron Irradiated, mg	Duration of Irradiation, hr	Calculated Cross Section, millibarns
A-1	24.4	16	3.73
A-2	36.5		3.60
A-3	46.1		3.31
A-4	37.6		3.75
A-5	--		--
B-1	18.7	60.5	3.24
B-2	32.3		3.63
B-3	50.8		2.31
B-4	47.4		3.56
B-5	48.5		3.61
Average	....	....	3.55
Standard Deviation	....	....	0.18

Irradiation of Nickel Oxide.--Samples of the nickel oxide were weighed into quartz tubes, which were sealed at one end and stoppered with a cork. Some of these tubes were placed in an irradiation container and were irradiated in Hole No. 22 of the ORNL Graphite Reactor for a 60.5-hr period. Other samples were irradiated in the same manner for a 28.5-hr period.

Determination of Cobalt-58.--The irradiated samples were allowed to decay for a period of 2 weeks since some sodium-24 ($t_{\frac{1}{2}}$ = 15 h) radioactivity was found by observing a gamma-ray spectrum of an irradiated sample. At the end of this time, a gamma-ray spectrum showed no radioactivity was present other than that due to cobalt. The radioactivity of the cobalt was determined then by nondestructive means. The samples were emptied from the quartz tubes into 10 x 75 mm pyrex culture tubes and were counted directly. The 0.81-Mev gamma-ray, full-energy peak of cobalt-58 was counted by means of a 20-channel gamma-ray scintillation spectrometer. From the area under the full-energy peak, the amount of radioactivity was measured and used in Equation 20 to calculate the cross section.

Data.--In Table 15 are listed the results obtained for the activation cross section of $Ni^{58}(n,p)Co^{58}$ reaction relative to a thermal neutron flux of 5×10^{11} neutrons/cm^2/sec.

Activation Cross Section of the $Fe^{56}(n,p)Mn^{56}$ Reaction

The $Fe^{56}(n,p)Mn^{56}$ reaction was not investigated because the (n,p) cross section has been reported in previous work by Reynolds[51] to be 0.05 mb for a thermal neutron flux of 5×10^{11} neutrons/cm^2/sec.

Activation Cross Section of the $Ni^{60}(n,p)Co^{60}$ Reaction

Attempts were made to measure the cobalt-60 radioactivity produced by the $Ni^{60}(n,p)Co^{60}$ reaction during the investigation of the $Ni^{58}(n,p)Co^{58}$ reaction. However, the full-energy peak of cobalt-60 could not be identified in the spectrum because of the distortion in the spectrum

brought about by the "sum" peak of cobalt-58 at 1.35 Mev. A sum peak results when the scintillator absorbs the full energy of two gamma rays that enter the scintillator at the same time. This region of interference is shown as the shaded area in Figure 20. It can also be seen from Figure 20 that there is no interference in the cobalt-60 spectrum by cobalt-58 in the 2.50-Mev region. Thus, if the radioactivity present in the 2.50-Mev region of the cobalt-58 spectrum was due to cobalt-60, the cross section of the $Ni^{60}(n,p)Co^{60}$ reaction would be approximately 0.09 mb based on a thermal neutron flux of 5×10^{11} neutrons/cm^2/sec. Again, this cross section applies only to Hole No. 22 of the ORNL Graphite Reactor.

TABLE 15

THE (n,p) CROSS SECTION OF NICKEL-58

Experiment	Weight of Nickel Irradiated, mg	Duration of Irradiation, hr	Calculated Cross Section, millibarns
A-1	51.1	60.5	4.02
A-2	52.7		4.97
B-1	36.4	28.5	5.70
B-2	58.2		5.01
B-3	73.2		5.10
B-4	28.7		5.80
B-5	41.0		5.58
C-1	65.8	60.5	5.28
C-2	72.9		5.29
Average	....	....	5.35
Standard Deviation	....	....	0.32

