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NEUTRON ACTIVATION ANALYSIS BY MEANS OF SHORT-LIVED ISOTOPES

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ACTIVATION ANALYSIS BY MEANS OF SHORT-LIVED ISOTOPES

James Lawton Brownlee, Jr.

ABSTRACT

The purpose of this research was to evaluate the application of short-lived isotopes to analysis by radioactivation and to develop rapid chemical separations of several short-lived isotopes from a variety of sample matrices. Radioactive tracer methods were used to determine the extent of chemical recovery following separation of vanadium-52, thallium-206 and niobium-94m. These isotopes were chosen as being representative of beta and gamma emitters, pure beta emitters and x-ray emitters, respectively. Special instrumentation, in the form of a dual memory 100-channel pulse height analyzer, was used and evaluated for the analysis of the beta and gamma radiation of counting samples.

Determinations were made of the amount of vanadium, as vanadium-52, in a series of petroleum process stream samples which included distillation residues and condensates. Samples from various refinery streams were sealed in polyethylene tubing for irradiation in the reactor. It was found that the vanadium in these samples could be deter-

mined non-destructively by gamma spectrometry of the irradiated gross samples. Determinations of vanadium in samples of petroleum cracking catalyst required chemical separation of the vanadium prior to gamma spectrometry because of interference from the photopeak of aluminum-28. A rapid separation of vanadium from aluminum and silicon was developed, employing solvent extraction of vanadium cupferrate into chloroform. This extraction followed fusion of the sample with sodium peroxide and removal of aluminum with 8-hydroxyquinoline. The chloroform solution of vanadium cupferrate was used for gamma analysis. This separation, requiring approximately 9-1/2 minutes, has been used to separate vanadium from several types of samples.

Determinations of vanadium made on the petroleum samples containing 10^{-6} to 10^{-7} grams of vanadium per gram of sample, showed standard deviations of 10-percent or less. Determinations of vanadium in cracking catalyst samples showed a higher standard deviation.

Determination of thallium, as thallium-206, was performed on rock and mineral samples. Thallium-206, being a pure beta emitter, was determined by decay curve resolution on separated thallium fractions. Several procedures were investigated for the chemical separation of thallium. Fusion and extraction of bromothallic acid into isopropyl ether were common to all procedures. Following extraction and evaporation of the ether, thallium(I) was precipitated as the iodide, the tetraphenylboron salt, or as the thionalide complex. These procedures were evaluated and used in the determination of microgram amounts of thallium in rock samples. Results show that amounts of thallium down to the order of 10^{-7} grams can be determined as thallium-206.

Niobium was investigated by means of its K x-ray, emitted in the decay of niobium-94m. Detection was achieved by means of a sodium iodide (thallium) scintillation detector, a krypton-filled x-ray proportional counter having proved to be of little use for quantitative work.

Several separation procedures were investigated for the post-irradiation separation of niobium from a variety of samples; only limited success was realized. Adsorption of niobium radiocolloid on silica gel showed chemical recovery of 30 - 35 percent from rutile samples, but could be applied only to samples containing little or no silica.
A pre-irradiation separation of niobium by paper chromatography was investigated and found to offer certain advantages over other methods.

CHAPTER I

INTRODUCTION

The rapid growth of technology carries with it the demand for newer, more sensitive methods of analyzing materials. Very often, materials are required for certain applications where ultra high purity is essential - where the level of trace contaminants must be less than fractions of a part per million. Many standard methods of analysis cannot be utilized to determine constituents in such low concentrations without resorting to the reduction of large sample volumes with consequent loss of material. Analysis by radioactivation has provided analysts with a method capable of extreme sensitivity without requiring large sample volumes.

As early as 1935, Hevesy and Levi (72) utilized the method to determine small amounts of dysprosium in yttrium. It was not until 1951, however, that the method was put to routine use by Leddicotte and Reynolds (111) at the Oak Ridge National Laboratory. Since that time, more reactor space has become available throughout the country (and the world); with the increase in amount of reactor space has also come an increase in the applications of activation analysis. Analytical chemists throughout the world have come to recognize activation analysis as a sensitive method for the determination of many elements throughout the periodic table.

Activation analysis, which utilizes nuclear properties of a sample rather than its chemical or atomic properties, is not without its disadvantages. For many elements, high sensitivity is attainable only by irradiation in a high flux of neutrons. Almost without exception, this requires the use of a nuclear reactor or other high energy source which can produce neutrons in high yield. In addition, irradiations for many isotopes are time consuming, requiring long periods of irradiation followed by meticulous separations of the element desired. Eliminating the former disadvantage is far beyond the scope of this report. However, for many elements, short-lived neutron-produced activities are known, and can be used for radioactivation determinations requiring no more time than more standard methods.

The investigations reported herein are concerned with the development of methods for the utilization of these short-lived isotopes in analytical determinations. Special techniques, instrumentation, and facilities necessary for irradiation, transfer, separation and analysis of neutron-induced short-lived activities are reported. Illustrations of a typical determination are presented, in addition to rapid separation procedures for short-lived vanadium, thallium, and niobium isotopes. The application of these procedures in the determination of these elements in a variety of sample materials is also considered.

CHAPTER II

THE ACTIVATION METHOD

Following the discovery of induced, or artificial, radioactivity by Curie and Joliot in 1933 (88), the application of this type of radioactivity to the solutions of analytical problems was soon recognized. The very fact that atomic nuclei undergo transformations when bombarded by nuclear particles forms the basis for the activation method of analysis, a relatively recent and powerful method for the determination of trace elements in a wide variety of samples. Briefly, activation analysis can be defined as a method of analysis based upon the quantitative measurement of the radioactivity induced in the constituents of a sample as a result of bombardment with nuclear particles. This definition implies that the bombarding particles may be either charged or neutral. Thus, Hevesy and Levi (72), in 1936, used thermalized neutrons to determine the amount of dysprosium in impure yttrium, and Seaborg and Livingood, in 1938, determined trace quantities of gallium in highly purified iron (174) by means of charged particle activation.

The choice of the proper nuclear reaction for an activation determination is generally dependent upon the physical, chemical and nuclear properties of the element being determined, other trace contaminants, and the matrix in which the element occurs, in addition to these properties of the activation products. These properties determine to a large extent the sensitivity with which a given element can be determined, the amount of interference to be expected from competing nuclear reactions or activation products, and the necessity for post-irradiation separations. In general, nuclear reactions involving charged particles have a small, or zero, cross-section at energies less than the threshold energy of the particular reaction. These threshold energies increase with an increase in atomic number of the target nucleus, thus activation determinations by means of charged particles are employed for the most part among the lighter elements, generally where neutron activation is the least effective. As the energy of the charged particles increases above the threshold, the yield of activation product increases, until competing reactions assume importance at which point the yield falls off. Also, "self-shadow" effects (147), i.e., absorption of a sizeable fraction of a particle flux by surface layers of the sample, are usually more severe than is the case with neutron activations. As a result of these disadvantages, and the relative availability of neutron sources having high particle fluxes, neutron activation determinations are much more widespread than charged particle activations.

As mentioned above, a knowledge of the nuclear properties of the elements is not only pertinent, but essential to activation analysis. Such information is readily available in the literature in a number of compilations, most of which are listed in "A Directory to Nuclear Tabulations"(63). The 1956 revision of the "Chart of the Nuclides" (181), and the "Trilinear Chart of the Nuclides" (186) present convenient sources of data for isotopic abundances, thermal neutron cross-sections of stable nuclei, and half-lives, modes of decay, and energies of decay. Strominger, Hollander and Seaborg (185) have compiled in tabular form experimental data for the nuclear properties of both stable and radioactive isotopes. A similar compilation, in card form, is found in the tabulations of the Nuclear Data Group of the National Research Council (199), which are supplemented and revised periodically.

Data available for neutron activations includes a compilation of cross-sections and resonance parameters (83); compilations of neutron activation calculations (178); sensitivities (111,127); slow neutron-induced activities arranged according to half-life (62); activation cross-sections and the half-lives of the radioisotopes produced (131); cross-sections for fast neutron reactions in a thermal reactor, and their applications and consequences to activation analysis. These are but a few of the more useful sources of nuclear data applicable to activation analysis. Other sources are to be found listed in such material as Nuclear Science Abstracts.

A. Theory of Neutron Activation Analysis

Before discussing techniques of activation analysis, it is of interest to examine the mathematical relationship between the amount of element present and the nuclear and irradiation parameters. Rigorous treatment of the general rate equations governing growth and decay in a neutron flux has been presented by Rubinson (158) and Lewis (114).

The rate of formation, $(dN^*/dt)_F$, of radioactive nuclei in a neutron field is given by:

$$(dN^*/dt)_F = N(t)\phi\sigma \qquad (1)$$

in which $N(t)$ is the number of target nuclei at time t, ϕ is the neutron flux in neutrons - cm^{-2} - sec^{-1}, and σ is the cross-section for activation, in $cm^2/$ nucleus. The rate of disintegration of the radioactive nuclei formed by neutron capture can be expressed:

$$(dN^*/dt)_D = -\lambda N^* \qquad (2)$$

in which λ is the decay constant, in units of $(\text{seconds})^{-1}$ (the decay constant is related to the half-life, t-1/2, by the expression:

$$\lambda = (\ln 2)/t\text{-}1/2 \qquad (3)$$

where t-1/2 is expressed in seconds).

The net time rate of change in the number of radioactive nuclei is given by the sum of the rate of disintegration and the rate of formation. Hence:

$$(dN^*/dt)_{net} = (dN^*/dt)_F + (dN^*/dt)_D = dN^*/dt \qquad (4)$$

Substituting Equations (1) and (2) into (4), this becomes:

$$dN^*/dt = N(t)\phi\sigma - \lambda N^* \qquad (5)$$

The number of target nuclei, N(t), is related to the number of target nuclei present at the time the sample is placed in the neutron flux (i.e., at time t = 0), N^o, by the expression:

$$N(t) = N^o - N^* \qquad (6)$$

Substituting this relation into Equation (5), and rearranging terms, the relation becomes:

$$dN^*/dt = N^o\phi\sigma - (\phi\sigma + \lambda)N^* \qquad (7)$$

which, when rearranged, and multiplied by the quantity $-(\phi\sigma + \lambda)$, gives rise to the expression:

$$\frac{-(\phi\sigma + \lambda)\ dN^*}{N^o\phi\sigma - (\phi\sigma + \lambda)N^*} = -(\phi\sigma + \lambda)dt \qquad (8)$$

Equation (8) can be integrated to give:

$$\ln\left[N^o\phi\sigma - (\phi\sigma + \lambda)N^*\right] = -(\phi\sigma + \lambda)t + C \qquad (9)$$

in which C is a constant of integration. If both sides of this expression are raised to the power e, the result is:

$$N^o\phi\sigma - (\phi\sigma + \lambda)N^* = Ke^{-(\phi\sigma + \lambda)t} \qquad (10)$$

in which the constant, e^C, has been replaced by the constant, K.

In order to evaluate K, it is necessary to have some further information; let us assume that at time $t = 0$, the number of radioactive nuclei, $N^* = 0$. Substituting these values for t and N^* into Equation (10), we obtain:

$$K = N^o\phi\sigma \qquad (11)$$

Hence:

$$N^o\phi\sigma - (\phi\sigma + \lambda)N^* = N^o\phi\sigma e^{-(\phi\sigma + \lambda)t} \qquad (12)$$

Solving for N^*, we obtain:

$$N^* = \frac{N^o\phi\sigma\ [1 - e^{-(\phi\sigma + \lambda)t}]}{(\phi\sigma + \lambda)} \qquad (13)$$

Recalling that $D = \lambda N^*$, where D is the number of disintegrations per second, and noting that N^o, the number of target nuclei, can be expressed:

$$N^o = \frac{wf\ N_o}{A} \qquad (14)$$

in which w is the weight in grams of the element sought, A its chemical atomic weight, f the fractional abundance of the stable isotope being activated, and N_o is Avogradro's number, Equation (13) can be written:

$$D = \frac{\lambda wfN_o\phi\sigma}{A}\frac{[1 - e^{-(\phi\sigma + \lambda)t}]}{(\phi\sigma + \lambda)} \qquad (15)$$

Solving for the weight of element sought, w, one obtains:

$$w = \frac{DA\,(\phi\sigma + \lambda)}{\lambda N_o f \phi\sigma \left[1 - e^{-(\phi\sigma + \lambda)t}\right]} \qquad (16)$$

The relation shown in Equation (16) has been derived assuming only that a single (n,γ) reaction,

$$X^{A} + n \rightarrow X^{A+1} + \gamma \qquad (17)$$

is taking place in the neutron field, and that reactions of the type

$$X^{A+1} + n \rightarrow X^{A+2} + \gamma \qquad (18)$$

take place only to a vanishingly small extent. An additional assumption can be made which will simplify Equation (16) considerably. If we assume that $\phi\sigma \ll \lambda$, i.e., σ is small and t-1/2 short, Equation (16) reduces to

$$w = \frac{DA}{N_o \phi\sigma f\,(1 - e^{-\lambda t})} \qquad (19)$$

Equation (19) is valid when the disintegration rate, D, of the irradiated sample is measured immediately on removing the sample from the neutron field in which it is activated. Should any chemical separations be necessary before the activity is measured, an additional term must appear in Equation (19) to correct for decay during the time required for separation. This is especially necessary when the activity to be measured is short-lived. When this term, which is taken from the radioactive decay relation for a single activity, is included, Equation (19) becomes

$$w = \frac{D'A}{N_o \phi \sigma f (1 - e^{-\lambda t_1})(e^{-\lambda t_2})} \qquad (20)$$

where: w = weight, in grams of the element being determined.

D' = disintegrations per second, measured t_2 minutes after removal of the sample from the reactor.

A = chemical atomic weight of the element being determined, in grams per gram-atom.

N_o = Avogadro's number, 6.023×10^{23} atoms per gram-atom.

ϕ = neutron flux, neutrons-cm^{-2}-sec^{-1}.

f = fractional abundance of the (stable) isotope being activated.

σ = cross-section for activation, cm^2 per nucleus.

λ = disintegration constant in sec^{-1}.

t_1 = time of irradiation.

t_2 = time interval between removal of the sample from the reactor and measurement of D'.

Equation (20), as written, can be used for analytical purposes only when values for ϕ and σ are known with good accuracy and precision.

In obtaining data from the literature for the activation analysis of many elements, it has been found that the activation cross-sections of these elements are not known with any great precision or accuracy. In addition, the neutron flux in most reactors is subject to slight variations, even during short irradiations. As a result, Equation (20) is not generally of practical use for most activation determinations. In place of Equation (20), however, a comparative method is most often used. In this method, a standard is irradiated at the same time as the sample, and in the same irradiation container, where possible. Often a standard is mixed homogeneously with the sample prior to irradiation. The activity of the unknown is then compared with that of the standard as follows:

$$\frac{A_x}{w_x} = \frac{A_s}{w_s} \qquad (21)$$

where: A_x = activity of the element in the unknown.
w_x = weight of the element in the unknown.
A_s = activity of the element in the standard.
w_s = weight of the element in the standard.

The comparative method of activation analysis circumvents the inconstancy of the neutron flux, and the lack of precision with which many activation cross-sections are known.

Precisions of the order of ± 10-percent are possible in non-destructive analyses for constituents occuring in the range of 0.1 - 10 parts-per-million by this method.

B. Short-lived Activations

While activation analysis, with its extreme sensitivities, small sample size, usual lack of reagent blank and relative ease of identification and measurement of activation products, has come into wide acceptance among the National Laboratories, its acceptance as a standard analytical tool in most college and industrial laboratories has been slow. The reasons for this lack of more general interest most probably can be stated in two words: cost and time. In order to utilize the advantages of neutron activation analysis, the analyst must irradiate his samples in a rather high flux of neutrons. Almost without exception, this means a nuclear reactor or other high energy source capable of producing copious amounts of neutrons. The cost of obtaining such a facility is tremendous, often amounting to at least several hundred thousand dollars. In addition, irradiation periods of several hours, days, weeks, or in some cases, months, are necessary to achieve the desired sensitivities. Here again, time is often measured in terms of cost, especially in industry. So long as these cost and time factors maintain their present status, one can expect that activation analysis will remain a tool used by industrial laboratories only for special purposes, with irradiations obtained through the co-operation of the National Laboratories, on a service basis.

The future for activation is far from being as dark as it might appear at first glance. For many types of samples, high neutron fluxes are not absolutely essential, and the portable radium-beryllium, antimony-beryllium and polonium-beryllium sources can be utilized. In addition, small laboratory neutron generators are becoming available in the price range of $20,000, which are capable of producing neutron fluxes intermediate between those of the portable neutron sources and many nuclear reactors. Units of this type are in the development stages at several companies, among them Texas Nuclear, Nuclear-Chicago, Schlumberger, Kaman Aircraft, and High Voltage Engineering Corporation.

Neutron generators of this type can go a long way toward improving interest in activation analysis. This still leaves the question of long irradiation periods. Until activation analyses can be completed in a day or less, activation analysis will not be accepted as a common tool along with other, more standard methods. One way of circumventing this disadvantage lies in the utilization of neutron-produced short-lived isotopes. In this way, long irradiations become unnecessary, resulting in large savings in the time required to obtain the results of an analysis.

Eliminating the problem of long irradiations by utilizing short-lived isotopes where they exist gives rise to still further problems. First to be considered is that of transporting the sample from the reactor to a radiochemistry laboratory where post-irradiation separations can be made when necessary. This problem has been overcome in the Phoenix Laboratory by installation of the pneumatic tube delivery system described in Chapter III. This system allows irradiation of samples, and their return following irradiation, to take place directly from hoods in the radiochemistry laboratory. Transportation of the sample to the reactor and back consumes a total of only 6-10 seconds, thus facilitating greatly work with short-lived isotopes.

Following irradiation in the reactor, samples contain many different activities in addition to those of elements being investigated. The problem which now arises is the removal by chemical or physical means (or both) of these contaminating activities before the isotope of interest has decayed to a level which is too low to measure. Removal by chemical means entails the development of radiochemical separation procedures which are capable of removing essentially all of the contaminating activities within a short time - generally within 10-15 minutes. Unfortunately, only a few simple chemical separation procedures are available which are capable of separating radiochemically pure isotopes from complex matrices. As a result, two or more of these simple procedures must be combined; finding the proper combination to effect the desired decontamination may require a good bit of experimentation and development. However the combination can usually be found to reduce contaminating activities to a tolerable level. When a sample is to be analyzed by means of its gross decay - i.e., when a Geiger tube, proportional chamber, or scintillation well crystal is to be used as a detector - the chemical separation procedure must remove those contaminating activities having half-lives very close to that of the desired isotope. By this means, a simple resolution of the resulting decay curve may be sufficient to obtain the amount of activity in the sample due to the isotope of interest. However, in order to obtain reasonably precise results by this method, essentially all of the longer lived activity must also be removed. In addition, some means of determining the fractional recovery of the element being determined must be incorporated into the separation procedure.

An alternative method makes use of physical means, either alone, or in combination with chemical separations, to remove or discriminate against contaminating activities. This discrimination takes the form of x- or gamma- ray spectrometry. Since the energy spectrum of one radioisotope is generally quite different from all others, it is often possible to measure that part of the spectrum which offers maximum detection sensitivity for the desired isotope and reduces or minimizes the effects of contaminating activities. In the case of several types of samples, chemical separations are not necessary, and the activity of the isotope of interest can be determined non-destructively by x- or gamma-ray spectrometry of the gross sample. However, this is the exception rather than the rule and some type of chemical separation is usually necessary. In this event, a chemical separation procedure can often be tailored to remove those contaminating activities having photopeaks which interfere with those of the short-lived isotopes of interest. As before, some means of determining fractional recovery of the element determined must be incorporated into the separation procedure.

By utilizing the methods outlined above, and the equipment described in the Chapters following, reasonably accurate analyses of a wide variety of samples can be performed by means of short-lived activities induced on neutron bombardment. Analyses by these methods have been performed successfully for silver, rhodium, and indium (167), copper (91), and cobalt (92) in a wide variety of matrices by means of their short-lived isotopes.

C. Techniques of Activation Analysis

The techniques required for activation determinations by means of short-lived isotopes utilizing facilities and equipment herein described perhaps can be best appreciated

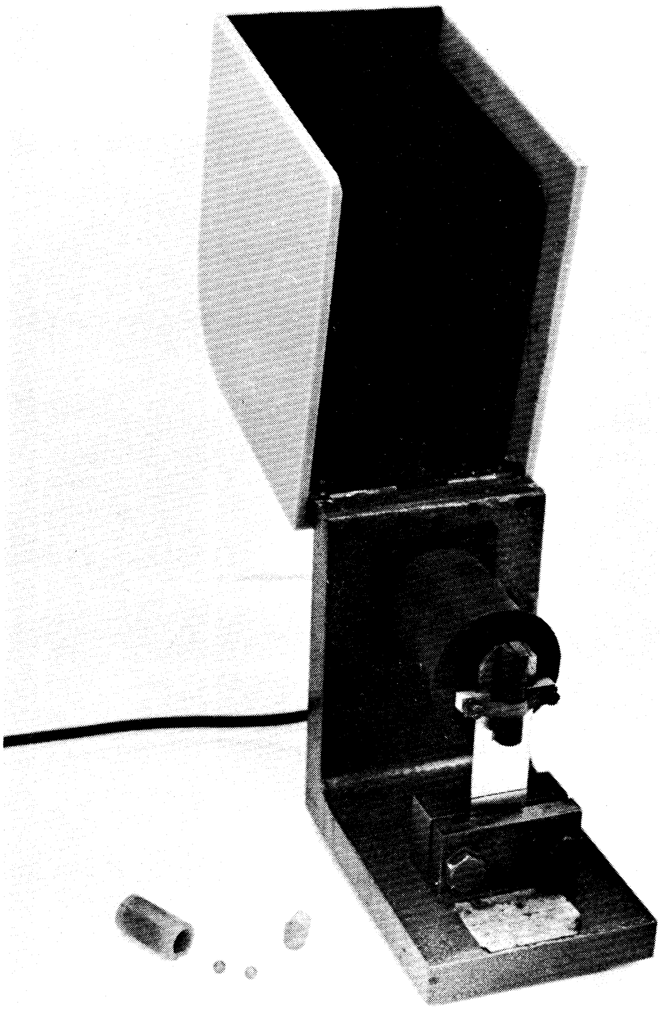


Figure 1. High Speed Vibration Mill with Agate Mortar and Balls.

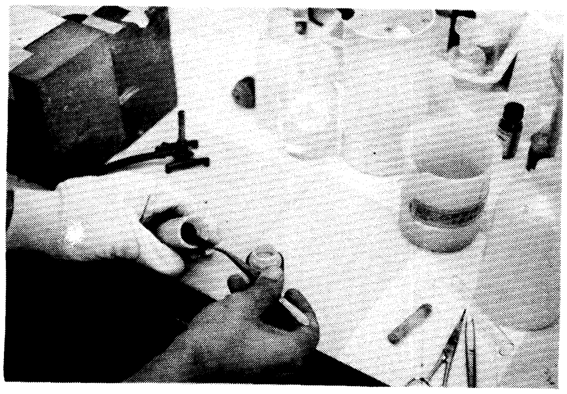
for placing in the reactor. A medicinal grade of polyethylene tubing - Intramedic Polyethylene Tubing (Medical Formulation PHF - PE 390, PE 410 or PE 430), Clay-Adams, Inc., New York - is used to contain samples, the ends being heat sealed readily over a micro burner. For certain types of samples, gelatine capsules also make convenient containers. The package containing the sample is then placed in an irradiation container, or "rabbit". The pictorial series following, Figure 2, a)-l), depicts the ensuing steps involved in a typical activation determination.

3. Calculation of Results

In order to obtain the results of an activation determination performed in a manner similar to the above illustrations, the numerical data is obtained from the tape and treated in the following manner: The photopeak of interest is located on the first cycle; the total number of counts under the photopeak is then obtained by summing the counts recorded in all of the channels comprising the peak. This total is then corrected for instrument dead time, as read from the dead time meter at the start of each counting cycle, as follows:

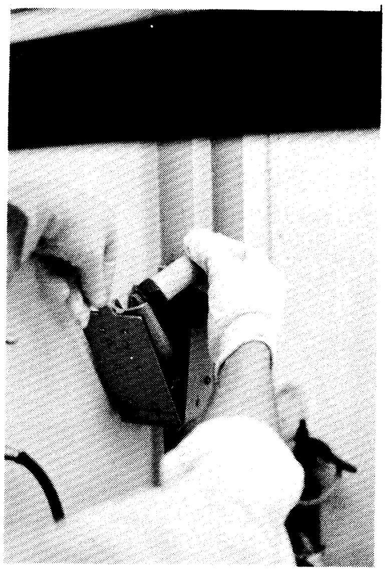
$$C = C_{obs} \times \frac{100}{100 - T} \qquad (22)$$

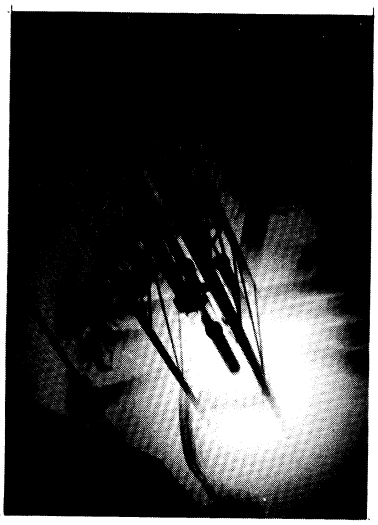
in which C = total count under the photopeak corrected for dead time.



a.) The sample is packaged in polyethylene or gelatine and placed in the irradiation container, or "rabbit."

b.) The "rabbit" is placed in the pneumatic tube system which carries it into the reactor, and...





c.) ...it is subjected to bombardment by neutrons for a predetermined period of time.

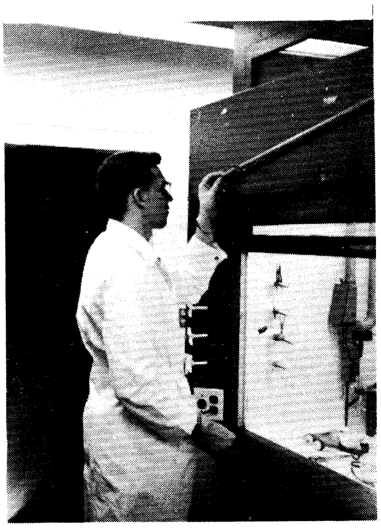
Figure 2. Pictures (a) through (l) Show a Typical Activation Determination Using Short-Lived Isotopes.

d.) The sample is returned automatically to the laboratory,

e). after which it is transferred to an inactive container for transfer through the secondary pneumatic tube system.

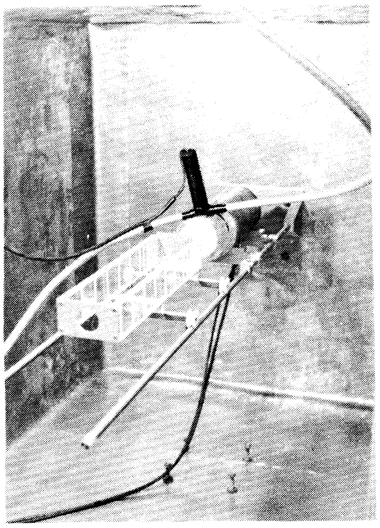
f.) A **chemical** separation may be necessary before transfer.

Figure 2. (Cont'd)



g.) The sample is loaded into the secondary pneumatic tube if the sample is solid.

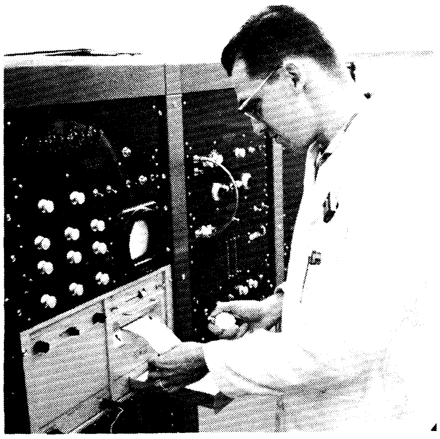
h.) If the separated counting sample is a liquid, the sample is carried to the counting room.

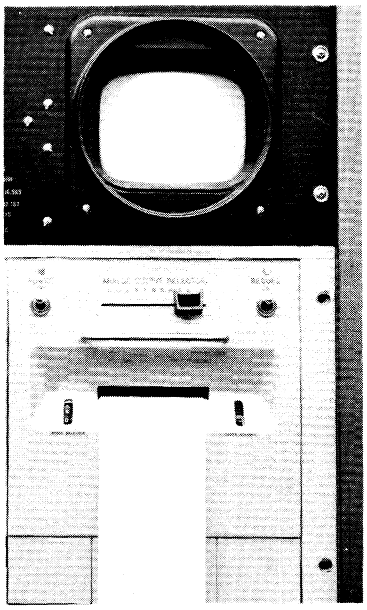


i.) Samples sent through the secondary system stop in the proper counting position in the cave which houses the scintillation detector.

Figure 2. (Cont'd)

j.) The dual 100-channel analyzer is started automatically by the sample, and...





k.) spectra are observed on the oscilloscope. Counts recorded in each channel during each counting cycle are recorded in digital form on tape...

l.) ...and plotted automatically by a linear x-y function plotter.

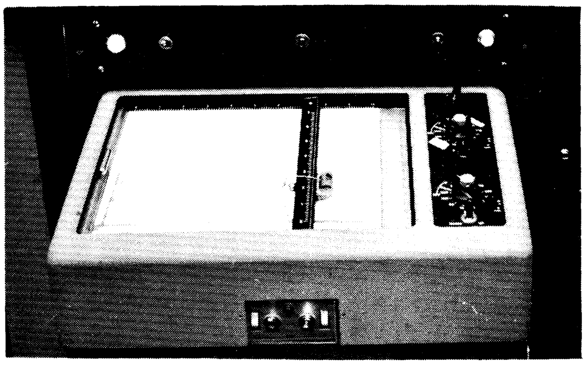


Figure 2. (Cont'd)

C_{obs} = total counts observed under the photopeak (obtained from the tapes).

T = observed dead time in percent.

The total count under the photopeak is then corrected for background, chemical yield and flux variations, and compared either to a standard curve, or to the counts under the photopeak produced by the activity induced in a single standard, in order to obtain the weight of element in the sample. Samples and standards must, of course, be irradiated and counted under identical conditions, and must be corrected for variations in neutron flux by means of monitor foils. It is also advisable to sum the counts under the photopeak for several successive cycles, making the necessary corrections for instrument dead time and background, and plotting these against time on semi-logarithmic paper in order to check the half-life of the photopeak. Several papers (34-36, 90, 107, 135) have appeared which provide an excellent discussion of the techniques of quantitative gamma spectroscopy and contain much information on the techniques and applications of the method.

CHAPTER III

FACILITIES FOR ACTIVATION ANALYSIS

The Ford Nuclear Reactor at the University of Michigan, and the Phoenix Memorial Laboratory building form an excellent, well integrated facility for work in activation analysis, especially that work which involves short-lived isotopes. This is made possible by pneumatic tubes which carry samples to the reactor and return them directly to hoods in the radiochemistry laboratory. This system is complemented by a small, secondary pneumatic system which allows transfer of an irradiated sample from the radiochemistry laboratory to a counting room in a matter of seconds. Use of these two systems allows transfer of samples from the reactor to the counting facility in well under one minute, thus forming an ideal arrangement for work with short-lived isotopes.

A. Ford Nuclear Reactor

This reactor is a swimming pool type of installation, the design of which is a modification of the Oak Ridge Bulk Shielding Facility. The core is heterogeneous, being composed of aluminum-clad enriched uranium plates, several of which are placed parallel to each other in the individual fuel elements. Surrounding the core on all four sides are graphite-filled aluminum cans which serve as neutron reflectors and moderator. This entire assembly is suspended in a large pool of water from a mobile bridge unit. The pool serves several functions, which include the following: it serves as a radiation shield, moderator, reactor coolant, neutron reflector, and a form of window through which the reactor core can be viewed.

Having gone critical in September, 1957, the reactor has been operating routinely at a power level of one megawatt since September, 1958. At this power level, the thermal neutron flux is of the order of 1×10^{13} neutrons-cm^{-2}-sec^{-1} within the core. Table I lists thermal neutron (2200 m/s) flux data for three of the four pneumatic tube exposure positions shown in Figure 3. The data are based on the activation of 1-mil thick gold foils weighing approximately 1.5 milligrams or less, and irradiated for various (short) lengths of time. The thermal cross-section for gold is taken as 98 barns (83). The values for the flux were obtained using Equations (19) or (20), solving for ϕ.

TABLE I

THERMAL NEUTRON FLUX DATA IN PNEUMATIC TUBES

Tube No.	Relative Thermal Neutron Activity	Thermal Neutron Flux (n-cm^{-2}-sec^{-1})	Cadmium Ratio
1	1.000	1.76×10^{12}	—
2	0.705	1.24×10^{12}	14.7
3	0.52	0.92×10^{12}	14.8

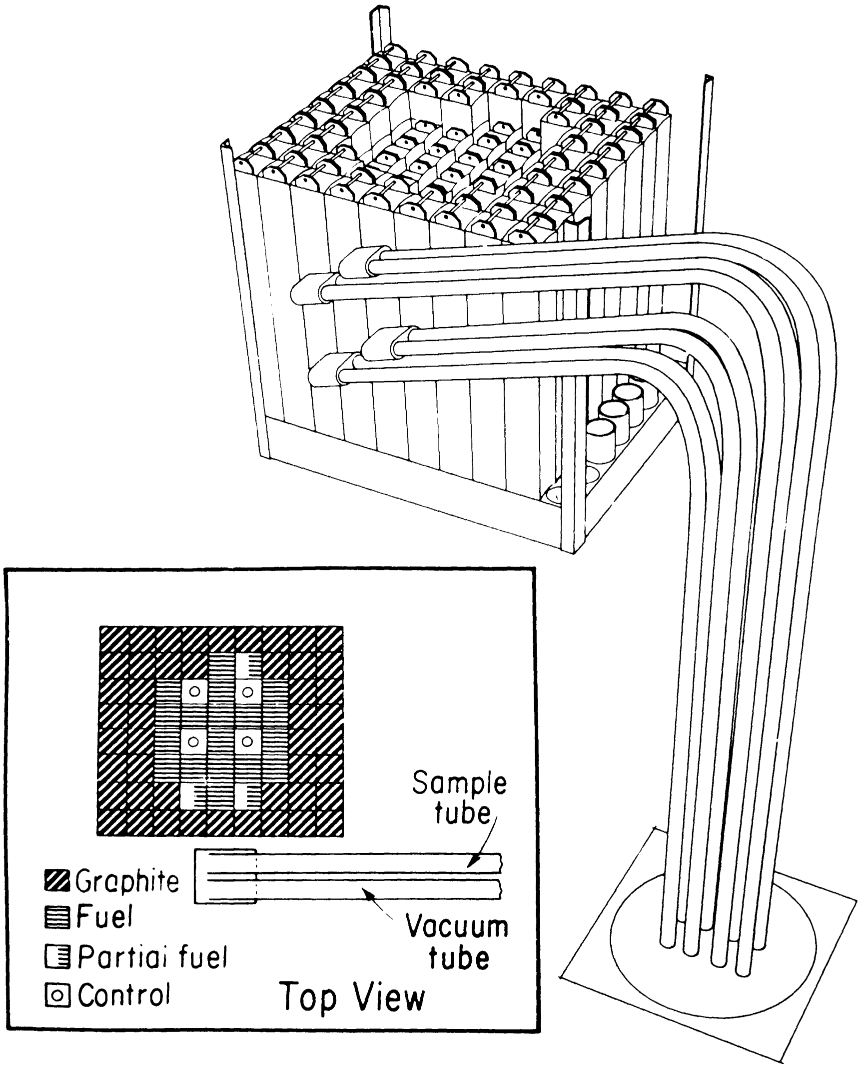


Figure 3   Schematic Diagram of Reactor Core.

The cadmium ratio, R_{cd}, is defined by the expression (81):

$$R_{cd} = \frac{A_{cd}}{A_{bare}} \qquad (23)$$

in which A_{cd} is the activity of a foil covered with cadmium, expressed as counts per minute per milligram of gold, and A_{bare} is the activity of the uncovered foil, also expressed as counts per minute per milligram of gold. The cadmium ratios reported in Table I were determined using gold foils enclosed in a cadmium envelope 20-mils thick.

