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STUDY IN ACTIVATION ANALYSIS

W. A. Brooksbank, Jr.

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Analytical Chemistry Division

STUDY IN ACTIVATION ANALYSIS

W. A. Brooksbank, Jr.

(Thesis - U.T. 1956
Masters)

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CHAPTER I

ACTIVATION ANALYSIS

A. Historical

Activation analysis may be defined as an analytical technique based upon the induction of radioactivity in stable isotopes of the element to be determined. An analogy may be drawn between activation analysis and a conventional colorimetric analysis. In the case of colorimetry, the ion to be determined is made to react with a chromogenic compound to yield a product whose color identifies the ion; and, within limits, is a measure of the concentration of that ion.

The reagent in activation analysis is the bombarding nuclear particle, the target material is the other reactant, and the radioisotope corresponds to the colored end product. The radioactive properties identify the element, and total radioactivity is a measure of the amount.

Activation analysis is a new technique reported for the first time in 1936 by Hevesy and Levi (1) for the determination of dysprosium in impure yttrium by means of thermal neutron irradiation. Charged particle irradiation was applied to activation analysis by Seaborg and Livingood in 1938 (2). They showed the presence of gallium in the parts per million range in very pure iron. Boyd (3), Leddicotte and Reynolds (4) give excellent review articles on activation analysis. The two latter authors describe the semi-routine method as it was systematized at Oak Ridge National Laboratory about 1950.

B. Principles

In practice, the sample to be analyzed is placed in a homogeneous flux of neutrons for a period long enough to induce a measurable amount of radioactivity. The activity produced may be calculated (4):

$$A = N f \sigma S \qquad (1)$$

A is the induced activity in disintegrations per second, f is the neutron flux in neutrons per sq. cm. per second, σ is the activation cross section, or a measure of the probability of the reaction between a neutron and an atom of the element (in "barns" or 10^{-24} sq. cm.), and S is the saturation factor. The saturation factor is the ratio of the activity produced at a time, t, compared to the activity produced at infinite time. It may be calculated from Equation 2 (5).

$$S = 1 - e^{-\lambda t} \qquad (2)$$

S is the saturation factor, λ is 0.693 divided by the half life, and t is the time of the irradiation. The half life and t must be in the same units of time (5). If we express the number of atoms, N, by the number of moles, $N = \frac{W \text{ (wt. in grams)}}{M \text{ (atomic wt.)}} \times$ Avogadro's Number (6.025×10^{23}), and rearrange Equation 1, we obtain Equation 3.

$$W = \frac{AM}{6.025 \times 10^{23} \times f \times \sigma \times S} \qquad (3)$$

It is assumed that the rate of formation is constant during bombardment, and that the number of target atoms remain essentially constant.

Activation analysis may be carried out in one of two ways: by the absolute method or by the comparator method. In the first, or absolute method, it is necessary that the flux be measured during the bombardment, that the cross section and half life be known accurately, and that the activity be measured absolutely. The flux may be obtained to within 10% readily (6). The literature lists the cross sections (7), but few are known to within ± 10%. The half-life tabulations show some discrepancies (8). It is extremely difficult to measure small amounts of activity absolutely, and the error in these measurements can be very large (9).

The comparator method of analysis is a method where a known amount of the element to be determined is irradiated simultaneously with the unknown. Since from Equation 3, the term $\frac{M}{6.025 \times 10^{23} \times f \times \sigma \times S}$ is the same for the unknown and for the comparator, they can be cancelled. A simplified equation results (2):

$$\frac{W \text{ in unknown}}{W \text{ in comparator}} = \frac{A \text{ in unknown}}{A \text{ in comparator}} \qquad (4)$$

In practice, the equation is complicated by yield corrections, decay corrections, sample weights and other factors which will be described later.

We shall be concerned with only neutron activation in the balance of this paper.

Certain samples to be analyzed for specific elements show only the activity due to these specific elements, and little activity due to the sample material itself (10). Such a situation will be discussed in the analyses of National Bureau of Standards' aluminum samples, numbers 85a, 86c and 87 for copper and manganese. In most analyses

chemical separations are necessary. In these, 10 to 20 mg. of an inactive isotope of the desired element is added after irradiation, and a compound of known composition of that element isolated and counted. The comparator is processed in the same way as the sample and the activity is measured under identical conditions. Carrier chemistry has the additional purpose, since the amounts added and recovered are known, of serving as a means of correcting for loss during the analysis.

C. Sensitivity

The range of the sensitivity of neutron activation analysis is from 10^{-11} grams to some elements which cannot be detected at all. Leddicotte and Reynolds (4) list the sensitivity of activation of elements from atomic number 1 through 83 which have half lives greater than ten minutes. They range from 10 to 100 γ of niobium to 0.0003 γ for europium and dysprosium for a flux of 4×10^{11} neutrons per sq. cm. per second and either at saturation or thirty days irradiation.

The factors which influence the sensitivity of neutron activation may be roughly classed into those factors which are fixed for any one element, and those which may be varied by the analyst. The activation cross section is the most important of the non-variable factors. The cross section of any element for a particular energy spectrum of neutrons, for example, pile neutrons, is fixed. The unit of cross section is the "barn," 10^{-24} sq. cm. of area. It ranges from 2.4×10^{-27} sq. cm. for iron to 7.38×10^{-22} sq. cm. for europium (4). The sensitivity for

detection is therefore proportional to the cross section; those with large cross sections will have greater sensitivity.

The flux of neutrons used for this work, and for most of the reported work from the Oak Ridge National Laboratory is 5×10^{11} neutrons per sq. cm. per second from the graphite reactor. The range of flux positions within this reactor is from 2×10^{8} neutrons per sq. cm. per second in the animal tunnels to 8×10^{11} neutrons per sq. cm. per second in Hole 10 and Hole 22. Higher fluxes are available in other reactors. The flux for a bombardment may be controlled by choosing the proper location in the reactor; the higher the flux, the greater the sensitivity.

The saturation factor may vary from 0 to 1.0. The maximum sensitivity occurs when it is 1.0. It is not necessary in many cases, nor practical in most, to irradiate to saturation. For example, if a radioisotope has a half life of thirty days, then in a thirty-day irradiation, one would build up 50% of maximum activity. In sixty days, it would be up to 75% of maximum. To reach maximum activity, it would be necessary to irradiate for three hundred days. Thus, for the first one-half of the activity it takes thirty days, for the second half, it takes two hundred and seventy days.

It is feasible on elements having short half lives; minutes, hours or even a few days, to reach saturation in a reasonable time.

Even though the time necessary to reach saturation is a constant depending on the half life of the radioisotope, the optimum irradiation time is chosen by the analyst.

As the sample weight increases then so does the sensitivity, as one would predict from Equation 3.

The activity, A, is constant for a given weight of element at a saturation bombardment. It is, however, expressed in disintegrations per second. No routine counting method is 100 per cent efficient; that is, it doesn't detect every one of the disintegrations from a source. If the emitted radiation is soft x rays, or very weak beta particles the actual efficiency may be only 1% or less. The more efficiently the separated fraction is counted, the greater the sensitivity according to Equation 4.

The accuracy of the activation method has been quoted as ±10% (4). It will be one of the purposes of this paper to evaluate this.

D. Errors in Activation Analysis

Activation analysis is unusually free of the conventional contamination errors common to most methods of trace element analysis (3,4). The sample is not chemically treated before irradiation, so that, if reasonable care is taken in preparing the sample for bombardment, this error is eliminated. The errors associated with activation analysis may be classed as either radiochemical or irradiation errors (11).

During the radiochemical separation, it is essential that the radioisotope and the carrier both exist in the same valence and ionic species at least once before the analysis is undertaken. This must be done in order to mix uniformly the active and inactive species. The process is called "exchange" (12). If exchange is not complete, the

ratio of active to inactive atoms will not be the same in the separated fraction as at the beginning of the analysis.

The carrier solution should not be contaminated with any radioactivity for obvious reasons.

A major source of radiochemical error is that of the activity measurement. If the activity measured is beta, then the source of error might be: self absorption, scattering, geometry, background fluctuations and instrumental errors (11). In the comparator method, if the standard samples are mounted identically with the sample, have close to the same yield of carrier spread over the same area and are counted consecutively, all errors but the instrumental errors cancel. If the beta activity is not energetic, like that of sulfur-35 or calcium-45, then self-absorption corrections are essential for valid results (12). Decay corrections are readily made in simple situations from the knowledge of the half life of the separated radioisotope (12). Instrumental errors may be monitored by using a long half-life source as a standard to measure the counting reproducibility.

Radiochemical purity is essential. The chemical separation must be extremely good; if not, a little extraneous activity might contaminate the separated fraction. The trend at Oak Ridge National Laboratory is not only to develop chemical methods, but to develop special methods of counting which discriminate against probable contaminants (13). The use of the well-type scintillation counter with special absorbers (14), the use of the gamma-ray scintillation spectrometer (15), and the discriminatory counter (16) are examples. The emphasis is now to develop

counting methods specifically designed for a given situation. Beta counting is used very infrequently. The only remaining analyses which are completed by beta counting are phosphorus-32, sulfur-35, calcium-45, silicon-31 and nickel-65. Whenever beta measurements must be made, it is necessary to verify the energy of the radiation by means of absorption curves and/or the half life, or by plotting the counting rate as a function of time (14). In this way, the presence of a particular isotope may be verified.

The counting methods and the errors associated with each will be discussed in some detail later.

The second type of error is that which occurs during the irradiation. If the neutron flux is not homogeneous over the sample container, the portions of the sample which received the lowest flux will be activated the least (11). This error is small unless a high-absorption cross section material, such as cadmium or boron is loaded into adjacent positions in the reactor. The error might be significant if the irradiation is made in a peripheral position next to the reflector where most neutrons would bombard the side of the sample nearest the center of the reactor.

The neutron flux would be attenuated as it traversed the sample if the sample or its container contained appreciable amounts of materials with high absorption cross sections (4,11). This would result in a lesser activation in the interior of the sample.

The same errors apply to the comparator standard, but the errors of neutron attenuation are magnified since the comparator will usually have a larger cross section than the sample. As a result of this attenuation

error, or "self shielding," specific activity will be low. Since the specific activity appears in the denominator of Equation 4, the results would be high. The error can be eliminated by diluting the comparators with low absorption cross-section materials, such as magnesium oxide, before irradiation or by irradiating a dilute solution of the comparator. Both methods reduce the effective cross section.

Optimum conditions for activation analysis are: 1) The sample material should have a low absorption cross section; 2) The sample material should have a low activation cross section or short half life; 3) The samples should be arranged concentrically around the comparator; 4) A comparator of high cross section should be diluted prior to irradiation; 5) Exchange must be complete when radiochemical separations are employed; 6) The counting method should be independent of the physical weight or shape of the separated mounts; 7) The counting method should differentiate between the radioactivity of interest and of contaminants; 8) The counting method should be efficient.

E. Statement of Problem

The method of activation analysis is a new analytical technique. It has been widely used within the Atomic Energy Commission to determine trace elements in a variety of materials. Since 1951 (4), this service has been available to any interested party. Some work has been performed by the Activation Analyses Group of the Oak Ridge National Laboratory on the relative precision and accuracy of this method as compared with

conventional chemical methods. Applied research has been inadequate because of the many pressing Atomic Energy Commission problems and the unavailability of known standards for many elements in the part per million range. This investigation will report studies of the precision and, if possible, the accuracy of activation analysis for the determination of copper, manganese, nickel, zinc, iron and titanium in National Bureau of Standards aluminum alloys. An attempt will be made to detect and to determine trace concentrations of other elements which may be present in the aluminum alloys although not detected by chemical methods.

CHAPTER II

NUCLIDES AND APPARATUS

A. Sample Preparation and Irradiations

All of the irradiations for this study were made in the Oak Ridge National Laboratory Graphite Reactor.

The reactor is a graphite cube, 24 feet on edge. The whole cube is surrounded by a 7-foot thick concrete shield. The sample-irradiation facilities used were Hole 22 and the graphite stringers.

Hole 22 is a pneumatic tube which enters the reactor from the side, perpendicular to the fuel channels. Samples are loaded into micarta containers, called "rabbits," and forced into the center of the reactor by compressed gas. This facility is used for short irradiations lasting from several seconds to sixty-two hours. The thermal neutron flux at the "in-pile" end of the tube is approximately 6×10^{11} neutrons per sq. cm. per second. The short half-life nuclides required by this study were produced here. These included copper, manganese, nickel, and zinc. At right angles to the fuel channels are removable graphite blocks. Holes enter from the top of these blocks to receive sealed aluminum containers called "stringer cans." This facility was used for irradiations of one week or multiples of one week, the time required for iron, cobalt, zirconium, antimony, silver and titanium.