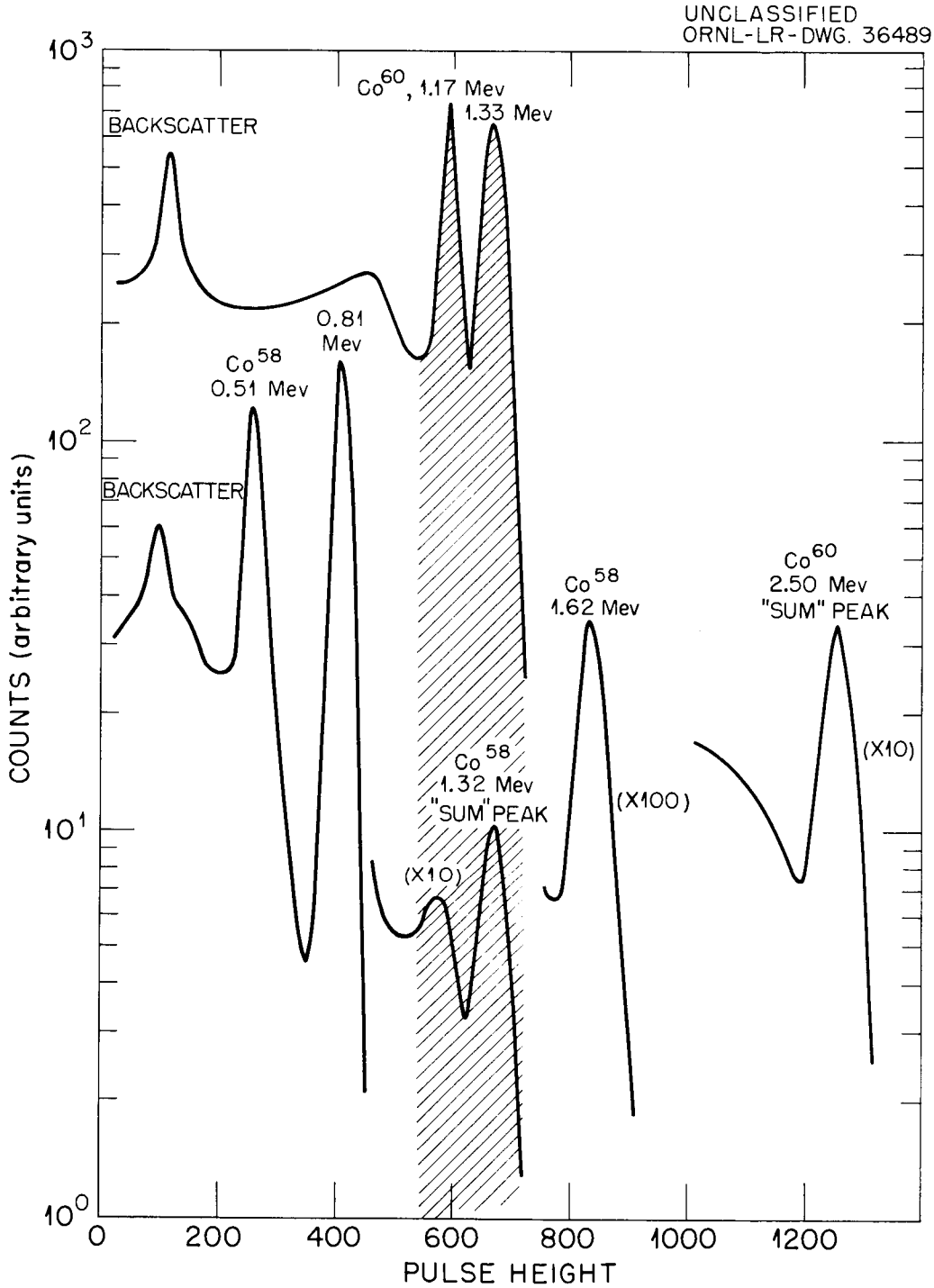

Fig. 20.--Cobalt-58 Gamma-Ray Spectrum and Cobalt-60 Gamma-Ray Spectrum Showing Regions of Interference.

Comparison

The cross sections of the (n,p) reactions for iron and nickel follow the trend expected from the Q values. The limits of quantitative measurement of iron and nickel determined by means of the (n,p) reaction as a method of activation analysis are given in Table 16.

TABLE 16

LIMITS OF QUANTITATIVE MEASUREMENT OF IRON AND NICKEL BY (n,p) REACTIONS

Element	Stable Nuclide	Relative Activation Cross Section, mb	Q, Mev	Radio-nuclide Produced*	Half Life	Limit of Quantitative Measurement, μg
Iron	Fe^{54}	3.55	- 0.344	Mn^{54}	312 d	600
	Fe^{56}	0.05	- 3.45	Mn^{56}	2.58 h	40
Nickel	Ni^{58}	5.35	+ 0.518	Co^{58}	72 d	8
	Ni^{60}	0.09	- 2.33	Co^{60}	5.3 y	20,000

* Duration of irradiation: one week or until saturation is achieved.

When the values from Table 16 for the limits of quantitative measurement for the determinations of iron and nickel by (n,p) reactions are compared with the values from Table 12 for the limits of quantitative measurement for the determinations of iron and nickel by (n,γ) reactions, it can be seen that the (n,γ) reactions provide lower limits. The (n,γ) reaction, then, would be the more practical reaction to use for these determinations.

The (n,p) reaction as a means of activation analysis for either iron or nickel has value only in very special cases. One of the cases is the determination of nickel in a sample that has been allowed to decay until all the 2.56-h nickel-65 radioactivity has disappeared. Since cobalt-58 has a half life of 72 d, it is possible to determine nickel in a sample that has been allowed to decay for several months.

The (n,p) Reactions of the Platinum-group Metals

It can be seen from Table 16 that the relative activation cross sections follow the trend predicted from a consideration of potential barrier and Q values for the reactions. Since they do, it was expected that the relative activation cross sections for the Platinum-group elements would be still lower than those of iron, cobalt, and nickel because of the increased potential barriers of these elements. For this reason the determination of the relative activation cross section for the (n,p) reactions of the Platinum-group elements was not attempted.

Limits in the Use of (n,p) Reactions

It is important to note that whereas the activation cross section of the $Ni^{58}(n,p)Co^{58}$ reaction is not sufficiently high to permit use of the reaction as a means of analysis, it is high enough that the reaction causes interference in a determination of cobalt in the presence of nickel. If cobalt is determined by neutron activation in the presence of nickel the following reactions take place:

$$Co^{59}(n,\gamma)Co^{60}$$

$$Ni^{60}(n,p)Co^{60}$$

$$Ni^{58}(n,p)Co^{58}$$

The radioactivity induced by these reactions can be calculated by Equation 19, which can be expressed as

$$A = CPW \tag{58}$$

where

$$C = \frac{fN}{M}$$

$$P = \text{the "activation factor"} = \sigma_{ac}\ \theta\left[1 - \exp(-\lambda t)\right]$$

The ratios of radioactivity resulting from these reactions are calculated as follows from the data given in Table 17.

TABLE 17

ACTIVATION DATA FOR (n,p) REACTIONS OF COBALT AND NICKEL

Stable Nuclide	Relative (n,p) Cross Section, cm^2	Natural Abundance, %	Saturation Factor*	Activation Factor
Co^{59}	36×10^{-24}	100	$\frac{0.693\ t}{5.3\ y}$	$4.8 \times 10^{-24}\ t$
Ni^{60}	9×10^{-29}	26.2	$\frac{0.693\ t}{5.3\ y}$	$3.1 \times 10^{-28}\ t$
Ni^{58}	5×10^{-27}	67.8	$\frac{0.693\ t}{0.197\ y}$	$1.2 \times 10^{-26}\ t$

* Saturation factor taken as λt for $t < 0.1\ t_{\frac{1}{2}}$.

The ratio of radioactivities due to cobalt-59 and nickel-60 are

$$\frac{A_{Co}}{A_{Ni}} = \frac{(CPW)_{Co}}{(CPW)_{Ni}} \cong 1.6 \times 10^6\ \frac{W_{Co}}{W_{Ni}}$$

where

$$C_{Co} \cong C_{Ni}$$

The ratio of radioactivities due to cobalt-59 and nickel-58 are

$$\frac{A_{Co}}{A_{Ni}} = \frac{(CPW)_{Co}}{(CPW)_{Ni}} \cong 400\ \frac{W_{Co}}{W_{Ni}}$$

for $$C_{Co} \cong C_{Ni}$$

Thus, as the amount of nickel increases relative to the amount of cobalt, the influence of the cobalt radioactivity induced from the nickel becomes appreciable. As the ratio of cobalt to nickel approaches 1 part in 10^5 parts, the determination of cobalt by neutron activation by means of the (n,γ) reaction becomes difficult because of the amount of cobalt-60 produced in the (n,p) reactions upon nickel-60.