Figure 4 is a plot of routine flux measurements taken in tube 2 with the reactor operating at a power level of 1000 kilowatts. The precision of the individual points should be no worse than ± 3 percent, based on errors in foil weighing, positioning in the irradiation container, and counting the samples. As before, gold foils 1-mil thick and weighing not more than 1.5 milligrams were irradiated to give counting rates within the useful range of the scintillation well counter. No corrections for self-shielding or flux depression by the sample have been made, since these should remain relatively constant for foils of the same thickness, weight, and relative positioning within the irradiation container. The configuration of the fuel rods and graphite moderator-reflectors in the core remains constant, except for special experimental runs. The

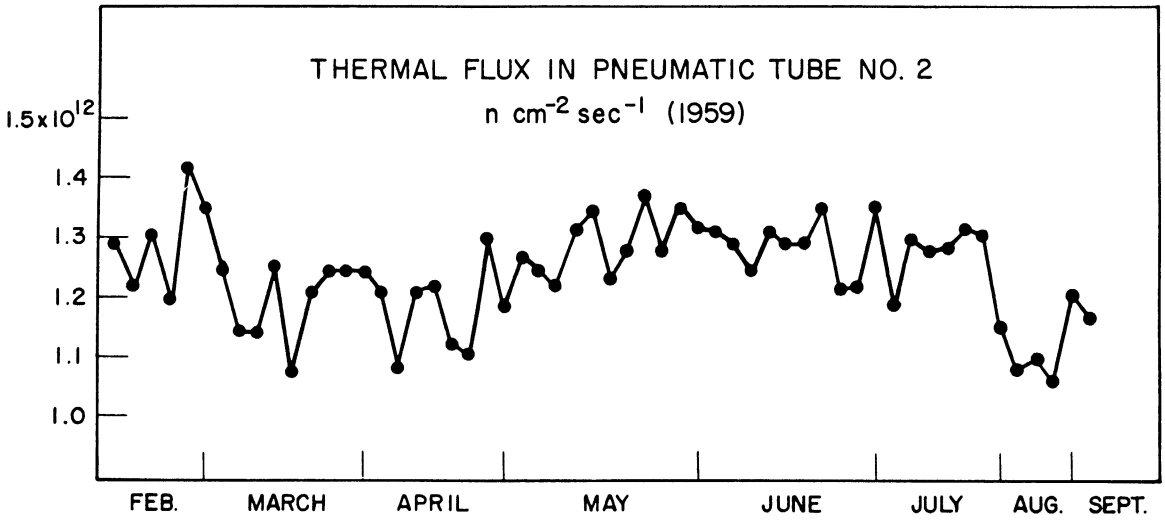


Figure 4. Thermal Flux in Pneumatic Tubes.

configuration presently in use is shown in the inset in Figure 3. With the reactor operating at a power level of 1000 kilowatts, the variation in power level has been found not to exceed 10-percent, thus giving rise to variations of the same order of magnitude in the measured flux.

In order to estimate the extent to which reactions such as the (n,p) and (n,α) reactions can interfere with the (n,γ) reaction during activation analysis, a knowledge of the fast flux at the pneumatic tube positions is necessary. After considering the standard threshold reaction (82, 194), the decay schemes of the radioisotopes involved, and the relatively short half-lives of some of the radioactive products, it was decided (196) that absolute gamma spectrometry of the foils, involving no chemical separation, would be the most advantageous counting technique. The reactions utilized for these determinations were:

$$Al^{27}(n,p)Mg^{27}$$
$$Mg^{24}(n,p)Na^{24}$$
$$Al^{27}(n,\alpha)Na^{24}$$

Experiment and calculation (196) proved that in the high purity foils used, any activities produced by the (n,γ) reaction involving impurities in the foils were below a detectable level.

The fast flux values, obtained after making suitable corrections for geometry, counting efficiency, decay schemes, and peak-to-total ratio, are given in Table II, along with the threshold energies for each of the reactions studied. The ratios of activity from fast neutron reactions in the pneumatic tubes were found to be close to the ratios for the thermal neutron flux listed in Table I. These ratios were combined with absolute flux measurements in tube 3 and form the basis for the flux values listed in Table II.

TABLE II

FAST FLUX DATA IN PNEUMATIC TUBES

		Fast Flux, n-cm^{-2}-sec^{-1}		
Tube No.	Relative Flux	$Al^{27}(n,p)Mg^{27}$ E_n 5.3 Mev	$Mg^{24}(n,p)Na^{24}$ E_n 6.3 Mev	$Al^{27}(n,\alpha)Na^{24}$ E_n 8.6 Mev
1	1.00	9.15×10^9	4.62×10^9	12.02×10^8
2	0.705	6.45×10^9	3.25×10^9	8.47×10^8
3	0.52	$4.76 \pm 0.26 \times 10^9$	$2.40 \pm 0.25 \times 10^9$	$6.25 \pm 0.25 \times 10^9$

At the relatively high neutron energies involved in these measurements, the shape of the fission spectrum (37) is approximated, even in the presence of a considerable amount of moderator. Thus, all three of the values listed for each pneumatic tube in Table II fall on the fission spectrum.

Experiments (196) conducted at power levels of five watts and 100 kilowatts have shown the existence of a flux inhomogeneity at the pneumatic tube positions. Variations of flux of approximately 8-percent along the length of the rabbit and approximately 30-percent from side to side have been observed. The self-shielding of the gold foils and the plastic rabbit appear to be negligible. These results are not inconsistent with the relative geometry of the pneumatic tube positions and the neutron flux attenuation in the water moderator. These data reveal that a certain amount of care must be exercised in positioning samples and flux monitors in the rabbit to insure a measure of reproducibility from one experiment to the next.

B. Pneumatic Tube System

The pneumatic tube system (1) provides for rapid delivery of samples to and from the proximity of the reactor. This is performed by a system of tubes which run from the reactor to laboratories in the Phoenix Building and the Reactor Building. The system has four irradiation positions at the reactor core, as shown in Figure 3. Eight possible sending stations are available, six in the Phoenix Building and two in the Reactor Building. These stations can be connected with any reactor irradiation position by means of the interchange system shown in Figure 5, located in the heat exchanger room under the beam port floor.

Samples to be irradiated in the pneumatic tube system are transported from the hoods in the radiochemistry laboratory in one of several types of sample carrier, or "rabbit" The rabbits supplied by Airmatics Systems Corporation were fabricated of aluminum, having a several-turn screw cap, and felt gaskets and bumpers. These proved unsatisfactory in that they became too radioactive to allow direct handling following irradiation. In addition, for work with short-lived isotopes, the several-turn screw cap was too cumbersome to allow rapid opening. In order to circumvent these disadvantages, quick opening rabbits were machined from nylon rod. These are simply pulled apart following removal from the reactor. The press fit of the top is sufficiently tight to prevent opening in the pneumatic tube, yet the rabbit can be pulled apart easily and rapidly to remove the sample. Figure 6A shows the construction details for the quick opening rabbits, while Figure 6B pictures these nylon rabbits and the Lustroid rabbits described below.

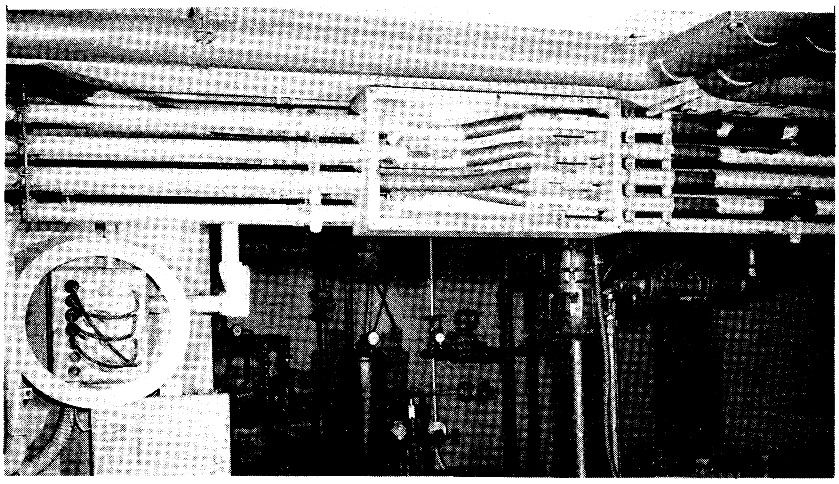


Figure 5. Pneumatic Tube Interchange.

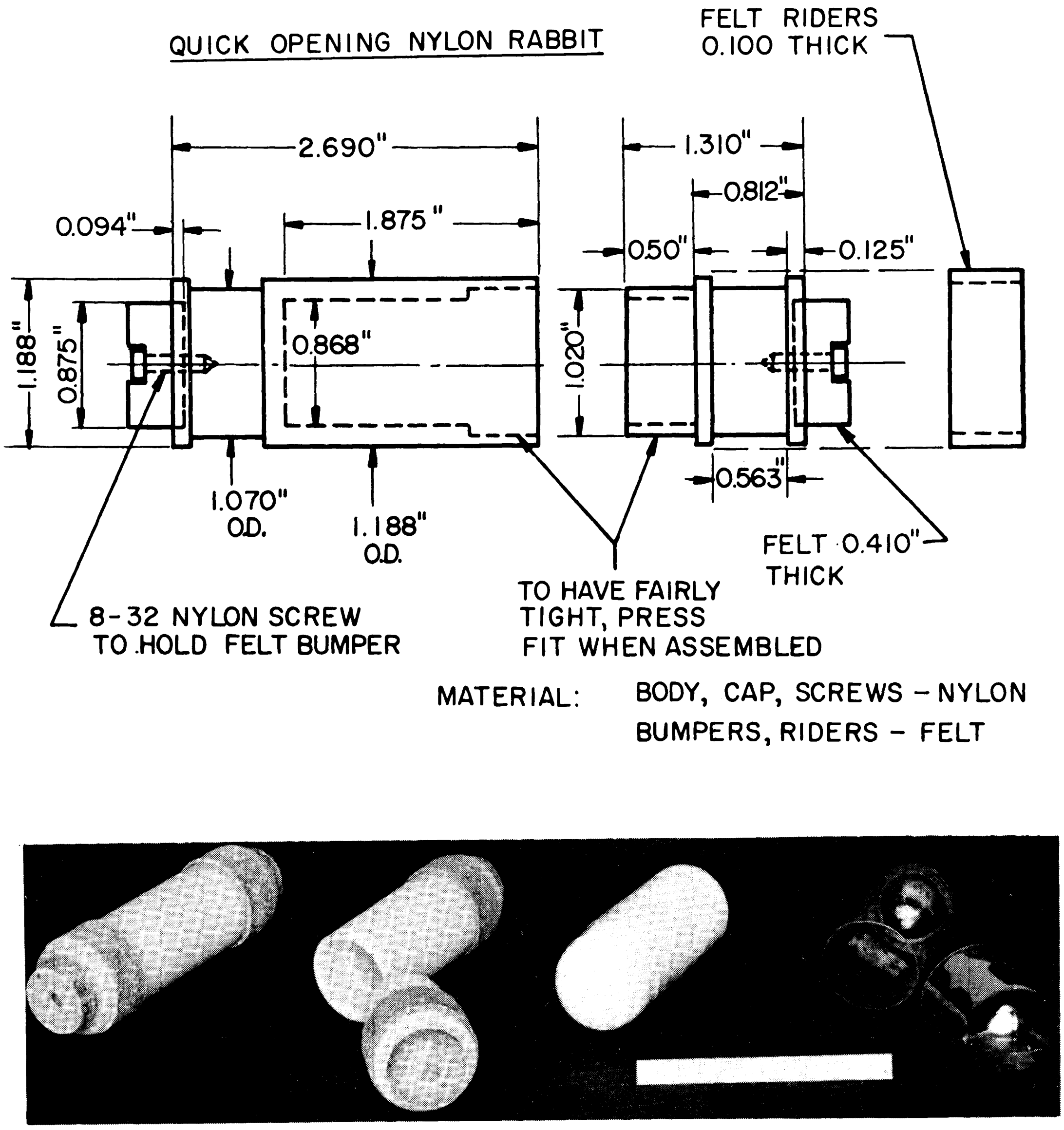


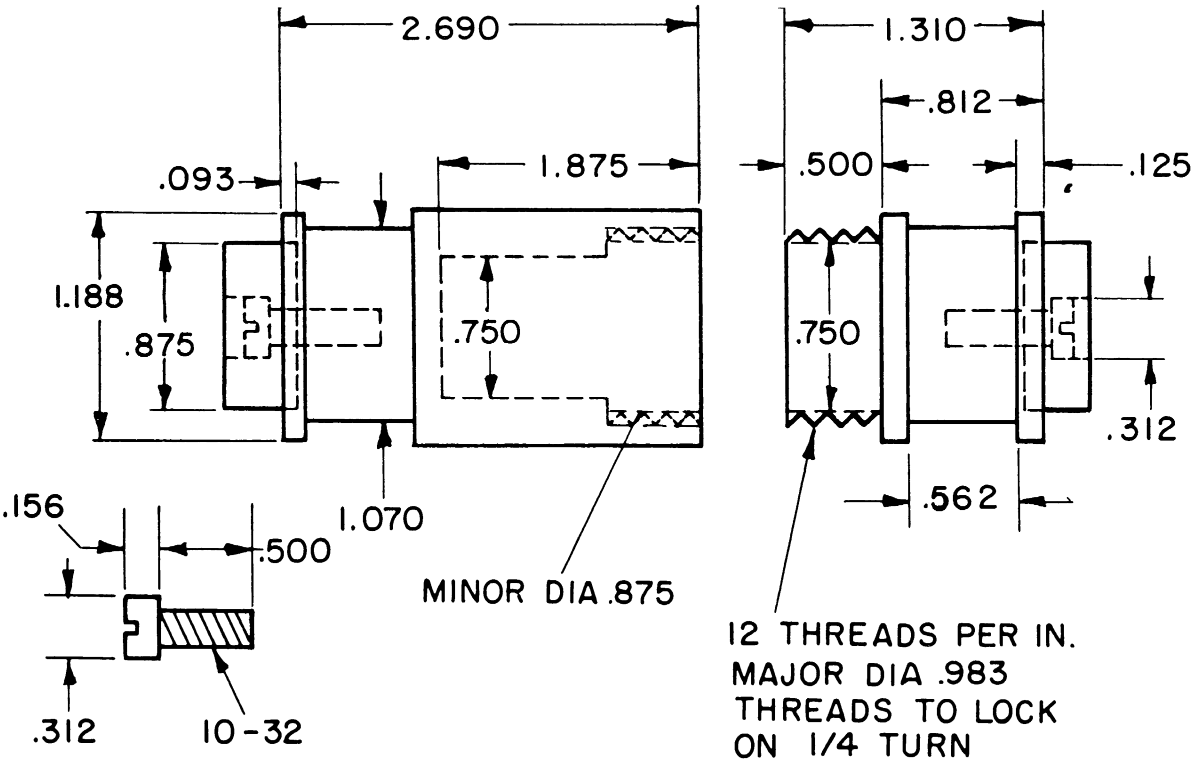
Figure 6. (A) Quick Opening Nylon Rabbit.
(B) Nylon and Lustroid Rabbits.

After several hours of irradiation at full power, it was found that the nylon bodies of the quick opening rabbits became quite brittle and developed cracks. In addition, a few of these have come apart in the pneumatic tube system, causing some concern on the part of the reactor operators. As a result, a new type of rabbit was designed, having a threaded cap which locks with a quarter turn. These were fabricated from irradiated polyethylene rod (4), and have been found to last 3-4 times longer than the original nylon rabbits. Figure 7 gives the construction details of these newer rabbits.

While the nylon for the original rabbits was chosen because of the low activity induced on irradiation, the dosage rates from the polyethylene rabbit bodies (felt gaskets and bumpers removed) are not much greater than for the nylon rabbit bodies. Dosage rates of the two materials are compared in Table III. These dosage values are still low enough to permit hand catching of the rabbits on removal from the reactor. However, it is advisable to make regular use of finger films to monitor the amount of dosage to which the hands are subjected while handling the rabbits and samples.

Simple Lustroid rabbits 1-1/4 inch diameter and 3-1/2 inches long (Figure 6B), consisting of two Lustroid tubes taped together, are also used for certain irradiations. The weights of these rabbits must exceed 20 grams; if they are any lighter, the rabbits may not open the exit door of the

QUICK OPENING POLYETHYLENE RABBIT



MATERIAL: BODY, CAP - POLYETHYLENE
SCREWS - NYLON
BUMPERS, RIDERS - FELT

Figure 7. Quick Opening Polyethylene Rabbit.

TABLE III

DOSAGE FROM RABBITS

Irradiation Time	Surface Dose Rates* (mr/hr) Polyethylene	Nylon
15 sec.	35	30
1 min.	140	100
2.5 min.	260	200
5 min.	310	250

---

*Measurements made 3 sec. after irradiation at 1000 kilowatts

pneumatic tube system sufficiently wide to break the vacuum and may be sucked back into the tube.

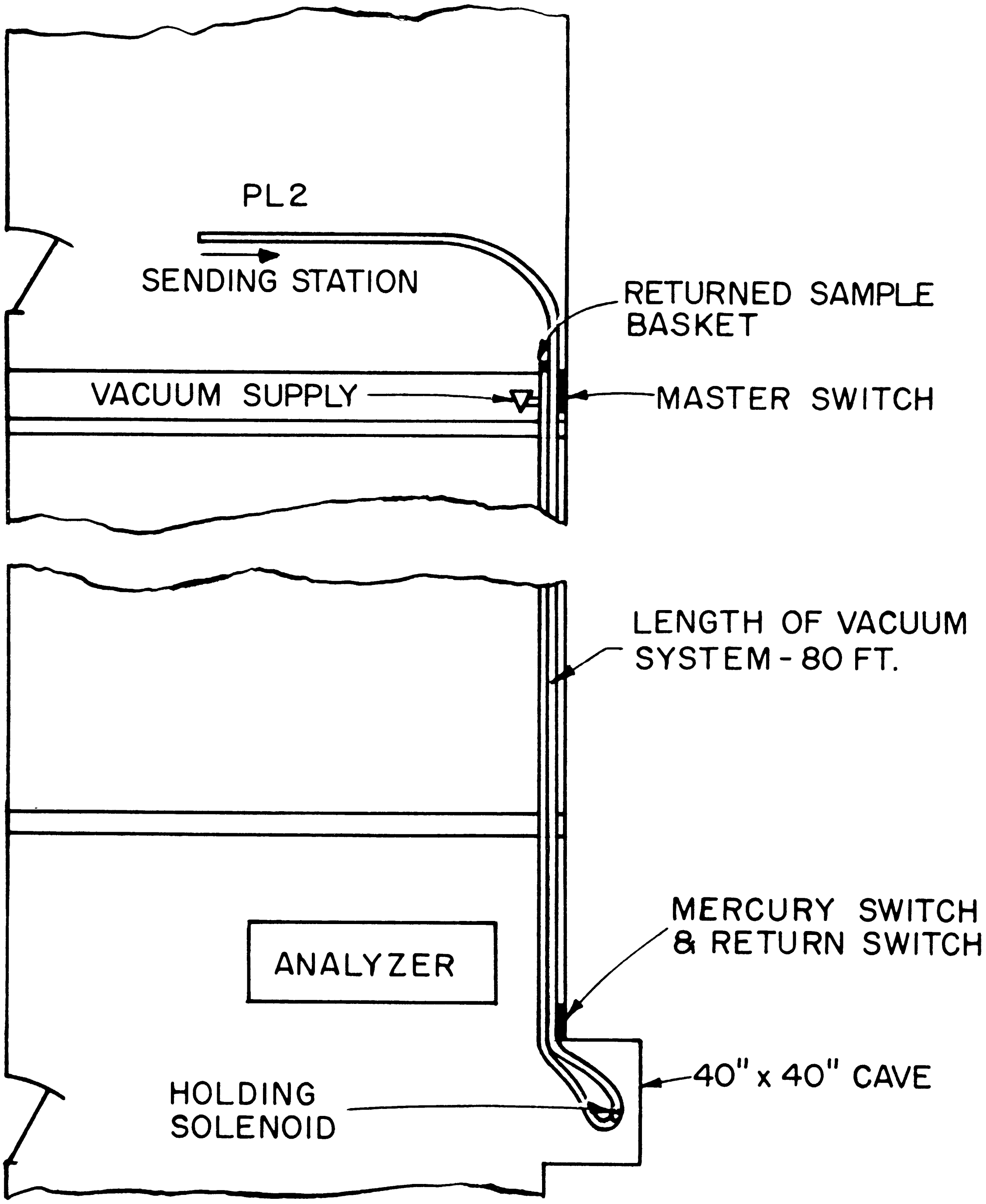
In general, the pneumatic tube system has operated rather efficiently and effectively through all but a small percentage of its approximately two year life. Minor problems have arisen due to corrosion of the microswitches which are used to energize or de-energize the relays controlling the vacuum. Also, small pieces of felt have broken away from the bumpers on the rabbits occassionally and become lodged in the vacuum system, thus resulting in an increase in the transit time of rabbits to and from the reactor above the usual three seconds. These difficulties have been remedied readily once the cause of the trouble was discovered.

C. "Bunny Rabbit" Pneumatic System

At the outset of the work involving short-lived isotopes, samples removed from the reactor had to be transported rapidly on foot some ninety feet from the radiochemistry laboratory to the room containing the 100-channel analyzer and associated counting equipment. This method of sample transportation has several disadvantages, among them the time required for transit, and the ever-present possibility of a spill, especially when the counting sample is in the liquid form. In an effort to overcome these objections, a 1-3/4 inch by 2-inch scintillation detector assembly, shielded by four inches of lead, was placed on the floor of the radiochemistry laboratory adjacent to hoods containing pneumatic tube terminals. With this arrangement, spectral measurements of irradiated samples could be started within a few seconds of their removal from the reactor. However, the sensitivity which could be attained with this detector was somewhat less than desirable due to its relatively low counting efficiency and the relatively high background of radiation present in the laboratory. A larger detector would have increased the detector efficiency, but would also have increased the background. Clearly, then, a larger detector for the radiochemistry laboratory was not the answer.

The answer to the transfer problem has been provided at least in part, by the installation of a secondary pneumatic tube system, named the "bunny rabbit" tube, connecting the laboratory with the 3-inch by 3-inch detector in its cave in the counting room. The system has the form of a loop starting in the laboratory, spiraling down into the detector cave, and then returning to the laboratory. The layout of the system is shown diagrammatically in Figure 8. The pneumatic tube itself is formed from 1/2-inch (i.d.) aluminum tubing used in aircraft fuel lines. Straight portions are made with hard tubing, and the bends of softer material. The whole is powered by a vacuum cleaner motor developing a negative pressure equivalent to approximately six inches of water.

The samples, once they are removed from the reactor pneumatic tube system, are transferred to small polyethylene test tubes which serve as rabbits in the bunny system. These are then placed in the bunny system, the entrance of which is located above a hood in the radiochemistry laboratory. The "send" control is located immediately before the entrance to the system, such that it can be activated as the sample is inserted. The sample then is transported to the counting room, the 90-foot trip requiring approximately two seconds. The samples are stopped at the detector position in the cave by a forked plunger, causing the pressure in the system to drop. This drop in pressure activates a mercury-filled pressure switch, closing the circuit which automatically starts the 100-channel analyzer, and shuts off the vacuum. The auto-start circuitry is described in Chapter IV; the



MATERIAL: 12-FOOT LENGTHS–ALUMINUM TYPE 20-24 T3,
ID 0.590", OD 0.625"
BENDS-ALUMINUM TYPE SO
COUPLINGS-ALUMINUM TYPE 20-24 T3, 3/4"
SEALING COMPOUND, GLYPTAL 1201, RED

Figure 8. "Bunny Rabbit" Pneumatic Tube Layout.

"bunny rabbit" pneumatic control circuits are shown in Figure 9. After the sample has been counted and analyzed, it is returned to the radiochemistry laboratory; the "return" control, located in the counting room, activates the solenoid which raises the forked plunger, and starts the vacuum cleaner motor. The sample is returned to the laboratory, where it is received in a basket at the terminus of the system. The vacuum is shut off on releasing the "return" control. The master control unit, allowing normal or continuous operation of the vacuum system, is located in the radiochemistry laboratory.

Installation of the bunny rabbit pneumatic system has made possible the study of radionuclides having half-lives of the order of seconds. In a typical experiment, the time lapse between removal of the sample from the reactor and the start of spectral analysis can be broken down into the following periods; approximately three seconds from reactor to hood, ten seconds for transfer of the sample to an inactive rabbit, and one to two seconds from laboratory to counting room. The total time lapse, therefore can be as short as 15 seconds, thus allowing work with isotopes down to the 11-second fluorine-20. The auto-start circuit allows an experimenter to control the analyzer from the laboratory once it has been placed in auto-start mode. Thus an experiment can be performed using very short-lived isotopes without assistance from the counting room.

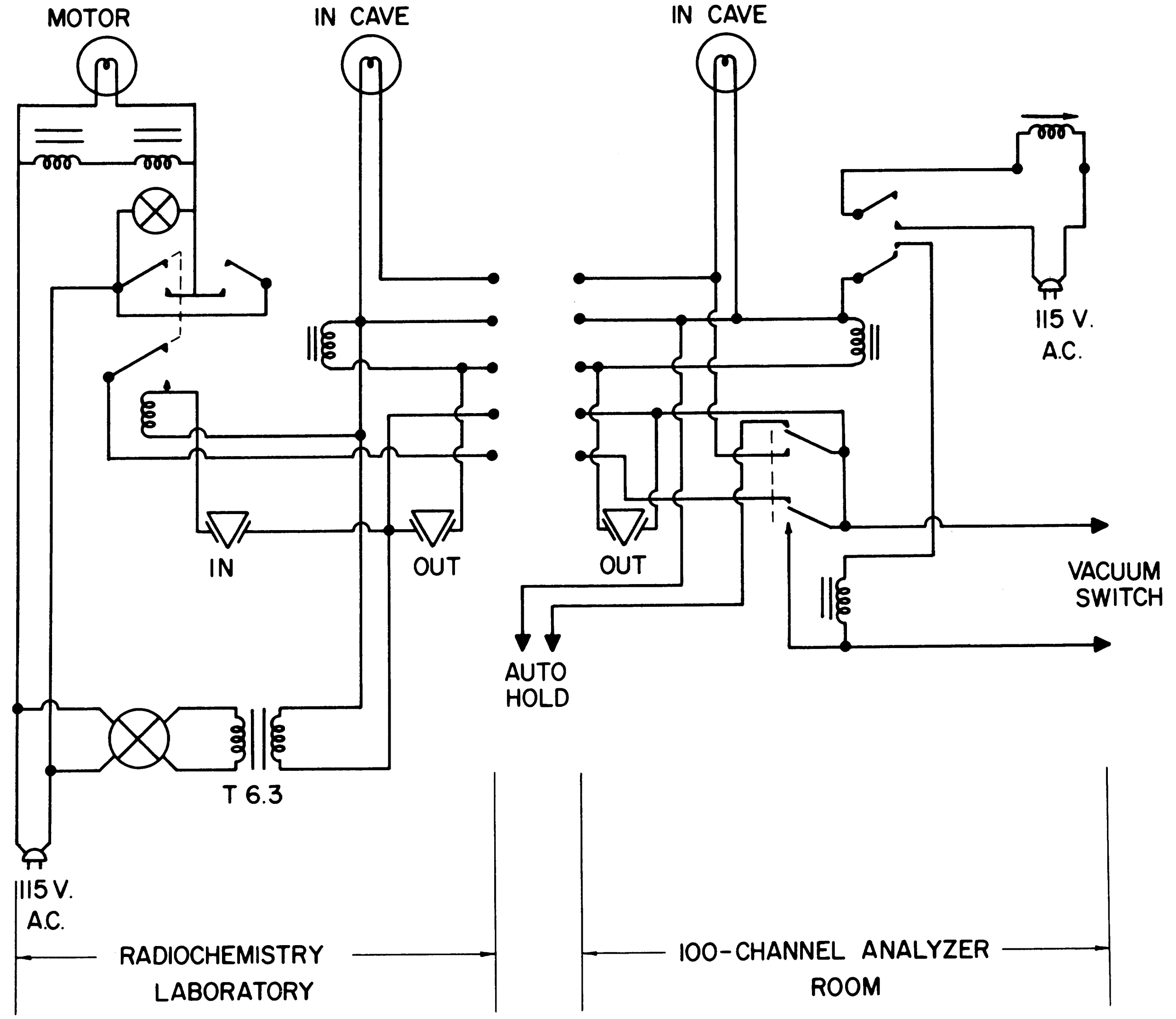


Figure 9. "Bunny Rabbit" Control Circuits.

CHAPTER IV

INSTRUMENTATION

The Ford Nuclear Reactor and the associated pneumatic tubes form a well integrated facility for work with short-lived radioisotopes. In order to utilize these facilities to the fullest extent, a rapid means of measuring or analyzing spectra is necessary. Prior to the start of the present investigations, scintillation and proportional counter detectors were available and in operation in these laboratories. They were, however, operated in conjunction with single-channel automatic sweep equipment which require a considerable amount of time to record a single spectrum. What was needed, then, was a multi-channel analyzer capable of analyzing spectra from radioisotopes having half-lives of the order of a few minutes or even several seconds. The unit finally obtained is described below, together with other counting equipment used in work with short-lived radioisotopes.

A. 100-Channel Pulse Height Analyzer

Several types of analyzers were considered (130), and included multi-channel analyzers with computer-type memories and multichannel analyzers with a visual register type of read-out.

Since there was no easy, reliable way to record spectra consecutively at short intervals, the latter type of analyzer was eliminated. This left the computer-type analyzer as the best type of instrument for work with short-lived isotopes. There were still some disadvantages to this type of instrument, however, with regard to the rapidity with which data could be read. The major limitation appeared to be in the type of printer available, and in devising a system for fast print-out of the information retained in the memory system. An answer to the problem was provided by the Radiation Instrument Development Laboratory of Chicago, who suggested an instrument with a dual memory system. In this proposed instrument, one of the magnetic core memory systems would store information in the form of pulses of various heights fed to it by the detector, while the second memory unit fed its stored information to a high speed printer. The units would then reverse functions at the end of a pre-set counting cycle.

1. Description

The instrument used in these laboratories is shown in Figure 10. It consists of a three-section double width relay rack six feet in height, which houses the following component sub-assemblies, reading from top to bottom, left to right: electronic timer, oscilloscope, high speed printer, printer control, x-y plotter, converter power supply, memory power supply; linear amplifier and pulse generator, converter, address scaler and "A" memory control, master input power controls, "A" memory unit and address current generator; detector high voltage supply, detector patch panel, address

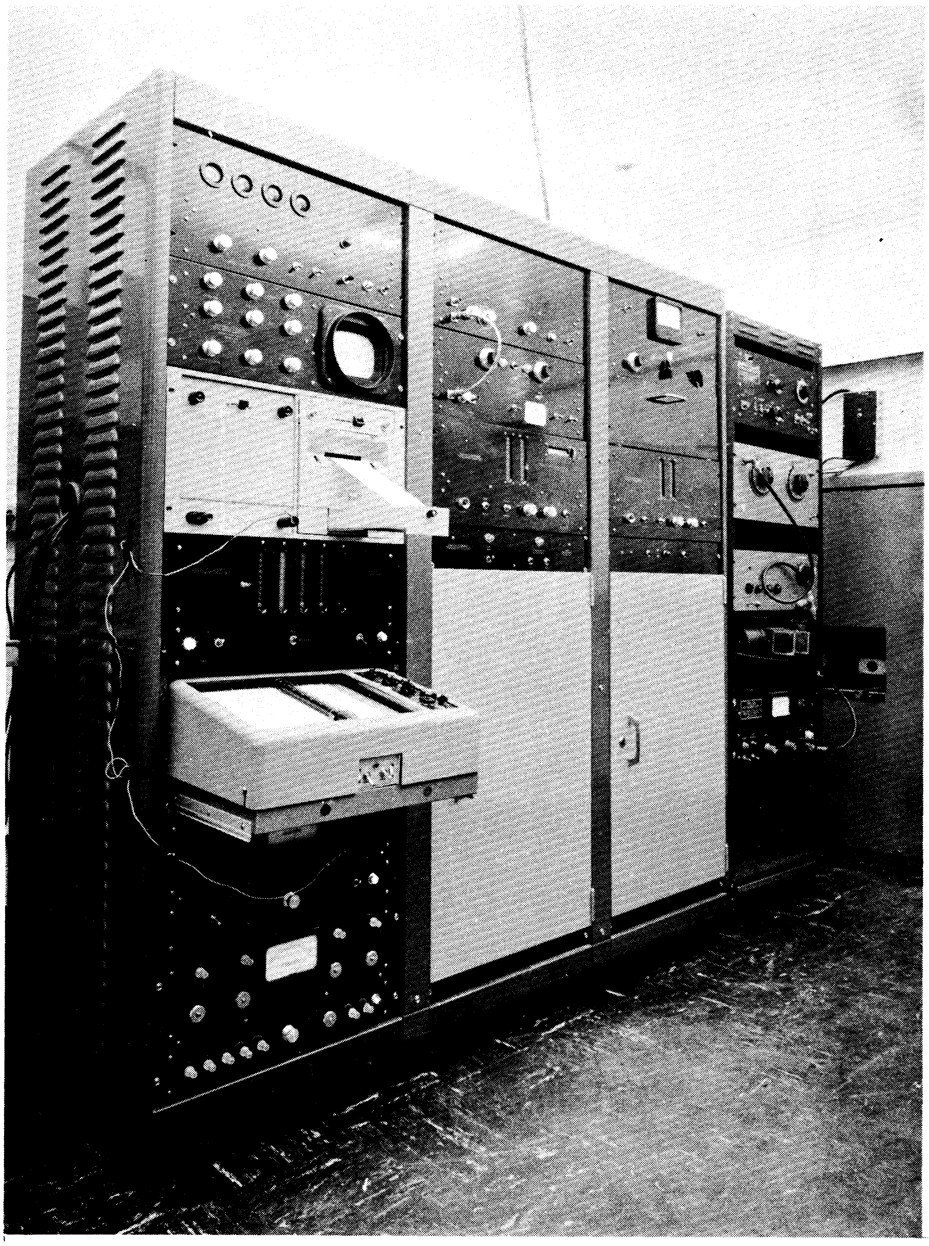


Figure 10. Dual Memory 100-Channel Analyzer.

scaler and "B" memory control, automatic start controls, and "B" memory unit and address current generator. The relationships of these units each to the other is shown schematically in the block diagram in Figure 11.

The analyzer consists of an analog-to-digit converter, a simple ferrite magnetic-core-memory type digital computer, and a data display system. It is a high speed unit designed to scan random voltage pulses, fed to it from a detector, which have a wide range of amplitudes and wave forms. These pulses are sorted on the basis of their amplitudes into any one of one hundred channels. The data, or pulses, so sorted, are stored in the memory in binary form, each channel being capable of storing a maximum of $2^{16}-1$, or 65,535 counts. The dead time of the unit is approximately (16 + 0.5N) microseconds, where N is the channel number in which the count is being stored.

The unit as provided can be used as either a single 100-channel analyzer or as an automatic dual 100-channel analyzer, in which role it is used most frequently. The major advantage of the analyzer, operating in the automatic mode, lies in its ability to record consecutive spectra for short-lived isotopes without losing data through the "dead" time of one second per channel associated with the printing cycle of an ordinary 100-channel analyzer. Since a special high speed printer (Hewlett-Packard Digit Recorder, Model 560A) is used, a complete print-out cycle for the data

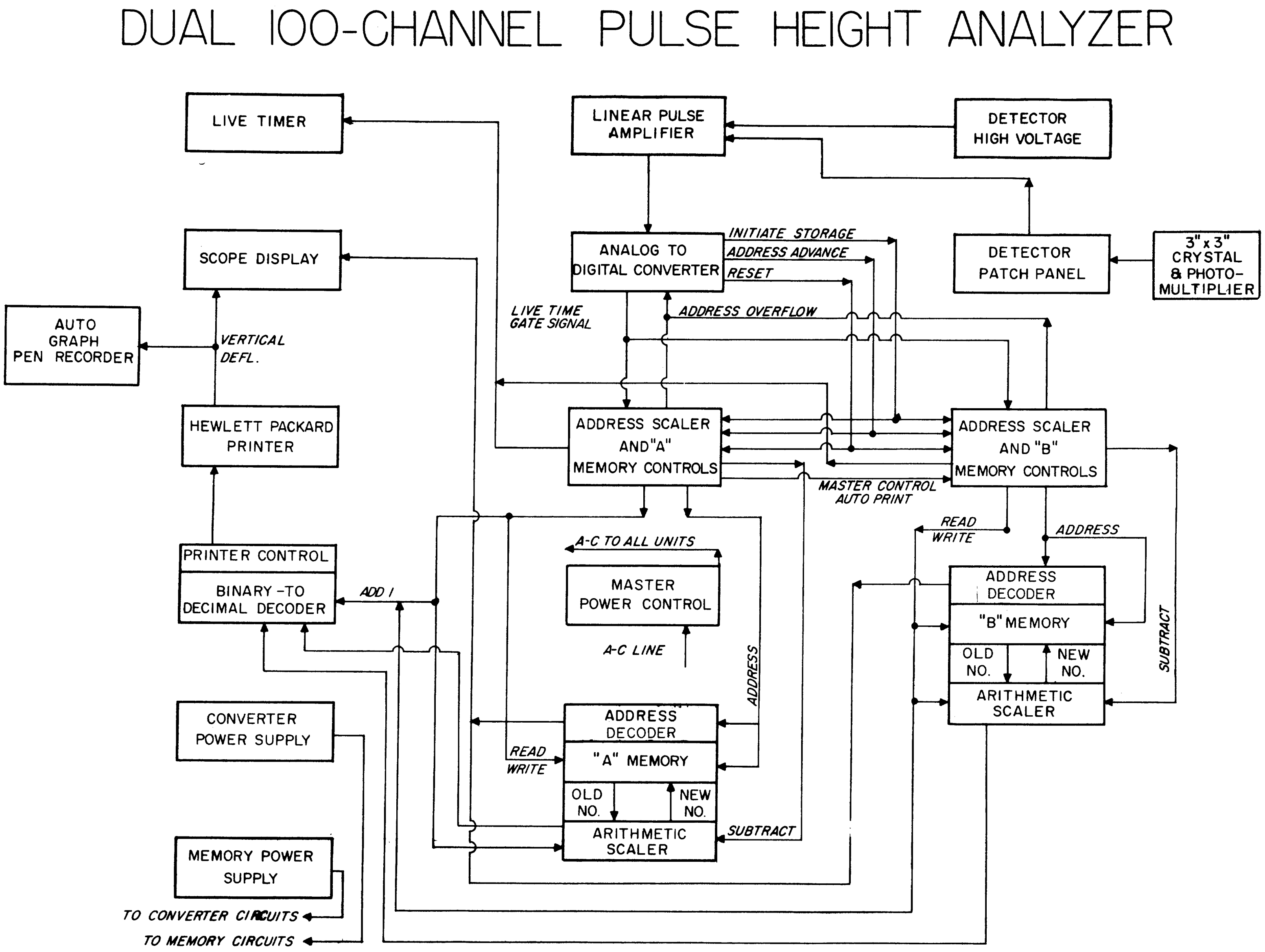


Figure 11. Block Diagram of 100-Channel Analyzer.

contained in the full one-hundred channels requires approximately twenty-four seconds. By adjusting the limit controls (I2 and I4, Figure 54), however, a short-lived peak may be shifted down to the first 20-30 channels, whereupon the data can be printed out in the order of six to ten seconds. Operation of the analyzer in this manner allows measurement of radioisotopes with half-lives of the order of six seconds with ease. The 7.4-second gold isomer, Au^{197m}, and the 10.7-second fluorine isotope, F^{20}, can be observed with little difficulty. The only limitation encountered is the time necessary to transfer the sample from the rabbit in which it was irradiated to a detector in the counting room or in the radiochemical laboratory.