To obtain the most homogeneous flux distribution, all samples were irradiated in "high flux" positions; that is, at the center of

the reactor. Neutron bombardment of the sample occurred from all directions, not unilaterally as in the peripheral positions.

The comparator materials were wrapped in 0.005-inch thickness 2S aluminum foil or placed in small quartz ampoules 5 mm. i.d. by 2 cm. long. The samples were wrapped in 3 x 5 cm. pieces of aluminum foil. The sample packets measured about 1 x 1.5 cm. These were packed into the irradiation containers along with the comparator and in such a manner that the comparator was always surrounded by sample packets. This was done so that any neutron flux attenuation caused by the samples would be reflected as a modified specific activity of the comparator. The chemical and physical forms of the comparators were chosen to have a low absorption cross section. For example, the molar cross section of the silver comparator was effectively lowered by irradiating silver nitrate rather than silver metal. The comparators were weighed and packed in duplicate. The weights were varied in order to detect any neutron flux attenuation in the comparator. If the attenuation error is significant, the larger comparator would have the lower specific activity.

Irradiation conditions are summarized in Table I.

B. Nuclear Properties of Radioisotopes

The nuclear properties of the radioisotopes induced in the stable isotopes of the elements being investigated are in Table II. The nuclear reaction in all cases, except titanium, is the (n,γ) capture reaction with thermal neutrons. In this reaction, a slow neutron is captured

TABLE I

SUMMARY OF IRRADIATION CONDITIONS FOR ACTIVATION ANALYSIS

Element	Facility	Length of Irradiation	Comparator
Cu	Hole 22	0.5 hour	Cu wire
Mn	Hole 22	0.5 hour	Mn powder
Ni	Hole 22	2.5 hours	Ni chips
Fe	Stringer - high flux	1 week	Fe wire
Zn	Hole 22	62 hours	Zn granules
Ti[a]	Stringer - high flux	2 weeks	TiO_2 powder
Ag	Stringer - high flux	1 week	$AgNO_3$ crystals
Co	Stringer - high flux	1 week	Co-Al alloy (0.038% Co)
Zr	Stringer - high flux	1 week	$ZrOCl_2$ crystals
Sb	Stringer - high flux	1 week	Sb powder

[a] The stringer can used was lined with 0.040 inche of pure cadmium metal to filter out thermal neutrons.

TABLE II

NUCLEAR PROPERTIES OF INDUCED RADIOISOTOPES (7,8)

Analysis for	Stable Isotope %	Radioisotope Formed[a]	Activation Cross Section (barns)	Half Life[b]	β^- (Mev)	γ (Mev)
Cu	Cu^{63}-69.1	Cu^{64}	3.9	12.80h	0.571 β^+-0.657	1.34
Mn	Mn^{55}-100	Mn^{56}	13.4	2.58h	0.65, 1.04, 2.81	0.822, 1.77, 2.06
Ni	Ni^{64}-1.2	Ni^{65}	2.6	2.56h	0.60, 1.01, 2.10	0.37, 1.12, 1.49
Fe	Fe^{58}-0.31	Fe^{59}	0.9	45.1d	0.257, 0.460	1.097, 1.295
Zn	Zn^{68}-18.6 Zn^{64}-48.9	Zn^{69m} Zn^{65}	0.10 0.50	13.8h 250d	--- 0.325	0.437 1.12
Ti	Ti^{46}-7.95 Ti^{48}-73.5	Sc^{46} Sc^{48}	(c)	85d 44h	0.36 0.64	0.89, 1.12 0.98, 1.0, 1.33
Ag	Ag^{109}-48.7	Ag^{110m}-Ag^{110}	2.8	270d	complex decay scheme	complex decay scheme
Co	Co^{59}-100	Co^{60}	36	5.28y	0.31	1.17, 1.33
Zr	Zr^{96}-2.80	Zr^{97} Nb^{97m} Nb^{97}	0.2	17.0h 60s 70m	1.91 none 1.27	none 0.747 0.665
Sb	Sb^{121}-57.3 Sb^{123}-42.7	Sb^{122} Sb^{124}	6.8 2.5	2.8d 60d	1.46, 1.94 complex	0.568 complex

[a] Symbol m following a mass number denotes a metastable state.

[b] h denotes hours, d denotes days, y denotes years, s denotes seconds, and m denotes minutes.

[c] No cross section for pile neutrons listed.

by the nucleus and a gamma is promptly emitted. The radioactive atom has a mass which is one mass unit greater than the target atom, but has the same atomic number. The active isotope will then decay, usually by β^- emission. Decay may be by electron capture, by β^+ (positron) emission, or by isomeric transition followed by one of the preceding types of decay.

Titanium-50 will add a thermal neutron to form titanium-51 which decays by beta-gamma emission with a half life of 5.82 minutes. However, in the presence of the tremendous amount of aluminum-28 (2.3 minutes), it is not feasible to use titanium-51 for the measurement of titanium in aluminum alloys. Fast neutrons will induce the following reactions (8):

1) $Ti^{48}(n,p)Sc^{48}$

2) $Ti^{46}(n,p)Sc^{46}$

These scandium isotopes are long lived and can be used. Scandium-48 can be formed only by energetic particle bombardment, while scandium-46 may be formed by neutron capture on stable scandium-45. If gamma scintillation spectra show the presence of scandium-48, and the ratio of the photopeaks at 0.89, 0.98, 1.12 and 1.33 m.e.v. are the same as for pure titanium metal, the absence of stable scandium is demonstrated.

The other case in which a knowledge of nuclear properties is essential is the parent-daughter sequence of zirconium-97. The following reaction will explain this (8):

$$Zr^{96}(n,\gamma)Zr^{97} \xrightarrow[\text{17 hours}]{\beta^-} Nb^{97m} \xrightarrow[\text{60 sec.}]{\gamma} Nb^{97} \xrightarrow[\text{70 min.}]{\beta^-,\gamma} Mo^{97}$$

At equilibrium the sample will decay with a seventeen-hour half life, even though the gamma activity comes from isotopes which have only sixty-second and seventy-minute half lives. If the chemical separation is effective in removing the niobium daughters, and the sample is counted soon after this separation, the sample count will increase as a function of time. To compensate for this, it is necessary to wait for the sample to reach equilibrium. Eight hours would be adequate for zirconium-97.

In some cases of short half-life isotopes decay corrections are necessary. Decay corrections are a simple exponential function of the half life and the time between measurements (12).

$$A = A_o e^{-\lambda t} \tag{5}$$

In Equation 5, $\underline{A}$ is the activity at time, $\underline{t}$; $\underline{A_o}$ is the activity at zero time; and $\underline{\lambda}$ is 0.693 divided by the half life of the radioisotope expressed in the same units as $\underline{t}$. Decay corrections are necessary whenever the time lapse between sample counts and comparator counts approaches or exceeds 1% of the half life. Decay corrections were made in the analyses for manganese, nickel and in some of the copper determinations. The radioelements and their numerical values of $\underline{\lambda}$ are: nickel-65, 4.51×10^{-3} min.$^{-1}$; manganese-56, 4.48×10^{-3} min.$^{-1}$; and copper-64, 902×10^{-4} min.$^{-1}$.

C. Radioactivity Measurement

The measurement of the radioactivity in activation analysis is the potential source of the greatest error in the method. When the net of the sample count minus background count is numerically the same, or

less than the background count, the analysis is very dependent upon fluctuations in the background count. Weakly radioactive fractions are susceptible to errors from contamination. Errors arising during beta particle measurement have been discussed. It is very important that the activity be identified and the purity checked.

An important contribution to radiochemical instrumentation has been the development of the NaI(Tl) scintillation spectrometer. The gamma radiation reacts with a NaI crystal to produce a flash of light. The intensity of the scintillation is proportional to the energy of the gamma ray. The light output is amplified by a photomultiplier tube and linear amplifier, and the output voltage is measured by an integral-differential discriminator. Two types of circuitry are in common use. In the single-channel circuit, only a narrow band of pulses in the spectrum is viewed at one time through an electronic slit. The slit is variable and can be moved to cover the entire spectrum. For convenience, the slit position is usually controlled by a motor-driven potentiometer. Successive sections of the spectrum are traced and recorded on a strip-chart recorder. In the multichannel circuit, there are many fixed slits which view simultaneously adjacent portions of the spectrum. Although some machines have as many as 256 channels, the twenty-channel machine is in common use. These machines differentiate between gamma rays of different energies, making it possible to emphasize the contribution of any desired energy to a scaling circuit. The background at a definite energy band is also low. This often results in a more favorable background-to-sample ratio, with an attendant increase in analytical precision.

The well-type scintillation crystal increases the counting efficiency by surrounding the sample with the detector crystal. In addition, since the sample occupies only a small portion of the void at the bottom of the well, geometry corrections are not necessary, since geometry is effectively 4π, or a sphere. The measuring device of choice for activation analysis is a well-type NaI(Tl) crystal as the detector, and either a single-channel or multichannel spectrometer to discriminate against unwanted activities. All samples to be counted for gamma were mounted in pyrex culture tubes (10 x 75 mm.)

Beta measurements should be avoided, if possible. The corrections required for self-absorption, scatter and for radiochemical purity are often difficult to ascertain. In the case of radioisotopes which have little or no gamma radiation, the use of the Geiger-Mueller or proportional counter is unavoidable.

Brief descriptions of the counting equipment used in these studies are given below.

1. Beta Counter

The detector is a thin mica-window Geiger-Mueller tube manufactured by Tracerlab, Inc., type TGC-2. It is mounted in a cylindrical shield with 2 inches of lead shielding. A scaler, with a scale of 64, completes the equipment. The high-voltage supply is contained in the same chassis. Nuclear Instrument and Chemical Corporation of Chicago built the scaler according to ORNL circuit drawing number Q-762.

2. Well-Type Scintillation Counter

The detector is a NaI(Tl) crystal, 2 inches in length and 2 inches in diameter with a central well 1.5 inches deep by 0.86 inche in diameter. The crystal purchased from Harshaw Chemical Company was optically coupled to a Dumont #6292 phototube. High voltage was obtained from a power supply manufactured by Atomic Instrument Company, Model #312. The scaler was also obtained from Atomic Instrument Company, Model #101B, research scaler, with scaling factor variable from 16 to 1024. Coincidence loss is 1% per 10^5 counts per minute. A linear amplifier was furnished as an integral part of the scaler.

Interchangeable liners were fabricated for the well, one of aluminum to act as a beta shield, and the other of lead to absorb weak gamma and x-ray radiation. Shielding consisted of 3 inches of lead.

3. Single Channel Scanning Spectrometer

The detector lead was the same as that described for the well-type scintillation counter, except that a RCA 5819 phototube was used because of greater stability. The discriminator circuit of the linear amplifier was manufactured by the Oak Ridge National Laboratory Instrument and Controls Division according to Drawing Q-1151. The coarse gain control limits the energy range studied; a setting of 4 corresponded to 0 to 4 m.e.v., 8 corresponded to 0 to 2 m.e.v., 16 corresponded to 0 to 1 m.e.v., etc.

Automatic scanning of the spectrum was accomplished by means of a potentiometer which was driven by the chart drive of the Brown Recorder.

The input signal to the recorder was from a linear count-rate meter fed by the discriminator circuit. Fifteen minutes were required to scan one energy range.

4. Multichannel Spectrometer

A twenty-channel spectrometer was used to obtain the data for the spectra shown in Figures 1 to 9. This instrument is manufactured by Atomic Instrument Company as Model 520, Twenty-Channel Pulse Height Analyzer. The detector is a NaI(Tl) crystal in the form of a right cylinder, 3 inches in length and 3 inches in diameter. The crystal is optically coupled to a Dumont 6363 phototube. The pulses are amplified by a Model 218 preamplifier and a Model 219 Linear amplifier and are then fed into a Model 521 Pulse Sorter Unit. In the latter unit the pulses are differentiated and fed into 20 separate scalers, each of which has a scaling factor of 16. Controls are available to select the width of each channel and to select a portion of the total spectrum to be viewed by each of the 20 channels. Suitable adjustment of the controls will enable the machine to view 20 adjacent channels. Six settings of 20 channels each are necessary to cover the energy range from 0 to 2.4 m.e.v., or from 0 to 1.2 m.e.v.

D. Special Reagents and Equipment

Activation analysis chemistry was conducted on a semi-micro scale, and 10 to 20 mg. of each carrier element were processed in a separation. Separations were carried out in 50-ml. centrifuge tubes. The usual chemical reagents were used. Final filtrations were performed on a

Coors 4/0 funnel using suction, and the precipitate was collected on filter paper discs 1.7 cm. in diameter. The precipitates were given a final wash with alcohol and dried at 105° for fifteen minutes.