The problem of determining the radioactivity of cobalt induced in the sample by the $Co^{59}(n,\gamma)Co^{60}$ reaction can be resolved by the use of a scintillation spectrometer, but it is necessary to use the 2.50-Mev sum peak of cobalt-60. Figure 20 shows the interference of the cobalt-58 gamma-ray spectrum with the cobalt-60 gamma-ray spectrum. Thus, it is important then in a determination of cobalt in the presence of nickel to use the sum peak of cobalt-60 for the determination of the radioactivity.

CHAPTER VIII

THE USE OF SHORT-LIVED RADIONUCLIDES IN ACTIVATION ANALYSIS

In past years the use of short-lived ($t_{\frac{1}{2}} < 30$ m) radionuclides in activation analysis has been impractical because of the difficulties encountered in measuring the induced radioactivity. The use of instruments such as beta counters generally requires that the radionuclide being measured be radiochemically pure and thus short-lived radionuclides decay away before chemical separations can be made. The advent of single-channel scintillation spectrometers offered no real solution to the measurement problem. Even though the radioactivity could be measured without chemical separation by means of a gamma-ray spectrometer the short-lived radionuclides decayed while the spectrum was being recorded in successive increments, and thus the parts of the spectrum were not in the proper proportion to each other.

Today, however, the development of gamma-ray multichannel spectrometers that can record the whole spectrum at once has made the use of short-lived radionuclides in activation analysis a practical method of analysis. Of course, the use of short-lived radionuclides depends not only on the measurement of the radioactivity but also on the time required for delivery of the irradiated sample from the source to a counter. At the Oak Ridge National Laboratory this delivery time is reduced to a minimum by measuring the radioactivity in a laboratory that is located

at the reactor in which irradiations are made. Total time required to deliver the sample from the reactor to the counter is approximately 1 min.

To determine the feasibility of using a short-lived radionuclide rather than a long-lived radionuclide for the determination of an element, the activation factor, P, (p. 83) of the short-lived radionuclide must be compared with the activation factor of the long-lived radionuclide.

Short-Lived Radionuclides of the Group VIII Elements

In the Group VIII elements there are several short-lived radionuclides that can be produced by (n,γ) reactions. These are listed in Table 18.

TABLE 18

SHORT-LIVED RADIONUCLIDES PRODUCED IN THE GROUP VIII ELEMENTS BY (n,γ) REACTIONS

Stable Nuclide	Natural Abundance, %	Activation Cross Section, barns	Radionuclide Produced	Half Life
Co^{59}	100	16	Co^{60m}	10.5 m
Rh^{103}	100	12	Rh^{104m}	4.4 m
		140	Rh^{104}	42 s
Pd^{108}	26.7	0.07	Pd^{109m}	4.8 m
Os^{189}	16.1	--	Os^{190m}	10 m
Ir^{191}	38.5	260	Ir^{192m}	1.45 m
Pt^{198}	7.2	4.0	Pt^{199}	31 m

Cobalt

Cobalt is normally determined by the measurement of the 5.3-y cobalt-60 radioactivity induced in an irradiation of cobalt. The activation cross section for the $Co^{59}(n,\gamma)Co^{60}$ reaction is 36 barns, and the activation cross section of the $Co^{59}(n,\gamma)Co^{60m}$ reaction is 16 barns.[52] However, the increase in the fraction of radioactivity induced in a given period of time more than makes up for the decrease in the cross section. The saturation factor (given approximately by λt) to produce cobalt-60 in a 1-week irradiation is 2.6×10^{-3}, whereas the saturation factor to produce cobalt-60m in a 10.5-min irradiation is 0.5. In this case, then, there is not only the advantage of short irradiation periods but also an increase in sensitivity for the determination of cobalt.

The gamma-ray spectrum of cobalt-60m is shown in Figure 21.

Rhodium

The stable nuclide, rhodium-103, has a natural abundance of 100%. There are two radionuclides formed by an (n,γ) reaction upon this nuclide, namely, rhodium-104m ($t_{\frac{1}{2}}$ = 4.4 m) and rhodium-104 ($t_{\frac{1}{2}}$ = 42 s). Meinke[53] has recently used the 42-s radionuclide for the determination of rhodium in ruthenium metal; the duration of the irradiation was 5 sec at a thermal neutron flux of 1.4×10^{11} neutrons/cm^2/sec.

In the investigation described herein, the gamma-ray spectrum of rhodium-104m ($t_{\frac{1}{2}}$ = 4.4 m) was obtained and is given in Figure 22. It can be seen from the decay scheme, also given in Figure 22, that there is no provision for the 0.097-Mev gamma-ray. An attempt was made to