In automatic operation, the "A" unit receives and stores information from the detector, while the "B" unit remains in a standby condition. At the end of the store cycle, the "A" memory feeds its stored information to the high speed printer, and then to an x-y plotter (F. L. Mosley Co., Pasadena, California, Model 3 Autograf X-Y Recorder), shown in operation in Figure 12 and 13. Data is thus presented in digital form on tape, and plotted on a standard-sized linear graph. While the "A" unit is printing out, the "B" memory stores pulses from the detector. The functions of the two units are reversed following the end of the second store cycle, and the "B" unit prints and plots its information. This cyclic operation is repeated for as long as the

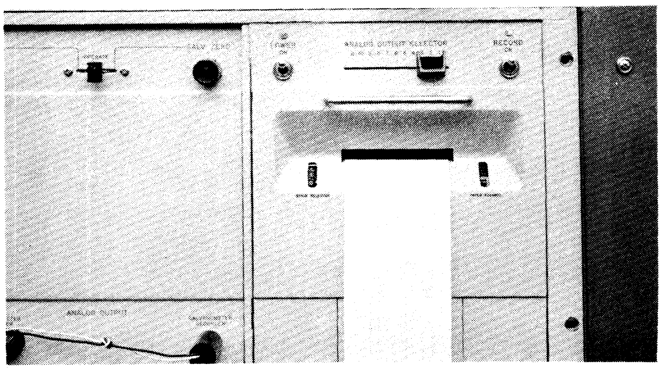


Figure 12. Hewlett-Packard High Speed Printer.

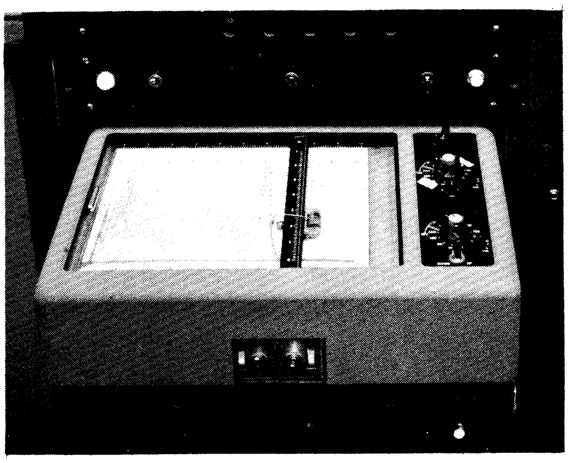


Figure 13. Mosley Autograf X-Y Recorder.

experimenter wishes; consecutive spectra are recorded in integral multiples of ten from 0.1 minute to 1000 minutes, providing a complete picture of the decay of short-lived radioisotopes, such as that shown in Figure 14.

The versatility of the dual 100-channel analyzer is further increased by means of the detector patch panel (Figure 15). By means of this panel, any one of the several detectors available can be coupled to the analyzer or the multi-scaler unti (Nuclear Chemical and Instrument Co., Chicago, Model 162), normally used to record the output of a 1-3/4-inch x 2-inch scintillation-well crystal (Harshaw Chemical Co., Cleveland, Ohio, Type 7F8). In addition, two remote detectors, one in the radiochemistry laboratory, the other on the beam port floor of the reactor building, can be used in conjunction with the analyzer.

Contained in a small chassis located behind the detector patch panel are several auxiliary circuits, Figure 16, which further increase the versatility of the instrument. This unit houses a summing circuit, coincidence signal inverting circuit, and an alternator electronic switch.

The summing circuit, due to Hoogenboom (77), is used in sum-coincidence work, and measures the spectra of gamma radiation emitted in cascade disintegrations. Use is made of a two-crystal scintillation spectrometer with the input to the 100-channel analyzer gated by a single-channel pulse height analyzer. The output of the single-channel analyzer

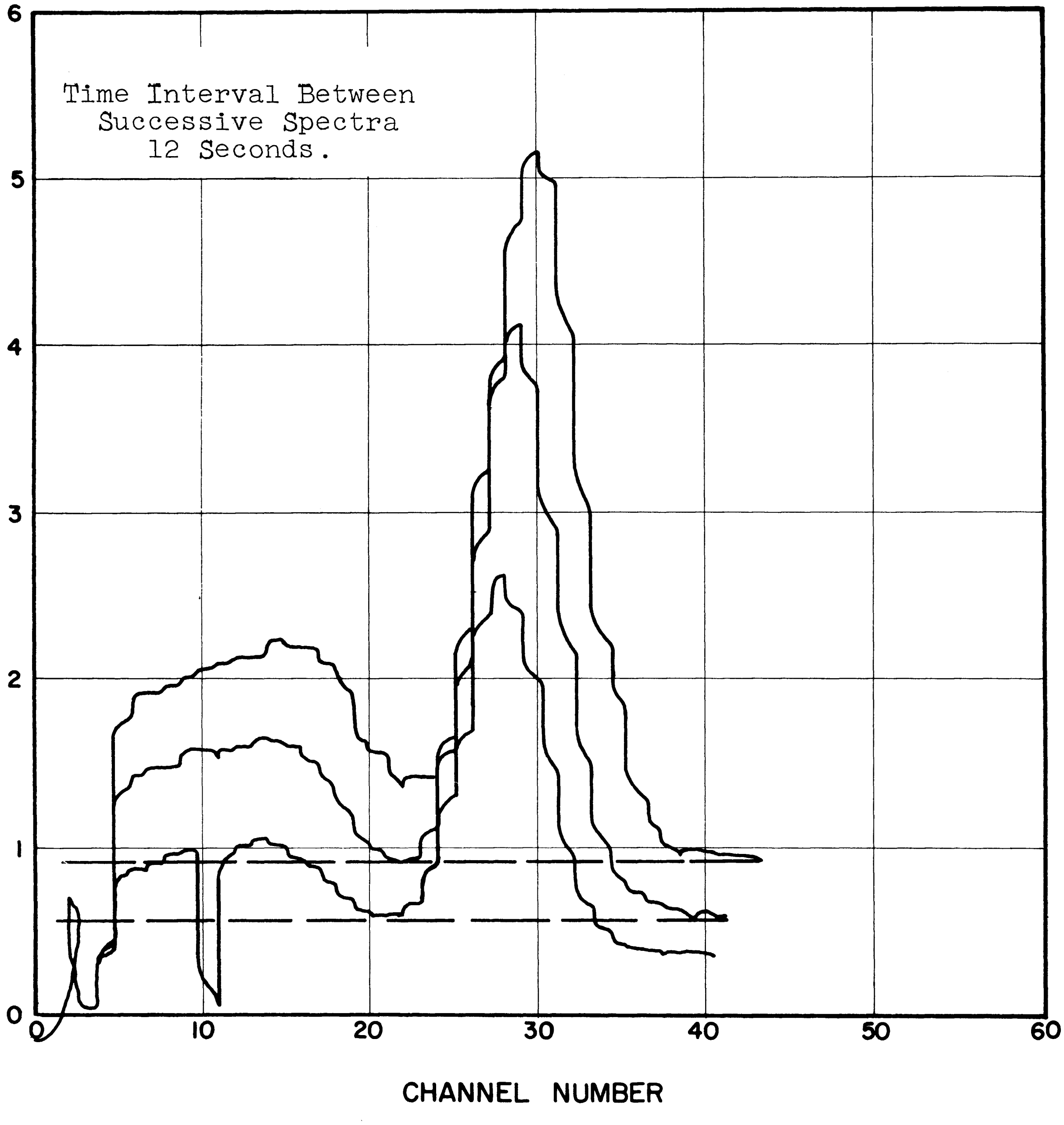


Figure 14. Decay of 10.7-Second Fluorine-20.

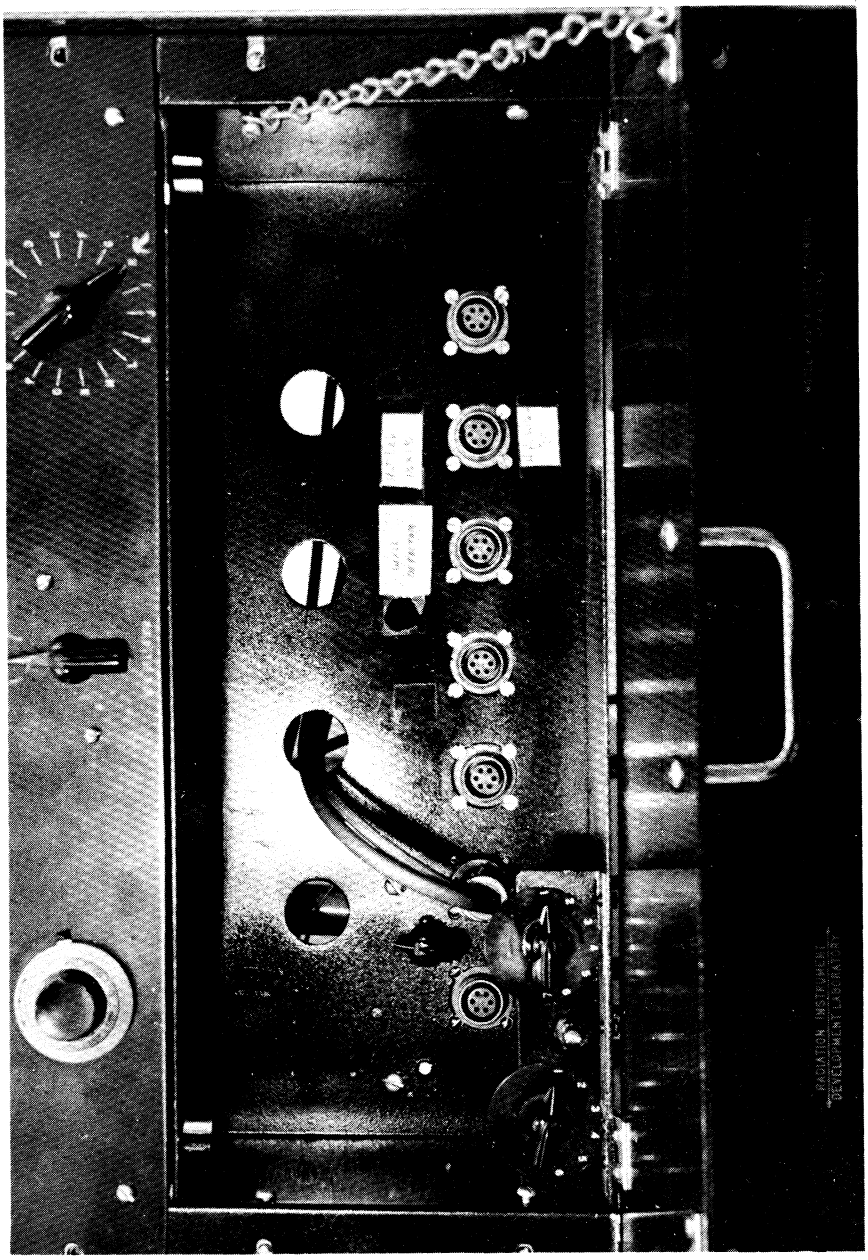


Figure 15. Detector Patch Panel.

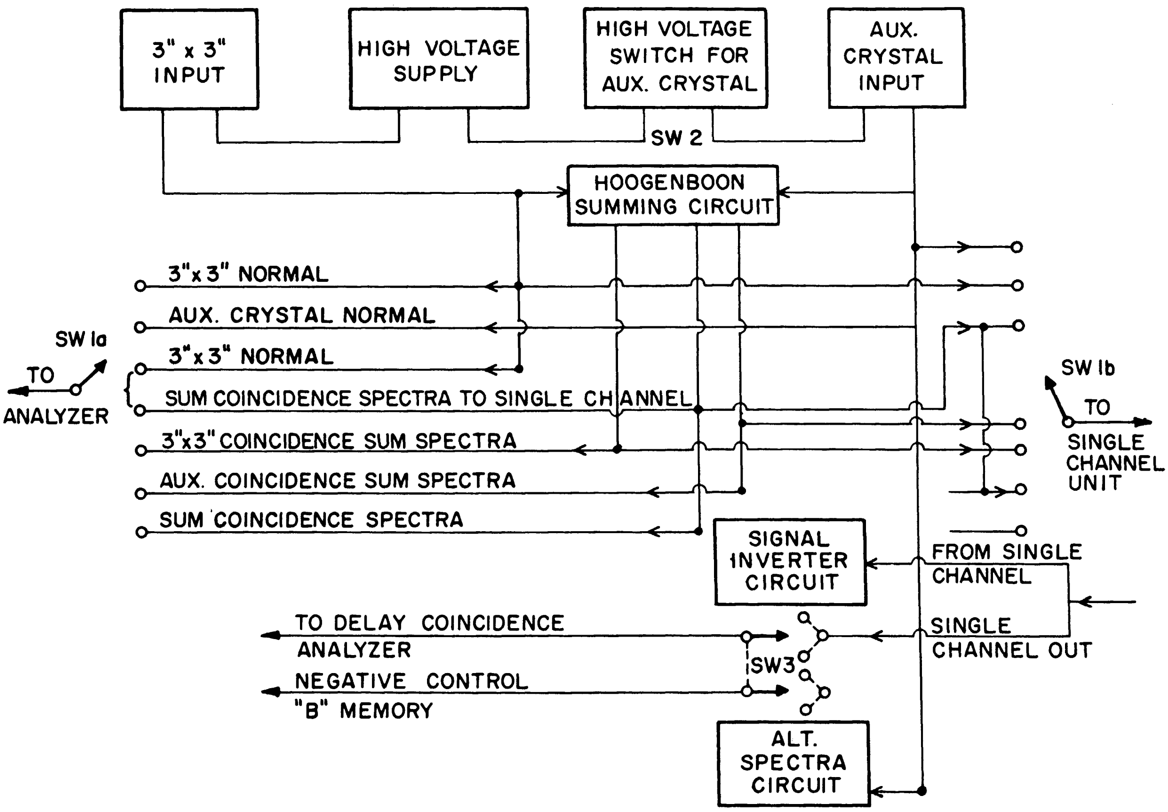


Figure 16. Block Diagram of Auxiliary Circuits Used with 100-Channel Analyzer.

gates the 100-channel analyzer whenever the sum pulse corresponds to the release in the crystals of the full energy available in the cascade. The pulse distribution shows only one peak, the "full energy" peak, for each gamma transition. There is no contribution to the spectrum from processes in which only a portion of the available gamma energy is absorbed. In addition, resolution of individual peaks is improved, and the detection efficiencies of coincident gamma rays are equal. The circuit schematic for this network is shown in Figure 17.

The signal inverting circuit is necessary for the analyzer to operate in anti-coincidence. This circuit operates to replace a negative pulse with a positive pulse in order that the delayed coincidence circuit within the 100-channel analyzer operate as an anti-coincidence gate. This circuit is of particular importance for the operation of the "beta paddle" in eliminating from gamma spectra a large portion of the bremstrahlung radiation found in many isotopes.

The alternator electronic switch was added to the auxiliary circuitry when it was suggested that alternate analysis of beta and gamma spectra of a single sample might be of interest in certain applications. By using a relay and the control lines in the analyzer, it is now possible to have the "A" memory store information from one crystal and the "B" memory store information from a second crystal,

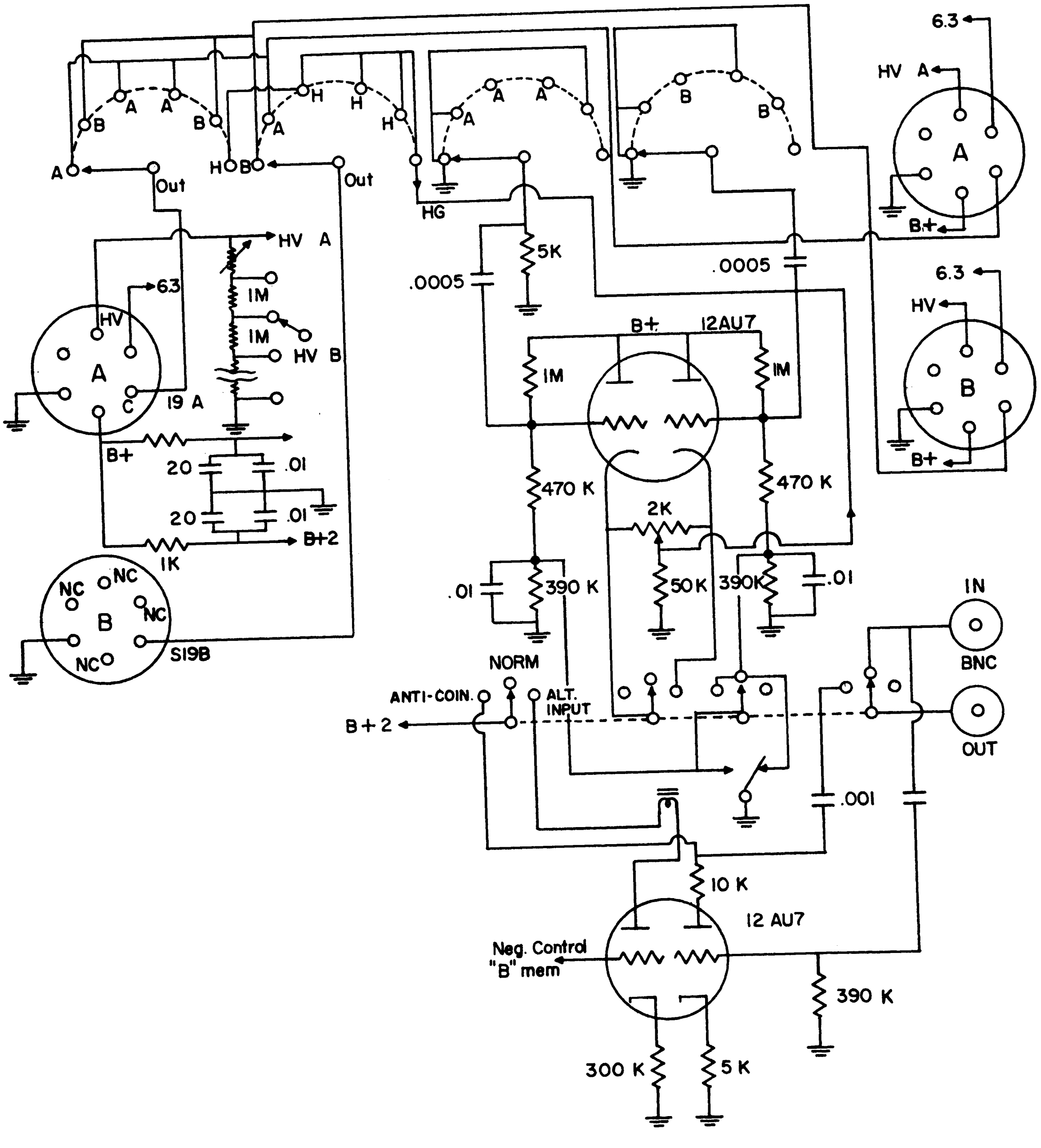


Figure 17. Hoogenboom and Alternate Input Gate Circuits.

both of which are "seeing" the same sample.

An additional circuit which was added to the analyzer following its receipt is a holding circuit which allows the analyzer to be placed in the automatic-recycle mode of operation and held there until released manually or by the "bunny" system described in Chapter III. This holding circuit consists of two relays, two Grayhill switches, and a mercury switch. Upon activating the system, the relays lock in the closed position, keeping "A" memory from storing while "B" unit remains inactive. The circuit, located behind panel P, Figure 54, allows the experimenter to place the analyzer in complete readiness prior to activating a sample, so that it is unnecessary to place each individual unit in operation manually, as was the case previously. When a sample is sent to the analyzer room by means of the "bunny system", the mercury switch in the vacuum line closes when the sample reaches the holding solenoid at the detector position, placing the analyzer in automatic recycle operation.

2. Detectors

a. Sodium Iodide(Thallium) Scintillators. The main detector used in conjunction with the 100-channel analyzer is a 3-inch x 3-inch sodium iodide (thallium activated) gamma scintillation detector (Harshaw Chemical Co., Cleveland, Ohio, Type R), coupled optically to a 3-inch multiplier phototube (DuMont, 6393) with Dow-Corning 200 Silicone Fluid

(6×10^4 centistokes viscosity). The phototube is surrounded by a mu metal shield to reduce the effects of magnetic fields. The entire assembly is enclosed in a light-tight housing which also contains a cathode follower preamplifier. The scintillation detector is shown in Figure 18, while Figure 19 gives the schematic diagram for the preamplifier and photomultiplier voltage divider network.

This detector is mounted in a cave having dimensions 40" x 40" x 40", extended out the east side of the Phoenix Memorial Laboratory Building below grade, as shown in the drawing of Figure 20. The experience of Heath and coworkers (70) indicated a housing of these dimensions to be necessary to reduce the effects of scattered radiation arising from interaction with materials surrounding the detector. A graded shield consisting of 0.0032-inch of cadmium and 0.005-inch of copper was included to reduce the x-ray background produced when scattered radiation interacts with the lead shield. The cadmium absorbs the fluorescent x-radiation of the lead, but gives rise, in turn, to a cadmium x-ray; the copper then absorbs this fluorescent cadmium x-radiation. Figure 21 shows a typical one hour background spectrum over the energy range from zero to four Mev. From this spectrum, it would appear that the lead shielding of the cave is probably contaminated with members of the radium decay chain. The potassium-40 photopeak is most probably due to small amounts of potassium contained in the sodium iodide detector

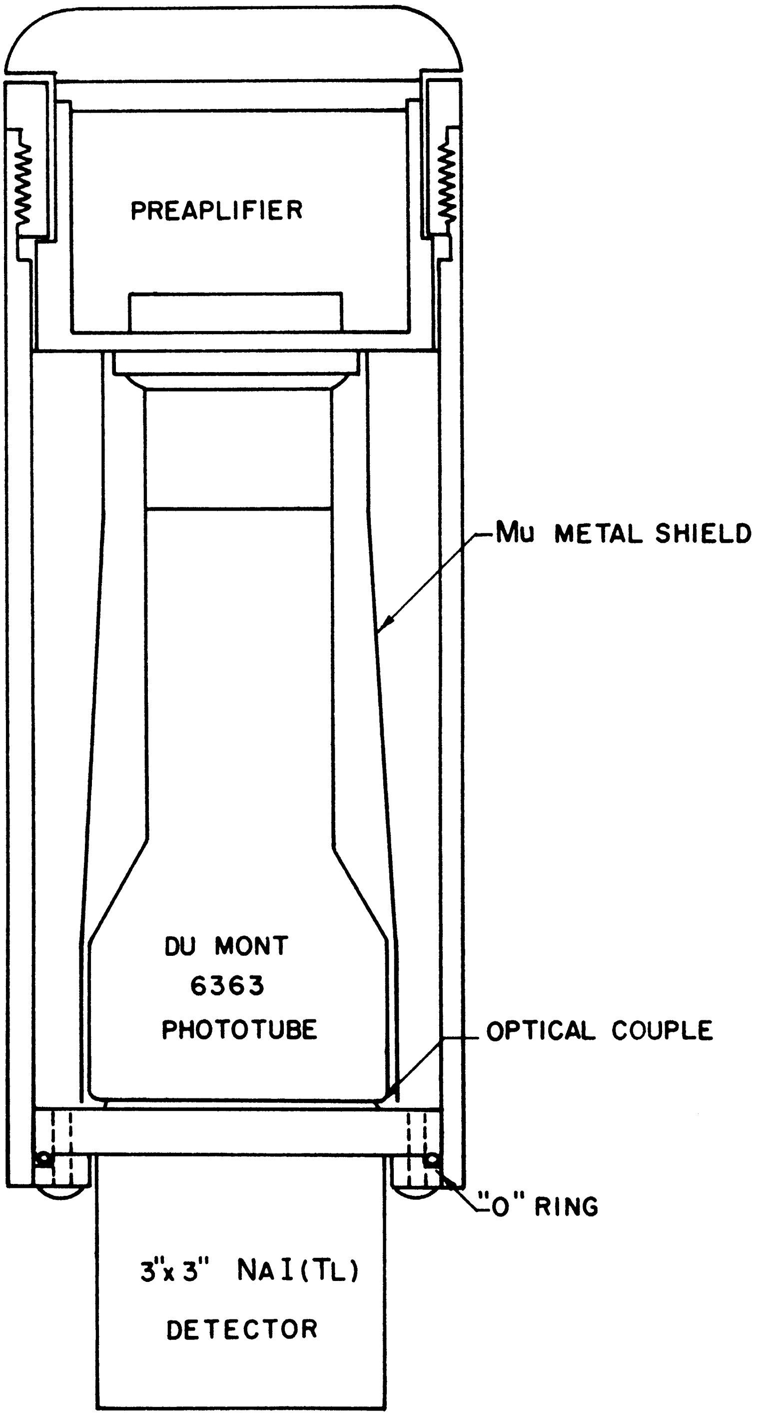
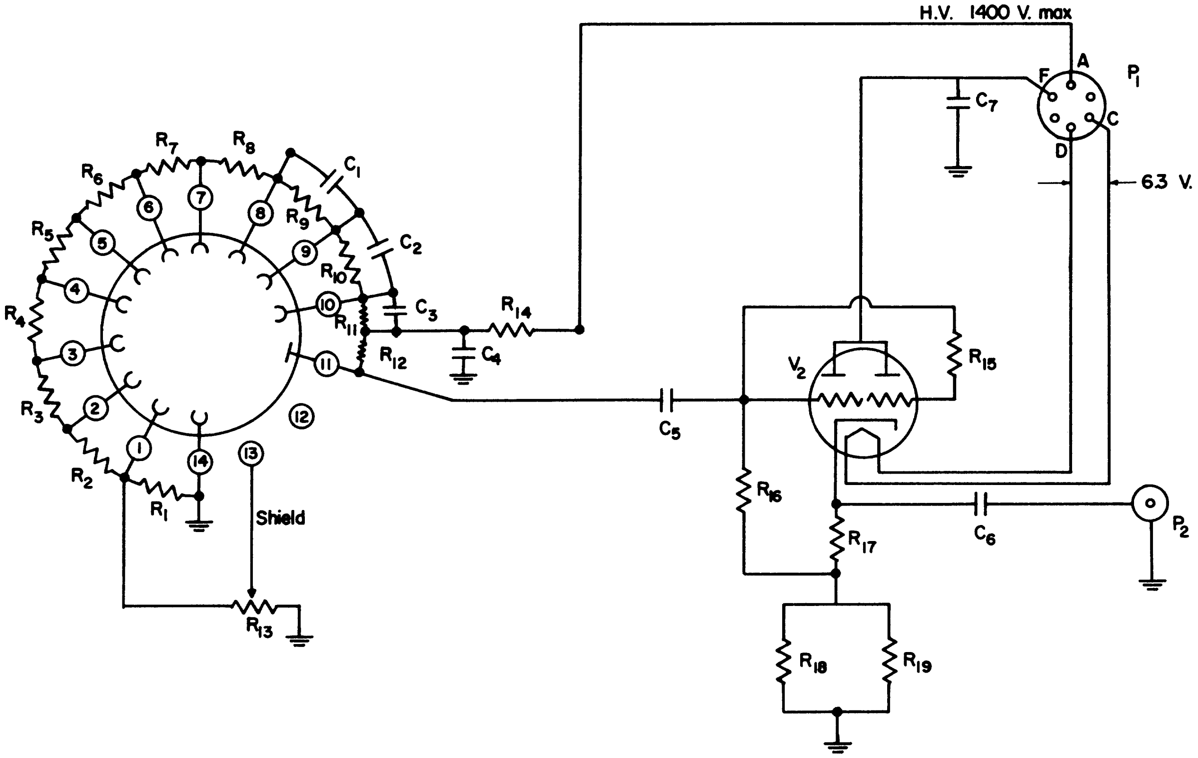


Figure 18. 3-Inch by 3-Inch Scintillation Detector Assembly.



R_1 - 200K, 1 w.
R_2 - 100K,1/2 w.
R_3-R_{10} - 50K,1/2 w.
R_{11} - 100K,1/2 w.
R_{12} - 50K,1/2 w.
R_{13} - 2.5M,1/2 w.

V_1 - DuMont 6363

R_{14} - 1K,1/2 w.
R_{15} - 22K,1/2 w.
R_{16} - 100K,1/2 w. (P)
R_{17} - 1K,1/2 w. (P)
R_{18} - R_{19} - 50K, 1 w. (P)

V_2 - 6J6

P_2 - Amphenol 831R

C_1 - C_3 - 0.005, 600v.
C_4 - 0.1, 300v.
C_5 - 0.001, 25 kv Mica
C_6 - 0.03, 600v.
C_7 - 0.47, 600v.

P_1 - Amphenol MS3106A14S6P

Figure 19. Scintillation Detector Preamplifier and Photomultiplier Voltage Divider Circuit.

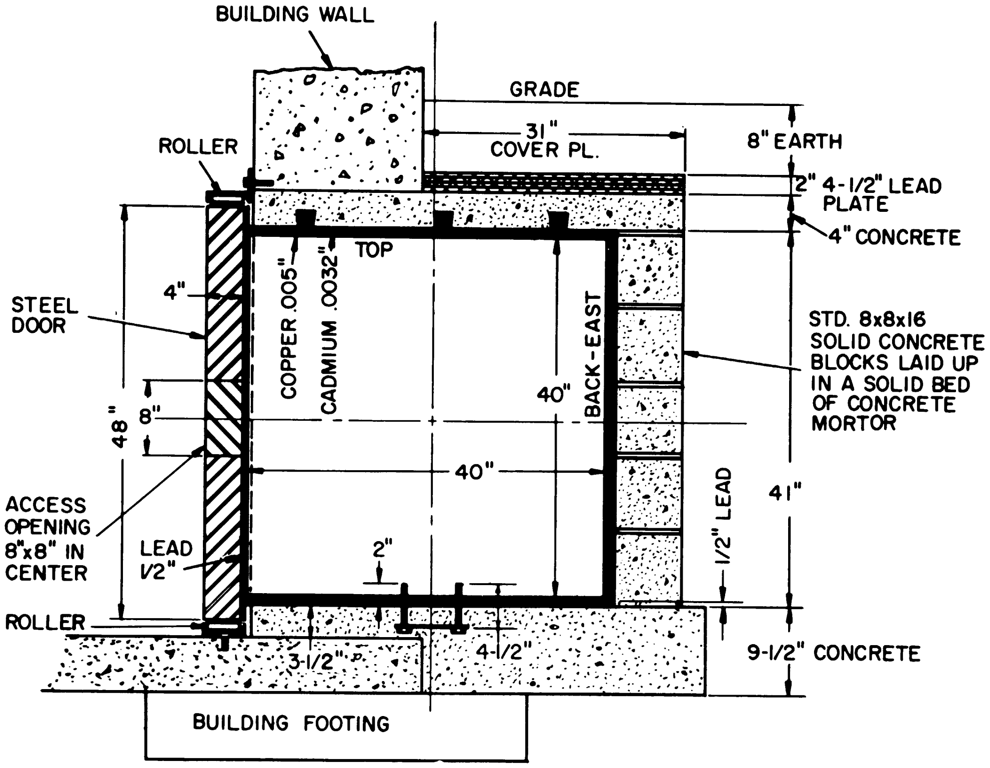


Figure 20. Cave for Scintillation Detector.

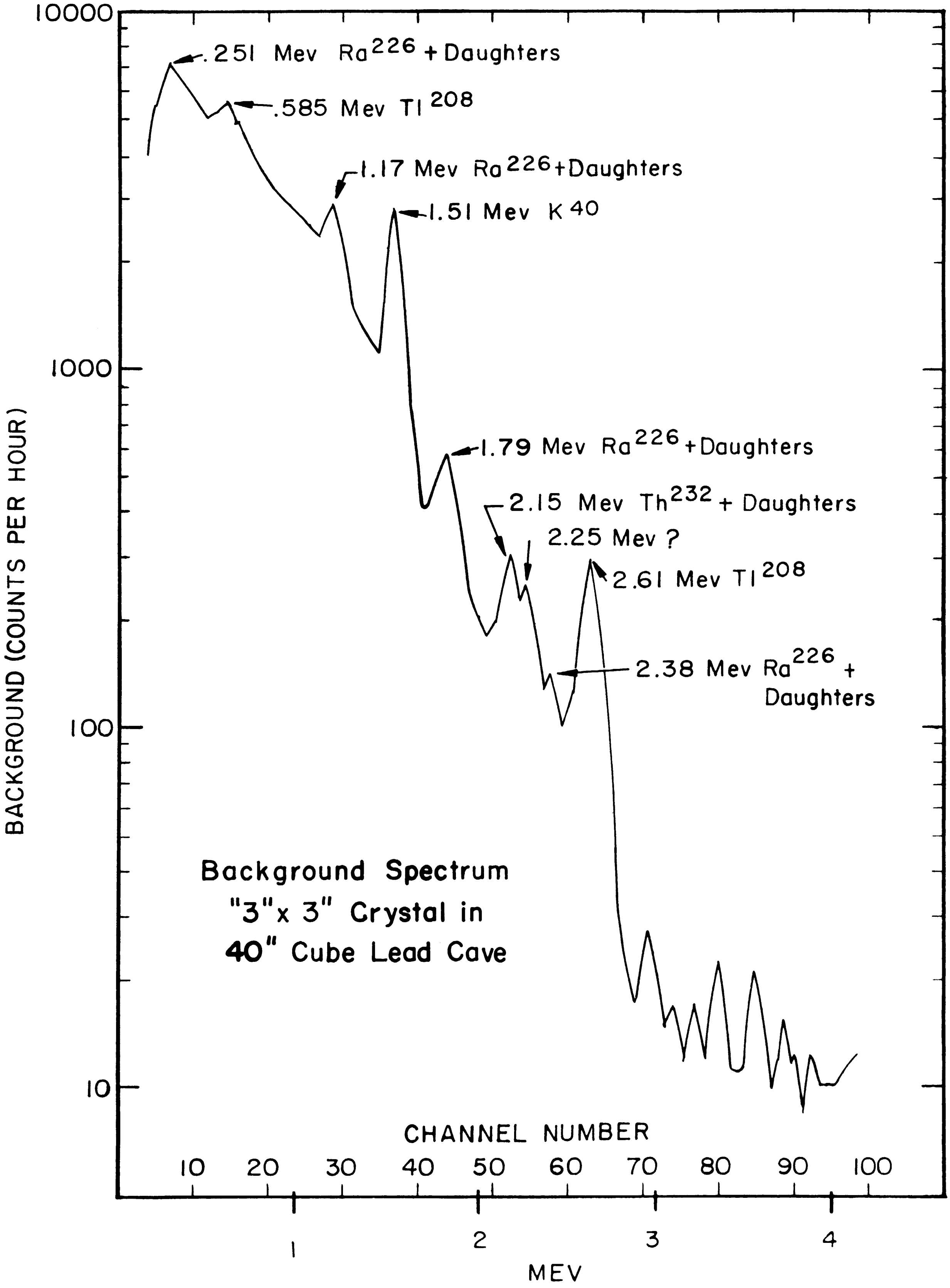


Figure 21. Background Spectrum of 100-Channel Analyzer.

or the Cs-Sb photo-cathode of the multiplier phototube. In general, backgrounds of this order of magnitude do not interfere seriously with routine work.

The scintillation detector assembly is mounted horizontally in the center of the cave on a track in such a way that the unit can be slid forward for repairs, or locked in place. Samples to be counted are placed in a graduated sample holder which slides in and out of the cave on nylon rollers. The holder is stopped by blocks placed on the track in front of the scintillation detector. This serves to insure reproducible geometry and protect the sodium iodide crystal and its aluminum can from accidental damage. The experimental arrangement within the cave is shown in Figure 22; the detector mounting and sample holder are shown in Appendix I. A large sheet of polyethylene is draped from the upper rear to the lower front of the cave, and serves to protect the walls and floor from contamination in the event of accidental spilling of a liquid sample.

The resolution of the 3-inch x 3-inch detector has been determined (196) as a function of gamma energy. The values obtained are plotted in Figure 23. These data are quite useful for rapid calculation of peak areas in activation analysis (135), and in determining the presence of multiple peaks lying in close proximity to each other.