Extractions were performed in 120-ml. separatory funnels.

All weighings of samples, comparators and separated precipitates were done on a Christian Becker Beam-o-lite Semi-micro Balance.

Carrier solutions (1.00 ml. equivalent to 10.0 mg. of carrier element) were prepared by dissolving an appropriate quantity of the metal salt or pure metal. Each carrier solution was standardized gravimetrically. Table III lists the carrier salts, solvents, and weighing forms.

"Hold-back" carriers were prepared in the same manner, but were not standardized. The nitrates of sodium, manganese, iron(III), cobalt(II), nickel(II), strontium, and copper(II), dissolved in 1 to 2M nitric acid, were used in this study.

TABLE III

CARRIER SOLUTIONS

Element	Salt	Solvent	Weighing Form
Ni	$Ni(NO_3)_2 \cdot 6\ H_2O$	0.5M HNO_3	Ni dimethylglyoxime
Fe	$FeCl_3 \cdot 6\ H_2O$	0.5M HNO_3	Fe_2O_3
Zn	$Zn(NO_3)_2 \cdot 6\ H_2O$	H_2O	$ZnHg\ (SCN)_4$
Ti	$Y(NO_3)_3 \cdot X\ H_2O$	2M HNO_3	$Y_2(C_2O_4)_3 \cdot 9\ H_2O$
Sb	$SbCl_3$	3M HCl	Sb_2S_3
Ag	$AgNO_3$	1M HNO_3	AgCl
Co	$Co(NO_3)_2 \cdot 6\ H_2O$	1M HNO_3	$K_3Co(NO_2)_6 \cdot H_2O$
Zr	$ZrOCl_2 \cdot 8\ H_2O$	3M HCl	ZrO_2

CHAPTER III

EXPERIMENTAL

The irradiated aluminum standards were allowed to decay for two hours after discharge from the reactor. In this span of time all of the aluminum-28 (2.3m) and most of the other short-lived isotopes decayed to negligible activity. The aluminum packets were unwrapped with six-inch long tweezers, the samples transferred to labeled 50-ml. centrifuge cones, and the wrappings discarded. The samples were treated with 3 ml. of 19M sodium hydroxide. After five minutes, 3 ml. of distilled water was added. When dissolution had ceased, the tubes were heated to boiling and maintained at the boiling point for three minutes. After cooling to room temperature, the solutions were acidified with 12M hydrochloric acid. In the analysis for silver, the solution was acidified with 15M nitric acid. Clear solutions resulted in all cases.

A. The Determination of Major Components

1. Copper

The copper analysis was done by the direct measurement of the photopeak area of the 0.511-m.e.v gamma ray. The spectrum of copper-64 is given in Figure 1. The 1.34-m.e.v. gamma ray associated with copper-64 is reported to be weak (8). The positrons emitted are annihilated and each annihilation gives rise to two quanta of 0.511-m.e.v. Sixteen hours after discharge, the activity measurement was made on the single-channel

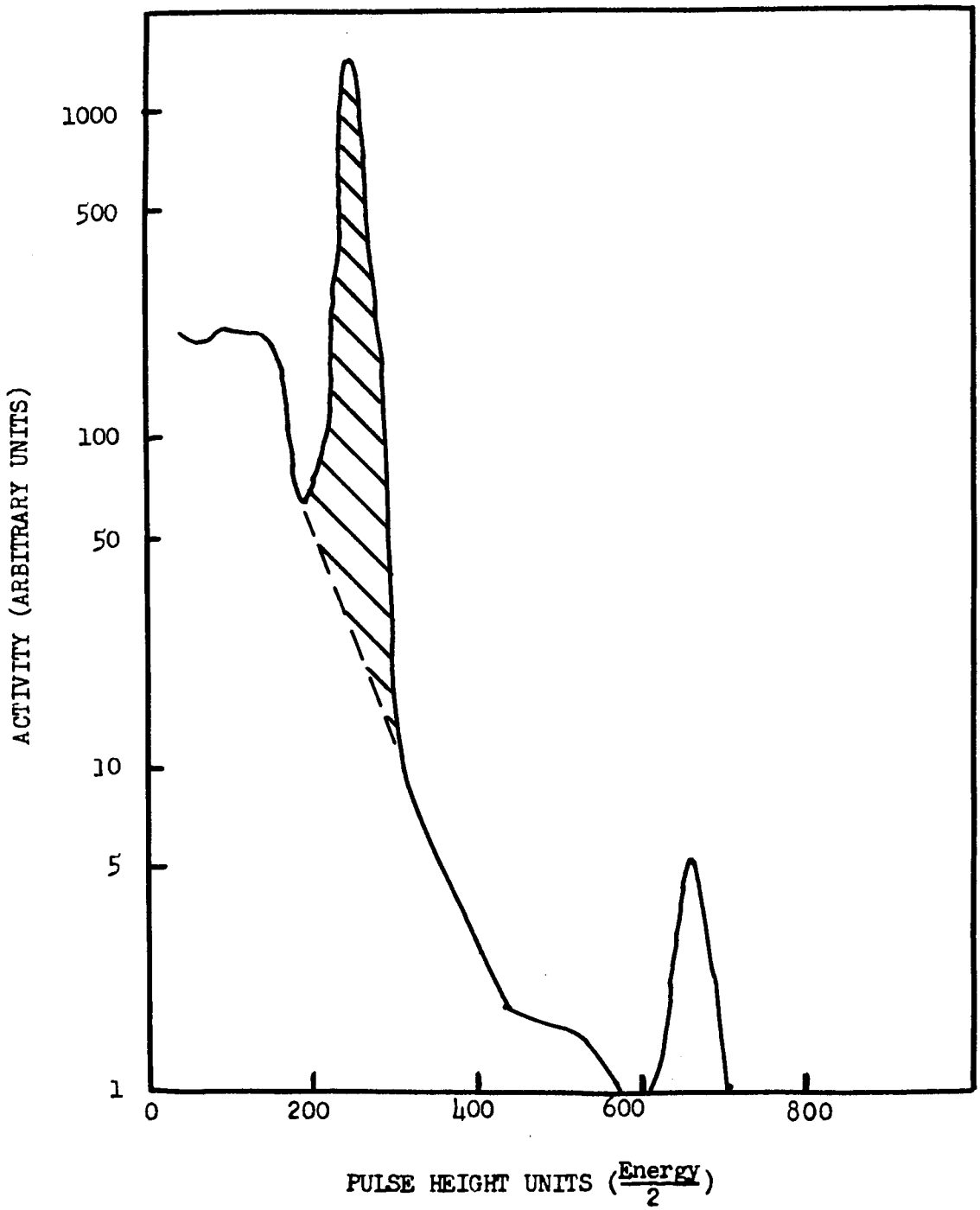

Figure 1. The gamma spectrum of copper-64
(shaded area measured)

Gain-8 Multichannel Spectrometer

recording spectrometer by scanning the region from 0.4 to 0.65 m.e.v. The base line under the photopeak of the Compton distribution was drawn at the same angle as shown by the background under the copper-64 comparator spectrum. The concentration of the comparator and the size of the sample aliquot was selected so that the activity could be read on the same count-rate scale. The smoothest envelope possible was drawn through the photopeak tracings. Triplicate measurements were made of the area under the photopeak by means of an Ott Planimeter. The results are expressed as units of area, A, on the counting rate scale.

The calculations were made as follows:

Comparator $$S = \frac{A \times D}{W}$$

S = The specific activity of the copper comparator in units of area per gram,

A = units of area measured,

D = that fraction of copper comparator solution measured divided into the total volume (Dilution Factor),

W = weight of copper metal used to prepare the comparator solution, in grams.

Sample $$\frac{A_S \times D_S}{S \times W_S} \times 10^{-4} = \%\ \text{Cu in sample}$$

A_S = Units of area measured on same count-rate scale as the comparator,

D_S = dilution factor of sample,

W_S = weight of aluminum sample taken, in grams,

S = specific activity, units of area per gram.

The results of the copper analyses are given in Table IV.

TABLE IV

THE DETERMINATION OF COPPER BY ACTIVATION ANALYSIS[a]

Sample Number	Sample Weight (grams)	Specific Activity of Comparator	Activity[b]	Decay Factor	Results grams/gram	Results %
85a-1	0.00317	3.96×10^5 units	33.4	1.000	2.66×10^{-2}	2.66
-2	0.00317	of area per gram	32.0	0.995	2.56×10^{-2}	2.56
-3	0.00234	on 5×10^3	24.3	0.990	2.64×10^{-2}	2.64
-4	0.00234	counts per	24.1	0.985	2.64×10^{-2}	2.64
-5	0.00241	minute range at	26.2	0.980	2.79×10^{-2}	2.79
-6	0.00241	1041.	24.0	0.975	2.58×10^{-2}	2.58
86c-1	0.0029	6.91×10^4 units	17.1	1.000	8.53×10^{-2}	8.53
-2	0.0029	of area per gram	17.3	0.996	8.63×10^{-2}	8.63
-3	0.0029	on 5×10^4 counts	16.6	0.992	8.28×10^{-2}	8.28
-4	0.0029	per minute range at 1000.	16.1	0.988	8.03×10^{-2}	8.03
87-1	0.0086	7.01×10^5 units	19.35	--	3.2×10^{-3}	0.32
-2	0.0059	of area per gram	13.6	--	3.3×10^{-3}	0.33
-3	0.0095	on 5×10^4 counts per minute range.	20.25	--	3.1×10^{-3}	0.31

[a] Irradiation conditions: thirty minutes in pneumatic tube in graphite reactor.

[b] Method of counting: 510 k.e.v. photopeak area integration from single-channel recording spectrometer by planimeter measurements.

2. Manganese

Manganese was determined by direct spectrometer measurement of the 0.822-m.e.v. gamma radiation. The tracing of the photopeak was obtained in the same manner as reported for copper-64 by scanning the energy region from 0.700 to 1.00 m.e.v. Figure 2 shows the gamma spectrum of manganese-56 recorded two hours after discharge from the reactor. The calculations are similar to those for copper except that all areas integrated were corrected for decay to a common time. The time chosen was the time when the first spectrum was recorded. The symbols given in the copper calculation are repeated for manganese:

$$\frac{\left(\frac{A_s}{e^{-\lambda t}}\right) \times D_s}{S \times W_s} \times 10^{-4} = \% \text{ manganese in sample}$$

The decay correction is given by $e^{-\lambda t}$ as described in Chapter II. The results appear in Table V.

3. Nickel

The aluminum samples were allowed to decay for two hours before the samples were dissolved. One milliliter of nickel carrier and all the hold-back carriers except nickel were added. The acidity was adjusted to 1M with hydrochloric acid and cupric sulfide was precipitated by passing a stream of hydrogen sulfide gas through the solution. The precipitate was removed by centrifugation. The supernatant liquid was filtered through 41H filter paper into a clean centrifuge tube. Hydrogen sulfide and colloidal metal sulfides were destroyed by boiling the solution with concentrated nitric acid and bromine water. The hydroxides