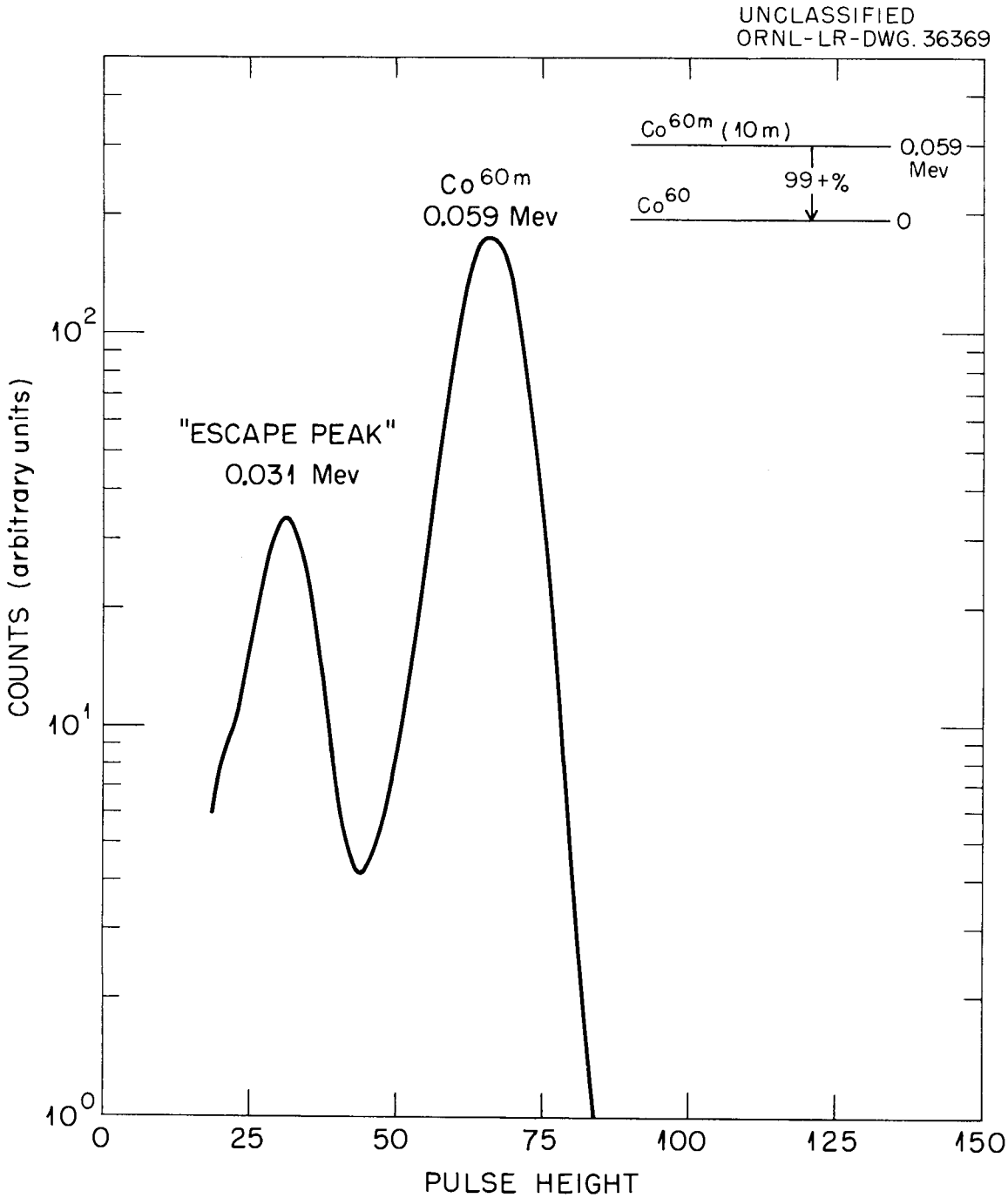

Fig. 21.--Gamma-Ray Spectrum of Cobalt-60m

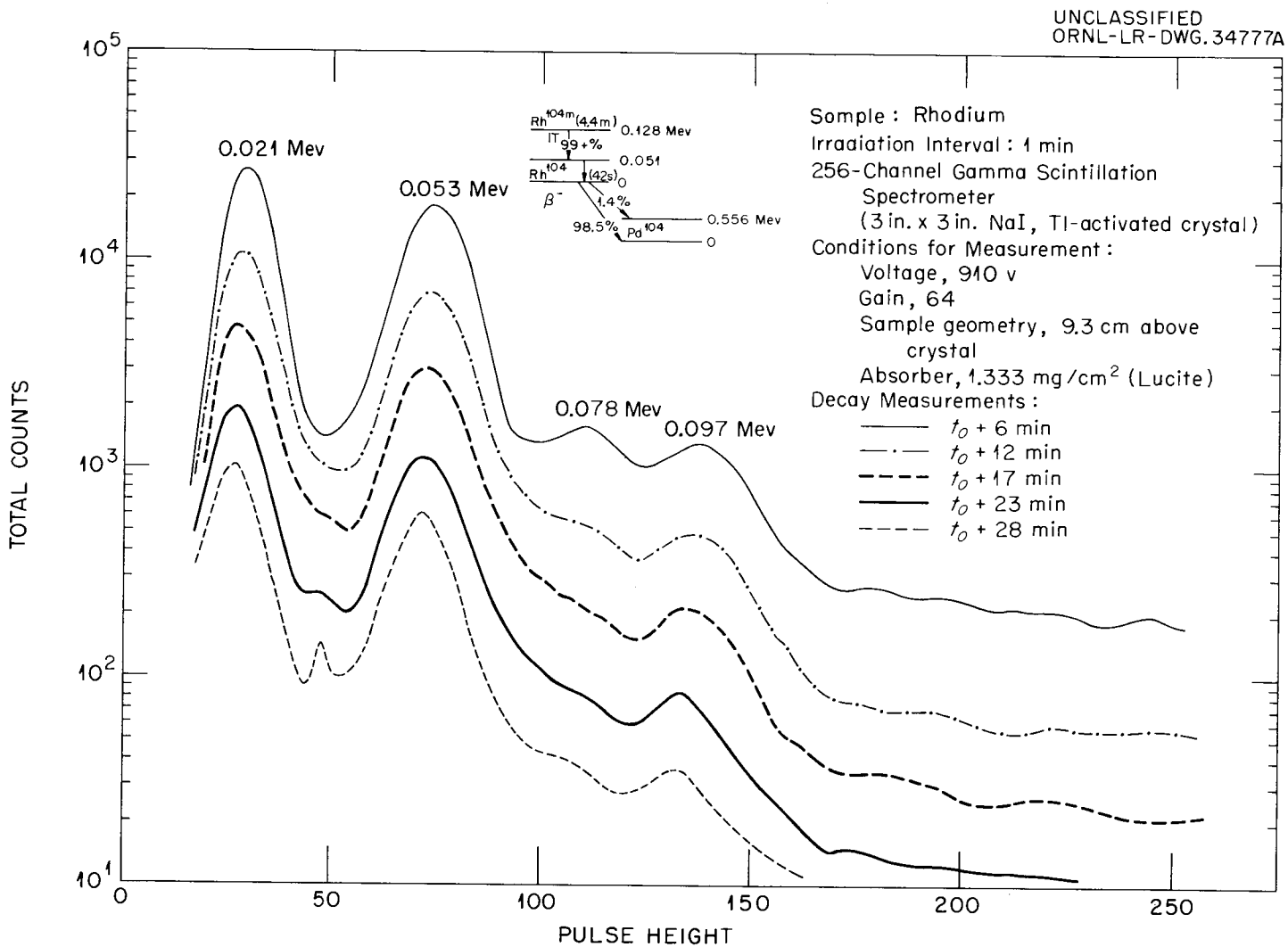

Fig. 22.--Gamma-Ray Spectra of Rhodium-104m Taken at Various Times after Irradiation

determine whether this gamma ray was a heretofore unknown gamma ray of rhodium. In order to do this a rhodium sample was irradiated, and a decay study was made. The results of this study are also shown in Figure 22. The 0.097-Mev gamma ray decays at the same rate as the full-energy peaks on the spectrum.