Several smaller gamma scintillation detectors, described elsewhere (6) are used, either in conjunction with

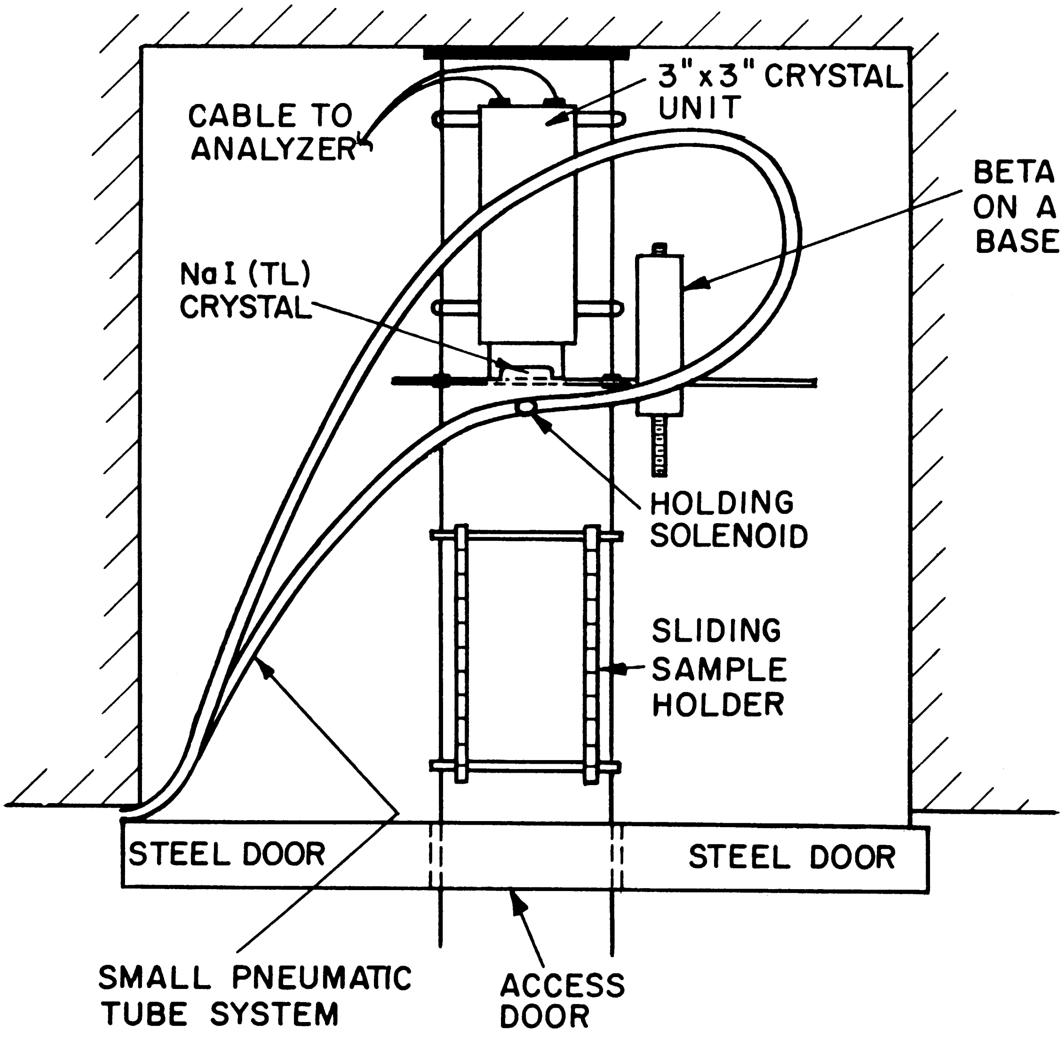


Figure 22. Schematic Layout of Cave Interior (Looking from Above).

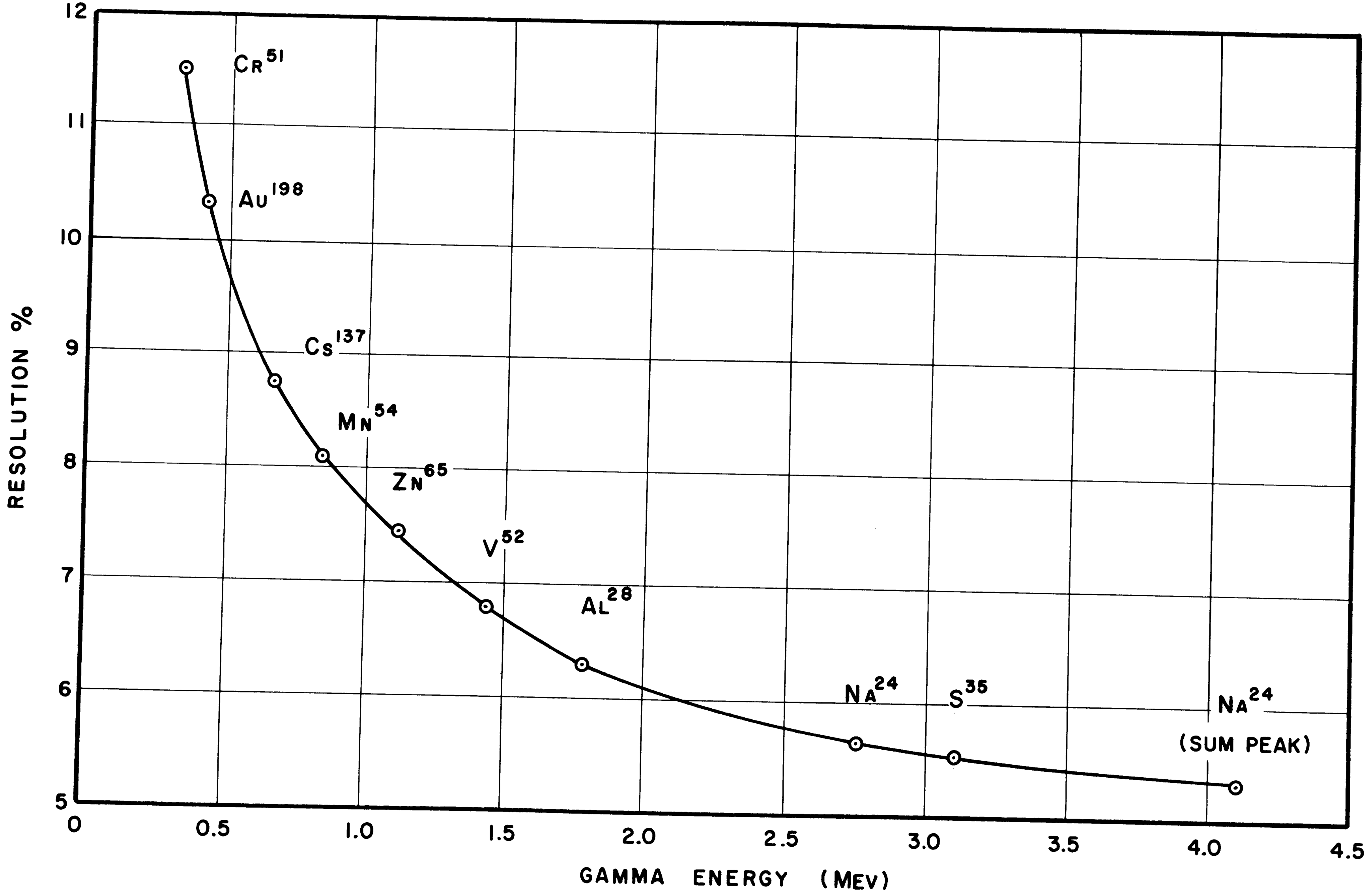


Figure 23. Resolution Curve for 3-Inch by 3-Inch NaI(Tl) Detector.

the 3-inch x 3-inch detector for coincidence work, or for operation remote from the 100-channel analyzer.

b. Beta Plastic Scintillators. Several hollow plastic beta scintillation detectors (14, 61) are available for use with the 100-channel analyzer. Little work has been done using these detectors since the majority of the work involves radioisotopes which have gamma radiation associated with their disintegration; gamma spectra are, in general, much more easily interpreted than beta spectra. In the work involving the activation determination of thallium-206, a pure beta emitter (Chapter VI), a flat beta plastic scintillator was used to record the beta spectra of the counting sample. These were recorded in an effort to obtain a "fingerprint" of the sample as evidence, in addition to the half-life, for the presence of thallium-206 in the counting sample.

The beta plastic scintillator actually used is a wafer of Sintilon plastic (National Radiac, Inc., Newark, N. J.) 1/4-inch x 1-1/2-inches in diameter. This is coupled optically to a DuMont 6292 with Dow-Corning 200. Typical spectra produced by means of this detector are shown in Figure 24. No attempt was made to perform a Kurie analysis of these spectra, since they were to be used only for comparison with a standard, rather than for beta end-point determinations.

In working with certain types of samples, it is found

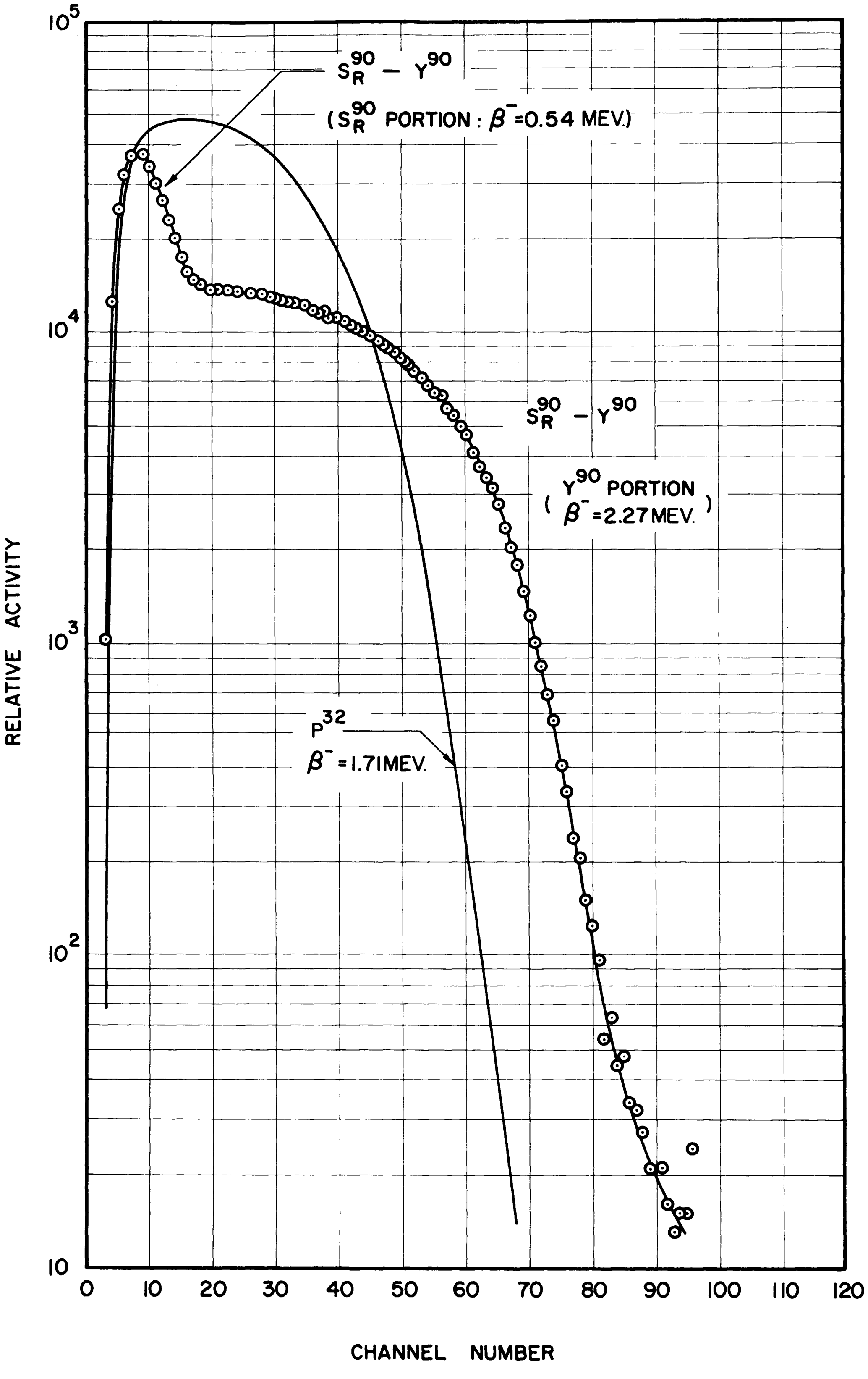


Figure 24. Typical Beta Spectra Analyzed with "Sintilon" Wafer Detector.

that bremstrahlung causes a large amount of interference in gamma spectra, especially in the low energy region. As a result, interpretation of data in this region is extremely difficult. One way of reducing this bremstrahlung is to place an absorber of low atomic number between the source and the detector. Absorbers of aluminum, beryllium or plastic (polystyrene, polyethylene, lucite, etc.) are generally used. These absorbers should be as thin as possible, since Compton electrons are generated in the absorber, and may result in a less sharply defined spectrum than is desirable.

Another, generally more effective means for reducing bremstrahlung in gamma spectra is by means of an anti-coincidence absorber, or beta paddle. Beta particles lose a portion of their energy in traversing the beta plastic scintillator material of the anti-coincidence absorber, then proceed to lose the rest of their energy in the 3-inch x 3-inch sodium iodide(Tl) detector. These two detectors are placed in anti-coincidence such that the beta particle produces no count when "seen" by both detectors. A gamma ray entering the sodium iodide(Tl) detector coincident with a beta particle entering the anti-coincidence beta absorber is not counted, so that the gamma count rate is reduced, but only by a relatvely small amount.

The anti-coincidence beta absorber is in the form of a 3-inch x 3-inch x 1/4-inch sheet of plastic scintillator

(Nuclear Enterprises, Ltd., Winnipeg, Canada, NE-102), coupled optically to a Plexiglass light-piper with Dow-Corning 200. Construction details are shown in Figure 25. The plastic scintillator and light-piper are enclosed in a single layer of household aluminum foil, the edges of which are sealed with Scoth 33 Electrical tape (Minnesota Mining and Manufacturing Co.). The base of the paddle is coupled with DC-200 directly to the photocathode face of a two-inch multiplier phototube (DuMont, 6292). This is contained in a housing which also contains the preamplifier, and is mounted on a swivel base so that the unit can be swung around out of the way when not in use. The arrangement of the anti-coincidence beta absorber within the cave is shown in Figure 26, while Figure 27 shows the effect of this unit on the spectrum of potassium-42.

c. X-Ray Proportional Detector. Inasmuch as the 0.042-Mev isomeric transition gamma of niobium-94m is converted almost completely (185; see also Chapter VII), an x-ray proportional counter was evaluated for use in analyzing the spectra of irradiated niobium-containing samples. The x-ray proportional detector used has been described by Anders (6), and consists of a 12.5-inch x 4.0-inch diameter brass tube filled to a pressure of two atmospheres with Krypton. A window of 0.1-inch x 2-inch (diameter) beryllium, sprayed with 27 milligrams of Glyptal lacquer dissolved in acetone (to seal any pin-holes present in the window),

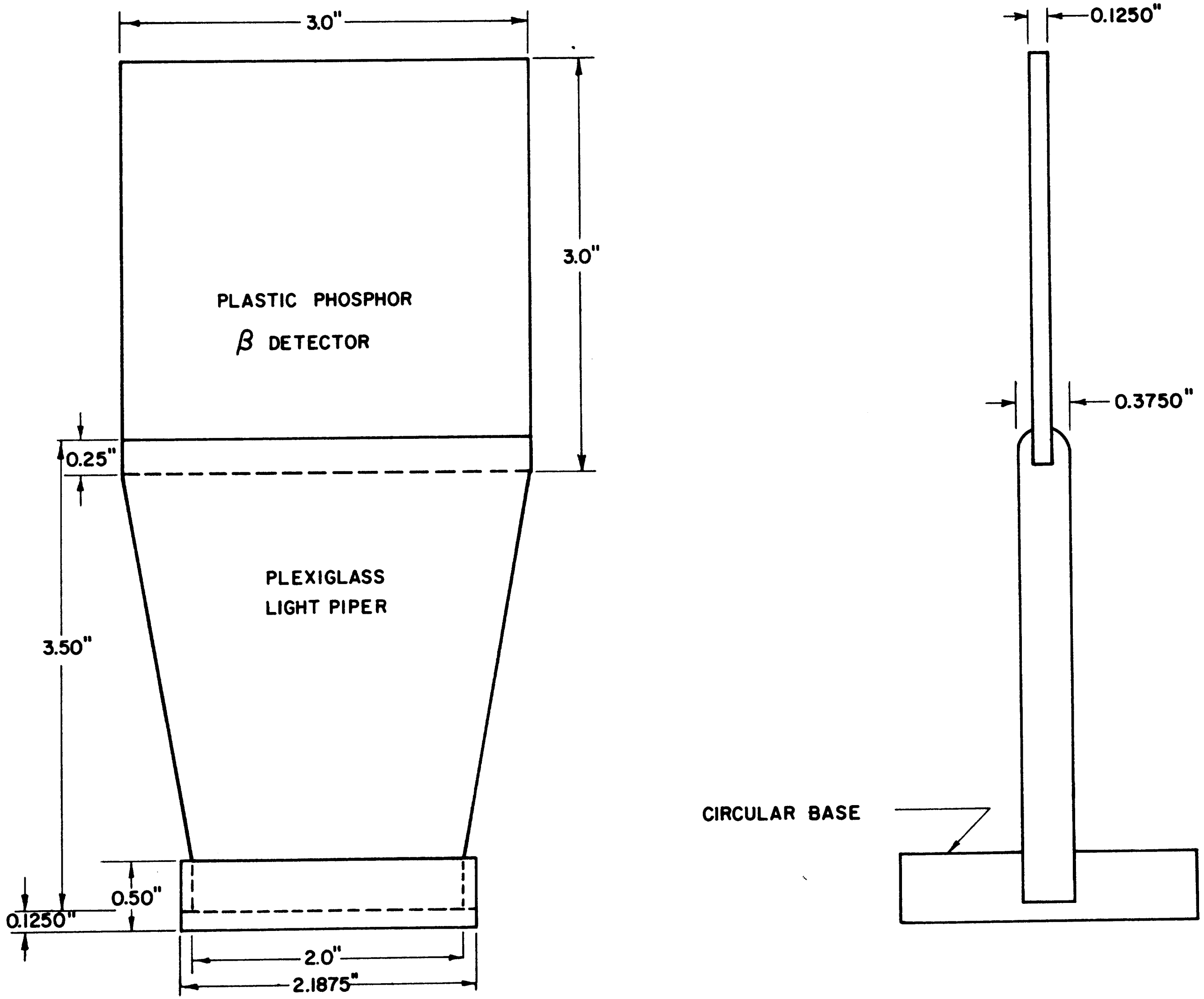


Figure 25. Beta Paddle Construction.

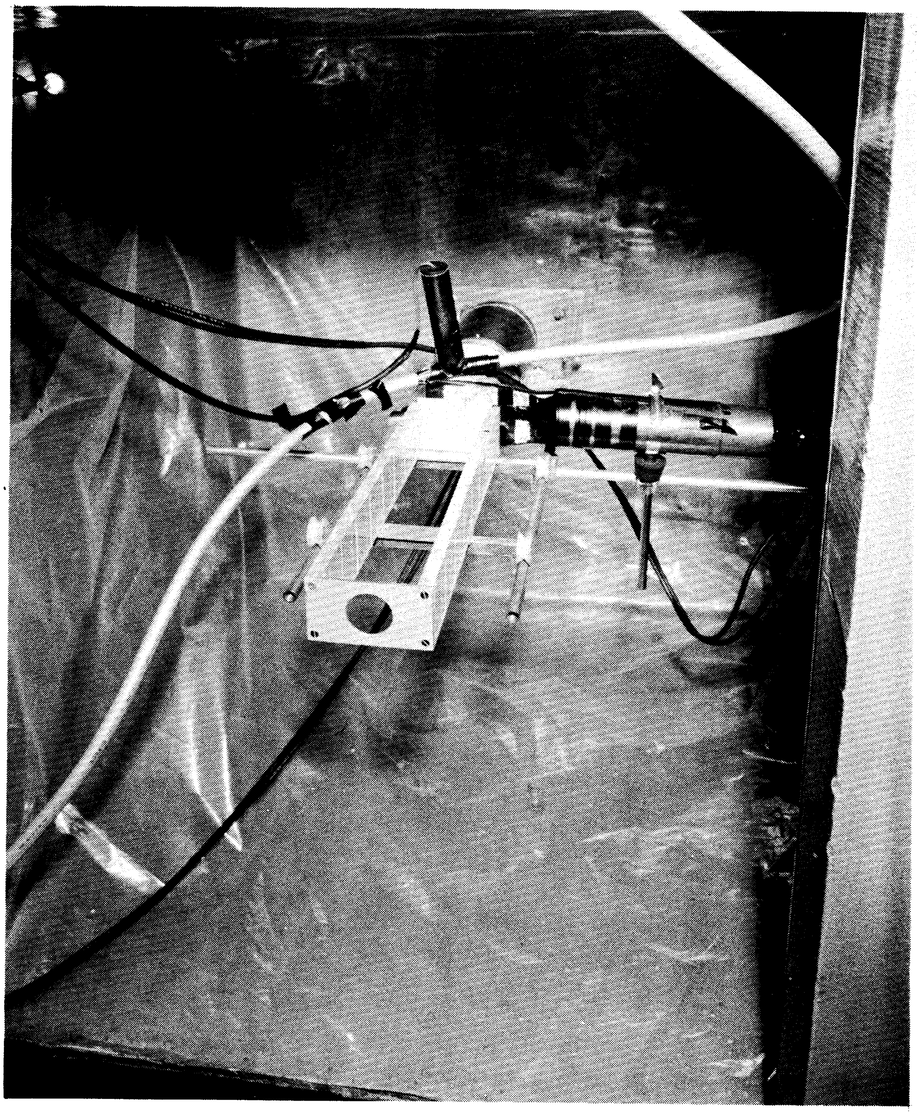


Figure 26. Beta Paddle in Analyzing Position.

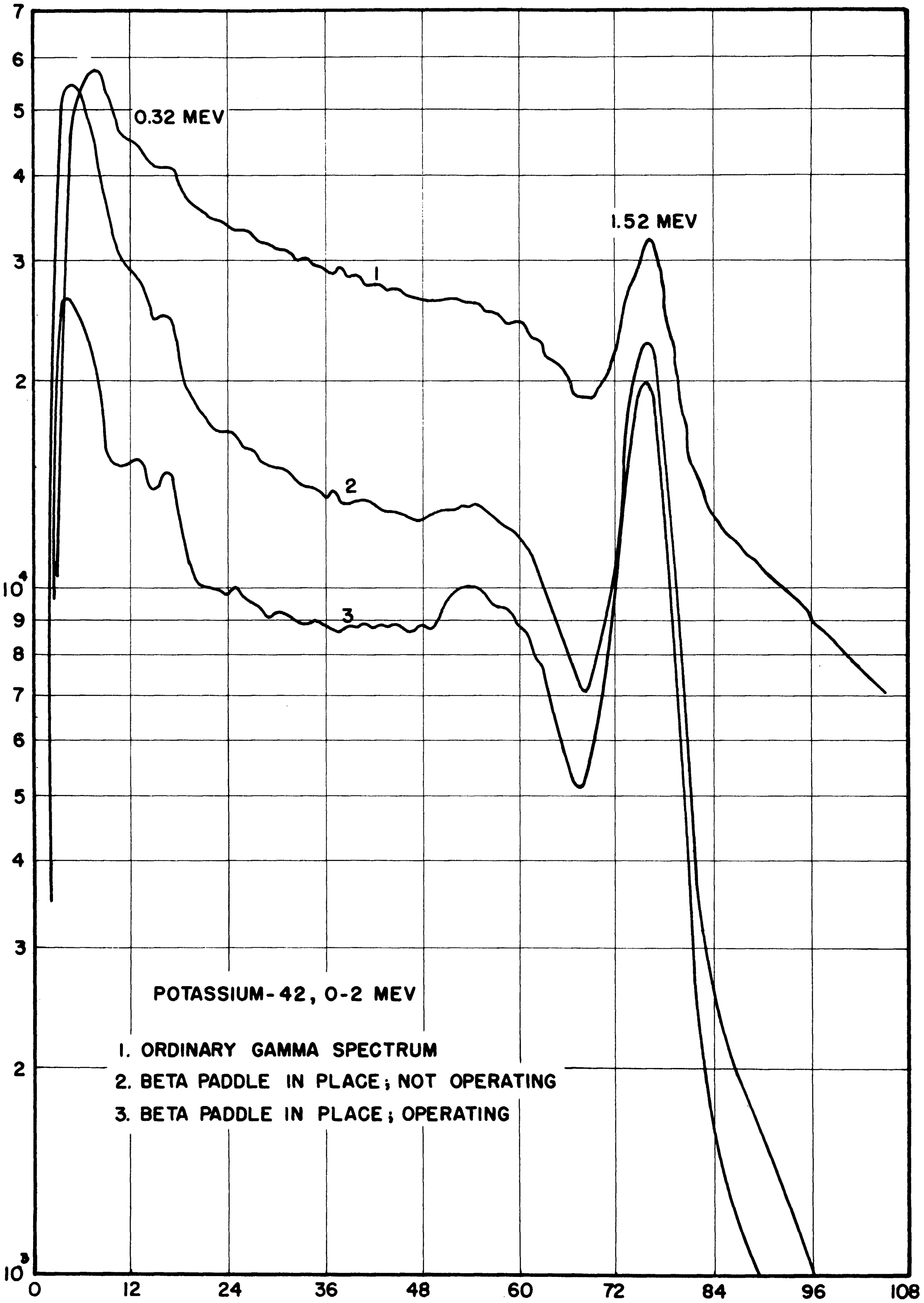


Figure 27. Effect of Beta Paddle on the Spectrum of Potassium-42.

served to admit x-radiation into the counter volume. The output of this detector was fed through a preamplifier circuit into the amplifier of the 100-channel analyzer (H, Figure 54) or into a separate non-overloading linear amplifier (Radiation Instrument Company, Silver Spring, Maryland, Model 107F). The x-ray spectra detected by this instrument was then analyzed by the 100-channel analyzer, with the data for each spectrum being presented in digital and graphical form. High voltage for the detector was provided by a highly regulated 5000-volt power supply, also obtained from Radiation Instrument Company.

3. Calibration

Calibration of the energy response of the 100-channel analyzer is easily accomplished by means of several long-lived isotopes having accurately known energies within the energy range to be scanned. The gamma energies of the isotopes used are plotted against the peak channel for each full energy photopeak. Such a plot is shown in Figure 28. Table IV lists several radioisotopes which have been used for this purpose.

It would appear to be worthwhile to construct a complete calibration curve over the energy range most frequently used (usually 0-2 Mev) before the start of each day of operation. This is especially important in the low energy region between 0 and 100 kev in view of the reported (50, 146) non-linear response of sodium iodide(thallium) gamma

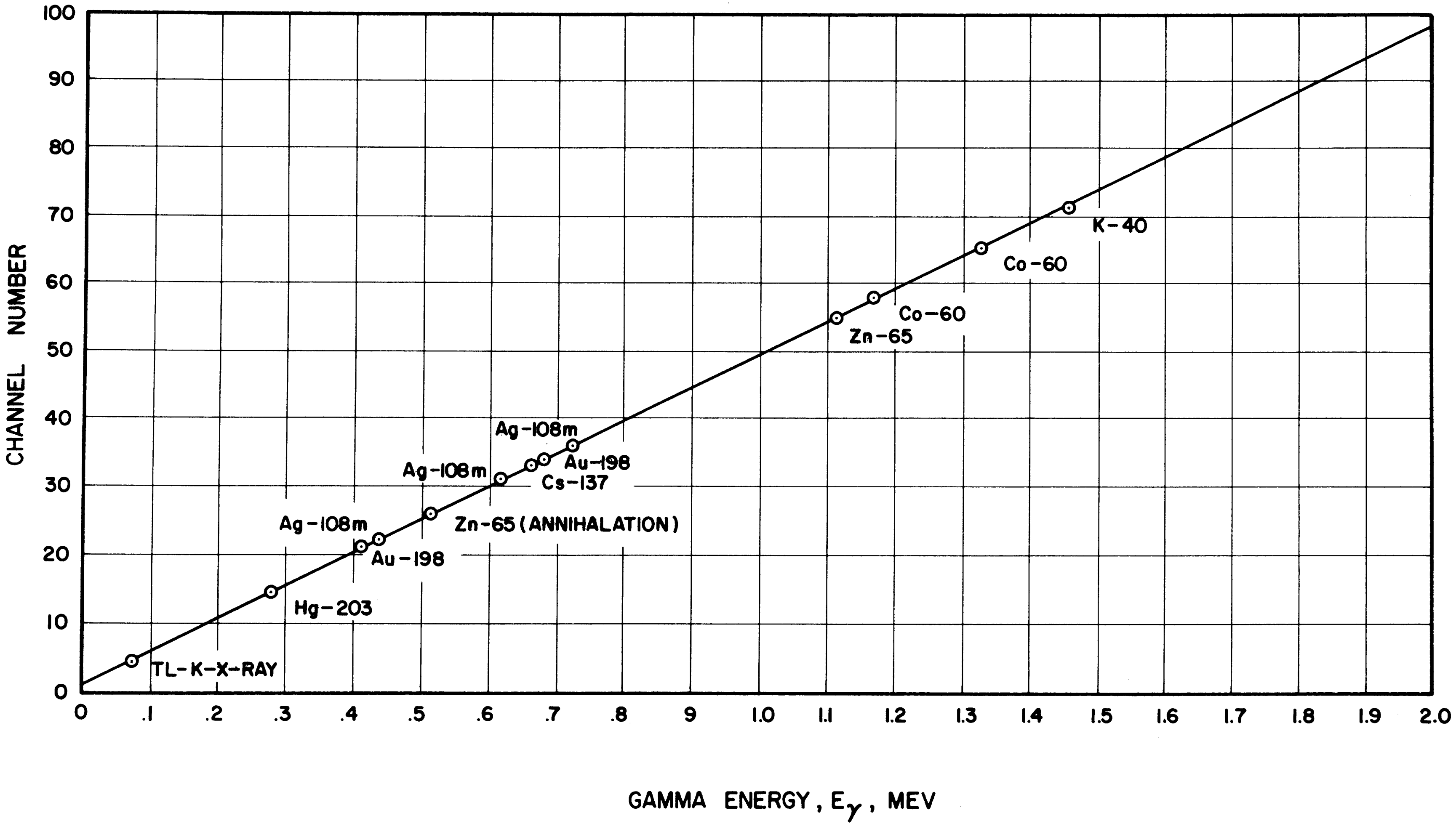


Figure 28. Typical Energy Calibration Curve.

TABLE IV

RADIOISOTOPES USED FOR ENERGY CALIBRATION

Isotope	Gamma Energy	Half-Life
Nb-94m	0.0168 ± 0.0007 (Nb K_{α}X-ray)	6.6 minutes
Cs-137	0.032 (Ba K_{α}X-ray)	27 years
Tl-204	0.071 (Hg K_{α}X-ray)	4.2 years
Hg-203	0.073 (Tl K_{α}X-ray)	47 days
Hg-203	0.279	47 days
Cr-51	0.325	27 days
Au-198	0.411	2.69 days
Zn-65	0.511 (Annihalation Radiation)	245 days
Mn-54	0.842	291 days
Cs-137	0.662	27 years
Zn-65	1.114	245 days
Co-60	1.17	5.24 years
Co-60	1.33	5.24 years
Na-24	1.368	14.9 hours
K-40*	1.46	1.3×10^{9} years
Cl-38	1.64	37 minutes
Cl-38	2.15	37 minutes
Co-60	2.50 (sum peak)	5.24 years
Na-24	2.754	14.9 hours
Na-24	4.112 (sum peak)	14.9 hours

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*Present in normal background

scintillators in this energy region. Sources such as those listed in Table IV, supplemented by standards such as those suggested by Matlack (122), and Cameron and Rhodes (32), provide sufficient points for a good energy calibration of the instrument. A single curve can then be used throughout the operating day, since there is only a very small amount of drift in the analyzer response during an eight-hour day.

4. Operation

In routine operation, the analyzer has performed in a highly satisfactory manner. In slightly over two years of operation the instrument has been unavailable for use by reason of faulty operation for only about five percent of the time during which the reactor was available for power operation. This presents approximately ten to fifteen percent of the total time since delivery of the unit.

As a result of the unique circuitry necessary for the automatic recycle operation, no satisfactory operating sequence has been available. A complete sequence is presented in Appendix II.

B. Beta Proportional Counter

For the analysis of samples of pure beta emitters (thallium-204 and -206), a thin window beta proportional counter was used. This counter, which has been described elsewhere (6, 105), was used in conjunction with a modified Low Alamos Pa-3 linear amplifier (Trott Electronics Company, Rochester, New York). The amplifier output was fed into a model SC-4 scaler, also built by Trott Electronics. A Glow Transfer Counter, Model 162A (Atomic Instrument Company, Cambridge, Mass.), was connected across the input to the driver tube for the mechanical register, thus allowing a much higher count rate to be recorded without jamming the register.

During this research, the counting chamber was operated at an anode potential of 4500 volts, using 99+ mol-percent methane (Phillips Petroleum Company, Bartlesville, Oklahoma) as the counting gas. The chamber was housed in a shield built with two-inch lead bricks which served to reduce the natural background to approximately 45-65 counts per minute.

In order to analyze the beta spectra of samples simultaneously with the measurement of their decay curves, a beta scintillation detector was used in conjunction with the beta proportional chamber. The experimental arrangement is shown in Figure 29.

C. Well Scintillation Counter

Much of the routine gamma counting during this research was performed with a 2-inch by 1-3/4-inch diameter sodium iodide(thallium) well scintillation crystal, type 7F8 (Harshaw Chemical Company, Cleveland, Ohio). This was coupled optically to a two-inch DuMont 6292 multiplier phototube in a standard unit also housing the preamplifier. The output

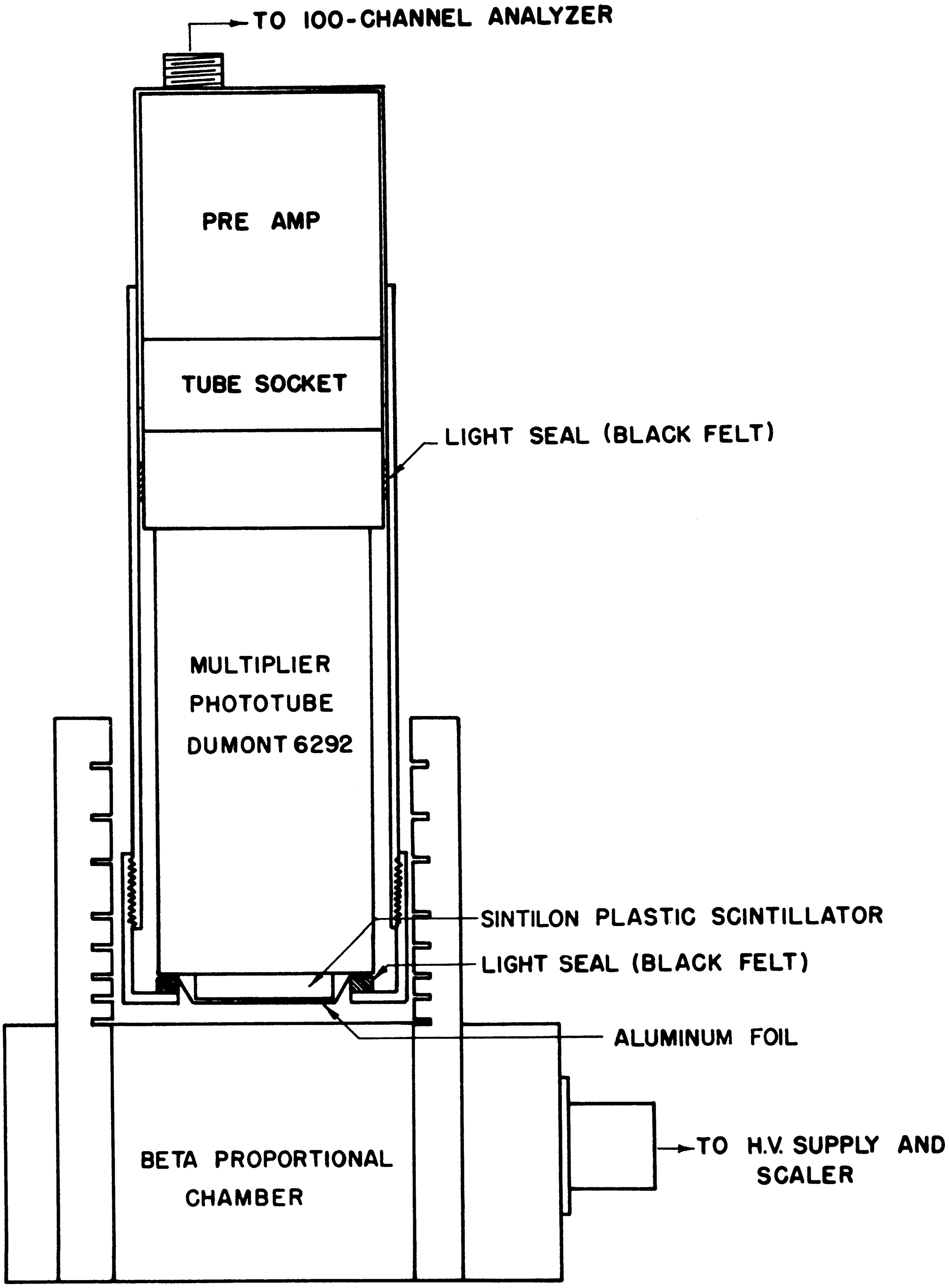

Figure 29. Experimental Arrangement for Simultaneous Measurement of Beta Spectra and Decay Curves.

is recorded with a modified Nuclear Instrument and Chemical Company Model 162 scaler. A Glow Transfer Counter was connected across the input to the driver tube for the mechanical register for use with samples having very high count rates. During this work the phototube was operated at a potential of 1290 volts. The unit was housed in a two-inch circular lead shield and had a background of the order of 240-300 counts per minute.

CHAPTER V

DETERMINATION OF VANADIUM

A. Nuclear Properties

The nuclear properties of vanadium make it an ideal element for rapid analysis by the activation method. Only two isotopes of vanadium are found in nature: vanadium-50 and -51. The natural abundances of these isotopes are 0.24- and 99.76-percent (71, 112), respectively. Since the two stable isotopes have consecutive mass numbers, only one radioactive nuclide is formed by the (n,γ) reaction, that of vanadium-52. Fortunately, the natural abundance of the stable isotope activated is almost 100-percent, thus favoring the determination by activation analysis with neutrons. Also, the thermal neutron activation cross-section for vanadium-51 is 4.5 barns (175), thus allowing neutron activations of high sensitivity, approaching 10^{-10} grams (127).