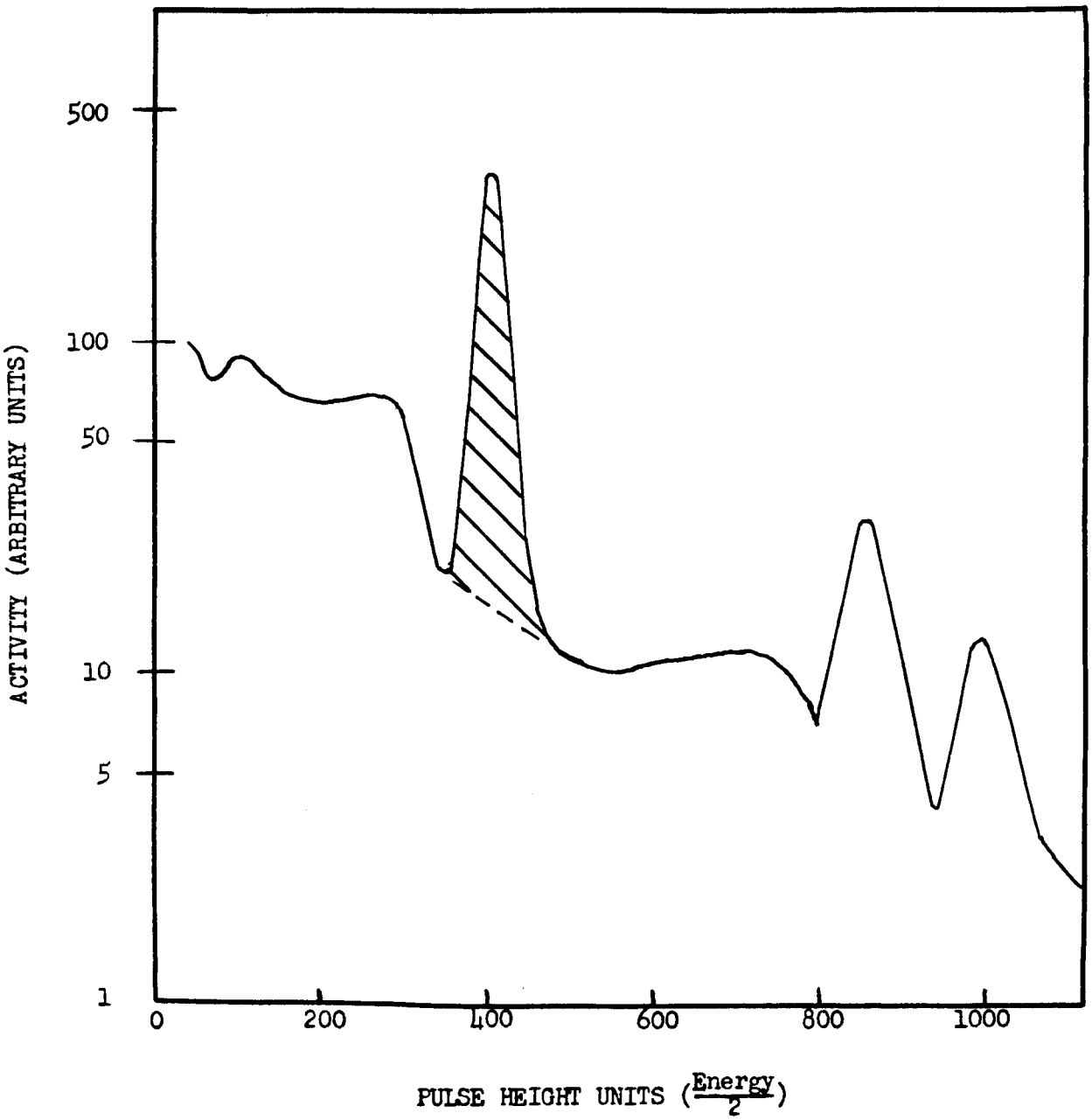

Figure 2. The gamma spectrum of manganese-56 (shaded area measured)

Gain-8 Multichannel Spectrometer

TABLE V

THE DETERMINATION OF MANGANESE BY ACTIVATION ANALYSIS[a]

Sample Number	Sample Weight (grams)	Specific Activity of Comparator	Activity[b]	Decay Factor	Results grams/gram	Results, %
85a-1	0.00317	1.73×10^6 units	35.9	1.000	6.5×10^{-3}	0.65
-2	0.00317	of area per gram	34.8	0.966	6.6×10^{-3}	0.66
-3	0.00234	on 5×10^4	25.9	0.931	6.9×10^{-3}	0.69
-4	0.00234	counts per	25.6	0.914	6.9×10^{-3}	0.69
-5	0.00241	minute range at	24.6	0.874	6.7×10^{-3}	0.67
-6	0.00241	1952.	24.1	0.842	6.9×10^{-3}	0.69
86c-1	0.0029	2.17×10^7 units	22.1	1.000	3.5×10^{-4}	0.035
-2	0.0029	of area per gram	22.8	0.973	3.7×10^{-4}	0.037
-3	0.0029	on 5×10^3 counts	22.2	0.953	3.7×10^{-4}	0.037
-4	0.0029	per minute range at 1900.	20.0	0.910	3.5×10^{-4}	0.035
87-1	0.0039	1.8×10^6 units of	25.85	1.000	3.6×10^{-3}	0.36
-2	0.0064	area per gram on	38.35	0.969	3.4×10^{-3}	0.34
-3	0.0069	5×10^4 counts per minute range at 2018.	41.20	0.943	3.5×10^{-3}	0.35
87-1	0.00132	5.45×10^6 units of	28.0	1.000	3.9×10^{-3}	0.39
-2	0.00132	area per gram on	26.7	0.981	3.8×10^{-3}	0.38
-3	0.00215	1.0×10^4 counts	37.0	0.955	3.3×10^{-3}	0.33
-4	0.00215	per minute range	36.8	0.931	3.4×10^{-3}	0.34
-5	0.00189	at 2056	31.3	0.910	3.3×10^{-3}	0.33
-6	0.00189		31.8	0.886	3.5×10^{-3}	0.35

[a] Irradiation conditions: Thirty minutes in pneumatic tube in graphite reactor.

[b] Method of counting: 820 k.e.v. photopeak area integration from single-channel recording spectrometer by planimeter measurement.

of iron(III) and aluminum were precipitated with 15M aqueous ammonia, the solution centrifuged, and the precipitates discarded. The nickel in the filtrate was precipitated as nickel dimethylgloxime. The precipitate was filtered, washed, dissolved and reprecipitated in the presence of cobalt(II), strontium and zinc hold-back carriers. The precipitate of nickel dimethylglyoxime was filtered, washed with water and then with alcohol, and dried at 105° for fifteen minutes. After cooling, the precipitate was weighed to determine the carrier yield, and mounted for beta counting. Mounting entailed placing the precipitate on a one-inch diameter watch glass and taping the watch glass to a 3 1/4 by 2 1/2 inch card and below a one-inch hole in the center, covered with a thin plastic film.

Counting was done at usual second shelf geometry on the Geiger-Mueller counter. Decay data was obtained every hour for five hours, and again at thirteen and twenty-three hours. This data was plotted and the contribution of the two and one-half hour component, nickel-65, was determined. The calculations are as follows:

Comparator $$S = \frac{\frac{A}{(Y)(e^{-\lambda t})} \times D}{W}$$

A = Activity at time of first count, in counts per minute,

Y = ratio of nickel dimethylglyoxime recovered to nickel dimethylglyoxime theoretically present,

D = dilution factor,

$e^{-\lambda t}$ = decay correction in time first sample was counted,

W = comparator weight, in grams.

The nickel content of a sample is given by:

$$\frac{\frac{A_s}{(Y_s)(e^{-\lambda t})}}{S \times W_s} \times 10^{-4} = \% \text{ nickel in sample}$$

A = activity at time of counting taken from the decay curve,

Y_s = chemical yield,

$e^{-\lambda t}$ = decay correction to time first sample was counted,

S = specific activity in counts per minute per gram,

W_s = weight of sample, in grams.

In all samples analyzed, a long-lived component appeared in the separated nickel-65 fraction. Spectral analysis showed the component to be sodium-24. Its contribution to the total count was readily obtained from the decay curves. The results of the nickel determinations are given in Table VI.

4. Iron

Iron was determined on samples which had been irradiated in graphite stringer cans. The cans were allowed to stand for one week before they were opened to allow for the decay of the fifteen-hour sodium-24 formed from the reaction $Al^{27}(n,\alpha)Na^{24}$. The samples were dissolved in the usual fashion. One milliliter of iron carrier, and the hold-back carriers of yttrium, copper(II), zinc, cobalt, strontium, and manganese(II) were added. Copper sulphide was precipitated, and the excess sulphide removed from the filtrate by boiling with concentrated nitric acid and bromine water. Ferric hydroxide was precipitated with 15M aqueous ammonia, washed and dissolved in 1M hydrochloric acid, and

TABLE VI

THE DETERMINATION OF NICKEL BY ACTIVATION ANALYSIS[a]

Sample Number	Sample Weight (grams)	Fraction of Carrier Recovered	Activity,[b] counts per minute	Results, grams/gram	Results, %
85a-1	0.0155	0.781	2355	4.4×10^{-3}	0.44
-2	0.0259	0.684	3330	4.3×10^{-3}	0.43
-3	0.0188	0.739	2890	4.7×10^{-3}	0.47
86c-1	0.0555	0.658	760	4.0×10^{-4}	0.040
-2	0.0475	0.719	642	3.6×10^{-4}	0.036
-3	0.0565	0.493	500	3.5×10^{-4}	0.035
87-4	0.0194	0.263	1588	7.1×10^{-3}	0.71
-5	0.0249	0.543	4200	7.1×10^{-3}	0.71
-6	0.0167	0.686	3800	7.5×10^{-3}	0.75

[a] Irradiation conditions: Two and one-half hours in the pneumatic tube in the graphite reactor. Specific activity of nickel metals comparator: 1) 4.36×10^7 counts per minute per gram for 85a and 87, 2) 5.18×10^7 counts per minute per gram for 86c. Method of analysis: Radiochemical, 9.3 mg. of nickel(II) carrier precipitated as 46.8 mg. of nickel dimethylglyoxime.

[b] Method of counting: Beta decay measurements on Geiger-Mueller counter extrapolated graphically to pile discharge time.

then reprecipitated with 8M sodium hydroxide. The precipitate was washed until free of excess sodium hydroxide. It was dissolved in 8M hydrochloric acid, and the acid solution was extracted once with an equal volume of isopropyl ether. The iron was stripped from the organic phase, precipitated as hydrated ferric oxide, and ferric hydroxide again precipitated, filtered, washed and ignited for twenty minutes at 700°. Ferric hydroxide was dissolved with 3M nitric acid and yttrium fluoride precipitated with dilute hydrofluoric acid. After centrifugation, the rare earth fluoride was discarded. The ferric oxide precipitates were transferred to individual culture tubes and counted by discriminatory gamma counting. A spectrum of the highest energy photopeak of the comparator is recorded using a wide slit. After the midpoint of the photopeak is determined, the slit is set so that it measures only this particular portion of the spectrum. Gamma radiation of lower energy is excluded. The Compton distribution from gamma radiation of higher energy than the photopeak used will be included in the measurement, but the effect is usually small. For iron-59, the gamma measured was 1.29 m.e.v. (See Figure 3). Sodium-22 ($t_{1/2}$ = 2.4 years) emits a gamma of 1.28 m.e.v. This was used as a standard to calibrate the slit. The relatively long half life of sodium-22 enables the operation of the spectrometer to be checked frequently over long periods of time and permits the accumulation of precise decay data for iron-59 ($t_{1/2}$ = 45.1 days).

The calculations were as follows:

Comparator $$S = \frac{\frac{A}{Y} \times D}{W}$$

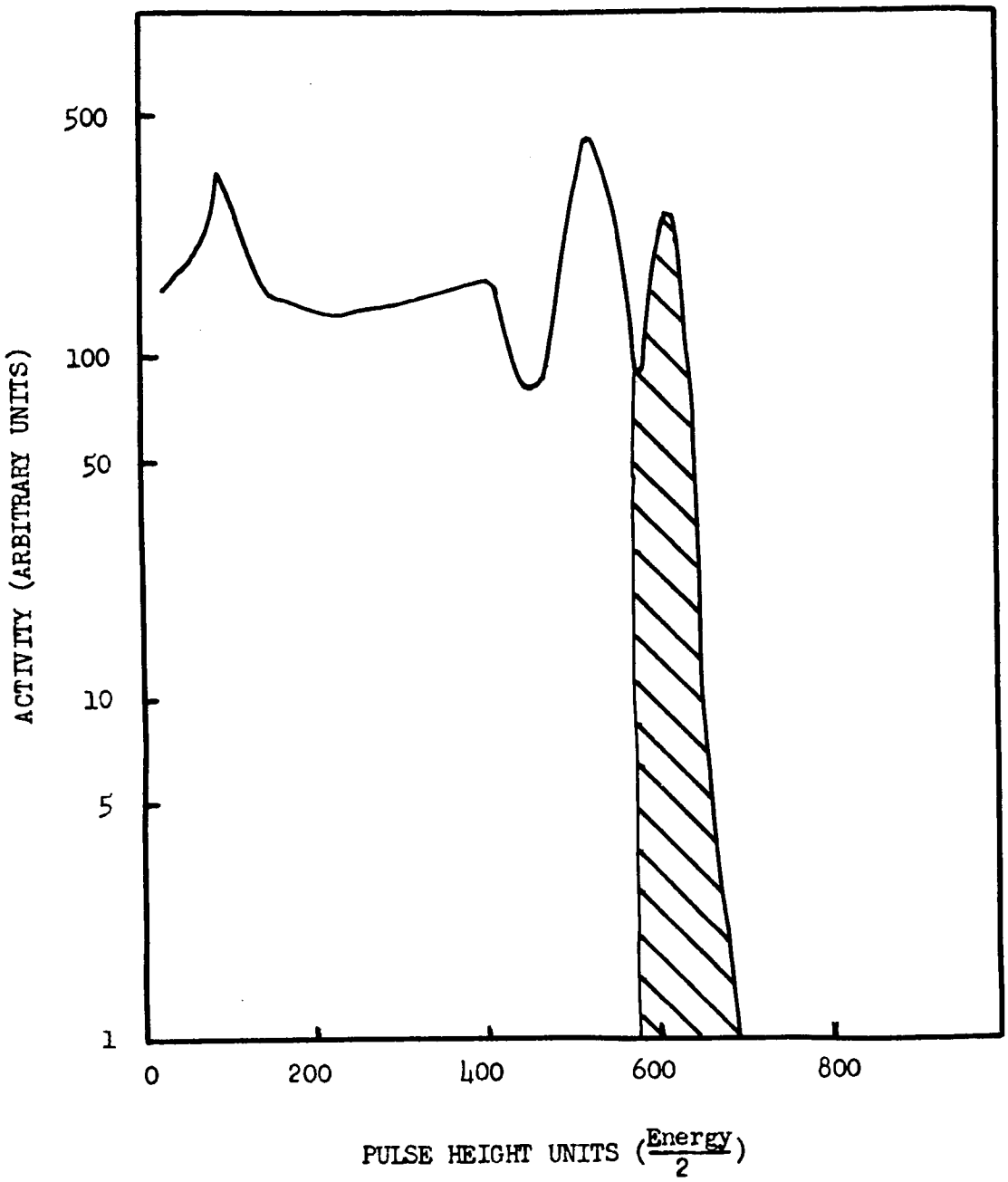

Figure 3. The gamma spectrum of iron-59 (shaded area counted)

Gain-8 Multichannel Spectrometer

Sample $$\frac{\frac{A_s}{Y} \times D}{S \times W_s} \times 10^{-4} = \%\ \text{Iron in Sample}$$

The results of the iron determinations are shown in Table VII.