It is possible that the 0.097-Mev gamma ray could result from the summing in the scintillator of some other gamma rays in the rhodium spectrum. If this were true, the spectrum would change shape as the distance of the sample from the scintillator changed. Thus, the gamma-ray spectrum of rhodium-104 was taken at different geometries, and the spectra obtained are given in Figure 23. It can be seen that no change in the spectrum with change in distance of the sample from the scintillator is evident.

In order to determine whether the 0.097-Mev gamma ray might be due to some unknown impurity in the sample, the spectra described above (Figs. 22 and 23) were taken on two irradiated samples of rhodium that came from different sources. If this gamma ray were resulted from the activation of an impurity, the amount of the impurity in the two rhodium samples could be expected to be different, and thus the shape of the spectra would be different. However, the spectra were the same, and thus it is concluded that the 0.097-Mev full-energy peak is truly a gamma ray of either rhodium-104m ($t_{\frac{1}{2}}$ = 4.4 m) or rhodium-104 ($t_{\frac{1}{2}}$ = 42 s). It could be that of either of these nuclides since rhodium-104m decays to rhodium-104.

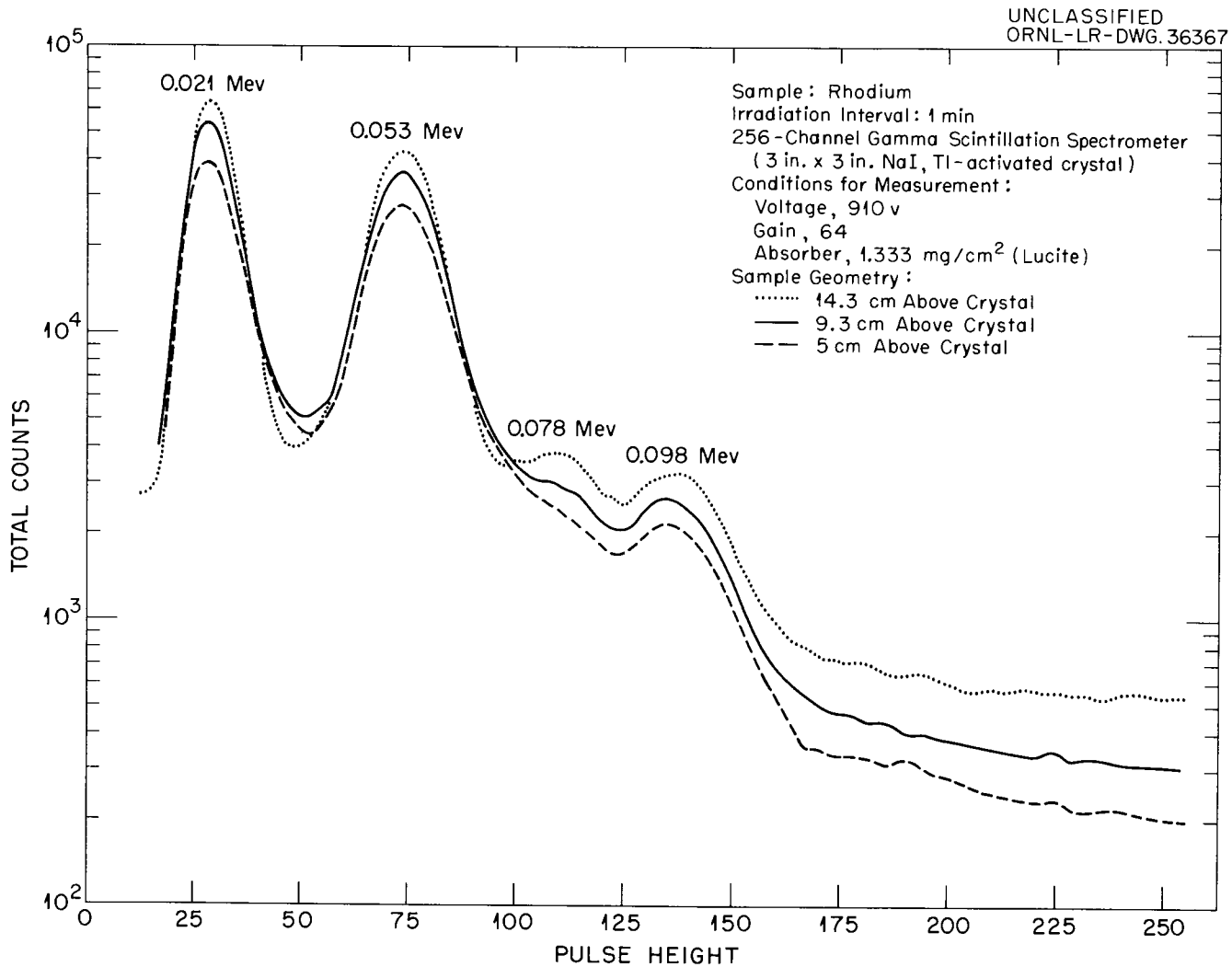

Fig. 23.--Gamma-Ray Spectra of Rhodium-104m Taken at Various Heights Above the Detector

Palladium

An irradiation of palladium metal was made, and 2 min after the irradiation a gamma-ray spectrum of palladium-109m was obtained by means of a 256-channel analyzer. From this gamma-ray spectrum it was determined that there was a short-lived radionuclide which produces a full-energy peak that could be used as a means to determine palladium. The spectrum obtained is given in Figure 24. Another spectrum was taken at a later time of the same sample; this spectrum (Fig. 24) shows that palladium-109m ($t_{\frac{1}{2}}$ = 4.8 m) decayed away leaving only palladium-109 ($t_{\frac{1}{2}}$ = 13.6 h).