The half-life for vanadium-52 is given as 3.74 minutes (120) to 3.77 minutes (97), thus allowing short activations but requiring rapid chemical separation procedures. The disintegration scheme (123, 200) is quite simple, consisting of a single beta particle and a single gamma-ray of 1.44 Mev, thus giving rise to a very simple gamma-ray spectrum.

B. Radiochemistry of Vanadium

1. General Properties

Metallic vanadium is stable and is not oxidized by moist air at ordinary temperatures. The metal burns in air to produce the pentoxide, as well as some lower oxides; it burns in an excess of dry chlorine gas to form the low-boiling vanadium tetrachloride, forming the basis for a rather useful separation (197).

Vanadium metal is attacked slowly by aqueous solutions of alkali chlorides, bromine, hydrochloric acid (hot or in the cold), hydrofluoric acid and hot concentrated sulfuric acid. Concentrated and dilute nitric acid, aqua regia, chloric and perchloric acids, bromic acid and potassium iodate all react with vanadium to produce vanadic acid. The metal can also be fused with sodium carborate, potassium hydroxide and potassium nitrate, forming soluble vanadates.

Vanadic acid and the vanadates of ammonium, lithium, and the alkali metals are relatively soluble in aqueous medium. The vanadates are characterized by the tendency to form condensed poly-vanadate compounds, much like the phosphates. The more common acidic anions (sulfate, chloride, fluoride) form soluble compounds with vanadium(IV), most of which are blue in aqueous solution. Vanadium(III) also forms aqueous-soluble compounds with most of the common reducing acids, as does vanadium(II). The latter state, however, is very easily oxidized and is not stable in the presence of oxidizing anions.

Pentavalent vanadium forms soluble complexes with sulfate, oxalate (156, 179), tartrate (179), fluoride (54), and peroxide (8, 159, 166, 193). Complexes involving hydroxide (45, 132, 157), cyanide (153), thiocyanate (60, 99, 115), oxalate (99), sulfite (98) and fluoride (45) ions with vanadium(IV) are known to exist. Among the complexes of vanadium(III), the halogens are most readily formed.

2. Oxidation-Reduction Behavior

Vanadium(V) is reduced in hydrochloric acid solution by the sulfite ion, or by bubbling SO_2 gas through the solution; vanadium(IV) is formed. The pentavalent state is also reduced by ferrous ion in acid, by passage through a Jones reductor, (reduction to vanadium(II), with the vanadium caught in ferric sulfate solution (188)), hydrogen sulfide gas (116), passage through a silver reductor in hydrochloric acid, and rapid stirring or shaking with mercury. The last three methods give rise to vanadium(IV) compounds.

Vanadium is oxidized to the pentavalent state by nitric acid, but the oxidation has been shown (94) to be only 99-percent complete. Boiling perchloric acid, persulfate in the presence of silver ions, and hot excess permanganate in acid solution also oxidize vanadium to the pentavalent state.

In neutral solution, iodine, dichromate and permanganate oxidize vanadium(II) to vanadium(III), if the addition is terminated at the phenosafranin change point. Iodine in a saturated solution of sodium carbonate oxidizes vanadium(IV) to vanadium(V). Ferric ion has also been used for this oxidation.

3. Precipitation Reactions - Coprecipitation Characteristics

Vanadium forms insoluble precipitates with many substances; however, only a few of these have been used for the radiochemical separation of vanadium. Batzel (11) obtained radiovanadium as lead metavanadate, $PbVO_3$, from an acetic acid solution of proton-irradiated copper foil following removal of insoluble sulfides and scavenging with manganese dioxide and ferric hydroxide. Cassatt (33) precipitated radiovanadium with cupferron in his separation of vanadium from deutron-irradiated titanium foil. The final precipitation of vanadium as lead metavanadate was made with a solution of lead acetate. Duval (46) studied the precipitation of vanadium(V) by several reagents, including mercury(I), lead, barium, manganese(II), silver, hexammino-cobalt(II), 8-hydroxyquinoline, cupferron, strychine, and α-nitroso-β-napthol. It would appear that several of these could be used for separation of radiovanadium. In addition small amounts of vanadium(V) can be precipitated as ammonium metavanadate (145) from an ammoniacal solution saturated with ammonium chloride. The precipitate forms only slowly, however, and is thus inapplicable for separating short-lived isotopes. A more complete list of the insoluble compounds of vanadium is presented by Brownlee (23), and may provide further information concerning precipitation reactions for use in the separation of radiovanadium.

Vanadium can also be removed from solution by coprecipitation with ammonium phosphomolybdate. Cain and Hostetter have shown (29) that pentavalent vanadium is quantitatively carried by ammonium phosphomolybdate provided that the amount of phosphorus added is 5-10 times the amount of vanadium. This procedure affords a good means of separating vanadium from copper(I and II), chromium(VI), nickel, aluminum, iron(III) and uranium(VI). Titanium hydroxide can also be used for this purpose; removal of vanadium may or may not be complete, depending upon the Ti:V ratio. Aluminum, ferric and chromic hydroxides have also been used (25).

4. Solvent Extraction

A search of the literature reveals that of the inorganic complexes of vanadium, only the vanadium(IV)-thiocyanate complex is extracted into organic solvents to an appreciable extent. The thiocyanate-methylisobutyl ketone system has been used (113) to separate radiovanadium from manganese(II) and chromium(VI). Heteropoly acids, for example, molybdovanadophosphoric acid, are extractable to some extent into organic solvents. However, there appears to be little reason for using systems of this type since better solvent extraction systems are available. In addition, high molecular weight amines (21, 38, 39, 48, 49, 110, 117, 140, 177) have been used for the extraction of vanadium.

Several solvent extraction systems involving vanadium chelates have been used for separation of vanadium from a wide variety of materials. Several of the more widely used chelating agents include cupferron (55, 58), 8-hydroxyquinoline (189), and acetylacetone (124, 125, 182).

The chelate formed by vanadium with cupferron (the ammonium salt of N-nitrosophenylhydroxylamine) has been found to be soluble in a number of organic solvents. The chelate reacts with many different metals, but good separations can be made with close control of pH and through the use of masking agents. The pH dependence of the cupferron extraction of vanadium into chloroform from dilute sulfuric acid solutions is shown in Figure 30 (57). This extraction suffers from the disadvantage that cupferron and many of its chelates are sensitive to heat and/or light. Fresh solutions of cupferron should be made daily, and extraction should take place in the cold.

The extraction of vanadium by thenoyltrifluoroacetone (TTA) has also been investigated (56). Figure 31 gives the pH dependence for the extraction of vanadium(IV) into benzene. Since large numbers of other elements are extracted by TTA in the pH range of maximum vanadium extraction, the method proved to be of little value for the rapid separation of vanadium(IV) from other elements. Vanadium(V) was extracted to a negligible extent, even after shaking for 30 minutes. Several other chelates are available which can be used to extract vanadium from aqueous solution. However, these offer few advantages, if any, over those mentioned above.

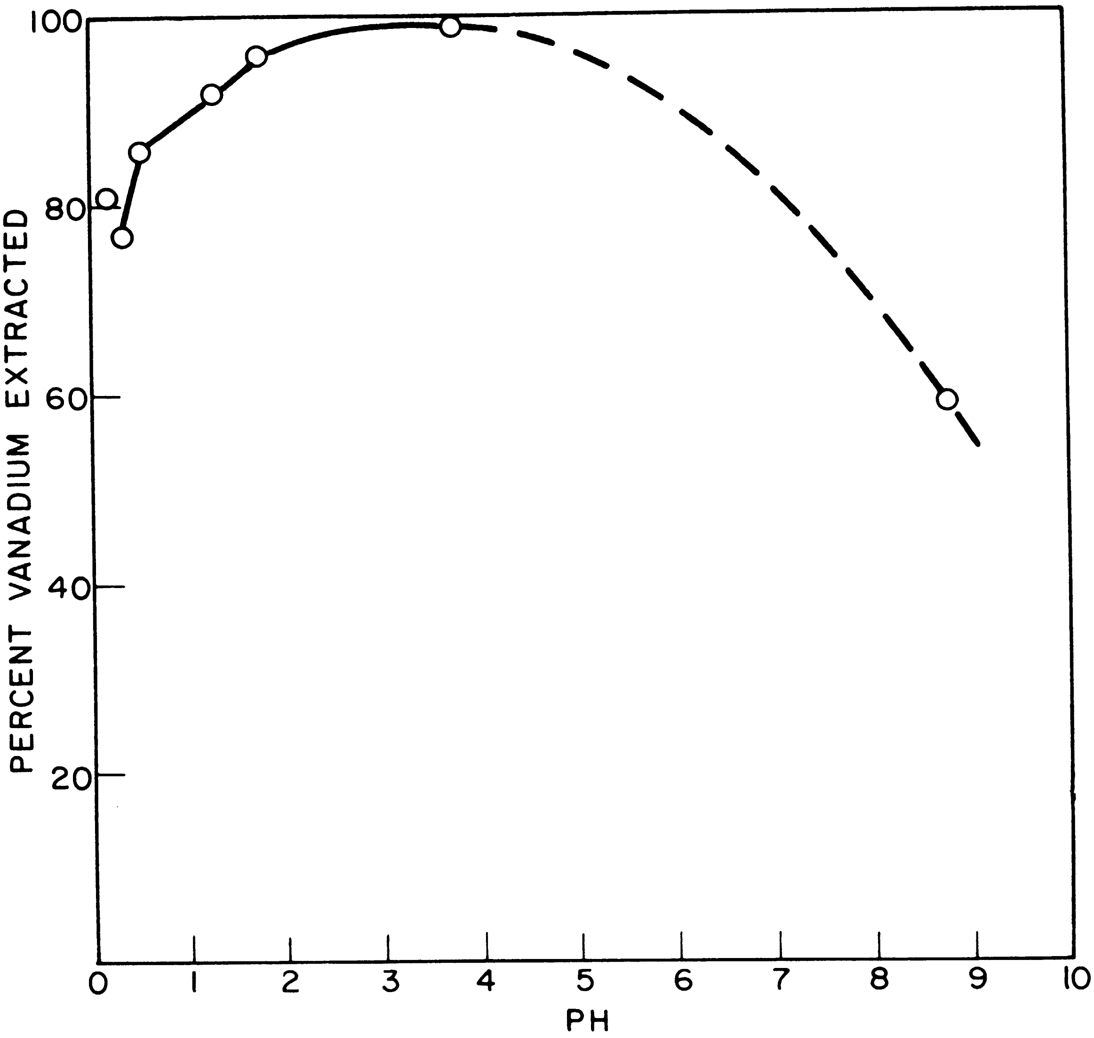

Figure 30. Extraction of Vanadium(V) Cupferrate into Chloroform.

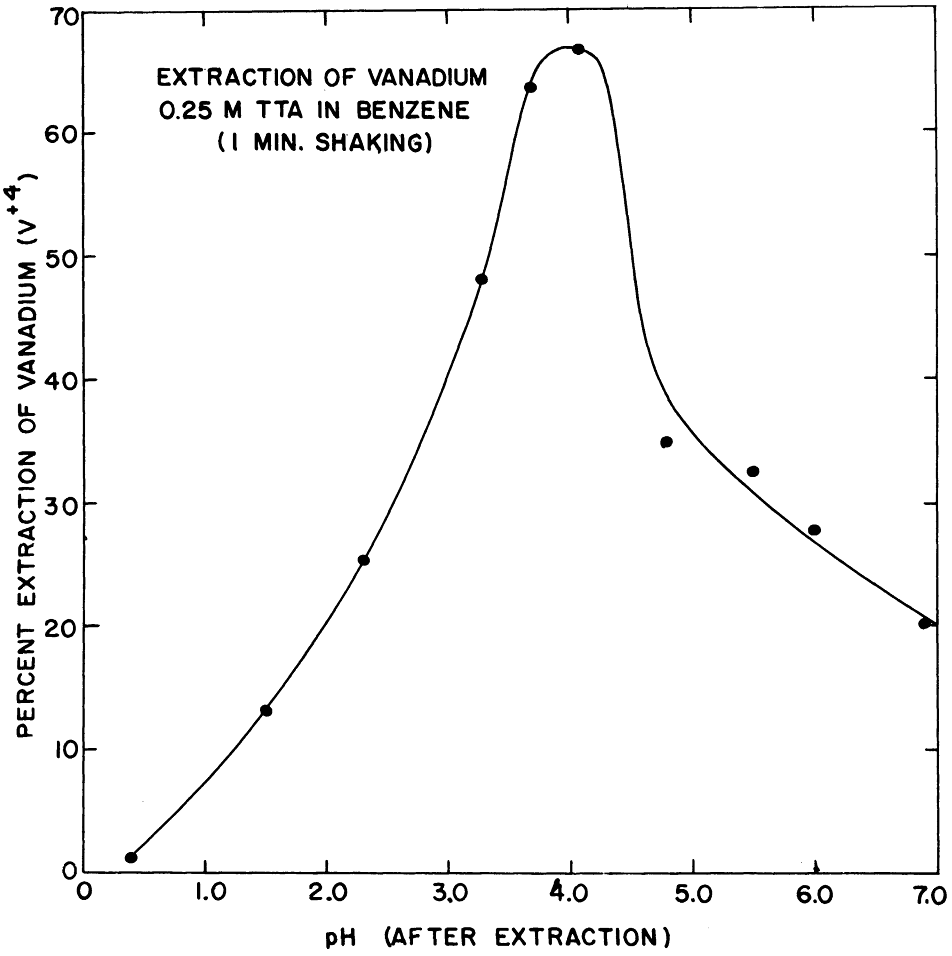

Figure 31. Extraction of Vanadium(IV) with TTA.

5. Ion-Exchange Behavior

A method for the separation of vanadium from rhenium has been published (160) in which the two ions in 0.3 N hydrochloric acid are placed on a column of MMG-1 anion exchange resin in the hydroxide form. Vanadium is eluted with 0.3 N hydrochloric acid; rhenium is removed from the column with 2.5 N sodium hydroxide. A second method for this separation involves elution of a neutral solution from a column of SBS cation exchange resin in the hydrogen form. Rhenium is eluted with dilute acid, while vanadium is eluted with 1:4 ammonium hydroxide. A separation of vanadium from tungsten involves adsorption of these ions at pH 1 on a column of anion-exchanging aluminum oxide. Vanadium is eluted by a solution containing hydrogen peroxide at pH 1, while tungsten is eluted with ammonium hydroxide.

Murthy (143) has investigated the elution of vanadium, as the vanadate, from Amberlite IRA-400 anion exchange resin. Only a part of the vanadium is adsorbed on the resin from a solution containing excess sodium carbonate; the remainder is eluted with 10-percent sodium carbonate. Vanadium is separated completely from uranium, which is strongly adsorbed as the carbonate complex.

Hicks and coworkers (74) have investigated the behavior of a number of metals toward anion exchange on Dowex-2 in the chloride form. They found that vanadium(II, III, IV) is eluted with concentrated hydrochloric acid, signifying little or no adsorption and exchange. On the other hand, vanadium(V) is adsorbed more strongly, and is eluted by 6-9 N hydrochloric acid, together with titanium(IV), platinum(II), zirconium(IV), hafnium(IV), and traces of silver and tantalum(V). These elements have, in general, widely different chemical properties, so that subsequent separation can be accomplished readily. The adsorption of vanadium(V) on Dowex-2 is shown in Figure 32 (101).

Erlenmeyer and Dahn (51) have investigated the use of 8-hydroxyquinoline as an adsorption agent in the chromatographic separation of several ions, in which adsorption takes place by means of chelate formation. The order of adsorption corresponds well to the order of solubilities of the 8-hydroxyquinolates; however, it is also somewhat dependent upon pH. The vanadate anion gives a grayish-black band which appears near the top of the column of oxine. The obvious disadvantage to this type of separation lies in the restrictions placed on the type of solution which can be used. Systems which attack or dissolve the adsorbant cannot be used, thus limiting the usefulness of the method. However, this points the way for investigations into the use of other chelate-forming materials as ion-exchangers.

C. Comparison of Analytical Methods for Vanadium

With the great interest shown in traces of vanadium in petroleum products, cracking catalysts (see Section D)

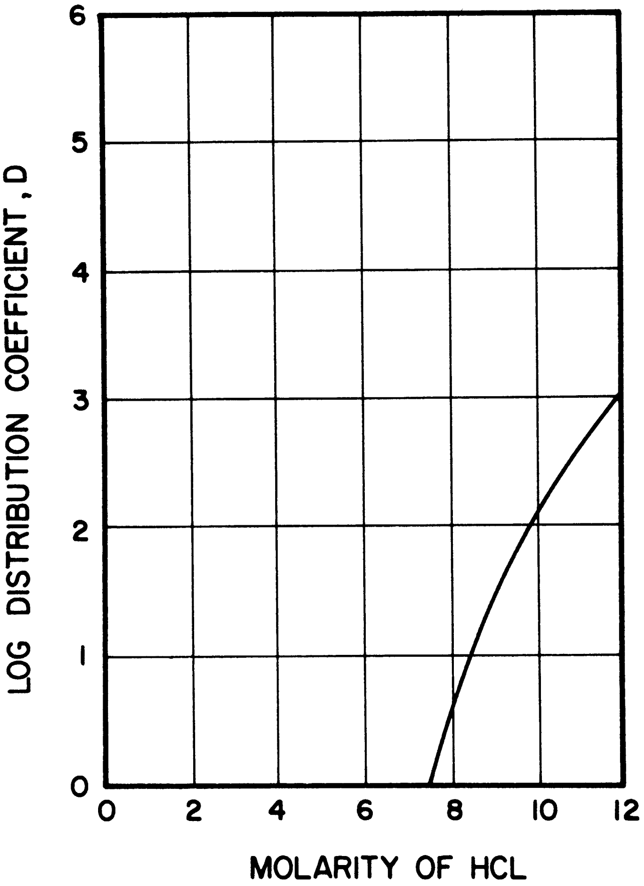

Figure 32. Adsorption of Vanadium(V) by Dowex-2 Anion Exchange Resin from Hydrochloric Acid.

and biological tissue, as well as in larger amounts in steels, uranium processing concentrates, etc., it is to be expected that a large number of analytical methods for determining vanadium will be developed. It may be of value to examine several of these methods with regard to the sensitivities of which they are capable, and see why activation has much to offer the analyst concerned with vanadium determinations.

Emission spectrography is usually considered to be about the most sensitive of the more conventional analytical methods. Vanadium has been determined spectrographically in the parts per million range by Anderson and Hughes (7), Malmstadt and Scholz (118) and others (30, 126, 148). In order to achieve this sensitivity, large samples must be taken and reduced in volume, consuming much time per sample and possibly resulting in some loss of vanadium. X-ray fluorescence spectroscopy has also been used with success. Davis and Hoeck (42) have determined vanadium in residual fuels and charging stock down to 0.4 parts per million with a precision of ± 10-percent. However, large samples (approximately 20 grams) must be taken and an ashing procedure used to reduce sample volume. Dyroff and Skiba (47) have used x-ray fluorescence to determine vanadium in cracking catalyst in amounts down to approximately 2 parts per million. Their procedure makes use of only two grams of sample, is non-destructive and requires only 15 minutes. The x-ray fluorescence procedure is one of the best from the standpoint of time required per sample, but lacks the sensitivity to be useful for many petroleum fractions in which the vanadium content is of the order of 0.1 parts per million.

Several colorimetric or spectrophotometric methods (40, 180, 204) offer sensitivities in the parts per million range. Most of these, with the exception of the procedure by Das Gupta and Singh (40), have a limit of detection of 5-micrograms, so that large samples must be taken. Das Gupta and Singh claim a detection limit of 5 x 10^{-3} micrograms, using benzohydroxamic acid. Amperometric titration (149) and coulometric determination (59) also have detection limits of the order of 1-5 micrograms.

Meinke (129) and Morrison (141) have compared vanadium sensitivities for several methods with that to be expected from neutron activation analysis. Meinke gives the following order of magnitude data for vanadium:

TABLE V

COMPARISON OF SENSITIVITIES FOR VANADIUM

Method	Sensitivity, μgm/ml
Emission spectrography; copper spark graphite d.c. arc	0.05
Flame spectrophotometry	2
Color Reaction	0.2
Amperometric titration	3
Activation analysis: Oak Ridge LITR*	5 x 10^{-5}

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*Assuming a thermal neutron flux of 10^{13} n-cm^{-2}-sec^{-1}

From this comparison, one sees that activation analysis is by far the most sensitive method for determining vanadium. In addition, since the half-life of vanadium-52 is only 3.74 minutes, radioactivation provides a rapid means for determining vanadium.

D. Occurance of Vanadium in Petroleum and Cracking Catalysts

A large amount of interest has been shown for several years in the determination of trace amounts of metals - for example, iron, nickel, vanadium and copper - contained in petroleum crude stocks, and deposited on cracking catalysts. Vanadium, although it is found in relatively low concentrations in many types of crude oil, contributes to a large measure toward the formation of hydrogen and carbon (12) during the catalytic cracking of relatively high-boiling distillates. In addition, a loss of sensitivity (136) is observed as vanadium is deposited on the catalyst. Also, corrosion of furnace brick is markedly increased (12) when residual oil from the cracking process, containing appreciable amounts of vanadium, is burned. Moreover, it has been found (137) that modern high temperature power-producing equipment - gas turbines and aircraft jet engines, for example - are particularly susceptible to corrosion by vanadium, even when present in less than parts per million amounts. As a result, analysis for vanadium in the parts per million and smaller range has become quite important to refiners and users of petroleum products.

having a wide range of molecular weight. Despite these relatively high molecular weights, many porphyrin-metal complexes are found in petroleum distillates. Available evidence (203) indicates that only those vanadium-porphyrin complexes having a relatively low molecular weight can contribute to the vanadium content of petroleum distillates.

Milner, et al. (137), and Horeczy and coworkers (78) have compared the various methods of concentrating the vanadium in petroleum samples as they relate to the volatility of vanadium-porphyrin complexes. Both groups compared the recovery of vanadium following wet ashing by sulfuric acid with that following ignition of crudes and distillation residues and overheads. Their conclusions were essentially the same: relatively little or no vanadium is lost on igniting distillation residues, whereas up to 50-percent or more of the vanadium is lost on ignition of crude and distillate overhead samples. In general, no loss of vanadium occurs on wet ashing these same materials.

In analyzing inorganic samples, volatilization of vanadium may or may not occur, depending upon treatment of the sample. In aqueous media, such loss is generally insignificant, at least at temperatures up to 175°C (75). This is explained by the fact that most volatile inorganic vanadium compounds are decomposed in the presence of moisture. In a relatively moisture-free system, however, volatile vanadium compounds can form and may be lost from the sample.

In the activation determination of vanadium described below, the loss of vanadium by volatilization does not occur with petroleum samples, since no chemical ashing or ignition is performed, the determination being completely non-destructive. On the other hand, loss of vanadium may or may not occur during the separation of vanadium from catalyst samples. However, correction for any such loss is automatic with determination of chemical recovery of vanadium by means of vanadium-48 tracer, since the two vanadium isotopes are chemically equivalent.

E. Experimental Procedures

At the start of experiments involving petroleum samples, several hundred milligrams of a South American crude and a domestic distillation residuum were absorbed on a piece of tared analytical grade filter paper. This was placed between two similar filter paper discs, which absorbed any excess of the sample. These were then placed in a small envelope formed from 1/4-mil cast Teflon film, and irradiated for ten minutes at a thermal neutron flux of approximately 0.95×10^{11} neutrons-cm^{-2}-sec^{-1}. At the end of the irradiation period, the filter discs were removed from the Teflon envelope and mounted for counting. Analysis of the gross activity of the sample was accomplished by means of gamma spectrometry, employing the 100-channel analyzer and 3-inch by 3-inch sodium iodide(thallium) detector. Spectra were recorded every thirty seconds throughout the energy range from 0 to 2 Mev, and corrected for instrument dead time and background activity. An excessive amount of bremstrahlung was present in the recorded spectra; this was traced to activity induced in the filter paper sample support. Several materials were irradiated and analyzed by gamma spectrometry in an effort to find the sample packaging material with the smallest amount of induced activity. Polyethylene tubing (Intramedic, Medical Formulation PHF, Clay-Adams, Inc., New York) was chosen as the best compromise between low induced activity and ease of packaging and handling. Petroleum samples were then irradiated after being sealed in short lengths of this tubing.

Gamma spectrometry was performed on several samples which were still sealed in polyethylene. When the vanadium photopeak of the sample had decayed out, however, a low intensity photopeak was found on the low energy side of the vanadium peak adding a part of its activity to the vanadium peak. This was subsequently identified as the 1.38-Mev peak of sodium-24 and had its origin in the polyethylene package. This interference was eliminated by transferring the irradiated sample to a tared 5-milliliter beaker, thus removing packaging material completely from the vicinity of the detector. The beaker and the sample were weighed following gamma scintillation analysis to obtain the weight of the sample.

1. Procedure for Petroleum Samples

A short length of polyethylene tubing (approximately 1 to 1-1/4 inches) was heat sealed on one end over a micro burner. About one milliliter of the petroleum sample to be analyzed was transferred by pipet into the tube. The open end of the tube was then heat sealed, care being taken not to volatize any of the sample. The container was then checked for leaks by squeezing. This was then wrapped in several thicknesses of Kleenex and placed in a nylon or polyethylene rabbit. A small accurately weighed gold foil (1-mil thick, weighing 0.1-0.5 milligrams) was taped inside the cap of the rabbit, directly over the center. The foil acted as a flux monitor and was used to correct for any variations in the neutron flux of the reactor from sample to sample. The rabbit was then placed in the pneumatic tube and sent into the reactor, where it was irradiated for a period of 10.00 ± 0.02 minutes.

At the end of the irradiation period, the sample was withdrawn from the reactor and the sample container removed from the rabbit. This was cut open on one end and the sample transferred into a tared 5-milliliter beaker of the type used to contain samples in a portable pH meter. Since the sample was not weighed prior to irradiation, transfer need not be quantitative. The beaker was then covered with a plastic planchet and taped to a counting card. The sample was transported to the counting room and placed atop the 3-inch by 3-inch scintillation detector (the crystal and housing were mounted vertically when these samples were being analyzed). Analysis with the 100-channel analyzer was begun at exactly two minutes following removal of the sample from the reactor, successive spectra being recorded over the range from 0 to 2 Mev every thirty seconds. Instrument dead time was recorded at the start of the first counting cycle and at the start of each subsequent cycle. Counting was continued over several minutes, or until the vanadium-52 had decayed below the limit of detectability. The sample was then removed from the detector cave, and the background activities recorded for 5-10 cycles. An average background was obtained from these measurements and subtracted from the vanadium spectra.

Petroleum samples which were solids or semi-solids at ambient temperatures required slightly different treatment. These could not be packaged easily in polyethylene tubing. Instead, samples of this type were melted, poured into 5-milliliter glass vials and allowed to solidfy. Approximately 3 milliliters of sample were transferred to the vial. The gold foil monitor was placed inside the vial, which was then wrapped in a piece of split rubber tubing, wrapped in Kleenex, and placed in a Lustroid rabbit. Irradiation was carried out as for liquid samples. On return from the reactor, the sample vial was removed from the rabbit and padding material, and the gold foil removed. The sample was then quickly melted over a burner, and poured into a tared beaker. Subsequent treatment was exactly the same as for liquid samples.

Soon after gamma analysis of the sample was completed, the beaker containing the sample was reweighed, care being taken throughout its handling to prevent touching the surface of the glass. The weights of samples were thus obtained by difference. The amount of vanadium in each sample was determined by summing the counts under the vanadium-52 photopeak recorded during the first counting cycle. This sum was then corrected for instrument dead time using Equation 22 (Chapter II), and background activity. The gold foil monitors were counted in the scintillation well counter; the gold activity was corrected to the time of removal of the sample from the reactor and converted to specific activity by dividing the observed activity by the weight of the foil in milligrams. Corrections for the variation in neutron flux from sample to sample were made by normalizing all observed photopeak activities to a (gold) specific activity of 7.00×10^6 counts per minute per milligram. The weight of vanadium was then read from the calibration curve, preparation of which is described in Section E, 3, below.

2. Procedure for Cracking Catalyst

Vanadium could not be determined non-destructively in catalyst samples due to interferences in the gamma spectrum caused by aluminum-28 and silicon-31 (see Figure 37). As a result, separation of vanadium from these two elements was necessary. The following procedure was developed to effect this separation.

Finely ground catalyst samples were weighed into gelatine capsules, from 40-100 milligrams being taken for analysis. The capsule was then wrapped in several layers of Kleenex and placed in a rabbit. An accurately weighed gold foil monitor (0.1 to 0.5 milligrams) was placed in the cap of the rabbit, which was then dispatched into the reactor, where it was irradiated for 10.00 ± 0.002 minutes. On removal of the sample from the reactor, the capsule containing the sample was placed in a nickel crucible containing a known amount of vanadium-48 tracer and 3-4 grams of molten sodium peroxide. The crucible cover was clamped down over the crucible immediately as the capsule was dropped into the flux. A violent exothermic reaction took place, heating the crucible bottom to a bright red. Once this reaction had subsided, the crucible was heated over a burner until the molten mass was clear. The melt was then cooled quickly by repeatedly dipping the bottom of the crucible into cold water.

The solidified melt was then dissolved in 100 milliliters of a solution containing 30 milligrams of aluminum and 5 milligrams of vanadium carriers, 16.7 milliliters of hydrochloric acid and 3 milliliters of 3-percent hydrogen peroxide. To this was added 30 milliliters of a 10-percent solution of 8-hydroxyquinoline in 1:4 acetic acid, followed by approximately 60 milliliters of ammonium hydroxide. The pH of this solution was 9-10, as determined with Hydrion pH paper. The resulting aluminum-8-hydroxyquinolate was filtered rapidly through a 120-millimeter medium glass filter frit and washed with 10-percent 8-hydroxyquinoline solution. The filtrate was acidified with hydrochloric acid, cooled by adding chipped ice or liquid nitrogen, and transferred to a 250-milliliter separatory funnel containing 5 milliliters of chloroform previously equilibrated with 1-2 normal hydrochloric acid. Six milliliters of 6-percent aqueous cupferron were added, and the mixture shaken for approximately one minute. The layers were allowed to separate and the reddish-brown chloroform layer was drained into a counting tube. Analysis of the gamma spectrum of the chloroform layer was begun exactly 10.0 minutes following removal of the sample from the reactor, and followed the same pattern as in the case of the petroleum samples. After gamma analysis of the sample was completed, the sample was set aside for a few hours, after which the vanadium-48 tracer was counted and compared to the amount added to the nickel crucible in order to determine chemical recovery of the separated vanadium.

3. Preparation of Standard Curves

Standard curves were constructed, relating the number of counts under the vanadium-52 photopeak to micrograms of vanadium. Three curves were constructed: for vanadium in petroleum samples irradiated at a reactor power level of 100 kilowatts; for petroleum samples irradiated at 1000 kilowatts; and for catalyst (and other) samples irradiated at 1000 kilowatts. These three curves are given in Figures 33 and 34, and were prepared in the following manner: 44.09 milligrams (for the vanadium curve for petroleum samples at 100 kilowatts) or 4.386 milligrams (for petroleum and catalyst samples at 1000 kilowatts) were dissolved in approximately 1 milliliter of nitric acid and diluted to 250 milliliters in a volumetric flask, using de-ionized water. Aliquots of the solution were pipetted onto 15-millimeter (diameter) ashless filter circles and evaporated to dryness between two additional circles. These were then placed in a small envelope formed from 1/4-mil Teflon and irradiated for 10.00 ± 0.02 minutes. On removal from the reactor, the three filter discs were removed from the rabbit and the Teflon envelope and mounted for gamma spectral analysis. Analysis was begun at exactly 2.00 minutes or exactly 10.00 minutes following removal, depending upon whether the curves were to be used with petroleum samples or with catalyst (or other) samples. The activity under the vanadium-52 photopeak in the first counting cycle was then corrected for instrument dead time, background activity,

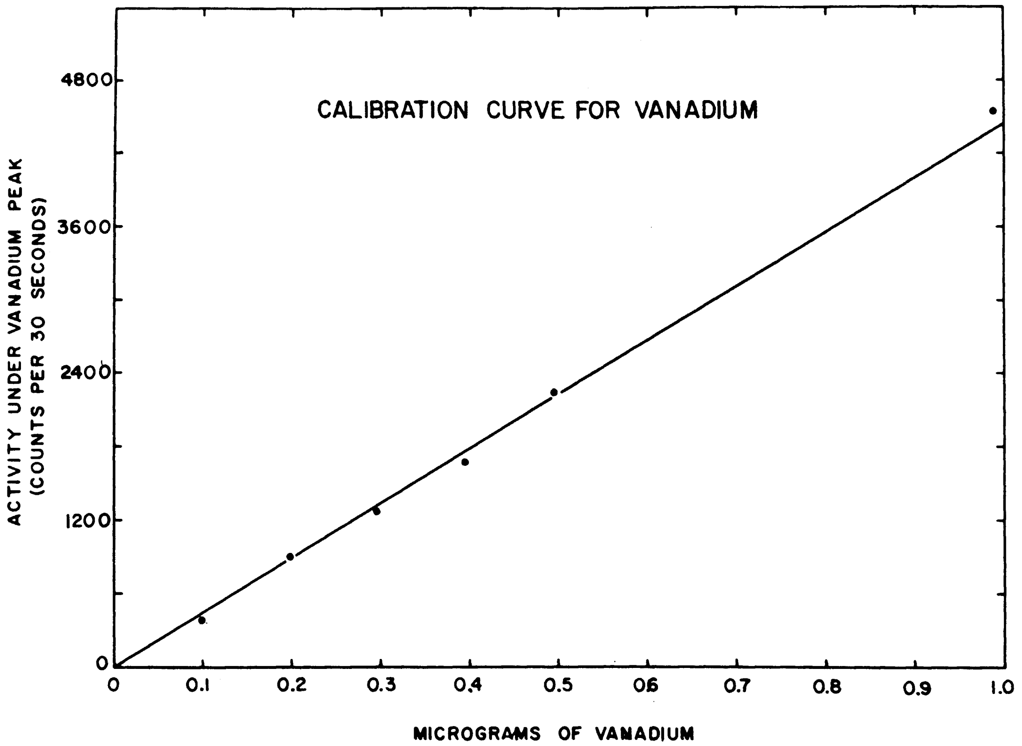


Figure 33. Calibration Curve for Vanadium in Petroleum. Reactor Power Level at 100-Kilowatts.

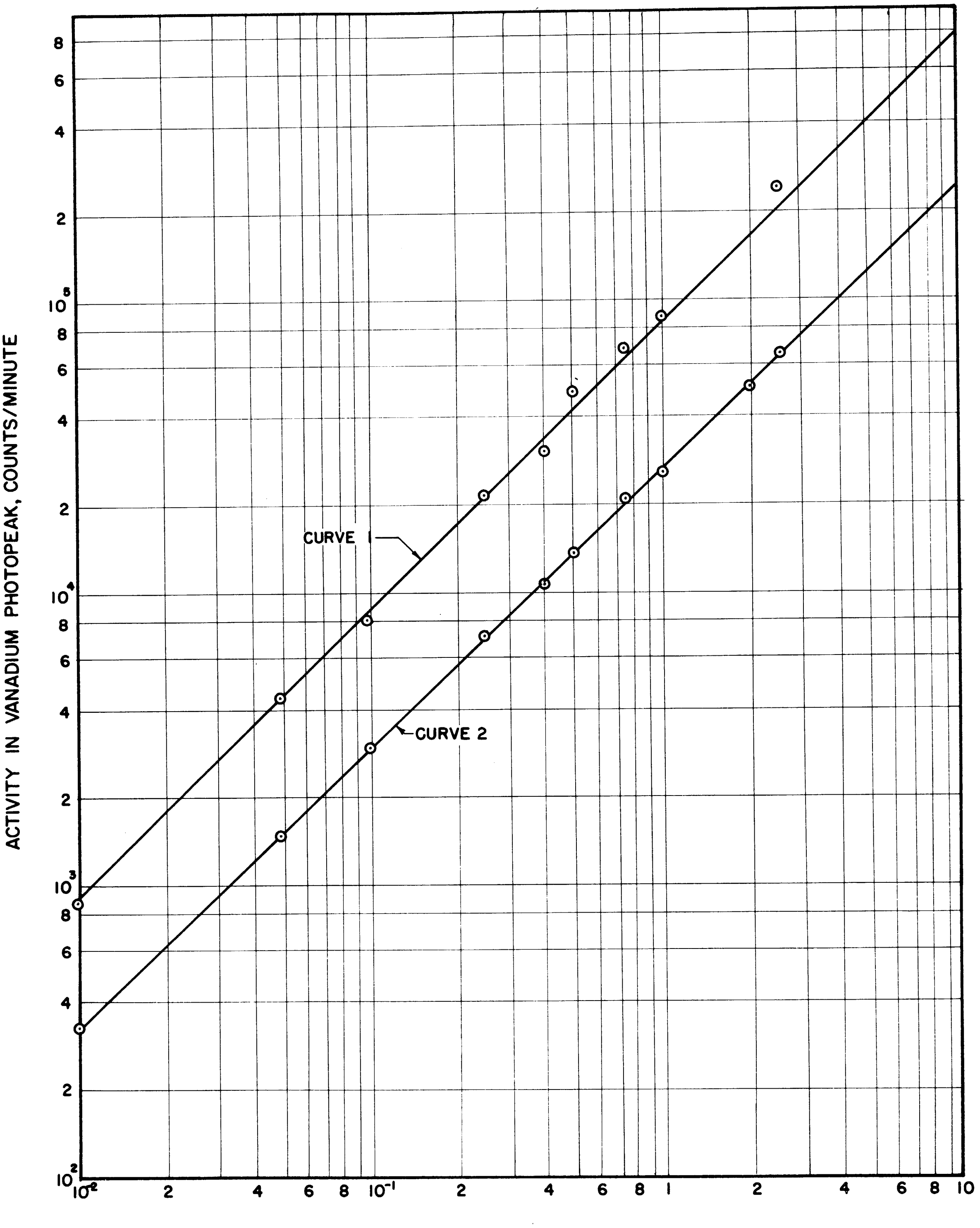


Figure 34. Calibration Curves for Vanadium. Reactor Power Level at 1000-Kilowatts.

and flux variations (in that order), and plotted against micrograms of vanadium.