5. Zinc

After irradiation the aluminum samples were allowed to decay for twenty-four hours. After dissolution in sodium hydroxide, 1 ml. of zinc carrier was added. The samples were acidified and all the hold-back carriers, except zinc, were added. Copper sulphide was precipitated and discarded. Excess sulphide was removed in the usual manner. The insoluble hydroxides were precipitated with sodium hydroxide, washed, and dissolved in the minimum amount of 12M hydrochloric acid. They were reprecipitated with 15M aqueous ammonia. The filtrate was acidified with hydrochloric acid, evaporated to incipient dryness, and the residue dissolved in 1M HCl. The resulting solution was extracted twice with a volume of 8% (w/v) tribenzlamine in chloroform equal to twice the volume of the aqueous phase. The organic layers were combined, washed with 1M hydrochloric acid and the zinc stripped with 0.1M hydrochloric acid (17). The zinc was precipitated as zinc mercuric thiocyanate, $ZnHg(SCN)_4$, filtered, dried and mounted for gamma counting. The gamma spectrum for a mixture of the separated zinc isotopes is shown in Figure 4. Spectral examination indicated that the zinc activity separated from the samples was very similar to pure zinc. For simplicity and accuracy, the samples were counted in the well-type scintillation counter. Energy discrimination was not attempted. Half-life determinations verified

TABLE VII

THE DETERMINATION OF IRON BY ACTIVATION ANALYSIS[a]

Sample Number	Sample Weight (grams)	Fraction of Carrier Recovered	Activity,[b] counts per minute	Results grams/gram	Results %
85a-1	0.0065	0.772	18	1.83×10^{-3}	0.18
-2	0.0057	0.772	21	2.42×10^{-3}	0.24
-3	0.0048	0.799	14	1.86×10^{-3}	0.19
86c-4	0.0040	0.803	50	7.95×10^{-3}	0.80
-5	0.0037	0.813	52	8.85×10^{-3}	0.89
-6	0.0038	0.696	45	8.75×10^{-3}	0.88
87-7	0.0066	0.701	48	5.28×10^{-3}	0.53
-8	0.0066	0.531	33	4.85×10^{-3}	0.49
-9	0.0073	0.808	57	4.95×10^{-3}	0.50

[a] Irradiation conditions: One week in high-flux stringer can in graphite reactor. Specific activity of iron metal comparator: 1.95×10^{6} counts per minute per gram. Method of analysis: Radiochemical, 15.66 mg. of iron(III) carrier precipitated as 22.4 mg. of iron oxide.

[b] Method of counting: Discriminatory gamma counting of 1.29 m.e.v. gamma.

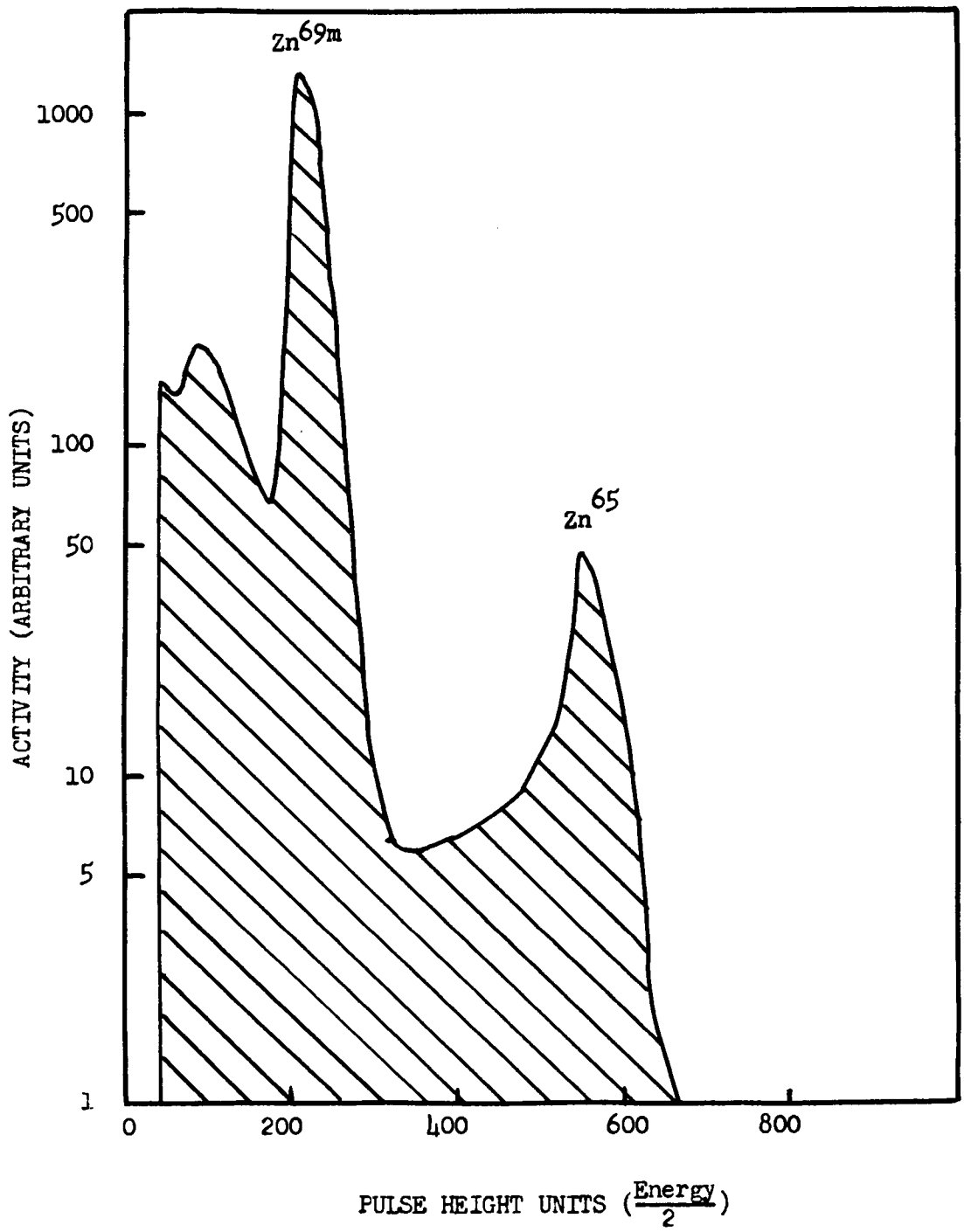

Figure 4. The gamma spectrum of Zn^{69m} and Zn^{65} (shaded area counted)

Gain-8 Multichannel Spectrometer

the absence of any activity except that due to 13.8 hour zinc-69m and one long-lived component, zinc-65.

The calculations follow the same pattern as for iron. Since counting was concluded in twelve minutes, no decay corrections were necessary. The results of the zinc determinations are given in Table VIII.

6. Titanium

Titanium-51 is unsuited for the determination of titanium in short-lived targets such as aluminum. The alternative to thermal neutron activation is fast neutron activation. Scandium isotopes are the end products of the fast neutron reactions. The gamma spectrum of the longer lived scandium isotope is shown in Figure 5. Since scandium behaves similarly to the rare earths, the more familiar chemistry of the lathanides was employed. The samples were allowed to decay for two weeks. One milliliter of yttrium carrier was added to the acidified solutions of the samples along with the usual hold-back carriers. Successive precipitations of yttrium fluoride and yttrium hydroxide were performed three times. Finally, yttrium oxalate, $Y_2(C_2O_4)_3 \cdot 9\ H_2O$, was precipitated and the individual samples were mounted for gamma counting. The activity separated was very low, as may be seen from Table IX. For this reason, the discriminatory counter was adjusted to count all gamma rays having an energy greater than 800 k.e.v. The activity was identified by placing all of the separated mounts on the face of the three-inch crystal and determining the spectrum by means of long, time-interval counts on sample and background and background individually. The spectrum

TABLE VIII

THE DETERMINATION OF ZINC BY ACTIVATION ANALYSIS[a]

Sample Number	Sample Weight (grams)	Fraction of Carrier Recovered	Activity,[b] counts per minute	Results grams/gram	Results, %
85a-1	0.0539	0.436	705	1.6×10^{-4}	0.016
-2	0.0553	0.407	787	1.85×10^{-4}	0.019
-3	0.0668	0.334	636	1.52×10^{-4}	0.015
86c-4	0.0345	0.494	50300	1.51×10^{-2}	1.51
-5	0.0418	0.379	46282	1.49×10^{-2}	1.49
-6	0.0427	0.351	44212	1.51×10^{-2}	1.51
87-4	0.0452	0.105	650	7.3×10^{-4}	0.073
-5	0.0579	0.286	2159	6.9×10^{-4}	0.069
-6	0.0531	0.222	1627	7.3×10^{-4}	0.073

[a] Irradiation conditions: Sixty-two hours in pneumatic tube in graphite reactor. Specific activity of zinc metal comparator: 1.88×10^{8} counts per minute per gram for 85a and 87. Method of analysis: Radiochemical, 10.4 mg. of zinc(II) carrier precipitated as 79.4 mg. of $ZnHg(CNS)_4$.

[b] Method of counting: Gamma counting in well-scintillation counter.

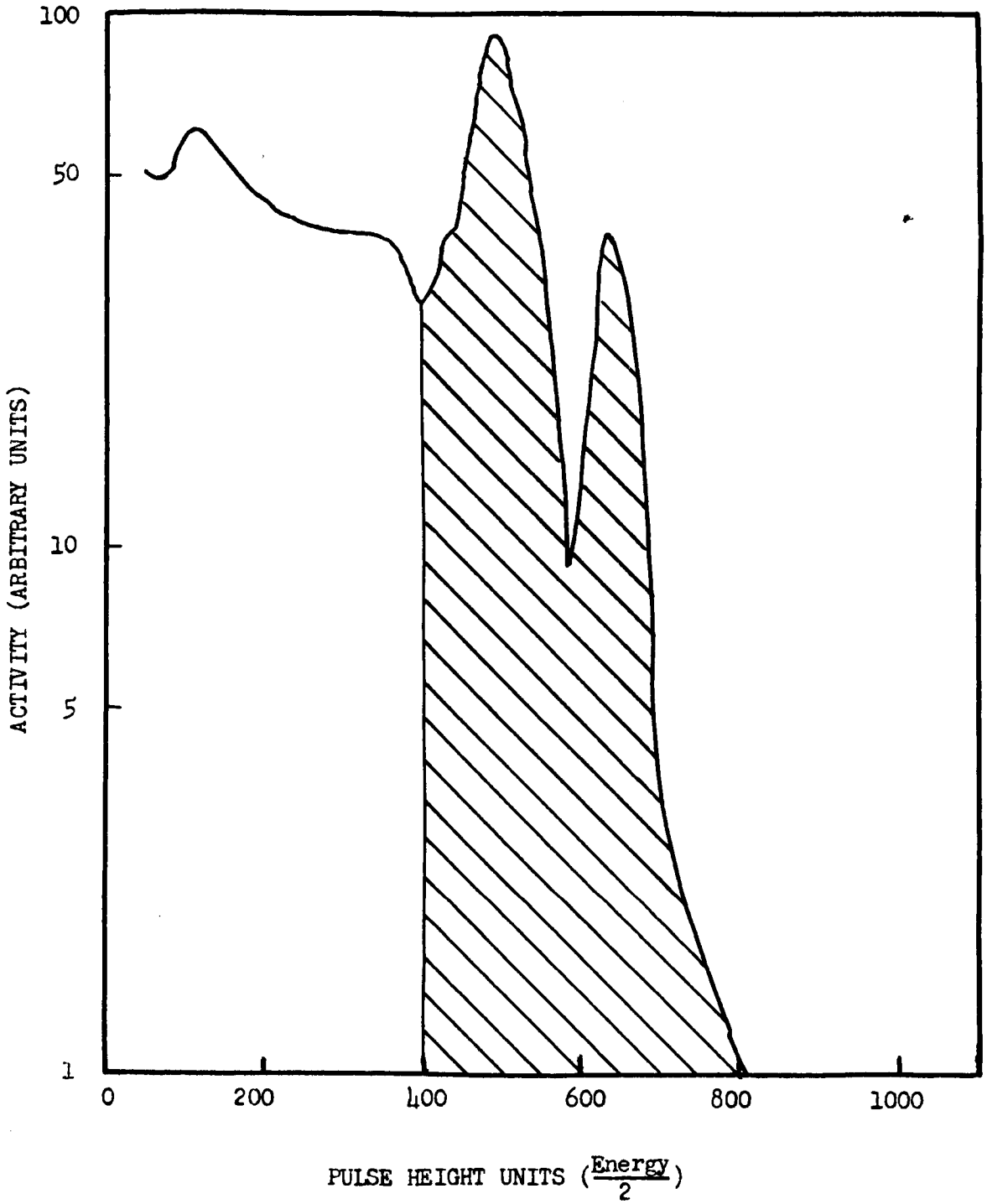

Figure 5. The gamma spectrum of scandium-46 (shaded area counted)