Osmium

A sample of osmium was irradiated, and a gamma-ray spectrum was taken 3 min after the irradiation with the intent of finding an osmium-190m ($t_{\frac{1}{2}}$ = 10 m) full-energy peak. In a decay study of the gamma-ray spectrum obtained, such a peak was not found. This radionuclide has been shown to be the daughter of iridium-190 [54] There has been no previous report of this radionuclide being formed by the (n,γ) on osmium-189. Thus it is concluded that this radionuclide cannot be used as a means to determine osmium.

Iridium

The element iridium is generally found as an impurity in any sample of the Platinum-group metals. Even in an activation analysis procedure for the determination of an element in a sample which may contain iridium as an impurity, the procedure is complicated; the stable nuclides of iridium which become activated have very high cross sections and the

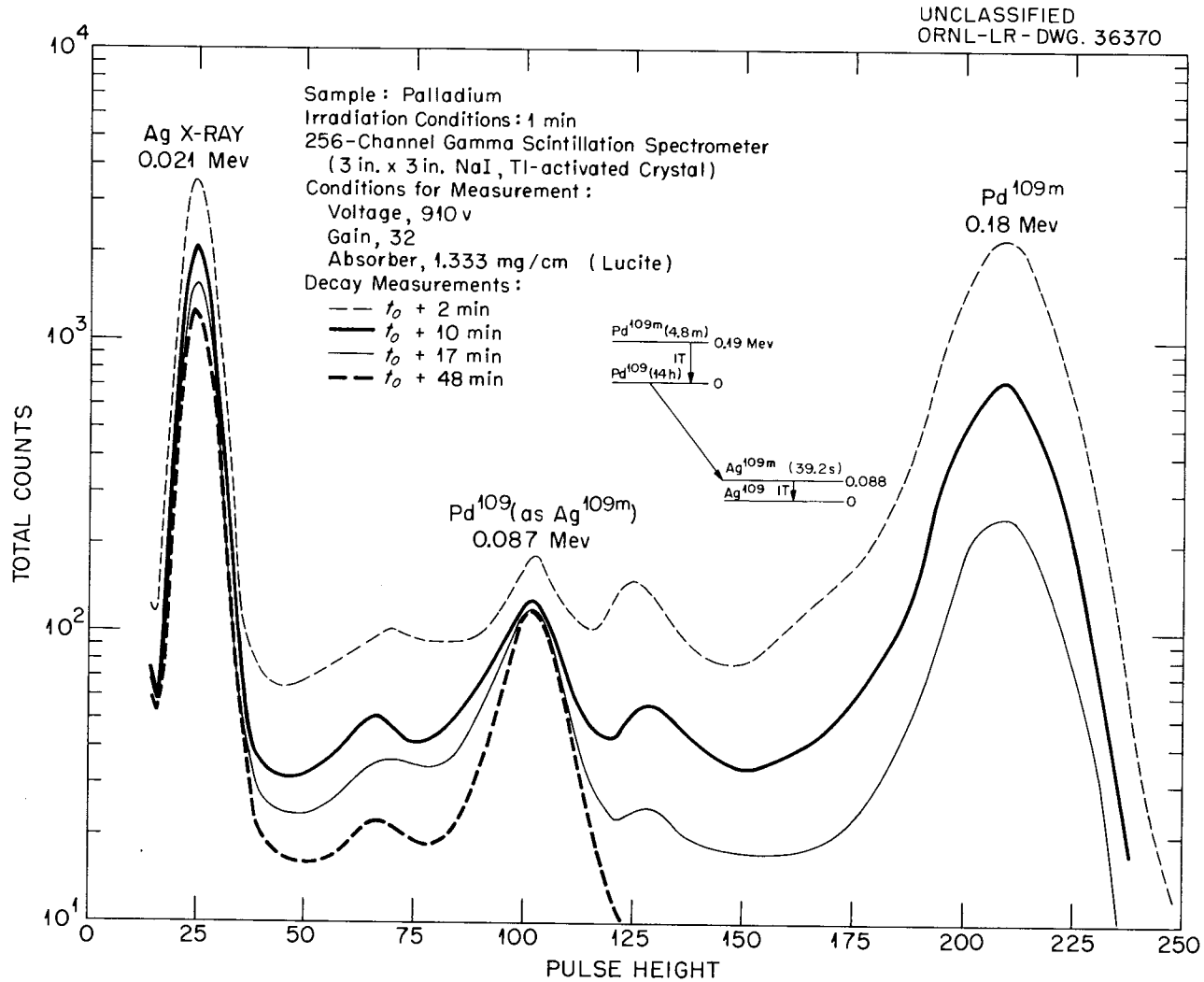

Fig. 24.--Gamma-Ray Spectrum of Palladium-109

radionuclides of iridium emit different gamma rays up to a maximum energy of approximately 1 Mev. The activation cross sections are tabulated in Table 1, and a gamma-ray spectrum of iridium-192 is shown in Figure 6. Thus, the interference of radionuclides of iridium in the activation analysis for other elements being determined by means of short-lived radionuclides was investigated.

Iridium as shown in Table 18 has only one short-lived radionuclide (iridium-192m, $t_{\frac{1}{2}}$ = 1.45 m). A sample of iridium metal was irradiated for 1 min and a gamma-ray spectrum taken 1 min after the sample was removed from the reactor. It was found that iridium-192m does not produce gamma-ray full-energy peaks that interfere with the determination of the other Platinum-group metals. Thus the determination of the Platinum-group metals by short-lived activation analysis would not be complicated by the presence of iridium impurities in the sample.

Platinum

Even though the radionuclide, platinum-199, produced by an (n,γ) reaction on natural platinum has a 31-m half life, it has been included in this section because of its relevance to the use of short-lived radionuclides.