An alternate procedure was also used: approximately 0.50 milliliter of the standard solutions were sealed in short lengths of polyethylene tubing and irradiated. Following return from the reactor, the polyethylene container was cut open on one end and aliquots of 1-250 λ of the active solution were pipetted onto filter circles. These were then analyzed by gamma spectrometry in exactly the same manner as the standards evaporated onto filter circles. Results by both methods were comparable, but the latter method, generally requiring less time and eliminating any activity due to the filter discs, was adopted for most measurements.

F. Results and Discussion

Calibration curves of activity under the vanadium-52 photopeak versus micrograms of vanadium were plotted from data obtained using the methods of Section E. Figures 33 and 34 show that the individual calibration points lie on a fairly straight line covering a wide range of activity and weight. Slight deviations of the individual points from a straight line are due, in all probability, to errors in handling the micropipettes used to take aliquots of the active solutions. Figure 33 gives the calibration curve for petrolium samples analyzed when the reactor was operating at a power level of 100 kilowatts. Curve 1, Figure 34, was used for petroleum samples activated with the reactor at a power level of 1000 kilowatts. Curve 2 was that used for catalyst samples, activated at 1000 kilowatts, where gamma analysis was begun exactly 10.0 minutes following removal from the reactor. Gamma analysis of all petroleum samples was begun exactly 2.0 minutes following removal from the reactor.

Gamma spectra obtained from petroleum process samples and from a typical crude oil are shown in Figures 35 and 36. The spectra observed were fairly simple, showing only one or two major photopeaks. Results for the determination of vanadium in several petroleum process stream samples are presented in Table VI. The results of the determinations show that reasonably accurate and precise determinations of vanadium can be performed non-destructively in the range of 0.1-1.0 parts per million. These determinations were completed in less than one hour. During this time, loss of sample by volatilization was negligible, amounting to only about 0.1 milligram for the most volatile of the samples used. Conceivably, for gasoline or other very volatile samples, the simple beaker and plastic planchet cover would need to be replaced by a glass-stopped vessel.

The results for the determination of vanadium in two cracking catalyst samples are presented in Table VII. These samples (kindly furnished by O. I. Milner of the Socony-Mobil Oil Company) have a silicon dioxide (90-percent) - aluminum oxide (10-percent) base, and may also contain

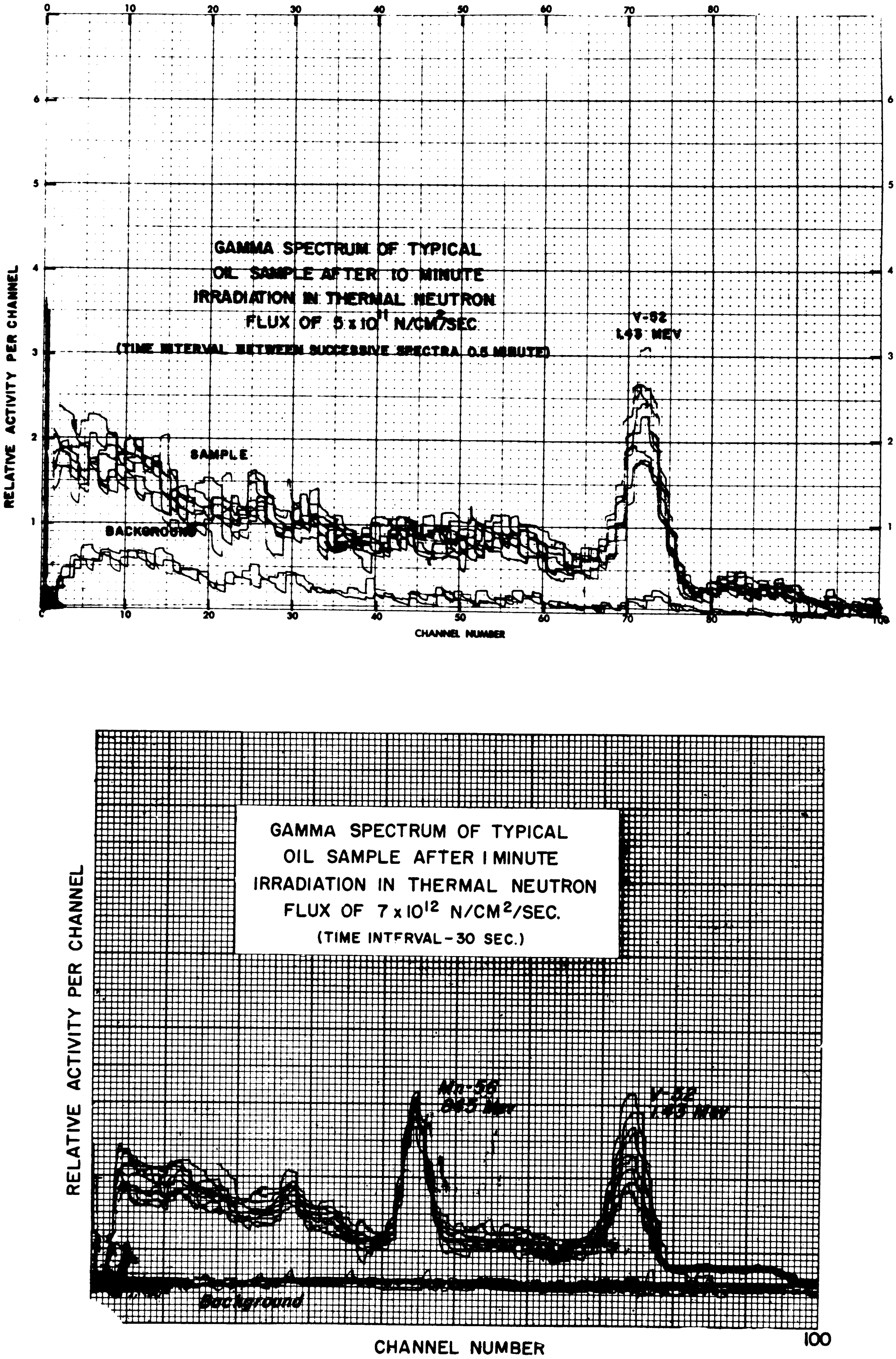


Figure 35. Gamma Spectra of Typical Petroleum Process Stream Samples.

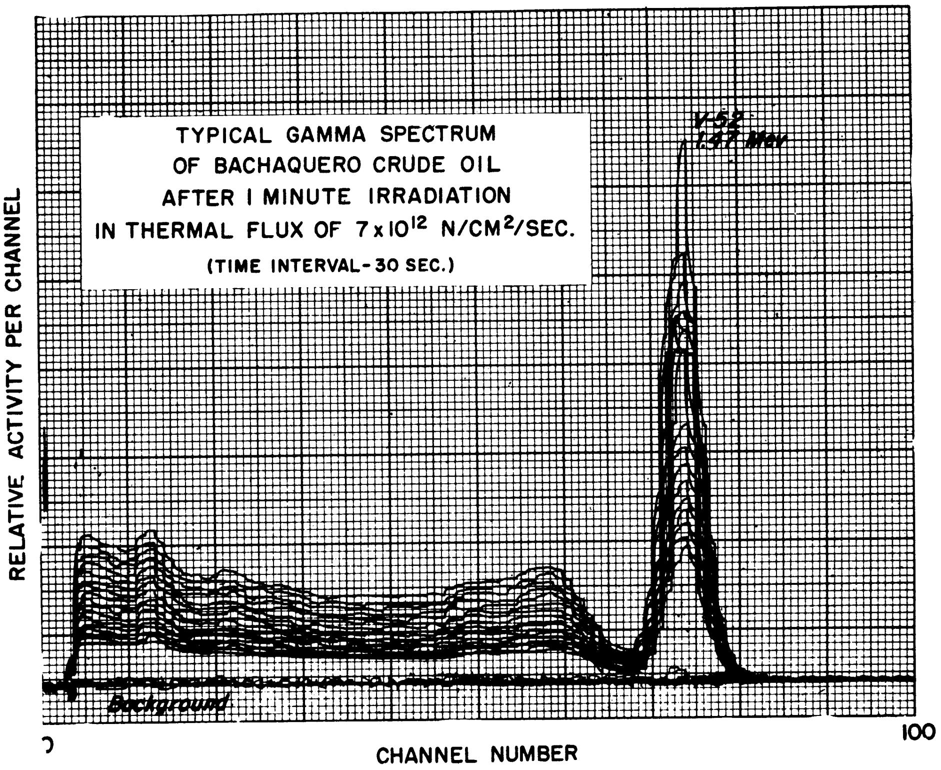


Figure 36. Gamma Spectra of Typical Crude Oil.

TABLE VI

VANADIUM IN PETROLEUM PROCESS STREAM SAMPLES

Sample No.	Wt. Sample, mg.	Corrected cts. per 30-sec. in V-52 photopeak	V ppm	Average $(\overline{X})$*	Chemical Det'n.,ppm**
1	576.6	1306	.509	0.490 ± 3.88%	0.47
	627.5	1321	.473		
	446.7	964	.489		
2	427.5	1900	1.68	1.65 ± 3.68%	1.66
	415.7	2902	1.58		
	303.8	2277	1.69		
3	424.1	1900	1.007	0.987 ± 1.65%	1.00
	366.2	1593	0.985		
	289.2	1265	0.987		
	237.3	1019	0.967		
4	595.7	380	0.146	0.135 ± 7.39%	0.11
	1071.3	656	0.138		
	1104.2	659	0.135		
	1011.7	548	0.122		

TABLE VI (Cont.)

Sample No.	Wt. Sample, mg.	Corrected cts. per 30-sec. in V-52 photopeak	V ppm	Average ($\bar{X}$)*	Chemical Det'n., ppm**
5	345.7	417	0.275		
	388.6	512	0.229		
	363.5	391	0.241	0.234 ± 10.1%	0.27
	878.5	913	0.233		
	1185.1	1102	0.217		
	985.9	891	0.207		

---

*The percent standard deviation is calculated by means of the relation

$$\%\sigma = \frac{1}{\bar{x}} \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n-1}} \times 100 \qquad (24)$$

where n is the number of determinations performed.

**Determined colorimetrically by the phosphotungstate method (137).

small amounts of nickel, iron, chromium, titanium and zirconium oxides. The gamma spectrum of a representative sample (Figure 37) shows a very large aluminum-28 photopeak, in addition to smaller vanadium-52 and silicon-31 photopeaks superimposed on the Compton continuum of the aluminum. It is because of the presence of this aluminum photopeak that a chemical separation of vanadium was deemed necessary for any reasonably accurate determination.

The major problem with this separation was encountered in the complete removal of aluminum, inasmuch as the other elements present in the samples gave rise to gamma photopeaks at much lower energies than that of vanadium-52, and hence did not interfere with the vanadium determination. Initially, it was felt that a simple extraction of vanadium as the cupferrate from dilute acid solution would suffice to separate vanadium from aluminum. It was found, however, that the counting sample contained a large amount of aluminum-28 contamination. Synthetic samples of aluminum oxide and vanadium pentoxide in the ratio of approximately 100:1, were analyzed by the method first tried (i.e., simple cupferron extraction from acid solution, following peroxide fusion). Not one of these showed more than the most minute contamination by aluminum, while catalyst samples consistently showed large amounts of contamination. It was then felt that perhaps the silicon played some part in the appearance of aluminum in vanadium cupferrate extracts; another series of synthetic samples, containing aluminum oxide, silica, and vanadium pentoxide, was then analyzed. The results were essentially the same as for the previous synthetic samples - no aluminum contamination. The procedure of section E was suggested by material in the literature (75) concerning the precipitation of aluminum with 8-hydroxyquinoline in the presence of several elements, including vanadium. The vanadium was complexed with 3-percent hydrogen peroxide to prevent formation of vanadium-8-hydroxyquinolate. Aluminum was removed completely from solution as the 8-hydroxyquinolate. The chemical recovery of vanadium in these procedures was determined by means of vanadium-48 tracer added to the nickel crucible prior to fusion.

As can be seen from results of vanadium determinations presented in Table VII, the reproducibility of the method is not quite as high as might be desired, even for trace determinations. This may well be due to such effects as thermal or photochemical decomposition of the cupferron reagent before use, thermal decomposition of the vanadium cupferrate, adsorption of vanadium on the aluminum-8-hydroxyquinolate precipitate, or mechanical losses incurred during the rapid separation. In general, mechanical losses are inconsequential as sources of error since determinations of chemical recovery compensates for any such loss. The wide variation in chemical recovery, from 18.4- to 71.4-percent contribute to poor reproducibility to the extent that

TABLE VII

VANADIUM IN CRACKING CATALYST

Sample No.	Wt. sample, mg.	V ppm	Average
1	76.0	6.01	9.66 ± 33.5%
	97.0	12.19	
	55.8	10.79	
2	59.4	22.38	24.09 ± 23.9%
	40.6	32.16	
	45.8	20.61	
	75.1	17.71	
	62.1	27.61	

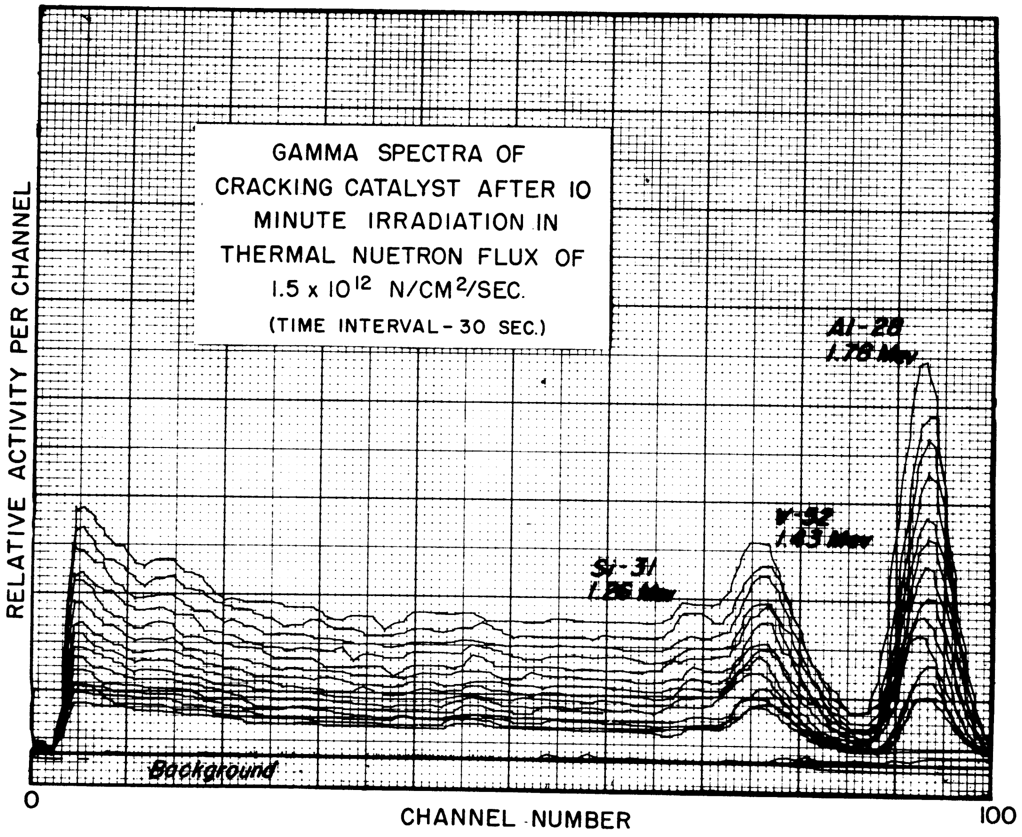


Figure 37 Gamma Spectra of Typical Cracking Catalyst.

samples with low recoveries exhibit poor counting statistics and lead to larger uncertainties in the amount of vanadium determined than for samples having higher recoveries.

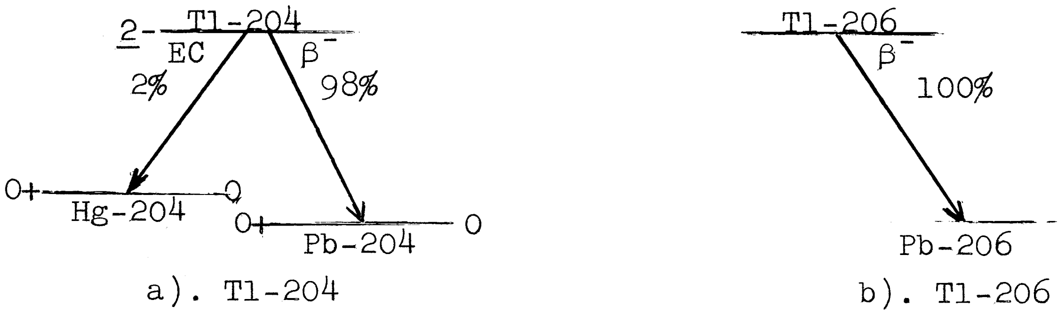
In activation analysis by gamma scintillation spectrometry, some amount of detection sensitivity is sacrificed for the rapidity with which an analysis can be performed; that is, smaller amounts of trace contaminants can be determined by means of gross gamma counting than by gamma spectrometry. The basis for this difference lies in the phenomenon of Compton scattering. The Compton effect entails an interaction between a gamma photon and an electron, in which the photon loses some, but not all, of its energy to the electron. In terms of activation analysis by gamma spectrometry, this means that the Compton-scattered photon does not appear in the full energy photopeak, and hence is not counted as activity of the isotope being used for analysis, but instead appears as a part of a continuum at lower energies. When a gamma emitter is analyzed by means of the decay of its gross activity, this Compton continuum is still present; in this case, however, it would be counted as part of the activity of a particular gamma emitting radioisotope, along with the full energy photopeak. The net result is a higher count rate than by gamma spectrometry, and a resultant increase in the sensitivity with which a given element can be determined. The disadvantages to gross counting, however, are the time required to measure the decay, and loss of precision as it becomes necessary to resolve components. In the case of vanadium, a rapid determination procedure was desired, consistent with reasonably good precision and accuracy. To this end, gamma spectrometry, coupled with a fast separation, provided the best compromise.

CHAPTER VI

DETERMINATION OF THALLIUM

A. Nuclear Properties

Naturally-occurring thallium consists of two stable isotopes, thallium-203 and -205. The abundances of these isotopes has been given (9) as 29.50- and 70.50-percent, respectively. Since the two stable isotopes do not have consecutive mass numbers, two radioisotopes are formed on bombardment of natural thallium by thermal neutrons. These two radioisotopes are thallium-204 (from thallium-203) and thallium-206 (from thallium-205), and have half-lives of 4.0 to 4.26 years (68, 79, 189) and 4.19 to 4.3 minutes (2, 52, 164), respectively. Thallium-204 decays by beta emission and electron capture, according to the decay scheme of Figure 38a (185), while thallium-206 is a pure beta emitter having the decay scheme of Figure 38b. As a result, thallium-206 produces no gamma spectrum, whereas thallium-204 produces a scintillation photopeak at 0.069 Mev, due to the mercury K x-ray.



a). Tl-204 b). Tl-206

Figure 38. Decay Schemes of Thallium-204 and -206.

The cross-sections for the activation of thallium-203 and thallium-205 are not such as to favor activation determinations by means of the short-lived isotope, thallium-206. These cross-sections have been reported (181) as being 11 barns for thallium-203 and 0.11 barn for thallium-205. Thus the utilization of thallium-203 for activation determinations is favored on one hand by its relatively high cross-section, but is discouraged on the other hand by its long half-life. The exact opposite is true in the case of thallium-205.

B. Radiochemistry of Thallium

1. Precipitation and Co-precipitation Reactions

Thallium is either monovalent or trivalent in its compounds. In the former state it resembles the alkali metals and silver in its reactions; the latter state resembles the heavy metals. Thallium(I and III) form several insoluble compounds capable of use in separation procedures. A few of these are discussed below as they relate to rapid separations of radiothallium-206.

In its monovalent state, thallium forms a bright yellow precipitate with iodide ion which is soluble in nitric acid and aqua regia, but insoluble in excess iodide. The solubility product of thallous iodide is approximately 3.7×10^{-10} at $20^{\circ}C$. Precipitation of thallium(I) as the iodide separates the element from cadmium, iron(II and III), aluminum, chromium(II and III), cobalt(II), nickel, zinc, alkaline earths, magnesium, and the alkali metals. Copper(I and II) and silver are also precipitated; the copper can be removed by digesting the iodide precipitate with dilute ammonium hydroxide. Silver can be removed by dissolving the precipitate in nitric acid, diluting, and precipitating silver as the chloride.

Thallium, by itself, is not precipitated as the thallic compound by hydrogen sulfide in strong acid solution. However, this should not be used as a means for thallium separations since thallium(III) forms compounds with members of the hydrogen sulfide group such as arsenic, antimony, tin or copper (75). In acid solution, thallic salts are reduced to thallous by hydrogen sulfide. Thallous ion can be precipitated completely as the sulfide, which is insoluble in alkalies and in acetic acid. Ammonium sulfide also precipitates thallous sulfide, which has a solubility product, $K_{sp4} = 10^{-24}$ (163). Mercury(II), lead and silver sulfides have been suggested (163) as coprecipitation agents for thallous sulfide.

Thallium(I) chromate and chloroplatinate also have low solubilities in aqueous solution, as do the cobaltinitrite and phosphotungstate. The chromate has been used in the separation of thallium(I) from meteorites (152) and fission products (150). For carrier free separation of small amounts of thallium(I), barium chromate has been suggested as a collector or coprecipitating agent. In the case of separation by means of the chloroplatinate, cobaltinitrite or phosphotungstate, potassium or rubidium have been suggested (163) as coprecipitating agents.

Kuznetsov and Alimarin (103) have reported an organic coprecipitation method for the separation of thallium from many elements. To a solution containing thallium in the monovalent state is added p-dimethylaminoazobenzene and methyl orange. The resulting precipitate carries down many elements, leaving monovalent thallium in solution. After oxidation of thallium in the filtrate with hypochlorite, it is coprecipitated in the pure form with the same coprecipitants. In this manner 10-0.1 micrograms of thallium per liter can be coprecipitated with 90-100-percent recovery (104).

Sodium tetraphenylboron has been used for the radiometric (3, 176) and gravimetric (201) determination of small amounts of thallium(I) in the presence of cadmium, zinc, lead, copper(II), indium(III), and iron(II and III). Interference from these elements is eliminated through the use of a saturated solution of ethylenediaminetetra-acetic acid. Samples for analysis were dissolved in a minimal amount of nitric acid, neutralized to pH 4-5 by means of an acetate buffer, and the saturated EDTA added. Amounts of thallium as small as 9 micrograms can be determined by this method in the presence of as much as 150 times this amount of lead.

Thionalide, or thioglycolic acid-β-aminonaphthalide, is a little used reagent for the precipitation of monovalent thallium. In a tartrate-cyanide solution containing sodium or ammonium hydroxide, thionalide is a specific precipitant for thallium(I), and has been used for its gravimetric determination (15, 16). The precipitation is made by adding a four- to five-fold excess of the reagent, dissolved in acetone, to a solution 1 M in sodium hydroxide, 5-percent in potassium cyanide and 5-percent in sodium tartrate. The precipitate is yellow, and finely divided. The solution is then brought almost to boiling, and cooled to room temperature, whereupon the precipitate agglomerates and can be filtered easily. For precipitation of 4.2-minute thallium-206, the boiling solution containing the precipitate can be cooled to room temperature quickly by using liquid nitrogen.

2. Oxidation-Reduction Behavior

The standard potential, at 25°C, for the Tl-Tl^+ (or Tl(Hg)-Tl^+) couple is given (106) as +0.336 volts vs. the standard hydrogen electrode. That of the thallous-thallic couple is -1.2466 volts.

Trivalent thallium can be reduced by sulfur dioxide in very dilute sulfuric acid (but not hydrochloric acid). Saturated sulfurous acid also is capable of reducing trivalent thallium to the monovalent state, as is a solution of hydroxylamine hydrochloride. Potassium iodide, in dilute acid solution, reduces thallic compounds to thallous, liberating iodine in the course of the reaction. This reaction forms the basis of an analytical method for the determination of thallium(III) in solution (66). Zinc, magnesium and aluminum in dilute hydrochloric or sulfuric acids reduces thallic salts to metallic thallium sponge. The sponge so obtained is oxidized easily by air or dissolved oxygen, hence most of the solution must be decanted and the residue washed quickly with recently boiled water. Hydrogen sulfide also reduces thallium(III) to thallium(I), and can result in the precipitation of thallous sulfide.

Thallium(I) is oxidized to thallium(III) by acidic potassium permanganate, potassium bromate or ceric sulfate. Bromine- and chlorine-water also oxidize thallium(I), in addition to hypochlorite. Aqua regia will oxidize thallium (I), but nitric acid alone will not. Thallous salts treated with potassium hydroxide and potassium ferricyanide are oxidized and precipitated as thallic oxide. The procedure has been made the basis for a gravimetric method of determining thallium(I) in solution (22). Thallium(I), like thallium(III), is reduced to a metallic sponge by zinc, magnesium and aluminum in dilute hydrochloric or sulfuric acid.

3. Solvent Extraction

Thallium(I and III) form complexes with bromide, chloride, and iodide which can be extracted into various organic solvents. Thallic bromide is extracted to the extent of greater than 90-percent over a wide range of hydrobromic acid concentrations (19, 86, 195). Figure 39 shows extraction of bromides into ethyl ether as a function of the concentration of hydrobromic acid. A good separation of thallium (III) from indium(III), iron(III) and gallium(III) can be made by keeping the concentration of hydrobromic acid between 0.5 and 1.0. Extraction into diethyl ether from hydriodic acid solutions is shown in Figure 40. The dotted curve for thallium(I) is valid only for microgram amounts. The use of hydriodic acid presents a problem, as the acid decomposes readily on standing. A solution of sulfuric acid, to which the appropriate amount of potassium iodide has been added, can be substituted for the free acid (86). By this means the concentrations of the acid and iodide can be varied over a wide range without loss of extraction efficiency.

Thallium(III) also extracts well into many organic solvents from solutions of hydrochloric acid, as shown in Figure 41. The extraction of gallium(III) and iron(III) are shown for comparison. Thallium(III) can be extracted from hydrochloric acid solutions so dilute that only small amounts of iron(III) and gallium(III) accompany it; the principal contaminant is then mercury(II) (85).

Dithizone has also been used for the extraction of thallium, in which the order of extractability (145) is $\mathrm{Pd} > \mathrm{Ag} > \mathrm{Hg(II)} > \mathrm{Cu(II)} > \mathrm{Bi} \geq \mathrm{Pt(II)} > \mathrm{Tl(III)} > \mathrm{Fe(III)} > \mathrm{Sn(II)} \overset{-}{>} \mathrm{Co} \geq \mathrm{Ni} > \mathrm{Zn} > \mathrm{Pb} > \mathrm{Mn} > \mathrm{Cd}$. Lead, Sn(II), Bi and Tl(I) react with the reagent in basic solution containing

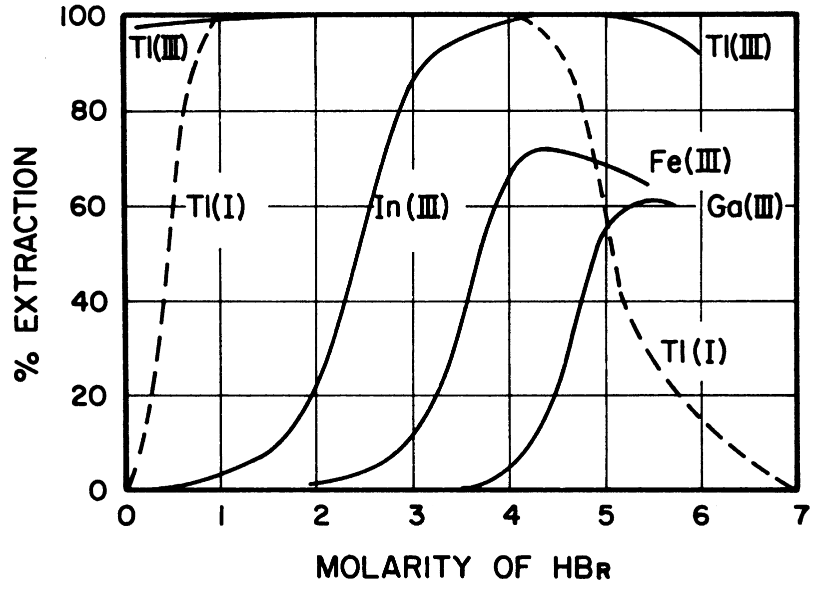


Figure 39. Extraction of Bromides into Ethyl Ether.

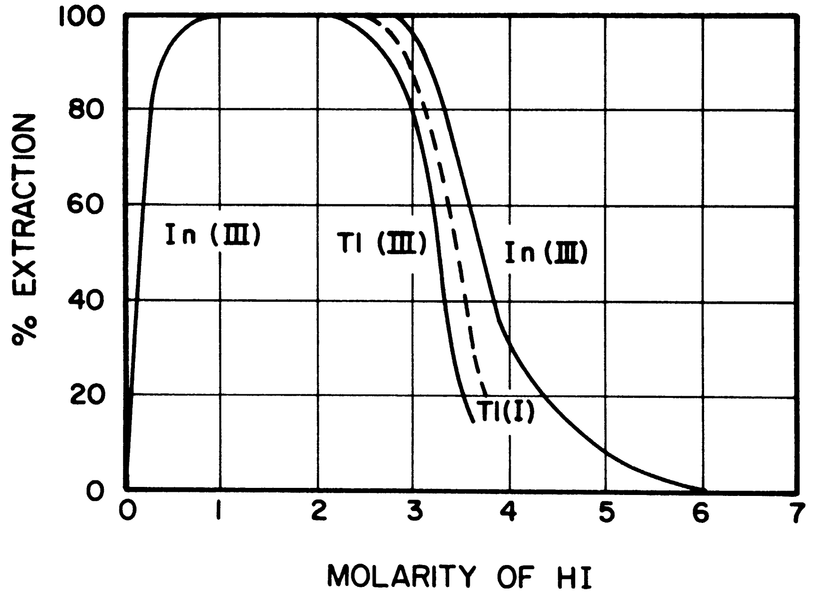


Figure 40. Extraction of Iodides into Ethyl Ether.

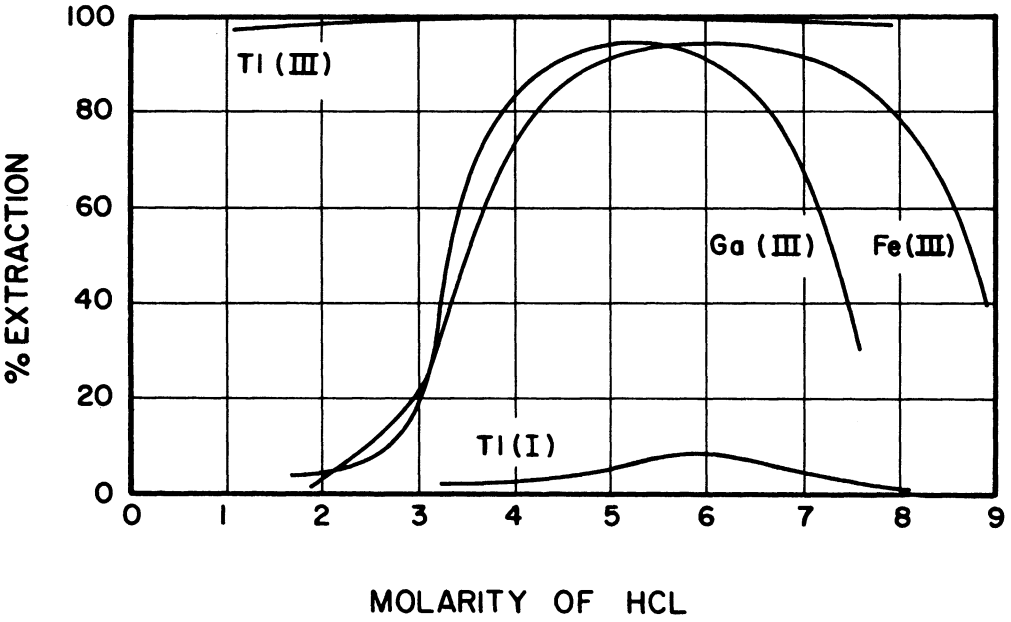


Figure 41. Extraction of Chlorides into Ethyl Ether.

cyamide. Ethylenediaminetetra-acetic acid prevents extraction of Pb, Zn, Bi, Cd, Ni and Tl(I and II) at any pH. The reaction between dithizone and thallium(III) does not attain completion; in addition, dithizone may be oxidized by the thallium(III).

Thenoyltrifluoroacetone (TTA) has found widespread use in radiochemical separations. Hagemann (67) studied the extraction of thallium(I and II) by 0.25 M TTA in benzene as a function of pH. His findings are presented in Figure 42.

4. Ion Exchange Behavior

The ion exchange behavior of thallium has not received a great deal of attention in recent years. Some work has been done, however, on the anion exchange behavior of thallium (I and III) from hydrochloric acid solutions using Dowex-2. Hicks, et al. (74), report that thallium(II) is eluted by 12 M hydrochloric acid in ten column volumes, along with the alkali metals, alkaline earths, rare earths, Sc, Y, Ti(III), V(II, III, IV), Ni, As(III), As(V), Se(IV), Pb, Bi, Cu(II), Al, Cr(III), Fe(II) and Mn(II). On the other hand, thallium (III) is not eluted by perchloric acid, ammonium hydroxide, nor sodium hydroxide, but is retained on the column. This behavior is in accord with the work of Krause, Nelson and Smith (102), who have studied the distribution coefficient of thallium(III) on Dowex anion exchange resin as a function of the molarity of hydrochloric acid. Their results are shown in Figure 43. Thallium is removed from the column by elution with 1.5 N sulfuric acid saturated with sulfur dioxide.

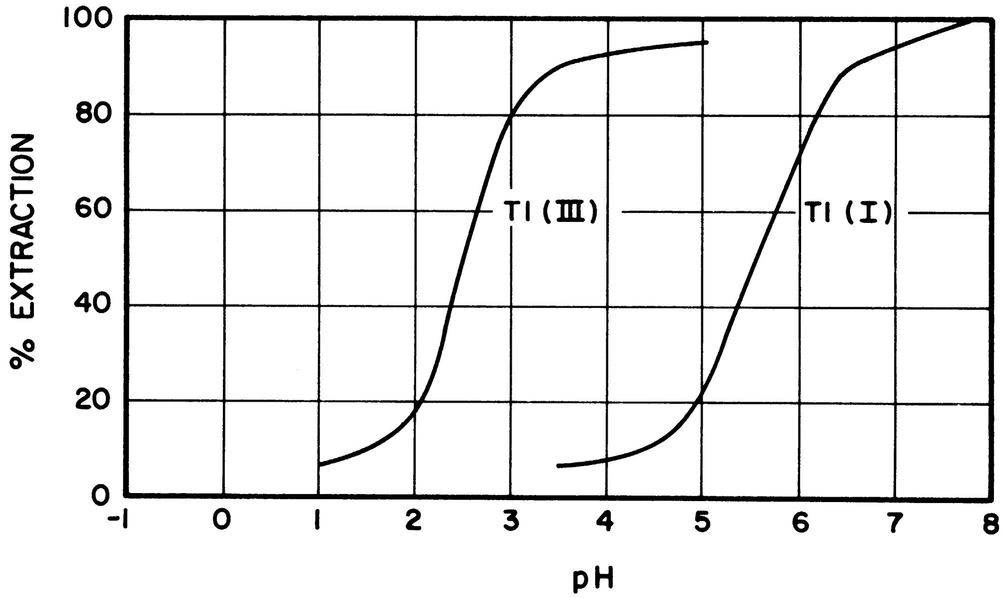


Figure 42. Extraction of Thallium by TTA.

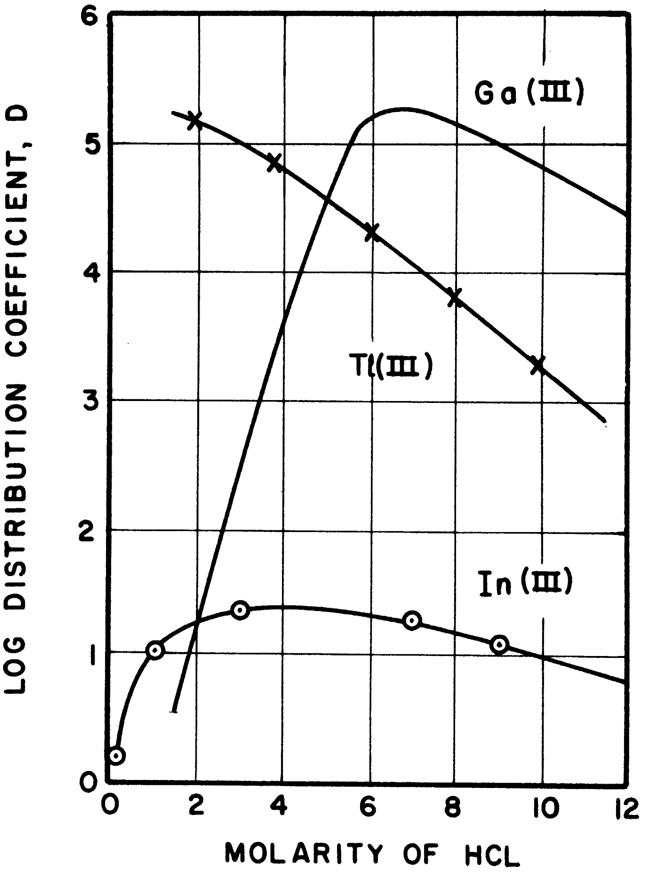


Figure 43. Distribution of Chlorides on Anion Exchange Resin.