Gain-8 Multichannel Spectrometer

TABLE IX

THE DETERMINATION OF TITANIUM BY ACTIVATION ANALYSIS[a]

Sample Number	Sample Weight (grams)	Fraction of Carrier Recovered	Activity,[b] counts per minute	Results grams/gram	Results, %
85a-1	0.0408	0.245	8	1.7×10^{-4}	0.017
-2	0.0451	0.935	7	1.3×10^{-4}	0.013
-3	0.0447	0.974	9	1.7×10^{-4}	0.017
86c-5	0.0435	0.925	21	4.1×10^{-4}	0.041
-6	0.0497	0.977	20	3.4×10^{-4}	0.034
87-7	0.0409	0.967	82	1.79×10^{-3}	0.17
-8	0.0452	0.948	94	1.89×10^{-3}	0.18
-9	0.0433	1.000	78	1.55×10^{-3}	0.15

[a] Irradiation conditions: Two weeks in cadmium-shielded stringer can in graphite reactor. Specific activity of titanium oxide comparator: 1.16×10^{6} counts per minute per gram titanium. Method of analysis: Radiochemical, 10.4 mg. of yttrium(III) carrier precipitated as 30.6 mg. of $Y_2(C_2O_4)_3 \cdot 9\ H_2O$.

[b] Method of counting: Integral gamma counting of all gammas with energy greater than 800 k.e.v.

was ill-defined, but prominent peaks could be identified at energies greater than 500 k.e.v.

Calculations resemble those for iron, except that the weight of the comparator (titanium dioxide) must be corrected for the difference in weight between titanium and titanium dioxide.

B. The Determination of Some Trace Constituents

Four elements were chosen to demonstrate the sensitivity of activation analysis: cobalt with a high activation cross section; antimony for its moderate activation cross section and short half life; zirconium because it had not been detected within the limits set by the National Bureau of Standards (0.001%); and silver, a very common contaminant of all copper whenever examined by activation analyses. The calculations are similar to those for iron in Section A-4.

1. Cobalt

The samples were dissolved after a decay period of two weeks. One milliliter of cobalt carrier and of all the hold-back carriers except cobalt were added. The copper group was removed as copper sulphide, the hydroxide group as the hydrous oxides, after excess sulphide had been removed, and then the basic sulphide group was precipitated. The latter was washed and dissolved in 15M nitric acid containing bromine. After evaporation to fumes several times with 12M hydrochloric acid to remove all nitrate ions, the cobalt carrier was precipitated with solid potassium nitrate, then dissolved in hydrochloric

acid and reprecipitated. The precipitate of potassium cobaltinitrite was mounted for gamma counting. The spectrum of cobalt-60 is shown in Figure 6. The method of discriminatory counting was used to measure the photopeak at 1.33 m.e.v. The results are given in Table X.

Since cobalt has a large cross section, the comparator was not pure metal, but an alloy of aluminum and cobalt (Co - 0.038%). The "self-shadowing" effect discussed earlier was thereby eliminated.

2. Zirconium

The stringer can was allowed to decay for twenty-four hours before it was opened. The samples were dissolved in the usual way, and 2 ml. of zirconium carrier and all the usual hold-back carriers were added. Copper and the other acid sulfide elements were removed first. After oxidation, the hydrous oxide group was removed and treated with 8M sodium hydroxide. The insoluble residue which contained the iron and zirconium was dissolved in 4M nitric acid, 2 ml. of 48% hydrofluoric acid added and barium fluozirconate, $BaZrF_6$, was precipitated by the addition of a saturated solution of barium nitrate. The foregoing cycle was repeated twice, and finally the zirconium was precipitated as hydrated zirconium oxide, ignited to zirconium oxide, and mounted for gamma counting. The comparator was processed in the same manner and concurrently with the samples. Comparators and samples were allowed to decay for eight hours in order to allow attainment of equilibrium with the gamma-emitting daughters. The gamma spectrum at equilibrium is shown in Figure 7. The results for zirconium are contained in Table XI.

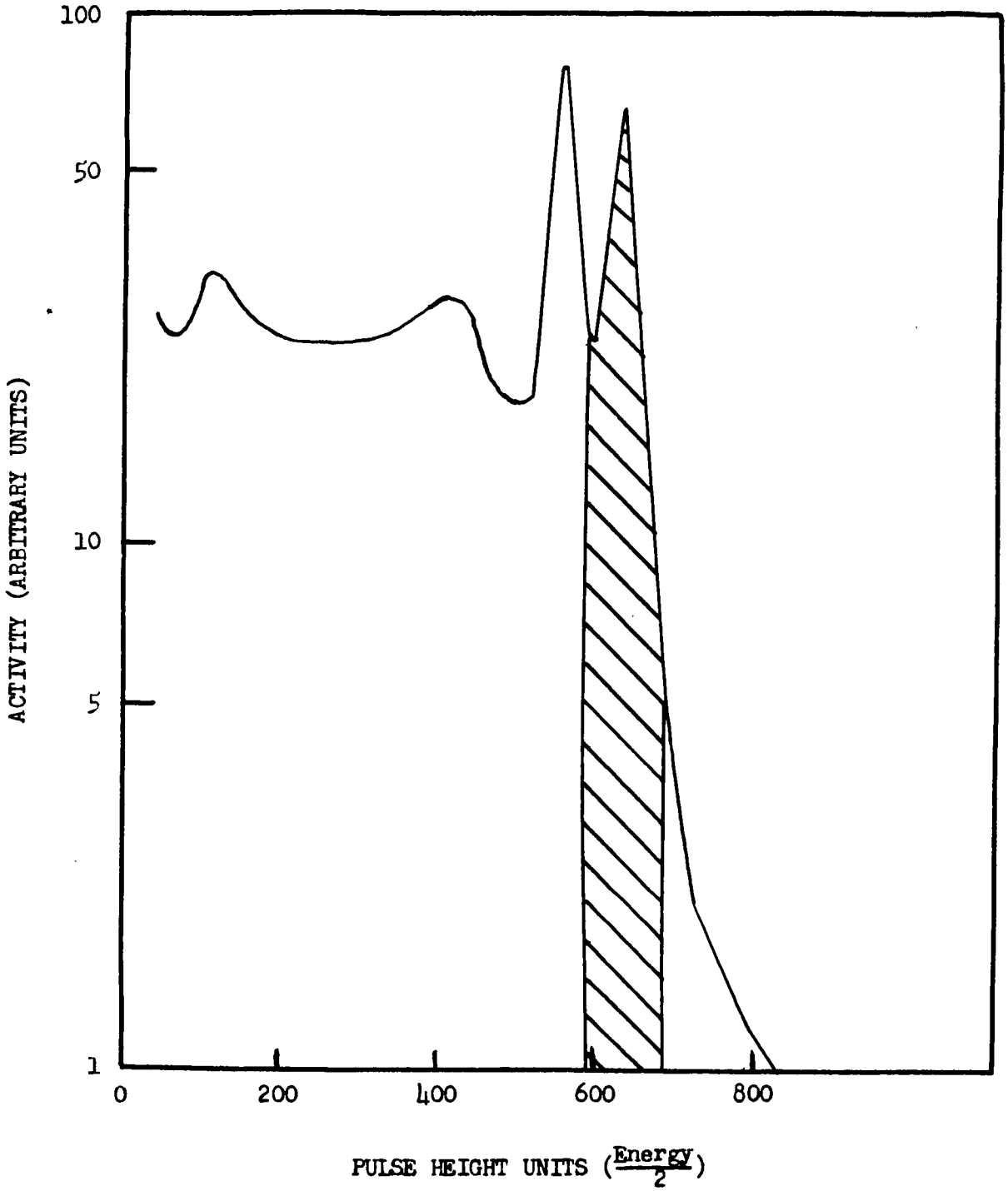

Figure 6. The gamma spectrum of cobalt-60 (shaded area counted)

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TABLE X

THE DETERMINATION OF COBALT BY ACTIVATION ANALYSIS[a]

Sample Number	Sample Weight (grams)	Fraction of Carrier Recovered	Activity,[b] counts per minute	Results grams/gram	Results, %
85a-1	0.0184	0.279	186	3.8×10^{-5}	0.0038
-2	0.0245	0.266	253	4.1×10^{-5}	0.0041
-3	0.0155	0.296	168	3.9×10^{-5}	0.0039
86c-4	0.0173	0.236	16	4.1×10^{-6}	0.00041
-5	0.0122	0.346	15	3.7×10^{-6}	0.00037
-6	0.0124	0.248	9	3.1×10^{-6}	0.00031
87-7	0.0112	0.189	107	5.3×10^{-5}	0.0053
-8	0.0114	0.159	77	4.5×10^{-5}	0.0045
-9	0.0128	0.177	114	5.3×10^{-5}	0.0053

[a] Irradiation conditions: One week in stringer can at high flux in graphite reactor. Specific activity of 0.4% Co-Al alloy comparator: 9.51×10^{8} counts per minute per gram cobalt. Method of analysis: Radiochemical, 9.5 mg. of cobalt(II) carrier precipitated as 75.7 mg. of $2\ K_3Co(NO_2)_6 \cdot 3\ H_2O$.

[b] Method of counting: Discriminatory gamma counting of 1.33 m.e.v. gamma.