If a radionuclide has a 10-m half life, a 1-min irradiation is generally sufficient. In the case of platinum, a 1-min irradiation produces sufficient platinum-199 radioactivity to influence the determinations of the other Platinum-group metals in which platinum is an impurity. Figure 25 shows the gamma-ray spectrum of platinum, and Figure 14 (p. 40) shows the composite gamma-ray spectrum of a rhodium-platinum mixture;

these spectra indicate the effect of platinum radionuclides on the rhodium spectrum for a 1-min period of irradiation at a thermal neutron flux of 5×10^{11} neutrons/cm^2/sec.

Comparisons of Activation Factors

Comparisons of the activation factors of those Group VIII elements which have both long-lived and short-lived radionuclides that can be used as a means of analysis are given in Table 19.

TABLE 19

COMPARISONS OF ACTIVATION FACTORS

Element	Radionuclide	Half Life	Activation Factor, P, barns	Duration of Irradiation
Cobalt	Co^{60m}	10.5 m	16	105 min*
	Co^{60}	5.3 y	0.009	1 week
Palladium	Pd^{109m}	4.8 m	0.018	48 min*
	Pd^{109}	13.6 h	2.9	136 hr*
Platinum	Pt^{199}	31 m	0.28	3.0 min*
	Pt^{197}	18 h	0.20	1 week

* 99.9% of saturation.

It can be seen from Table 19 that cobalt and platinum both have higher activation factors for the short-lived radionuclides than for the long-lived radionuclides. This indicates that the ratio of radioactivity to weight of element represented by that amount of radioactivity is greater for the short-lived radionuclides than for the long-lived radionuclides. However, the activation factor for short-lived palladium-109m

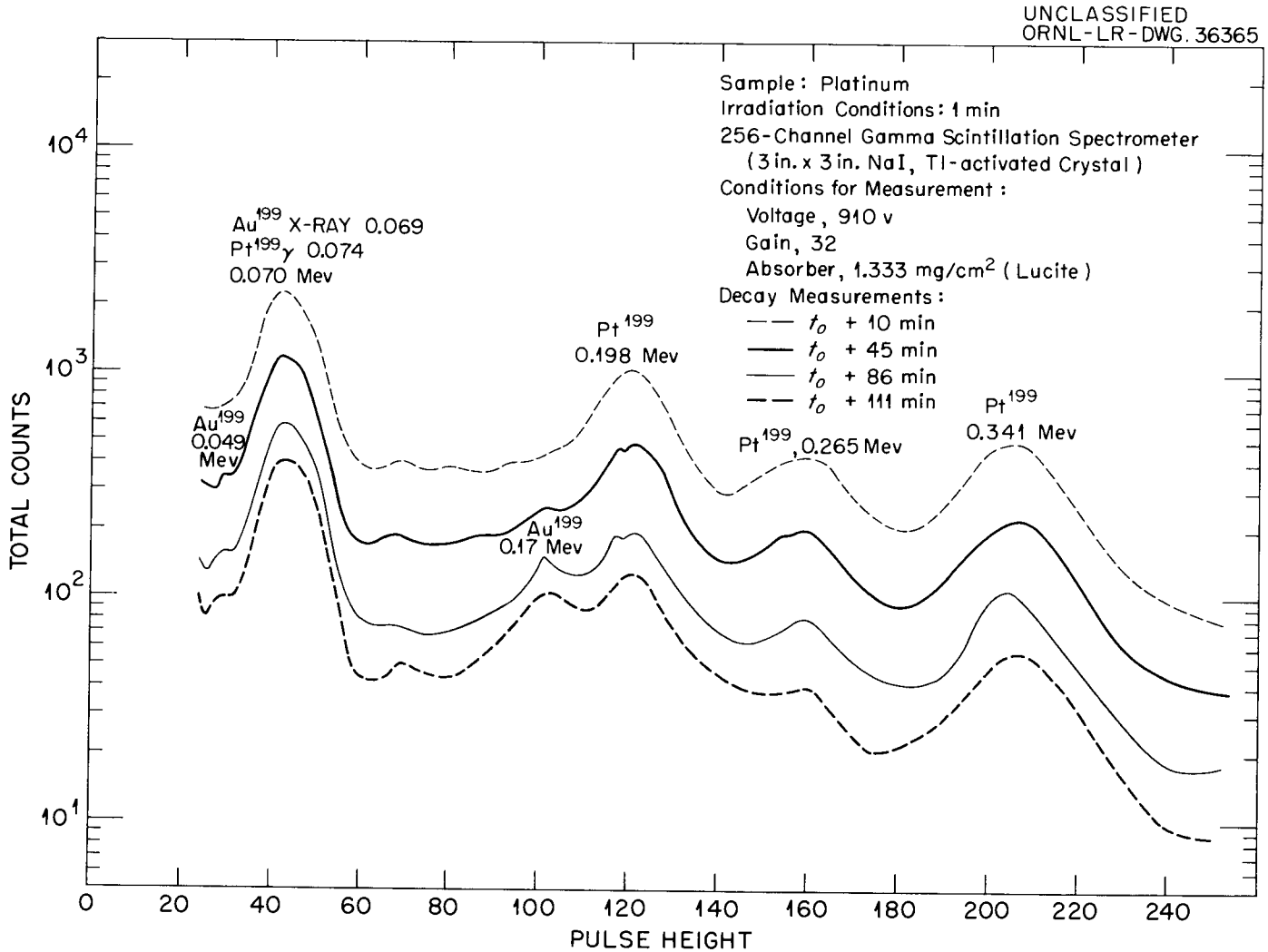

Fig. 25.--Gamma-Ray Spectrum of Platinum-199

is less than that of palladium-109 indicating that the ratio of radioactivity to weight of element represented by the amount of radioactivity is smaller for the short-lived radionuclide than for the long-lived radionuclide.

Conclusions

The conclusions that are reached from this investigation of short-lived radionuclides of the Group VIII elements are that cobalt-60m, rhodium-104m, palladium-109m, and platinum-199 can all be used to good advantage. In the case of palladium-109m the limit of quantitative measurement will be higher by use of the short-lived radionuclide than by use of the long-lived radionuclide. However, the short duration of irradiation provides some advantage in the length of time required to perform a determination of palladium.