The behavior of many elements toward anion exchange from fluoride solutions has been reported (53) recently. Thallium(I) was not adsorbed by a Dowex-1 anion exchange resin; thallium(III) was adsorbed only to a limited extent.

Cation exchange behavior of thallium has been studied by Bonner (20) and Davidson, et al. (41). From the information available, it would appear that anion exchange is the more useful of the two types of ion exchange for most separations involving thallium.

5. Amalgam Exchange

A rapid and selective radiochemical separation procedure has been developed by Devoe, Kim and Meinke (43) using techniques of amalgam exchange. Separation of a radioisotope takes place as a result of rapid exchange of inactive element in the amalgam with the radioelement in solution. If there is a relatively small amount of inactive element in solution as compared to that in the amalgam, most of the radioactivity will be exchanged into the amalgam. Using a 2-percent thallium amalgam, and stirring vigorously for two minutes, 85-percent of the thallium-204 present (21 micrograms) in a 0.5 M sodium nitrate solution was exchanged. This method appears to have useful potential for the separation of short-lived isotopes. However, care must be taken to remove any of the noble metals which might be present in the solution before thallium exchange is attempted.

This can be accomplished easily by shaking the solution first with pure mercury to reduce and remove noble metals. In addition, elements which are reduced to the metallic state by thallium amalgam may also amalgamate as the thallium is exchanged.

C. Comparison of Analytical Methods

A variety of analytical methods is available for the determination of thallium. Meinke (129) has compared activation analysis with other methods and gives the sensitivities listed in Table VIII. In addition to the methods listed, several others have been developed in recent years. For example, Buser and Tiptsova (27) have developed a gravimetric-amperometric procedure in which thallium(III) is precipitated as the bromothallic acid complex with diantipyriylmethane in the presence of Cu(II), Zn, Cd, Bi, Fe(III), and Sb(III and V). These authors claim the method is capable of detecting 10^{-6}-10^{-7} percent thallium. A second method (26) by these same authors involves amperometric titration of thallium(III) with Complexone III, using 1-(2-pyridazo)-2-naphthol as an indicator. By this method, the authors determine amounts of thallium less than 0.69 milligrams in 20-25 milliliters of solution. Martin and Shain (121) have developed an analytical procedure for analysis of thallium by differential voltammetry using a hanging mercury drop electrode. The limit of sensitivity of this method is the order of 10 micrograms in 1-2 milliliters.

Hume (84) reports an ultra-violet spectrophotometric determination of thallic chloride complexes in the range from 4 to 20 parts per million with a precision of approximately 10-percent. A colorimetric method is available (134) for thallium determinations down to 10 parts per million.

TABLE VIII

COMPARISON OF SENSITIVITES FOR THALLIUM

Method		Sensitivity $\mu g/ml$
Spectrography: graphite d. c. arc		0.2
Flame spectrophotometry		1.0
Activation Analysis:	Oak Ridge X-10 Reactor*	0.6
	Oak Ridge LITR**	0.03

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*Neutron flux approximately 5 x 10^{11} n-cm^{-2}-sec^{-1}

**Neutron flux approximately 1 x 10^{13}n-cm^{-2}-sec^{-1}

As a comparison with some of the above methods, Koch (96), cites the limit of detection for thallium by activation analysis as 1 x 10^{-3} micrograms, using the reaction $Tl^{203}(n,\gamma)Tl^{204}$, and 7 x 10^{-4} micrograms for the reaction $Tl^{205}(n,\gamma)Tl^{206}$. Conditions for obtaining these detection limits are irradiation in a flux of 10^{14} neutrons-cm^{-2}-sec^{-1} to saturation, or for a maximum of 30 days. The limits of detection represent that weight of thallium which, when activated under these conditions, yields sufficient radioisotope to provide 1000 disintegrations per minute. Using the 4.2 year thallium-204, Reed, Kigoshi and Turkevich (152) have determined thallium in meteorites in amounts as low as 0.65×10^{-10} grams per gram of sample. Again, as in the case of vanadium, activation analysis offers the most sensitive method by far for determining thallium.

D. Experimental Procedures

Three procedures have been developed for rapid separation of thallium from a wide variety of samples. Initially, work was done on the analysis of botanical samples; this was later extended to include meteorites, rocks and ores. Three procedures have evolved from this work and have been compared with respect to time required for each separation, chemical recovery of thallium, and radiochemical purity of the counting sample.

Since thallium-206 is a pure beta emitter, there are some problems encountered in analyses by means of this isotope that are not found in the case of gamma emitting isotopes. Contaminating activities having half-lives of the same order of magnitude as that of thallium-206 must be removed completely. So long as short-lived gamma emitting contaminants, present in a gamma emitting sample, have energies less than that of the isotope of interest, the contaminants do not interfere with the analysis. With beta emitters, however, this is not the case, since resolution of radioisotopes is performed on the basis of half-lives. This imposes severe restrictions on the level of contamination of the final counting sample.

In an effort to determine the nature of contaminating activities present in any of the counting samples, the counting chamber of a proportional counter was inverted and a gamma or beta scintillation detector placed in close proximity to the sample in the arrangement shown in Figure 29, Chapter IV. This allowed measurement of beta or gamma spectra of the sample simultaneous with measurement of its decay curve. Attempts were made to compare the recorded beta spectra with that from a standard sample of thallium-206. The gamma spectra were essential in determining the nature and amounts of contaminating gamma activities.

1. Separation By Precipitation as Thallous Iodide

Finely powdered samples, weighing between 200 and 1000 milligrams, were weighed into gelatine capsules. These were then wrapped in several layers of Kleenex, placed in a rabbit along with an accurately weighed gold foil monitor, and irradiated in the pneumatic tube position for 10.00 ± 0.02 minutes. The sample was then removed from the rabbit and placed in a covered nickel crucible containing 3.5-4.0

grams of molten sodium peroxide and a known amount of thallium-204 activity. The crucible cover was then clamped down over the crucible immediately as the capsule was added. A violent exothermic reaction took place, heating the crucible bottom to a cherry red. Once this reaction had subsided, the crucible was heated over an open burner until the molten mass was clear. The crucible was then cooled quickly by dipping the bottom of the crucible into cold water.

Once the melt had cooled sufficiently, it was dissolved with 20 milliliters of 1 N hydrobromic acid, followed by 20 to 25 milliliters of concentrated hydrobromic acid. The concentrated acid was swirled around until the inside of the crucible was clean. The solution was diluted to approximately 40 milliliters, and 10 milligrams each of aluminum, copper(II), manganese(II), potassium, thallium(I), and zinc added. Five milliliters of bromine water were added to insure oxidation of the thallium carrier to the trivalent state. This solution, having a hydrobromic acid concentration between 1 and 3 M, was then transferred to a separatory funnel and extracted twice with 20 milliliter portions of isopropyl ether. The combined ether extracts were then transferred to a second separatory funnel and washed with three 15 milliliter portions of 1 M hydrobromic acid.

After washing with dilute hydrobromic acid, the ether extract was transferred to a beaker containing 10 milliliters of de-ionized water; the ether was then removed by evaporation on a hot plate. The beaker was then placed in an ice bath and the solution saturated with sulfur dioxide. An excess of saturated potassium iodide was then added; the solution was then heated almost to boiling, and the agglomerated thallous iodide removed by filtration. The precipitate was washed with de-ionized water and acetone, mounted between Teflon film and Scotch tape over a hole, slightly larger than the filter paper, cut into a standard counting card. The gamma spectrum of this sample was measured using a 1-3/4-inch x 2-inch (diameter) sodium iodide(thallium) scintillation detector simultaneous with measurement of its decay curve by means of a proportional counting chamber.

Samples known to have a high percentage of silica were treated with a mixture of sulfuric and hydrofluoric acids in a platinum crucible also containing a known amount of thallium-204 activity. The mixture was carefully heated to fumes of sulfur trioxide, cooled quickly, more hydrofluoric acid added, and fumed again. The mixture was then transferred to a beaker containing 7 milliliters of concentrated hydrobromic acid, 10 milliliters of bromine water, and 10 milligrams each of aluminum, copper(II), manganese(II), potassium, thallium(III), and zinc. The extraction of this solution with isopropyl ether and subsequent treatment was exactly the same as outlined above.

2. Separation by Precipitation with Thionalide

Samples analyzed for thallium were treated in the same manner as those analyzed by means of the thallous iodide precipitate up to, and including the reduction to thallous ion by sulfur dioxide. Once this reduction was completed, 15 milliliters of 20-percent sodium tartrate were added, followed by a few drops of phenolphthalein indicator. Approximately 8 milliliters of 6 N sodium hydroxide were then added to neutralize the solution, followed by 15 milliliters of a 20-percent solution of potassium cyanide. An additional 8 milliliters of 6 N sodium hydroxide were then added, making the final concentration of sodium hydroxide approximately 1 M. A solution of 50 milligrams of thionalide in 10 milliliters of acetone was then added, giving rise to a bright yellow opalescence. The solution was brought to a boil over an open burner. To the hot solution was added liquid nitrogen; the contents of the beaker were swirled and more liquid nitrogen added as necessary until the solution had attained approximately room temperature. The resultant safron-yellow precipitate was quickly filtered, washed with de-ionized water, and mounted as in the case of thallous iodide. Decay curve measurement and gamma spectral analysis took place exactly as for the thallous iodide.

3. Separation by Precipitation of Thallous Tetraphenylboron

As with the preceding separation, samples were treated initially in the same manner as those whose separation involved the thallous iodide precipitation. However, following isopropyl ether extraction of bromothallic acid, the combined ether extracts were evaporated over 10 milliliters of 2 N sodium acetate. This solution was then saturated with sulfur dioxide, reducing thallium to the monovalent state. The thallium was then precipitated as the tetraphenylboron compound on addition of 10 milliliters of a 2-percent solution of sodium tetraphenylboron which was 5×10^{-3} M in aluminum nitrate and sodium hydroxide. The white precipitate was filtered, washed with de-ionized water, mounted and analyzed in the same manner as the previous samples.

4. Preparation of the Standard Curve

As mentioned previously, since thallium-206 is a pure beta emitter, severe restrictions are imposed on the level of radioactive contamination in the counting sample. As a result of this restriction, samples must be free from sizeable amounts of contaminating activity in order for relatively precise results to be possible. In the construction of a standard curve for thallium, this point gave rise to a serious problem, inasmuch as most of the thallium metal and compounds available contained relatively large amounts of trace contaminants at least by the standards of activation analysis. For example, Fischer C. P. thallous nitrate contained several parts per million of sodium and chlorine, amounts small enough by ordinary analytical standards, but relatively large by activation analysis standards. Purification of the thallium to remove these contaminants proved to be a challenging task.

Approximately 500 milligrams of "chemically pure", lead-free thallium was dissolved in a few milliliters of sulfuric acid in a platinum crucible. Approximately 2 milliliters of nitric acid were added and the mixture heated to fumes of sulfuric acid. This was repeated two additional times, the solution was cooled and diluted to approximately 50 milliliters with de-ionized water. The resulting solution was electrolyzed under slow stirring at a potential of 3-6 volts for two hours. The material deposited on the platinum gauze cathode was carefully washed with de-ionized water and dried with reagent grade acetone. On activation of a small amount of this material, a slight improvement in the level of contamination was noted, but not nearly enough to allow construction of a good thallium calibration curve.

In an effort to decrease further the amounts of trace contaminants in the electrodeposited thallium, the following procedure was tried and adopted: the electrodeposited thallium was placed in a new, scrupulously clean, fused silica crucible and melted over an open burner in a well ventilated hood. The molten metal was kept at the melting point for approximately two minutes, then poured quickly into a scrupulously clean beaker containing de-ionized water. This quenched thallium was removed from the water, and the melting-quenching procedure repeated. Essentially all of the slag remained in the crucible when the molten metal was quenched; the quenched thallium was bright and shiny. When activated in the reactor, a small amount of this material showed a much lower level of contamination than any of the metal or its compounds had shown previously. This material was used, without further attempts at purification for the standard curve relating activity of thallium-206 to weight of thallium.

The standard curve was constructed in the following manner: 13.3 milligrams of the doubly quenched thallium were placed in a clean 250.0-milliliter volumetric flask with approximately 5 milliliters of reagent grade nitric acid and 10 milliliters of de-ionized water. This was allowed to dissolve at room temperature, and was then brought to volume with de-ionized water. Approximately 500-microliter aliquots of this solution were sealed in short lengths of polyethylene tubing and irradiated, along with an accurately weighed gold foil, for 10.00 ± 0.02 minutes at a reactor power level of 1000 kilowatts. On removal from the reactor, various aliquots of the active solution were pipetted onto filter paper discs which were mounted in the same manner as the samples. The decay curves of these aliquots were then measured and resolved. The thallium-206 activities of the various aliquots, taken at several different times following removal from the reactor, were normalized to the same specific activity of the gold foil monitors, 10.00×10^6 counts per minute per milligram. These data were then plotted on log-log paper against the weight of thallium in each aliquot to give the standard curve.

E. RESULTS AND DISCUSSION

A calibration curve (Figure 44) has been constructed for use in the analysis of samples irradiated for 10 minutes at a thermal neutron flux of approximately 0.95×10^{11} neutrons-cm^{-2}-sec^{-1} and analyzed at 10 minutes following removal from the reactor. Decay curves for samples whose analysis was begun at some time in excess of 10 minutes following removal from the reactor were back-extrapolated to this time in order to determine the activity of thallium from the curve in Figure 44.

Several different types of sample were analyzed for thallium by one or more of the methods presented in the preceeding section. The separated thallium was analyzed by either beta or gamma spectrometry simultaneous with measurement of its decay curve by means of the experimental arrangement shown in Figure 29, Chapter IV. Gamma spectra, analyzed using a 1-3/4-inch by 2-inch sodium iodide(thallium) scintillation detector, were recorded in order to determine the presence of gamma-emitting contaminants in the counting samples. Beta spectra were compared with those produced by pure thallium as evidence, in addition to the half-life, for the presence of thallium-206.

Preliminary results using the thallous iodide precipitation were disheartening due to the presence of several thousand counts per minute of long-lived activity. Some of this activity was traced to manganese-56 and copper-64

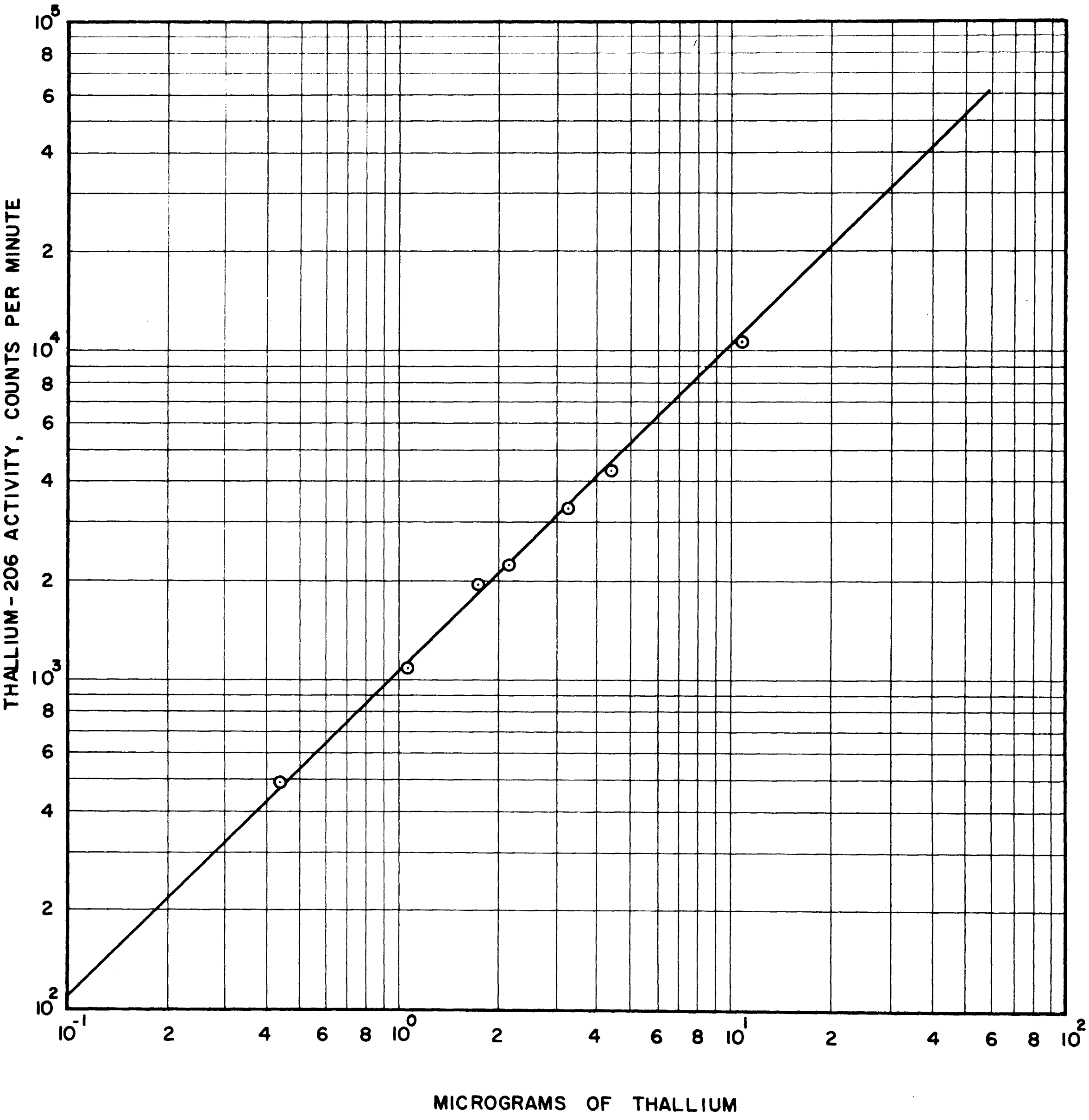

Figure 44. Calibration Curve for Thallium as Thallium-206.

and -66. In addition, other activities were felt to be present which had no observable gamma radiation associated with its decay. The back-washing of the isopropyl ether with 1 M hydrobromic acid removed some of the contaminating activity, but not all. The majority was removed only after three washings of the extract using fresh hydrobromic acid for each extraction. Results for the determination of thallium in lepidolite, a lithium mica, are presented in Table IX. These samples were analyzed by procedure 1, above; separation of the thallium required 10-12 minutes and gave chemical recoveries ranging from 43- to 71-percent. Chemical recovery was determined by either of two methods: comparison of the activity due to thallium-204 in the counting sample with that present initially, or by comparison of the weight of thallium in the counting sample with that added as carrier at the start of the procedure. Recoveries determined by both methods for a single sample produced values which agreed to within 1-percent. A typical decay curve for a thallous iodide counting sample is shown in Figure 45. Figure 46 shows a comparison of the beta spectrum of thallium in lepidolite with that of a pure thallium sample.

Lepidolite, microcline, and certain other types of samples having relatively large amounts of silica gave colloidal precipitates of silicic acid when the solidified peroxide melt was dissolved in hydrobromic acid. In order to avoid this difficulty, samples known to contain large

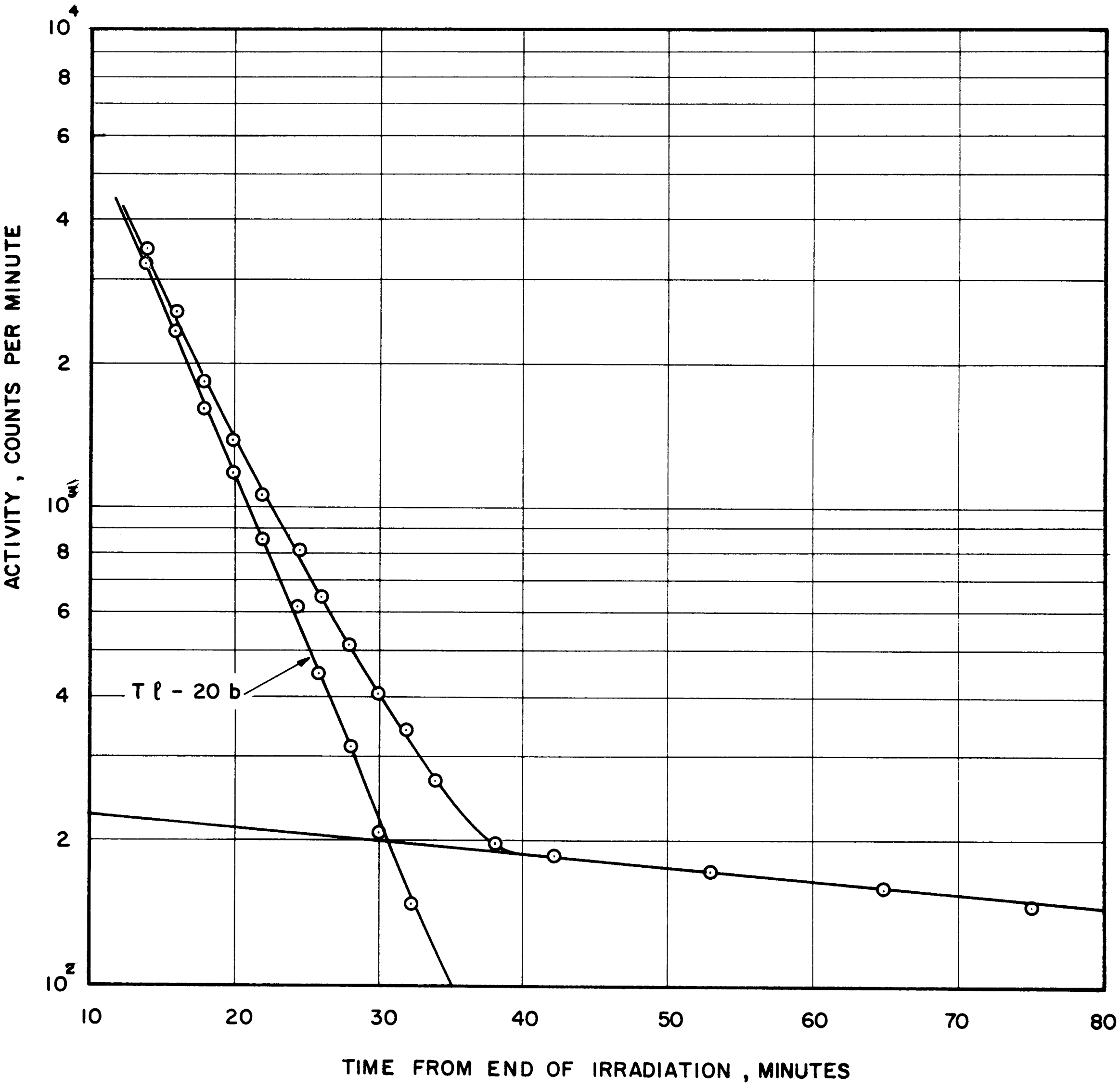

Figure 45. Decay of Thallium-206 in Lepidolite. Thallium Separated as Thallous Iodide.

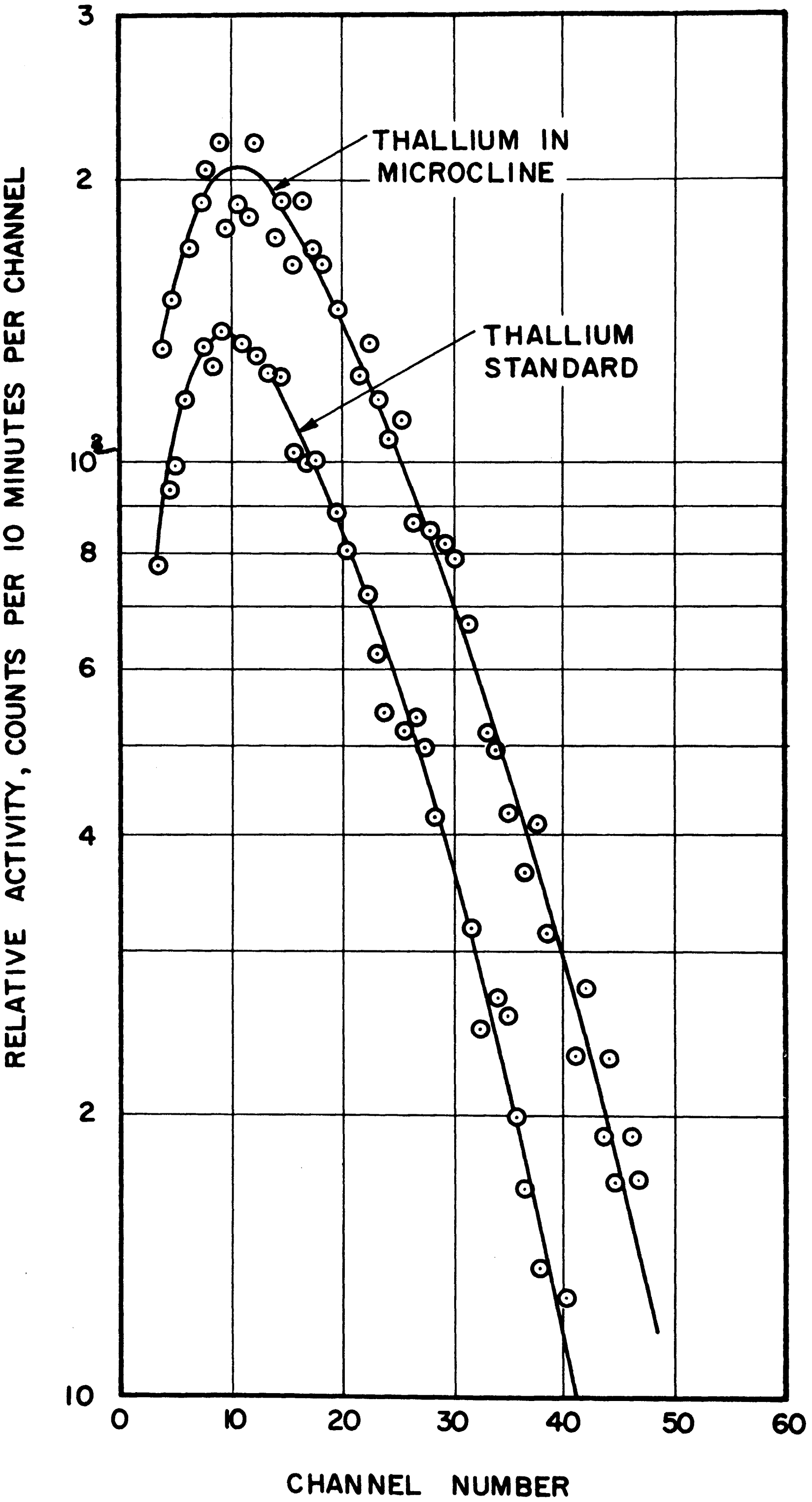

Figure 46. Comparison of Beta Spectrum of Thallium-206 in Microcline with that of a Thallium Standard.

amounts of silica were digested in a mixture of hydrofluoric and sulfuric acids in platinum. The mixture was heated to fumes of sulfuric acid, cooled, approximately 1 milliliter of hydrofluoric acid added, and the crucible reheated to fumes of sulfuric acid. This procedure removed all silicon interference and required approximately the same length of time as the peroxide fusion.

TABLE IX

THALLIUM IN LEPIDOLITE

Sample No.	Wt (mg)	Chemical Recovery of Tl (%)	Wt Tl found mg x 10^{-3}	Tl ppm	Average (Std deviation)*
1	64.3	65.0	3.10	74.2	
2	84.2	71.0	4.60	77.0	79.7 (± 9.15%)
3	127.	43.5	4.86	88.0	

*The standard deviation was obtained using Equation (24).

Samples of microcline, a potassium aluminum silicate, and a stony meteorite were analyzed by procedure 2, above, involving precipitation of thallium(I) with thionalide. This procedure requires somewhat longer to complete than that involving thallous iodide; however, the chemical yield is higher, and in several cases has reached 100-percent. Results for the determination of thallium in microcline are presented in Table X. Separation of the thallium from these samples by the methods of procedure 2 required 14-16 minutes. The procedure offers only one advantage which the thallous iodide precedure does not: the thallium-thionalide precipitate dissolves almost completely on boiling the solution from which the thallium(I) was precipitated, thus allowing for the removal of contaminating substances from the precipitate.

TABLE X

THALLIUM IN MICROCLINE

Sample No.	Wt (mg)	Chemical Recovery of Tl (%)	Wt Tl found mg x 10^{-3}	Tl ppm	Average (Std deviation)*
1	417.6	89.10	26.3	63.0	
2	469.9	100.0	34.8	74.1	68.5 (± 8.10%)
3	470.4	100.0	32.2	68.5	

*The standard deviation was obtained using Equation (24).

Samples of Holbrook meteorite, analyzed for thallium by the method of procedure 2, showed less than 2 x 10^{-8} grams of thallium per gram of sample, or less than 0.02 parts per million. These results are in accord with analyses for thallium in Holbrook meteorite performed by means of 4.20 year thallium-204 (151). Care must be taken to avoid terrestrial contamination of these samples during preparation for irradiation. Anders (5) reports that agate contains small amounts of thallium which might cause contamination of samples powdered with an agate mortar and pestle.

The method outlined in procedure 3, precipitation of thallium(I) with sodium tetraphenylboron, was tried on several unweighed samples of lepidolite and microcline. Considerable amounts of copper and manganese activities were found in the final precipitate, even after careful backwashing of the isopropyl ether extract. The level of contamination remained essentially the same even when ethylenediaminetetra-acetic acid was added. The time required for the separation of thallium by this procedure was approximately 16 minutes; chemical recovery amounted to 60-65-percent. It was felt that the procedure offered no advantage over the iodide or thionalide procedure.

The determination of thallium by means of short-lived thallium-206 has the advantage of being more rapid than determination by means of the 4.2-year thallium-204. Several determinations can be completed in a single day when the short-lived isotope is utilized, especially if chemical recovery is determined by weighing the final precipitate. Analysis by means of thallium-204 requires several days of continuous irradiation as well as several hours for counting. However, utilization of this isotope allows higher sensitivities to be attained than is the case for thallium-206.

Methods have been presented for the rapid separation and analysis by radioactivation of thallium in a variety of samples. The methods presented can be adapted for use with either the short-lived thallium-206, or the long-lived thallium-204. A choice between the two depends upon the amount of thallium expected, and the time available for the determination.

CHAPTER VII

DETERMINATION OF NIOBIUM

A. Nuclear Properties

Naturally occurring niobium contains 100-percent of the stable isotope niobium-93 (163, 202), and has an absorption cross-section for thermal (2200 m/sec) neutrons which has been reported as 1.17 ± 0.02 barns (89) and 1.1 ± 0.1 barns (83). This cross-section appears (181) to be for production of the niobium-94m isomer. The half-lives of the two isomers formed, niobium-94 and -94m are 6.6-minutes (161), and from 1.8 x 10^4 years (155) to 2.2 x 10^4 years (44), respectively.

The energy level diagram for niobium-94 and -94m is shown in Figure 47 (44, 185). From this diagram, we see that niobium-94 emits gamma photons of energy 0.705, 0.878, and 1.58 Mev. It would appear from the diagram that the 6.6-minute niobium-94m isomer gives rise to an isomeric transition gamma photon of 0.042 Mev. In practice, however, one finds an x-ray of energy 0.0168 ± 0.0007 Mev as a result of internal conversion.

The nuclear properties of the 94m isomer appear to be such as to favor its use in activation analysis. However, the chemical behavior of niobium, coupled with the large conversion coefficient causing the appearance of the niobium x-ray, presents some problems. It would seem reasonable to

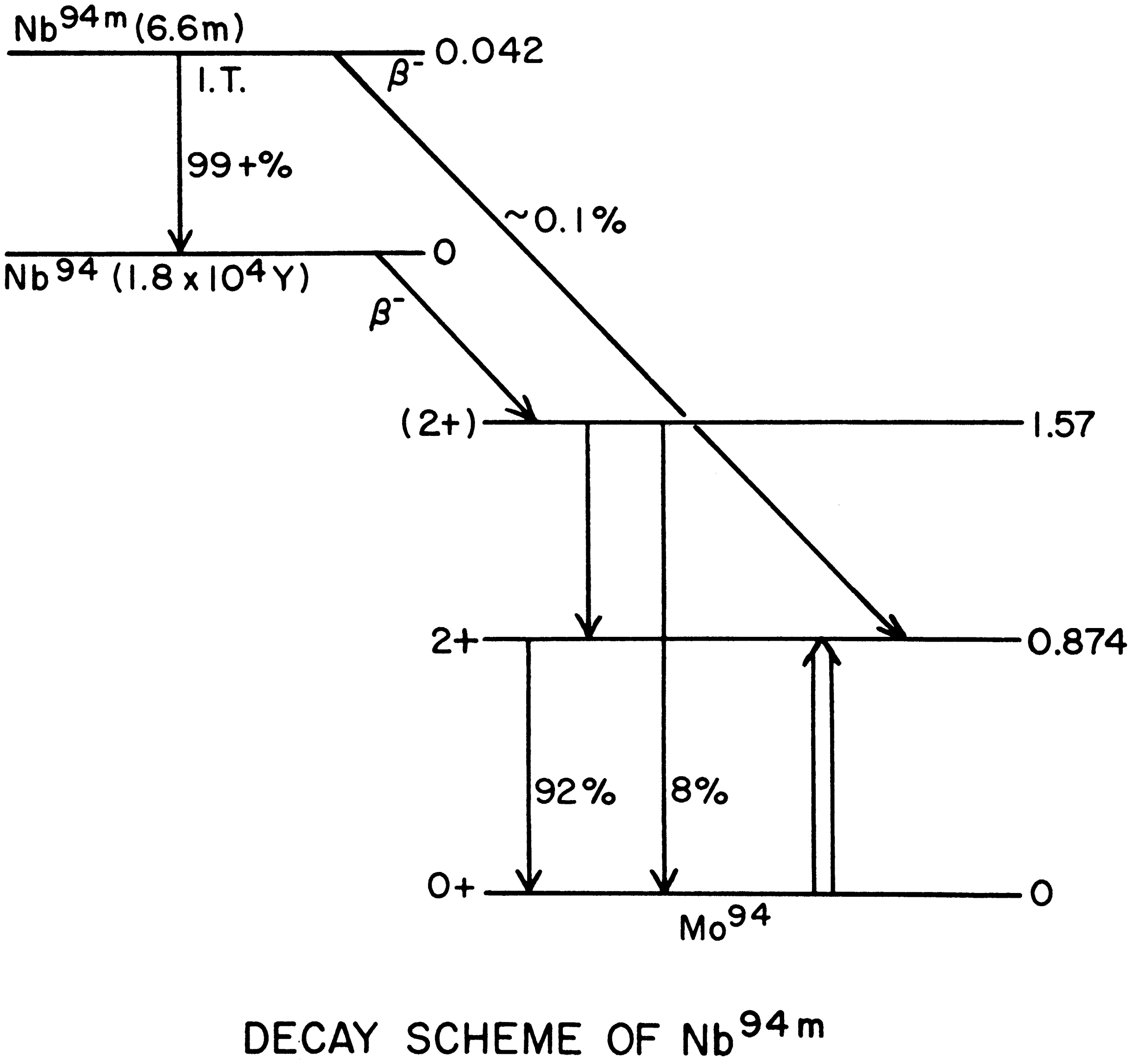

Figure 47. Decay Scheme of Niobium-94 and -94m.

count niobium-94m samples as solids, covered only with thin films, rather than as liquids in glass or plastic containers in view of the relatively high absorption of x-radiation by these containers. However, the chemical behavior of niobium appears to be such as to make a rapid separation of niobium in a short time, and in good yield, rather difficult.

B. Radiochemistry of Niobium

1. Precipitation and Coprecipitation Behavior

Niobium is most often precipitated in a form that can be converted to the oxide on heating. One of the classical precipitation methods involves the use of tannin as the precipitating agent (170). Niobium(V) reacts with tannin to produce a finely divided brick-red precipitate. From a barely acid oxalate solution containing large amounts of ammonium chloride, niobium(V), tantalum(V), and titanium(IV) precipitates as the tannates, leaving zirconium(IV), hafnium (IV), thorium(IV), uranium, beryllium and aluminum in solution (169). Titanium(IV) can be removed by dissolving the tannate in a solution containing nitric and salicylic acids, when the niobium(V) and tantalum(V) are precipitated hydrolytically as the hydrated oxides, titanium(IV) remaining in solution as the salicylate complex. Tartrate can be used in place of the salicylate with the same results. Tantalum(V) can then be removed by dissolving the oxides in a minimum of hydrofluoric acid and adding an excess of boiling potassium fluoride solution. The solution is evaporated to a small volume (approximately 15 milliliters) and cooled. Tantalum (V) separates first as potassium fluotantalate, the niobium remaining in solution as the oxyfluoride (133). This method works best with large amounts of niobium and tantalum, but is rather time-consuming.

Steinberg (183) has separated niobium from fission products by hydrolytic precipitation of $Nb_2O_5 \cdot x\ H_2O$ after ether extraction of uranyl nitrate. The niobium precipitate, containing some zirconium, was dissolved in oxalic acid and reprecipitated by destruction of the oxalate with chloric acid. This procedure gave good decontamination from all of the fission products except for zirconium when phosphate was present.

Belekar and Athavale (13) have separated niobium(V) from tantalum(V), titanium(IV), tin(II) and antimony(III) from a tartrate solution buffered at pH 6 with 8-hydroxyquinoline. However, the precipitate is easily contaminated by small amounts of manganese(II) and sodium.