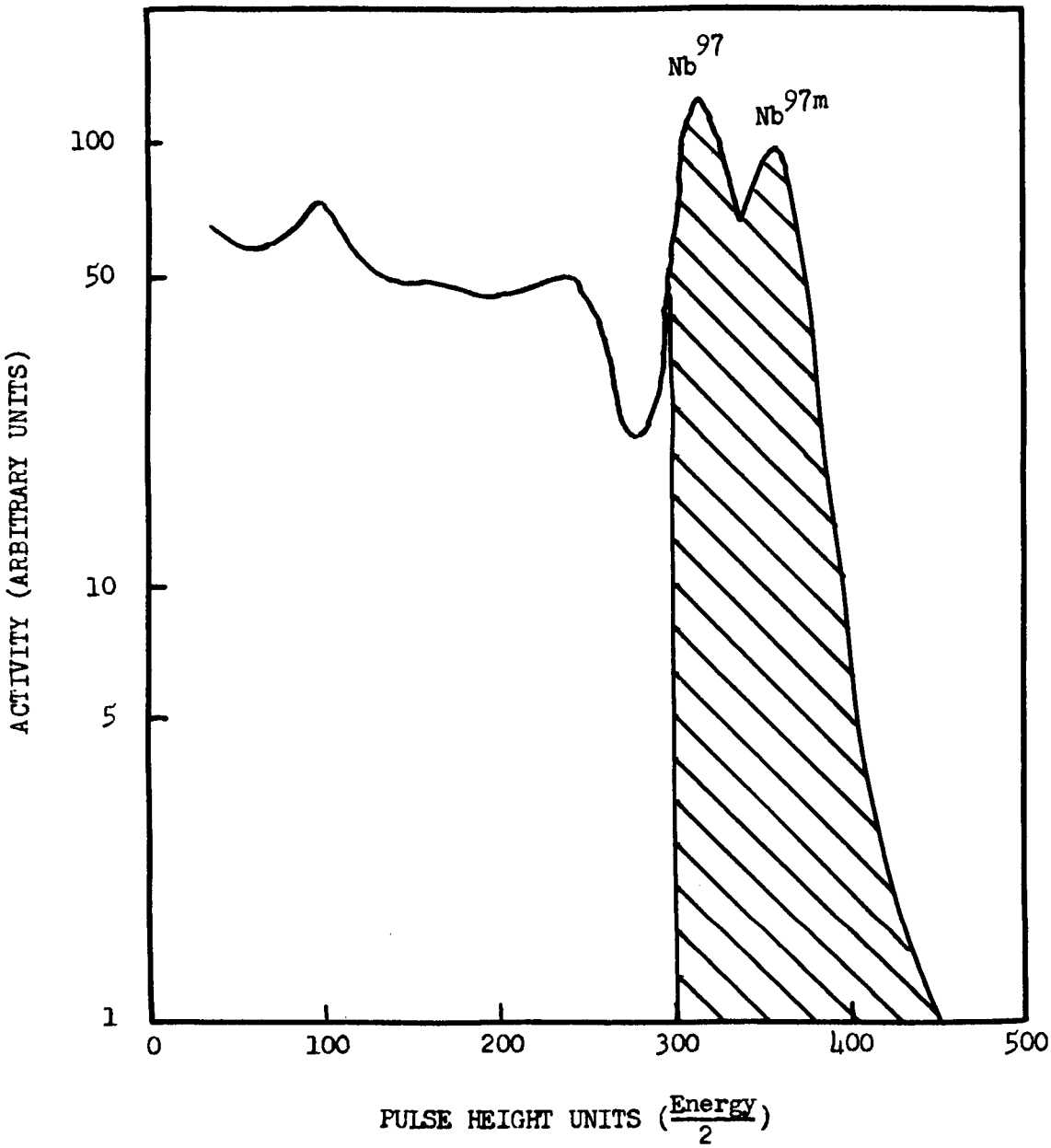

Figure 7. The gamma spectrum of the equilibrium mixture of Zr^{97} - Nb^{97m} - Nb^{97}. (shaded area counted)

Gain-8 Multichannel Spectrometer

TABLE XI

THE DETERMINATION OF ZIRCONIUM BY ACTIVATION ANALYSIS[a]

Sample Number	Sample Weight (grams)	Fraction of Carrier Recovered	Activity,[b] counts per minute	Results grams/gram	Results, %
85a-1	0.0443	0.433	59	8.22×10^{-6}	0.0008
-2	0.0610	0.536	109	8.92×10^{-6}	0.0009
-3	0.0593	0.617	110	8.05×10^{-6}	0.0008
86c-4	0.0558	0.805	118	7.00×10^{-6}	0.0007
-5	0.0584	0.529	74	6.42×10^{-6}	0.0006
-6	0.0632	0.744	127	7.19×10^{-6}	0.0007
87-7	0.0566	0.513	152	10.9×10^{-6}	0.0011
-8	0.0569	0.658	187	13.3×10^{-6}	0.0013
-9	0.0572	0.629	121	9.0×10^{-6}	0.0009

[a] Irradiation conditions: One week in stringer can at high flux in graphite reactor. Specific activity of $ZrOCl_2 \cdot 8\ H_2O$ comparator: 3.73×10^8 counts per minute per gram zirconium. Method of analysis: Radiochemical, 17.8 mg. of Zr(IV) carrier precipitated as 24.0 mg. of zirconium oxide.

[b] Method of counting: Integral gamma counting of all gammas having energies greater than 630 k.e.v.

The discriminatory counter was adjusted to count all gamma rays having energies greater than 0.63 m.e.v. Naturally occurring zirconium contains hafnium, and since radioactive hafnium isotopes are always formed in high yield by slow-neutron capture, it was necessary to discriminate against these isotopes. Fortunately, all hafnium isotopes have gammas less energetic than 0.63 m.e.v.

3. Antimony

Antimony is frequently found in trace concentrations in metals and alloys. After irradiation the samples were allowed to decay for three days before processing. Antimony carrier and the usual hold-back carriers added and the acid sulfide group separated from a solution 1M in hydrochloric acid. The sulfide precipitate was dissolved in aqua regia. Hold-back carriers of cobalt, iron(III) and zinc were added and the antimony precipitated from the solution as antimonic oxide by vigorous boiling with 15M nitric acid. The precipitate was dissolved and reprecipitated once more, and then dissolved in hydrochloric acid. A hold-back carrier of tin was added, and the antimony was precipitated with hydrogen sulfide in oxalic acid solution. The precipitate was dissolved, and the sulfide precipitation repeated twice; additional tin carrier was added each time. The final precipitate of antimony(III) sulfide was dried and mounted for gamma counting.

Spectral examination indicated little contaminant activity. The samples were counted by means of the well-type scintillation counter. Figure 8 shows the spectrum of antimony-122 (2.8d) and antimony-124 (60d)

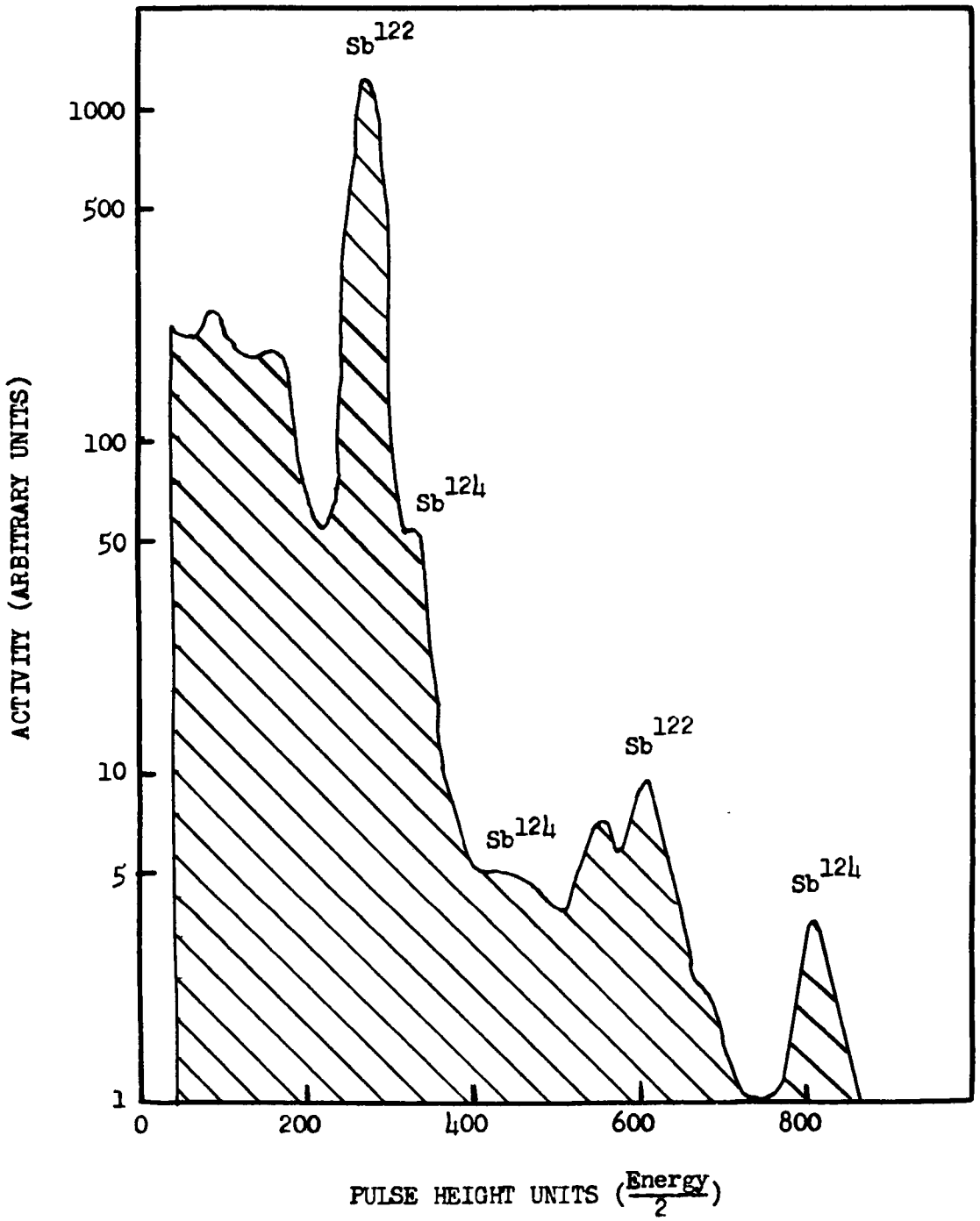

Figure 8. The gamma spectra of Sb^{122} - Sb^{124} (shaded area counted)

Gain-8 Multichannel Spectrometer

three days after discharge from the pile. The results of the analyses are compiled in Table XII.

4. Silver

The samples were allowed to decay for two weeks. The fundamental part of the sample dissolution was the same as for the other elements; however, because of the insolubility of silver chloride, nitric acid was substituted for hydrochloric acid in all operations. Silver carrier and the usual hold-back carriers were added and the silver precipitated as silver chloride. The precipitate was washed and dissolved in 15M aqueous ammonia, iron(III) hold-back carrier was added, the hydrous oxides precipitated and discarded, and the silver chloride reprecipitated by the careful addition of nitric acid followed by heating. The silver chloride was washed, filtered, dried and mounted for gamma counting. There was no evidence for radioactivity other than that shown in the silver-110m - silver-110 spectrum shown in Figure 9. The samples were counted in the well-type scintillation counter. Analytical results are given in Table XIII.

TABLE XII

THE DETERMINATION OF ANTIMONY BY ACTIVATION ANALYSIS[a]

Sample Number	Sample Weight (grams)	Fraction of Carrier Recovered	Activity,[b] counts per minute	Results grams/gram	Results, %
85a-1	0.0504	0.559	358	3.5×10^{-7}	0.00004
-2	0.0440	0.748	341	2.9×10^{-7}	0.00003
-3	0.0389	0.825	370	3.2×10^{-7}	0.00003
86c-4	0.0491	0.367	6198	9.5×10^{-6}	0.00095
-5	0.0535	0.720	17330	10.4×10^{-6}	0.00104
-6	0.0423	0.175	3037	11.2×10^{-6}	0.00112
87-7	0.0579	0.423	23653	26.7×10^{-6}	0.0027
-8	0.0435	0.773	30920	25.5×10^{-6}	0.0026

[a] Irradiation conditions: One week in stringer can at high flux in graphite reactor. Specific activity of antimony metal comparator: 3.61×10^{10} counts per minute per gram. Method of analysis: Radiochemical, 20.5 mg. of antimony(III) carrier precipitated as 28.6 mg. of Sb_2S_3.

[b] Method of counting: Gamma counting in well scintillation counter.