This investigation has also shown that osmium does not have a short-lived radionuclide that can be used as a means of analysis. It has been shown that the short-lived radionuclide of iridium does not produce radioactive interferences in the determination by activation analysis of the other Platinum-group metals.

A 0.097-Mev gamma ray has been found in the gamma-ray spectrum of rhodium-104. This gamma ray has not previously been accounted for in the decay scheme of rhodium-104.

CHAPTER IX

SUMMARY

Neutron activation as a method of analysis for the determination of any group of elements can be described only in general terms. Its greatest advantage over other methods of analysis is that it is a specific assay method for each individual element of a group. It has been the purpose of the work described herein to investigate the general application of this method of analysis to the determination of the Group VIII elements and its specific application to the determination of individual elements within this Group.

In this work, the mathematical description of the neutron activation of an element being determined is given. From the equations derived, the direct proportionality between the weight of the element and the radioactivity induced in this element is shown.

Since the measurement of radioactivity is the most important measurement that is made in any activation analysis, the measurement of the radioactivity by beta counting, gross gamma counting, and differential gamma counting were considered. Methods of determining the radioactivity are described for both an absolute and a comparator-sample method. For each of these methods, the basic relationship between the radioactivity, measured in counts per unit time, and the weight of element are shown. In the application of differential gamma counting for

the determination of radioactivity from a gamma-ray spectrum, equations describing Gaussian curves have been applied. A method of calculating disintegration rates of radionuclides from standard equations has also been presented.

For certain radionuclides produced by (n,γ) reactions on the Group VIII elements, a statistical comparison of beta, gross gamma, and differential gamma counting based on experimental data obtained was made. When the counting methods were evaluated for the determination of iron-59, cobalt-60 and iridium-192, it was found that the gross gamma counting method gave the smallest relative standard error for each of these nuclides. However, it was found that nickel-65 can be determined with the least relative standard error by gross gamma counting if the gross gamma counting rate is above 546 counts/min and by beta counting if the gross gamma counting rate is below this. The methods of counting radionuclides from elements other than iron, cobalt, nickel, and iridium were not investigated because more than one radionuclide is produced in the irradiation of each of these elements. If more than one radionuclide is produced, the method of counting that is used will depend upon the relative amounts of each of the radionuclides. These amounts vary with time and thus the method of counting varies with time.

Also, from a study of background radioactivity, a method of determining the net counting rate of the sample has been established so that a preset error in the net counting rate may be obtained. The basis of the method is the calculation of a proportionality constant that relates the net counting rate of the sample to the error in the background

measurement. A background count must be taken with every sample count; therefore, as the net counting rate of the sample approaches the background counting rate, the error in the background count becomes very significant. From these experiments, the limits of quantitative measurement for the determinations of the Group VIII elements by means of (n,γ) reactions were calculated. The limits were based upon a 640-sec measurement of the gross gamma activity and a 5% relative standard error in the net counting rate of the sample at a background counting rate of 6 counts/sec. For the determination of each of the Group VIII elements, the limits of measurement was found to be 10 μg or less.

Two special methods of analysis by neutron activation were applied to the Group VIII elements. The first of these was the use of the (n,p) nuclear reaction in place of the (n,γ) nuclear reaction to induce radioactivity into an element. Measurements of the activation cross section for the (n,p) reactions of iron and nickel were made. These cross sections were calculated from the data taken in experiments in which a thermal neutron flux was used as a measure of the effective neutron flux. Relative cross sections so calculated are valid only for the irradiation facility used which in this case was Hole No. 22 of the ORNL Graphite Reactor. The cross sections of the $Fe^{54}(n,p)Mn^{54}$, $Ni^{58}(n,p)Co^{58}$, and $Ni^{60}(n,p)Co^{60}$ reactions were calculated to be 3.55, 5.35, and 0.09 mb, respectively. The $Fe^{56}(n,p)Mn^{56}$ cross section calculated in this same manner has previously been reported to be 0.5 mb.[55] These experimentally measured cross sections agree with the trend expected when reaction Q values are considered. The larger cross sections are associated

with the reactions which have the more positive reaction Q values. Considerations of reaction Q values and potential barrier values indicate that the (n,p) reactions of the other Group VIII elements have smaller cross sections than those measured for the (n,p) reactions on iron and nickel. Thus, the (n,p) cross sections of these elements were not measured.

It was shown that the cobalt-58 produced by the (n,p) reaction upon nickel-58 may seriously interfere in an activation analysis determination of cobalt in the presence of nickel unless the 2.50-Mev sum peak of cobalt-60 is used to measure the induced radioactivity. Even when this is done, cobalt cannot be determined by means of the (n,γ) reaction if the ratio of cobalt to nickel is less than 1×10^{-5} because of the cobalt-60 produced by the (n,p) reaction upon nickel-60.

The second special method of analysis by neutron activation investigated was the use of short-lived radionuclides as a means of determination of the Group VIII elements. The gamma-ray spectra of cobalt, rhodium, palladium, and platinum were obtained. It was shown that specific full-energy peaks in each of these spectra except in that of palladium could be used as a means of analysis with no decrease in the sensitivity from that obtained through the use of the long-lived radionuclides. There is a loss in sensitivity in the use of the full-energy peak of the short-lived radionuclide rather than that of the long-lived radionuclide of palladium.

No short-lived radioactivity corresponding to osmium-190m ($t_{\frac{1}{2}}$ = 10m) was found in a gamma-ray spectrum of irradiated osmium. It was also

determined in this investigation of short-lived radionuclides that the gamma-ray spectrum of iridium-192m ($t_{\frac{1}{2}}$ = 1.45m) does not interfere with the gamma-ray spectrum of the other short-lived radionuclides of the Group VIII elements. Thus, the presence of iridium as an impurity in a sample would not necessitate a chemical separation after a short irradiation (~ 1 min) as it does after a long irradiation (hours).

Although several techniques for the determination of the Group VIII elements by the method of activation analysis have been described herein, there are other techniques, many of them more specialized, which fit specific cases. Examples of these are the gamma-gamma coincidence techniques for the determination of cobalt in iron which has been reported by Salmon,[56] and the method for the quantitative determination of iridium in platinum presented by Airoldi and Germagnoli.[57] The methods described herein and methods such as those mentioned above are applicable to routine analysis of the Group VIII elements.

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