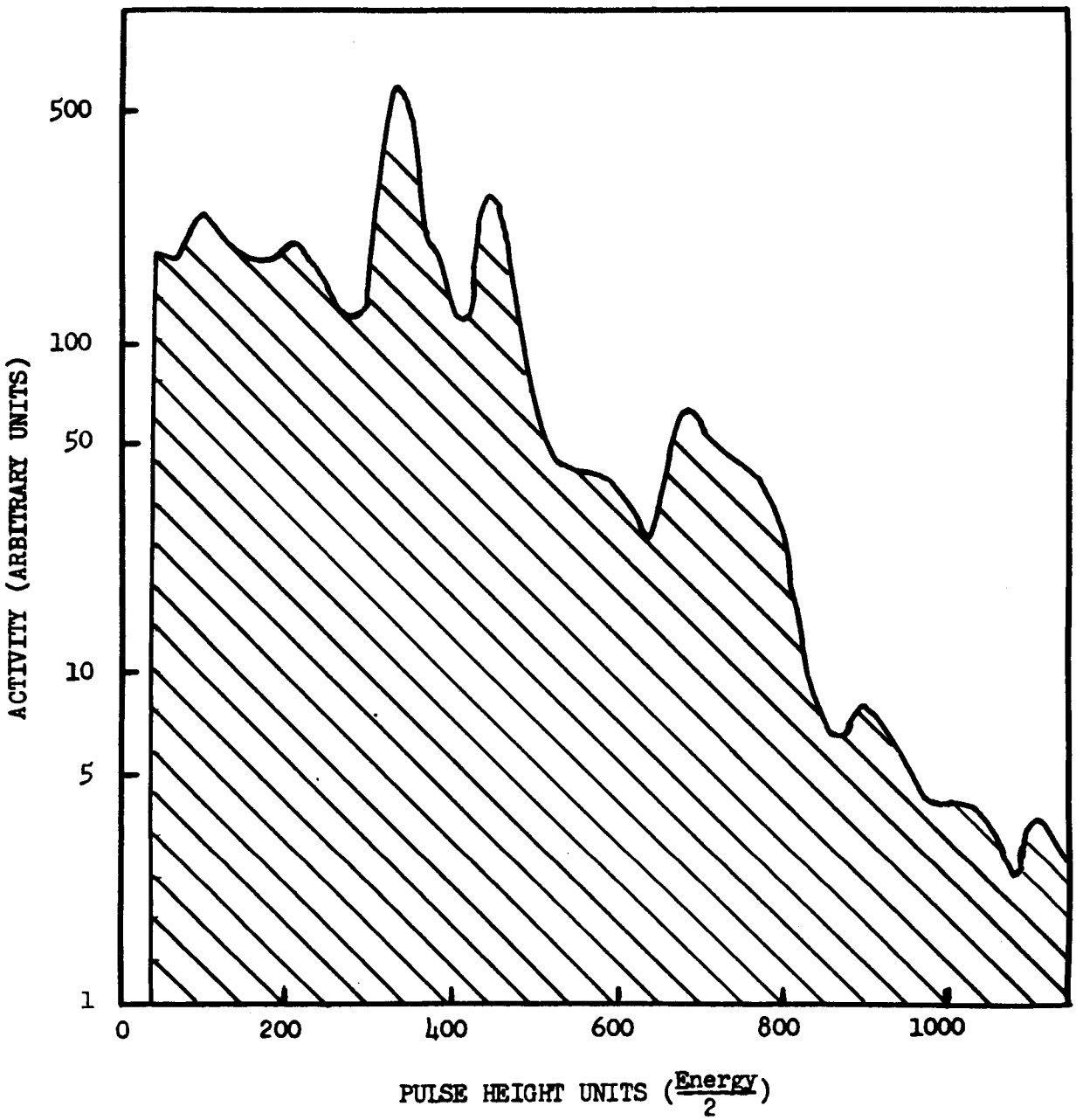

Figure 9. The gamma spectrum of Ag^{110m} - Ag^{110}
(shaded area counted)

Gain-8 Multichannel Spectrometer

TABLE XIII

THE DETERMINATION OF SILVER BY ACTIVATION ANALYSIS[a]

Sample Number	Sample Weight (grams)	Fraction of Carrier Recovered	Activity,[b] counts per minute	Results grams/gram	Results, %
85a-1	0.0267	0.791	194	2.4×10^{-6}	0.00024
-2	0.0347	0.810	252	2.3×10^{-6}	0.00023
-3	0.0314	0.911	279	2.5×10^{-6}	0.00025
86c-1	0.0285	0.381	190	4.5×10^{-6}	0.00045
-2	0.0272	0.824	336	3.9×10^{-6}	0.00039
-3	0.0287	0.886	410	4.2×10^{-6}	0.00042
87-1	0.0325	0.833	75	0.7×10^{-6}	0.00007
-2	0.0375	0.952	127	0.9×10^{-6}	0.00009
-3	0.0379	0.948	118	0.9×10^{-6}	0.00009

[a] Irradiation conditions: One week in stringer can at high flux in graphite reactor. Specific activity of $AgNO_3$ comparator: 3.87×10^9 counts per minute per gram of silver. Method of analysis: Radiochemical, 15.8 mg. of silver(I) carrier precipitated as 21.0 mg. of AgCl.

[b] Method of counting: Gamma counting in well scintillation counter.

CHAPTER IV

RESULTS AND CONCLUSIONS

Tabulations of the results obtained by neutron activation analysis with the values listed on the National Bureau of Standards' Certificates for the three aluminum alloys are given in Tables XIV to XVI. The results of the trace element determinations appear in Table XVII. The data appearing in Tables IV to IX were treated statistically. No statistical treatment of the counting data was included.

The paired values of the weight of element found, and the weight of element calculated to be present, may be used to plot the analytical results. If the curve has a slope of unity and passes through the origin, then the analytical method shows no constant error. An alternate way is to use the method of least squares to determine the slope of the best line through all of the points. The standard deviation of this slope is readily calculated. If the slope is unity, within the limits of standard deviation of the slope, then the analytical method has no bias. On the other hand, if the slope deviates from unity, then the intercept is calculated in order to determine the constant error. When the quotient of the intercept and its standard deviation, called the statistic $\underline{t}$ exceeds the critical value, then the line does not go through the origin. A bias exists in the method. The methods for the statistical treatment of the data were taken from Youden (18).

TABLE XIV

COMPARISON OF RESULTS OF ANALYSES ON NATIONAL BUREAU OF STANDARDS ALUMINUM ALLOY 85a

Element	Certified Value, %	Value Found, %
Copper	2.48 ± 0.02[a]	2.65 ± 0.09[a]
Manganese	0.66 ± 0.02	0.68 ± 0.02
Nickel	0.41 ± 0.02	0.45 ± 0.05
Iron	0.208 ± 0.008	0.20 ± 0.08
Zinc	0.019 ± 0.006	0.017 ± 0.005
Titanium	0.016 ± 0.004	0.016 ± 0.006

[a] With associated standard deviation at the 95% confidence level.

TABLE XV

COMPARISON OF RESULTS OF ANALYSES ON NATIONAL BUREAU OF STANDARDS ALUMINUM ALLOY 86c

Element	Certified Value, %	Value Found, %
Copper	7.92 ± 0.054[a]	8.37 ± 0.48[a]
Manganese	0.041 ± 0.008	0.036 ± 0.002
Nickel	0.030 ± 0.010	0.037 ± 0.002
Iron	0.90 ± 0.02	0.85 ± 0.12
Zinc	1.50 ± 0.06	1.50 ± 0.14
Titanium	0.035 ± 0.002	0.038 ± 0.012

[a] With associated standard deviation at the 95% confidence level.

TABLE XVI

COMPARISON OF RESULTS ON NATIONAL BUREAU OF STANDARDS ALUMINUM ALLOY 87

Element	Certified Value, %	Value Found, %
Copper	0.30 ± 0.02[a]	0.32 ± 0.02[a]
Manganese	0.30 ± 0.00	0.35 ± 0.02
Nickel	0.59 ± 0.02	0.72 ± 0.05
Iron	0.46 ± 0.02	0.50 ± 0.04
Zinc	0.077 ± 0.014	0.072 ± 0.005
Titanium	0.16 ± 0.02	0.17 ± 0.03

[a] With associated standard deviation at the 95% confidence level.

TABLE XVII

RESULTS OF TRACE ELEMENT DETERMINATIONS

Element	Aluminum Alloy 85a Value Found, %	Aluminum Alloy 86c Value Found, %	Aluminum Alloy 87 Value Found, %
Antimony	0.00004	0.00095	0.0027
	0.00003	0.0010	0.0026
	0.00003	0.0011	
Silver	0.00024	0.00045	0.00007
	0.00023	0.00039	0.00009
	0.00025	0.00042	0.00009
Cobalt	0.0038	0.00041	0.0053
	0.0041	0.00037	0.0045
	0.0039	0.00031	0.0053
Zirconium	0.00008	0.00007	0.00011
	0.00009	0.00006	0.00013
	0.00008	0.00007	0.00009

A. Results

1. Copper

From the statistics of the straight line, the slope differs significantly from unity in a positive direction. Therefore, a bias exists. Aluminum alloy 85a exhibits a bias of +0.16 with an associated deviation of ± 0.07 at the 95% confidence level. For sample 86c a positive bias of 0.45 ± 0.429 exists. Only three determinations were made on sample 87; consequently, no attempt was made to evaluate the results except by means of the curve for all the samples.

The reason for the existing bias is not immediately apparent, but some correlation between the zinc content of the sample and the higher copper result is possible. Zinc-69^m has a gamma ray of 0.437 m.e.v. The resolution of the spectrometer, that is, the width of the photopeak at half height divided by the energy at the midpoint of the photopeak, is 10%. The gamma ray of copper was measured at 0.510 m.e.v. Overlap between the peaks is probable, so that a smooth envelope drawn through the tracing of the copper peak could include some gamma radiation from zinc-69^m. Further investigation of this possibility is warranted at some future time.

2. Manganese

No bias exists for the manganese determination on sample 85a. Using the "F test" (19), the calculated value for the variance is larger than the critical value; therefore, the agreement between averages is not acceptable as measured by the agreement between determinations within

the sets on sample 86c. However, if only the values for manganese obtained by the colorimetric method are used to evaluate the standard sample, then results are reconciled. One value listed on the Certificate of Analysis, obtained by the persulfate-arsenite method, differs markedly from all other values. When this value is excluded, no bias exists. An unexplainable bias of +0.05 ± 0.016 exists for sample 87.

3. Nickel

The data for nickel was plotted in the usual way. The curve had a slope of unity, but an intercept was detected. The data from samples 86c and 85a fell on one line, but the data from sample 87 was discontinuous although parallel with this line. Since 86c and 87 were analyzed at the same time, and calculated from the same nickel metal comparators, the difference had to be the purity of the separated fraction, rather than comparator errors. The major difference in composition between 87 and the other samples is the high silicon content (6.21%). The neutron reaction on silicon is $Si^{30}(n,\gamma)Si^{31}$ which decays by beta emission with a 2.62-hour half life. No specific chemistry was designed to eliminate silicon during the nickel separation, and no silicon hold-back carrier was used. For this reason, it is reasonable to assume that the bias present in the nickel analysis was caused by silicon-31 contamination. Beta absorption and decay measurements would not indicate the presence of silicon-31 in the separated nickel-65 fraction. This is one reason for the avoidance of beta counting with its inherent lack of specificity in favor of the more discriminating method of gamma counting.

4. Iron

The plot of the data, and a treatment by least squares, showed a slope of unity, and no bias.

5. Zinc

The plot of the data from samples 85a and 87 indicate that the curve passes through the origin and has a negative bias. Sample 86c shows no bias.

6. Titanium

The plot of the data and a treatment of least squares indicates that the slope does not differ significantly from unity and that no bias exists.

7. Trace Elements

The trace element analyses could not be compared with standard values since none were listed on the Certificates. The results for cobalt are known to be high. The cobalt-60 used as a means of measuring the stable isotope of cobalt, cobalt-59, can also be formed from the fast neutron reaction on nickel, $Ni^{60}(n,p)Co^{60}$. When such is the case, then another fast neutron reaction, $Ni^{58}(n,p)Co^{58}$, will occur. The latter reaction is the only prolific way to produce this isotope with uncharged particles. Cobalt-58 has a gamma ray of 0.81 m.e.v.; and 15% of the decay proceeds through a positron. The spectrum would, therefore, have two gammas, at 0.81 and 0.51 m.e.v. These two peaks were evident in the separated cobalt mounts from the samples. The ratio of peak areas

for the cobalt-58 and cobalt-60 isotopes separated were not well enough defined to determine the mode of formation of the cobalt-60 following the fast neutron reaction. The cobalt results, in any case, could not exceed the value calculated on the assumption that all of the cobalt-60 came from the slow neutron-capture reaction. Actually this is not true, but the results given in Table X are calculated as equal to this figure.

B. Conclusions

From the foregoing data, it may be concluded that activation analysis is adequate for the determination of manganese, iron and titanium in aluminum alloys. The positive bias exhibited by the results for copper and nickel may be eliminated by the use of proper chemical separation techniques for the copper, and by a silicon removal step in the nickel procedure. The data is not sufficiently detailed to explain the negative bias in the zinc determination.

The proper choice of counting conditions is pointed up by the error in the nickel determination revealed only by the statistical treatment of the results. The accuracy of the activation analysis method appears to be better than 10%. The sensitivity of the method has been demonstrated for antimony, silver, cobalt and zirconium to be greater than the sensitivities employed by the National Bureau of Standards in their analyses of the aluminum alloys.

CHAPTER V

SUMMARY

Neutron activation analysis has been applied to the determination of copper, manganese, nickel, iron, zinc and titanium in National Bureau of Standards aluminum alloys 85a, 86c and 87. The accuracy and precision of these analyses have been ascertained by the statistical treatment of the data. No bias was found for manganese, iron and titanium methods. A positive bias was discovered for both the copper and nickel analyses. This bias can be explained satisfactorily by the degree of radiochemical purity of the counted fractions. The copper mount was contaminated with zinc-69^m and the nickel fraction was contaminated with silicon-31. A negative bias was detected for two of the samples in the zinc determination. No explanation is advanced.

The sensitivity of activation analysis was demonstrated by determining antimony (0.4 to 25 p.p.m.), silver (0.9 to 4 p.p.m.), cobalt (4 to 50 p.p.m.) and zirconium (0.7 to 1.0 p.p.m.).

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