Kosta and Ravnik (100) describe the precipitation of thorium(IV), zirconium(IV) and niobium(V) with sodium hypophosphate using titanium(IV) as a carrier. Precipitation from 6 M hydrochloric acid is nearly quantitative. Thorium (IV) is removed as the fluoride, and zirconium(IV) as the barium fluozirconate precipitate, niobium(V) remaining in solution as the fluoride or oxyfluoride complex.

Niobium(IV) coprecipitates with a number of reagents. Schoeller (168) precipitated niobium with calcium oxalate from an oxalate-salicylate solution. The salicylate served to keep titanium(IV) in solution. Manganese dioxide (64), and lanthanum fluoride and oxalate (10) have also been used. While not a precipitation method, the procedure of Roake (154) results in the separation of niobium(V) from dilute acid solution in the form of a solid. This procedure depends upon the adsorption of a niobium colloid onto silica gel from a dilute nitric acid solution. Roake investigated the adsorption of radiocolloids of niobium and zirconium onto silica gel, filter aids and Pyrex glass wool from solutions of irradiated uranyl nitrate. He found that silica gel adsorbed 86.6-percent of the niobium and 87.0-percent of the zirconium present in a fission product mixture. His procedure required maintenance of the solution and adsorbant at 100°C for a period of 17 hours. In a second set of experiments, niobium(V) was adsorbed onto porous Vycor and Super Filtrol filter aid from a solution at pH 0.8 to the extent of 93.1- and 98.5-percent, respectively, after only 2 hours. The radioniobium and zirconium was desorbed readily by leaching with 0.05 M oxalic acid at 100°C for a few minutes. The method provides a good separation of niobium and zirconium from the other fission products.

2. Oxidation-Reduction Behavior

The most stable oxidation state of niobium in aqueous solution is the pentavalent state. Niobium(III) also exists in aqueous solution, but is quite sensitive to oxidation. Solutions containing niobium(III) or its complexes are made by cathodic reduction, or by reduction with zinc, of solutions of niobium pentoxide in sulfuric, hydrochloric or hydrofluoric acids. Niobium(III) so obtained is easily oxidized to niobium(V) by air (slowly), mercuric chloride, and most other oxidizing agents.

The potential of the Nb^{+3}-Nb^{+5} couple has been measured by Kiehl and Hart (95) in various concentrations of sulfuric acid against a saturated potassium chloride calomel electrode. In a solution containing equal concentrations of niobium in the two oxidation states and 3.14 M in sulfuric acid, they obtained a potential of 0.373 volts for the couple; in 9.87 M sulfuric acid, the potential was 0.426 volts. The increase in potential has been ascribed to the formation of very stable niobium(V) sulfate complexes.

3. Solvent Extraction

Niobium forms only a few complexes with inorganic ligands which are useful for the extraction of niobium into organic solvents. Of these complexes, those involving fluoride, chloride and thiocyanate ions are the most commonly used for this purpose.

Relatively few studies have been performed on the extraction of elements as fluoride complexes, partly because of the difficulties involved in the manipulation of hydrofluoric acid solutions. However, extraction of the niobium-fluoride complex into various organic solvents has been studied by a number of investigators. Bock and Herrmann (14) studied the extraction of the fluoride complex into ethyl ether. Their results showed that niobium(V) is extracted to the extent of 65.8-percent from solutions 20 M in hydrofluoric acid. Other elements which extract appreciably under these conditions include tantalum(V), tin(II and IV), and rhenium(VI); arsenic(V), molybdenum(VI), selenium (IV) and tellurium(IV) are partially extracted. Stevenson and Hicks (184) have also studied the extraction of the niobium-fluoride complex; diisopropyl ketone equilibrated with the aqueous phase was used as solvent. They achieved niobium extraction of better than 90-percent, and were able to separate tantalum(V) and niobium(V). Walterbury and Bricker (198) used 4-methyl-2-pentanone and extracted an average of 99.9-percent niobium(V) from a hydrofluoric-sulfuric acid mixture. Moore (139) used diisobutylcarbinol as extracting agent and obtained a 98-percent extraction of niobium.

Hicks and Gilbert (73) have separated niobium from cyclotron targets by dissolving the target in hydrochloric acid containing niobium carrier as the oxalate complex. Niobium was then precipitated hydrolytically by destroying the oxalate ion with nitric acid, redissolved with concentrated hydrochloric acid, and extracted into diisopropyl ketone. The niobium was then back-extracted into 6 N hydrochloric acid. No information concerning interference by other elements was given, but at this high concentration of hydrochloric acid, gold(III), antimony(V), gallium(III), germanium(IV), indium(III), and scandium are partially extracted (142). Brunnix and Irwine (24) have studied the solvent extraction of niobium(V) and tantalum(V) from hydrochloric acid solutions by several organic extractants. They determined that the system 4-methyl-2-pentanone - 6.7 M hydrochloric acid was the most preferred of those investigated for the separation of niobium and tantalum because of the large separation factor for both elements.

A large amount of interest has been shown in recent years in long chain aliphatic and aromatic amines, in addition to organic phosphorus compounds, as extracting agents. Leddicotte and Moore (110) used methyldioctylamine in xylene to extract niobium and tantalum selectively and quantitatively from hydrochloric acid. Tribenzylamine in either chloroform or dichloromethane has also been used (48) for the extraction of niobium(V) and tantalum(V) from concentrated hydrochloric or sulfuric acid. Hydrochloric acid has been found to be the more desirable medium because of the lower extraction of tantalum(V).

Among the organic phosphorus compounds, dibutylphosphoric acid (containing some monobutylphosphoric acid), in the form of a 0.6 M solution in n-butyl ether, extracts niobium(V) to the extent of 98-percent (165). Zirconium(IV), yttrium, holmium(III) and indium(III) are also extracted quantitatively under these conditions; tin(IV) and tantalum (V) are extracted to the extent of 50- and 35-percent, respectively. Most other elements are extracted to the extent of less than 5-percent. Niobium is back-extracted from the organic phase with 4 M hydrofluoric acid.

Another organic phosphorus compound coming into use for the extraction of niobium is tri-n-octylphosphine oxide (TOPO). Studies have been conducted (80) on the extraction of niobium and tantalum by 0.5 millimoles of TOPO in cyclohexane from solutions containing citric, tartaric, or lactic acid as a function of hydrochloric acid concentration. The results of this study are shown in Figure 48. In addition, niobium, stabilized by thiocyanate, is also extracted by TOPO in cyclohexane from hydrochloric or sulfuric acid; extraction also takes place from catechol-stabilized solutions. In 6 M sulfuric acid, niobium is extracted to the extent of 98-percent. The thiocyanate complex is also extracted in other organic solvents, e.g., ethyl acetate; this extraction has been employed (65) in the determination of microgram amounts of niobium in rock samples.

Among the organic chelating agents, cupferron and 8-hydroxyquinoline have been used to extract niobium(V) from aqueous solution. Niobium(V) and zirconium(IV) cupferrates are extracted (119) almost quantitatively into chloroform

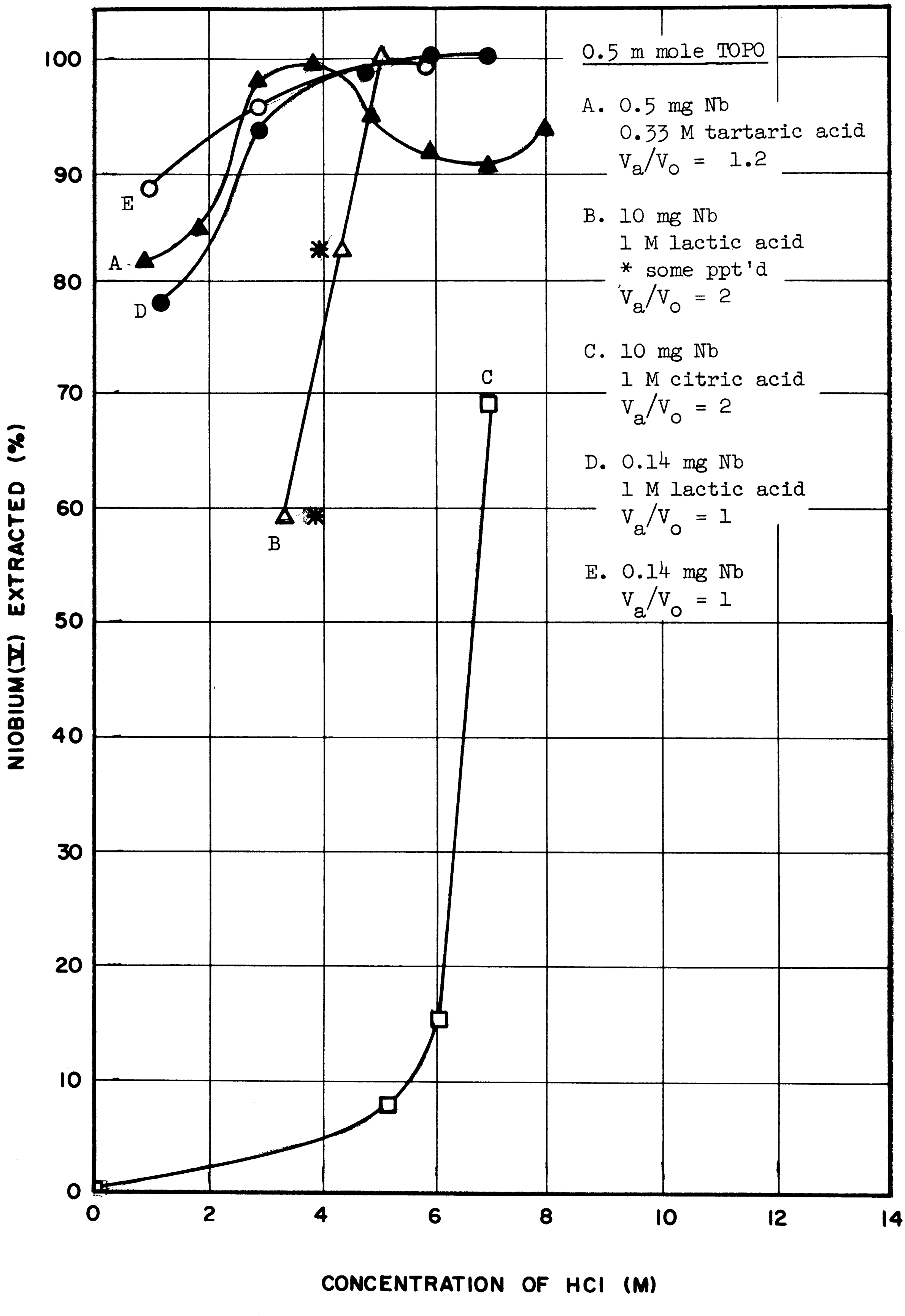

Figure 48. Extraction of Niobium from Hydrochloric Acid by TOPO.

from a solution of irradiated uranyl nitrate which is 6 M in hydrochloric acid and 0.05 M in sulfur dioxide. A second extraction, followed by a wash with 6 M hydrochloric acid, serves to remove almost all contaminating activities due to the other fission products. The chloroform layer can then be evaporated, and the solid cupferrates of niobium and zirconium destroyed with concentrated nitric acid. The zirconium is then removed by diluting the nitric acid solution until the solution is 2 M in nitric acid, followed by extraction with 0.5 M thenoyltrifluoroacetone in benzene (69).

Niobium is extracted as the oxinate into chloroform from a citrate solution which is 1 M in ammonium hydroxide. This extraction has been used in the spectrophotometric determination of niobium in steels (93).

4. Ion Exchange Behavior

Hoffman, et al. (76), have studied the anion exchange behavior of the chloro complexes of niobium(V), zirconium(IV), hafnium(IV), and tantalum(V) on Dowex-2 resin. The distribution coefficients of niobium and zirconium are such as to provide the means for a very convenient separation of the two elements. The mixture in 1 milliliter of 6-7 M hydrochloric acid is adsorbed on a column of Dowex-2 and washed with an addition 3 milliliters of acid. The eluant and wash contain the zirconium. Niobium is eluted from the column with 4 milliliters of 1.5-4.0 M hydrochloric acid.

Tantalum(V) and niobium(V) have been separated by anion exchange in the determination of these two elements (28). A solution of these elements in 3 M hydrofluoric acid, placed on a column of Deacidite FF anion exchange resin, is eluted with a solution 3 M in hydrochloric acid and 0.1 M in hydrofluoric acid. The niobium is eluted rapidly under these conditions, while tantalum is recovered by elution with 4 M ammonium chloride and 1 M ammonium fluoride. The separation is purported to be quantitative. A similar procedure, using Dowex-1, anion exchange resin, was developed by Bergstresser (17) for the determination of microgram quantities of niobium in tantalum.

Studies of the cation exchange behavior have not been possible, since niobium(V) does not exist in stable form in aqueous solution as the simple Nb^{+5} ion. However, cation exchange resins have been used to adsorb niobium as the colloid (171-173).

C. Comparison of Analytical Methods

Niobium is one of the more difficult elements to determine with reasonably good precision, especially when present in trace amounts. Colorimetric methods are limited to the colored complexes of niobium with hydrogen peroxide, thiocyanate and phosphomolybdate. Niobium reacts with hydrogen peroxide in a strong sulfuric acid solution to produce a yellow color (163). The reaction is not especially sensitive, but it has been used to determine niobium in amounts down to 20 micrograms.

The niobium thiocyanate complex has been used to determine microgram amounts of niobium in standard rock samples (65) following extraction into ethyl acetate. This complex has a strong yellow-orange color; colorimetric or spectrophotometric determinations based upon measurement of the intensity of this color are capable of greater sensitivity than is the case for the peroxy complex. The method appears to be sensitive to 1-2 micrograms of niobium.

The niobium determination by the molybdenum blue method (144), in which the intensity of the blue niobiophosphomolybdate complex is measured, is capable of a sensitivity greater than 15 micrograms. At this level, niobium can be determined to ± 13.7-percent.

Two x-ray techniques have been developed for niobium in oxide mixtures (31, 138). Amounts of niobium down to approximately 200 parts per million (as niobium pentoxide) have been determined to a precision of about 10-percent. Analysis of the separated oxide takes about 15 minutes.

Meinke (129) gives the comparison of activation analysis of niobium with other methods listed in Table XI. Koch (96) has calculated that niobium can be determined as niobium-94m by activation analysis with a detection limit of 3×10^{-5} micrograms, utilizing a (thermal) neutron flux of 1×10^{14} neutron-cm^{-2}-sec^{-1}, and irradiation to saturation or for thirty days. One would expect then, that the determination of niobium by neutron activation would be a very sensitive method.

TABLE XI

COMPARISON OF SENSITIVITIES FOR NIOBIUM

Method		Sensitivity μgm/ml
Spectrography:	copper spark	0.2
Flame spectrophotometry		20.
Colorimetry		50.
Activation analysis:	Oak Ridge X-10 Reactor*	10.
	Oak Ridge LITR Reactor**	0.5

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*neutron flux approximately 5 x 10^{11} n-cm^{-2}-sec^{-1}

**neutron flux approximately 1 x 10^{13} n-cm^{-2}-sec^{-1}

D. Experimental Procedures

Since niobium-94m is observed by means of its K x-ray, it was felt that counting samples containing this isotope would have to be in the form of a solid in order to minimize the effects of energy absorption. As a result, the following procedures are all attempts to obtain the niobium-94m in a solid matrix. Since niobium is adsorbed by glassware, all glass equipment was treated with Siliclad, an organic silicone compound (Clay-Adams, Inc., 141 East 25th Street, New

York), to prevent contact of niobium-containing solutions with the surface of the glass.

1. Adsorption Procedure

Approximately 100-800 milligrams of a finely powdered sample were activated in the pneumatic tube position for 15.00 ± 0.02 minutes. The irradiated sample, enclosed in a gelatine capsule, was then placed in a nickel crucible containing 3-4 grams of molten sodium peroxide and an accurately known amount of niobium-95 activity. Following decomposition of the gelatine capsule, which heated the bottom of the crucible to a bright red, the mass was heated over an open burner until the flux was free of undissolved sample (approximately 1-3 minutes). The crucible and contents were cooled rapidly by dipping the base of the crucible repeatedly into cold water.

The solidified melt was dissolved in 50 milliliters of (1 + 1) nitric acid containing 10 milligrams of titanium(IV) carrier. Approximately 0.50 gram of silica gel (100-200 mesh) was added to the solution, followed by an additional 50 milliliters of concentrated nitric acid. The mixture was then brought to a boil and kept at the boiling point for approximately two minutes. The silica gel was filtered quickly through a stainless steel frit, washed with de-ionized water, and dried with acetone. The dried silica gel was transferred to a piece of glassine paper, and distributed evenly in the depression in a counting card, formed by cutting a hole in the center of the card with a number 13 cork borer and covering the opening on one side with Scotch tape. The sample was then covered with Scotch tape, and analyzed by means of the 100-channel analyzer. The high voltage applied to the multiplier phototube was increased to approximately 1150 volts so that the energy range analyzed at an amplifier coarse gain setting of 1 was of the order of 0-70 Kev. The amount of niobium-95 in the counting sample was compared with the amount of niobium-95 added at the start of the procedure as soon as any contaminating activities had decayed. By this procedure, the fractional recovery of niobium was determined.

2. 8-Hydroxyquinoline Procedure

Approximately 100-400 milligrams of finely powdered sample were irradiated for 15 minutes in the pneumatic tube position. On removal from the reactor, the sample was transferred from the gelatine capsule in which it was irradiated to a platinum crucible containing approximately 4 grams of molten potassium pyrosulfate and a known amount of niobium-95 activity. The crucible was heated over an open burner until the molten mass was clear, or for a maximum of 5 minutes. The crucible and the melt were then cooled by dipping into cold water, and transferred to a beaker containing 30 milliliters of 5-percent (w/v) ammonium tartrate, 10 milligrams of manganese(II) and 10 milligrams of sodium. This was heated until the solidified melt disintegrated and dissolved. The crucible was removed from the beaker with forceps and was rinsed with a minimum of de-ionized water. The hot solution was filtered and the filtrate diluted to 50-75 milliliters. Four grams of ammonium chloride were then added and the pH adjusted to approximately 6.0. The solution was warmed and 10 milliliters of a 10-percent solution of 8-hydroxyquinoline in methanol were added. The resultant precipitate was filtered, washed with a solution containing 0.1-percent 8-hydroxyquinoline and 1-percent each of ammonium tartrate and ammonium chloride. The precipitate was mounted on a standard counting card and analyzed in the same manner as the silica gel samples.

3. Hydrolytic Precipitation Procedure

Finely ground samples were irradiated for 15 minutes as in the previous procedures. Upon removal from the reactor, the sample was transferred from the gelatine capsule in which it was irradiated to a platinum crucible containing approximately 4 grams of molten potassium pyrosulfate, a known amount of niobium-95 activity, and approximately 15 milligrams of niobium pentoxide. The crucible was heated until the molten mass was clear, or for a maximum of 5 minutes, then cooled until the melt solidified. The crucible was then placed in a beaker containing 25-30 milliliters of 5-percent ammonium tartrate and 10 milligrams of manganese(II) and heated until the melt disintegrated and dissolved. The crucible was then removed from the beaker with forceps and rinsed with a minimum of de-ionized water. The solution was filtered, and the filtrate made approximately 4 M in hydrochloric acid. Ten milliliters of perchloric acid were also added, and the solution brought to a boil for about 2 minutes. A few milligrams of cellulose power were added to the boiling suspension; a similar amount was placed in a filter chimney and slurried with water. The suspension was then poured into the filter chimney and allowed to stand for 30 seconds before a gentle suction was applied. As the cellulose powder formed a mat on the filter paper, the suction was slowly increased. The precipitate was washed with de-ionized water, mounted and analyzed in the same manner as previous samples.

4. Co-precipitation of Niobium with Calcium Oxalate

Finely ground samples were irradiated and fused with potassium pyrosulfate as in the previous procedure, but without adding niobium pentoxide to the molten pyrosulfate. The solidified melt was digested in 35 milliliters of de-ionized water containing 5 milliliters of saturated oxalic acid and 2 drops of niobium(V) carrier solution (10 milligrams per milliliter). The solution was then filtered; the precipitate was rinsed with 15 milliliters of a solution containing 1 milliliter of saturated oxalic acid diluted to 100 milliliters. To the filtrate was added 150 milliliters of hydrochloric acid and the solution transferred to a separatory funnel. The aqueous solution was extracted three times with 15 milliliter portions of 4-methyl-2-pentanone equilibrated with 9 M hydrochloric acid. The combined organic layers were collected in a second separatory funnel and back-extracted three times with 15 milliliter portions of a solution containing 4 milliliters of saturated oxalic acid in 100 milliliters of water. The combined aqueous layers were boiled briefly to expel any dissolved 4-methyl-2-pentanone. One hundred milligrams of calcium, as calcium nitrate carrier solution, were added, followed by a few drops of concentrated ammonium hydroxide. The fine white precipitate was collected on a filter disc, rinsed with a dilute solution of calcium nitrate, mounted and analyzed in the same manner as previous samples.

5. Pre-irradiation Separation of Niobium by Paper Chromatography

A finely powdered sample was fused with approximately 4 grams of potassium pyrosulfate. The melt was cooled, and treated as in the previous procedure. After extraction into 4-methyl-2-pentanone and back-extraction into dilute oxalic acid, the resulting aqueous solution was evaporated almost to dryness on a hot plate. The remaining solution, having a volume of only a few drops, was treated with a drop or two of 3-percent hydrogen peroxide and reheated. The solution was transferred quantitatively to a strip of chromatographic paper and eluted by ascending chromatography with 4-methyl-2-pentanone saturated with concentrated hydrofluoric acid for approximately 30-45 minutes. During this period, the solvent front traveled a distance of approximately 100 centimeters from the initial point. A pilot strip containing a known amount of niobium-95 activity was chromatographed simultaneously as an aid in locating the position of the niobium band on the sample strip. The strips were dried under an infra-red lamp, and the niobium band located on the pilot strip. The corresponding area of the sample strip was separated from the remainder, care being taken to avoid unnecessary handling. This was then carefully wrapped in a piece of 1/4-mil Teflon film and irradiated for 15 minutes in the pneumatic tube position. Following removal from the reactor, the paper section was mounted and analyzed in the same manner as the previous samples.

E. Results and Discussion

The niobium x-ray was observed initially by means of the 3-inch by 3-inch sodium iodide(thallium) scintillation detector. The presence of the x-ray, rather than the expected isomeric transition gamma photon of 42 Kev, suggested the use of an x-ray proportional chamber as the detector. Consequently, a sample of irradiated niobium carrier solution was analyzed by means of a krypton-filled x-ray proportional chamber (6), the output of which was fed into the 100-channel analyzer. A double peak was observed (Figure 49) which decayed with the proper half-life, but which did not appear to lend itself to use in quantitative determinations.

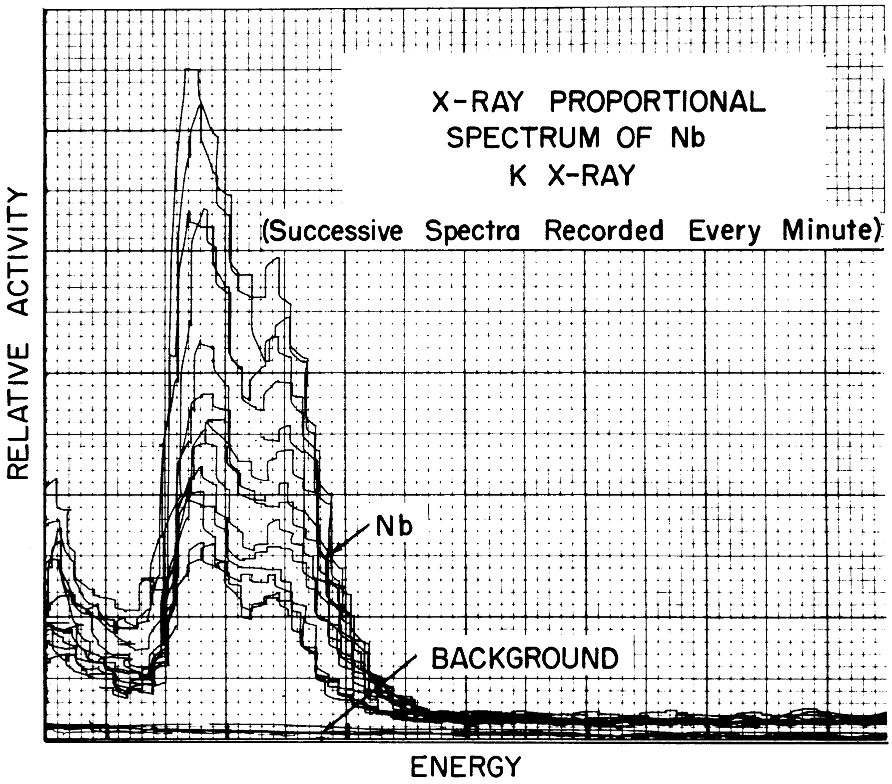


Figure 49. X-Ray Proportional Spectrum of Niobium.

In all subsequent work, the 3-inch by 3-inch sodium iodide (thallium) detector was used.

A calibration curve (Figure 50) has been constructed for use in analysis of samples irradiated for 15 minutes at a thermal flux of approximately 0.95 x 10^{12} neutrons-cm^{-2}-sec^{-1} and analyzed at 10 minutes following removal from the reactor.

The results of the determination of niobium in rutile, which is primarily titanium dioxide with small amounts of niobium and vanadium oxides, are shown in Table XII. Separation from the sample of the irradiated niobium was performed by adsorption onto silica gel, according to procedure 1, above. Analysis of the gamma spectra showed a large amount of titanium contamination to be present on the silica gel. However, this contamination presented no serious interference in the niobium determination since the energy of the niobium x-ray is so much lower than that of the titanium gamma radiation. The spectra observed for niobium in rutile, measured over the range of 0-70 Kev, is shown in Figure 51; a barium K x-ray is included for purposes of comparison.

That the removal of niobium from solution was due to adsorption by silica gel rather than precipitation was shown by adding successively increasing amounts of niobium(V) carrier to the solution in which the peroxide melt was dissolved. It was found that the amount of niobium-95 tracer adsorbed by 0.5 gram of silica gel decreased as the

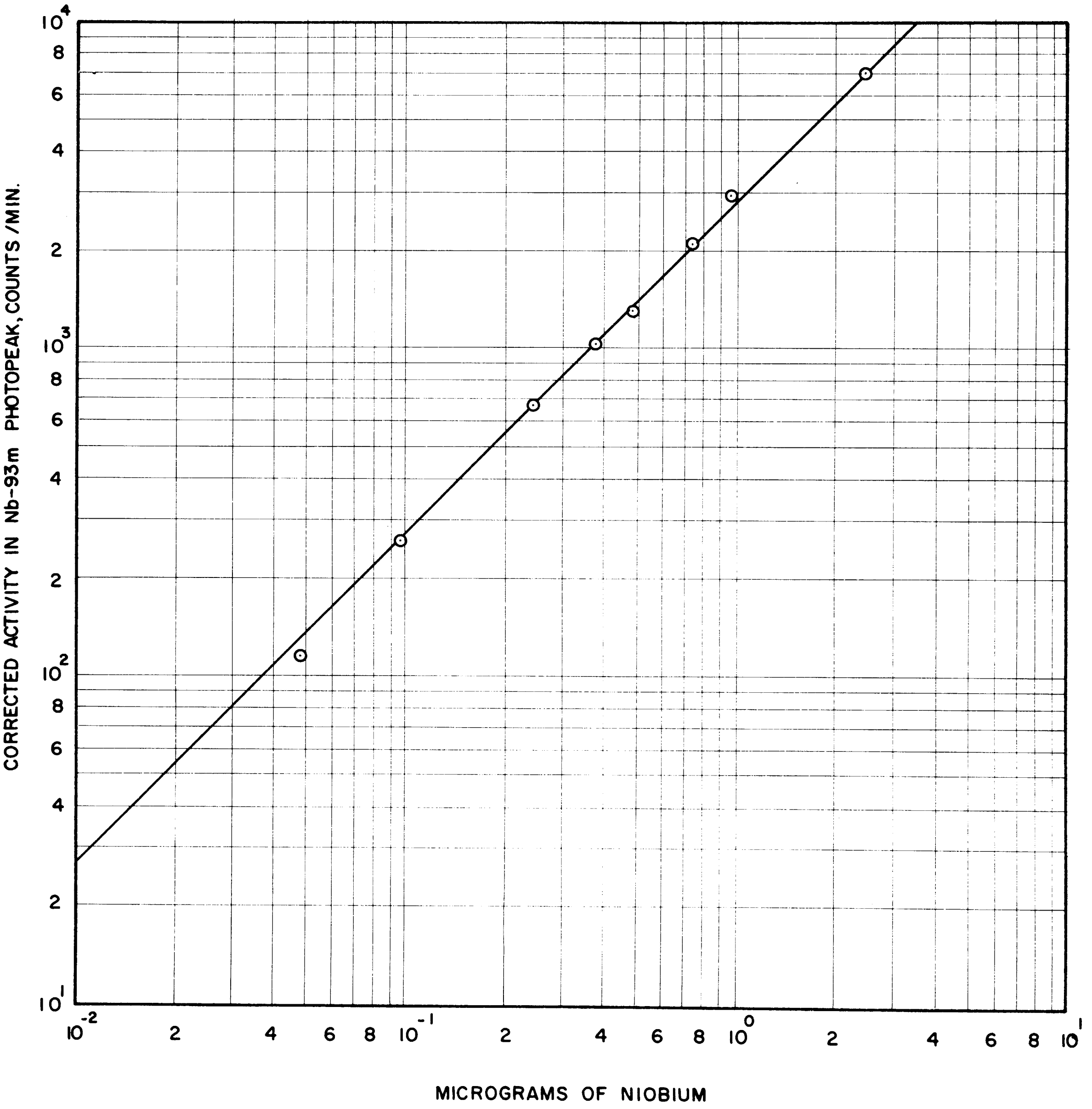


Figure 50. Calibration Curve for Niobium as Niobium-94m.

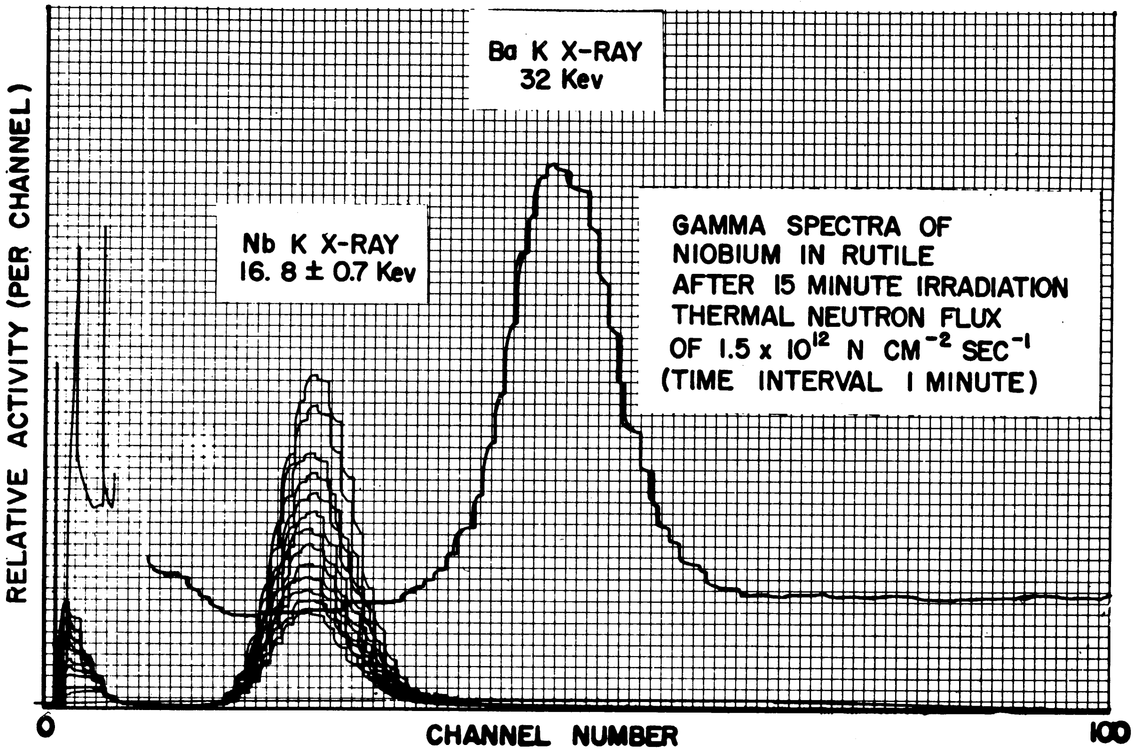


Figure 51. Gamma Spectra of Niobium in Rutile.

TABLE XII

NIOBIUM IN RUTILE

Sample No.	Wt (mg)	Chemical Recovery of Nb (%)	Wt Nb found mg x 10^{-3}	Nb ppm	Average (Std deviation)*
1	104.2	35.17	59.0	566	
2	79.0	32.13	50.5	639	583 (± 8.52%)
3	66.5	30.18	36.2	544	

*The standard deviation was obtained using Equation (24).

amount of carrier increased. The presence of titanium in the counting sample was possibly also the result of adsorption of titanic acid or pertitanates. This adsorption of titanium is a possible cause for the relatively low chemical recovery of niobium. The procedure required 9-9.5 minutes.

Samples having appreciable amounts of silica could not be analyzed by the adsorption procedure following peroxide fusion. This was due to the formation of colloidal silicic acid on acidification of the solution used to dissolve the peroxide melt and subsequent adsorption of niobium on the gelatinous mass. A mixture of hydrofluoric and sulfuric acids was tried to bring silica-containing samples into solution; the mixture was heated to fumes of sulfuric acid, cooled, and transferred to a beaker containing nitric acid. Any insoluble material present was filtered; silica gel was added to the filtrate and treated as in procedure 1.

Only 6-percent of the niobium-95 present initially was recovered from each of four samples. Essentially the same results were obtained when potassium pyrosulfate was substituted for sodium peroxide as a flux.

The modified 8-hydroxyquinoline precipitation of Belekar and Athavale (13), procedure 2, resulted in recovery of only about 18-percent of the niobium-95 initially present. In addition, the sample was badly contaminated with radioactive manganese, copper, sodium and chlorine - so much so that the x-ray energy region of the spectrum became useless for the detection of niobium x-ray. The use of various complexing agents, such as ethylenediaminetetra-acetic acid, did little or nothing to decrease the contamination levels. The inclusion of a solvent extraction step prior to precipitation increased the chemical recovery to approximately 23-percent and reduced levels of contamination somewhat, but the overall procedure remained unsatisfactory.

The investigation initiated by Fukai (56) into the rapid separation of niobium by hydrolytic precipitation was rechecked and attempts made to increase the reported yield of 50-percent. When samples were treated by procedure 3, a milky precipitate of hydrated niobium pentoxide was formed. This finely divided precipitate either passed through the filter, or clogged the pores so that filtration of the solution required an hour or longer. This situation was improved markedly by the addition of a few milligrams of cellulose powder to the mixture and to the filter chimney. The cellulose was added to the filter chimney just prior to the start of the procedure and slurried with de-ionized water. By this means, an estimated 75-percent of the precipitate was retained on the filter, and filtration took place rapidly. The yield of this procedure, however, was only 25-30 percent, approaching that of the adsorption procedure. A larger amount of niobium(V) carrier (up to 50 milligrams of niobium) was added in an effort to increase the yield, but to no avail. The largest recovery amounted to 40-percent, but the precipitation occurred too slowly to be of much use in a rapid separation. In addition, manganese and tungsten accompanied the precipitate in large amounts. The inclusion of a solvent extraction step prior to precipitation of the oxide did little to lower the contamination level. In addition, precipitation of the oxide following solvent extraction occurred more slowly than was the case when large amounts of carrier niobium were present and no extraction step was used.

Coprecipitation of niobium with calcium oxalate appeared to be the most promising of the procedures studied involving the post-irradiation separation of niobium. Analysis of a wider variety of samples was possible by this procedure than by the procedure involving adsorption of niobium by silica gel. The chemical recovery of niobium was approximately the same as that of the absorption procedure:

30-32 percent. An increase in the amount of oxalic acid used to back-extract the niobium into aqueous solution from 2 milliliters per 100 milliliters of water to 4 milliliters per 100 milliliters resulted in a three-fold increase in the niobium-95 tracer recovered. It is probable that a further increase in oxalate concentration in the back-extraction step would result in a corresponding increase in the chemical recovery of niobium. However, as the amount of precipitate increases, the amount of energy absorbed by the precipitate would also increase. What seems necessary for niobium is a reagent which would react rapidly and quantitatively with small amounts of niobium to form an easily filtered precipitate.

The methods and procedures thus far discussed have all involved post-irradiation separations of radioniobium from other elements in the samples. The method outlined in procedure 5 represents a complete reversal in thinking, in that it involves separation of niobium in a pure form prior to irradiation. Admittedly, in this or any other pre-irradiation separation, a blank determination must be performed for traces of niobium (or other elements of interest) contained in the reagents, thus losing one of the greatest advantages of activation analysis. However, the amount of contamination and the low yields of the procedures discussed previously appeared to justify study of a pre-irradiation separation.

An unweighed sample of microcline, a potassium aluminum silicate, was subjected to the separation outlined in procedure 5. A pilot sample of niobium-95 chromatographed simultaneously with the sample, and, after drying, cut into seven 1/2-inch wide strips. These were analyzed for their niobium-95 content by means of the 100-channel analyzer. Results showed that 96.06-percent of the total niobium-95 activity was contained on the strip farthest from the starting point, and containing the solvent front. The remaining 3.94-percent of the activity was found on the adjacent strip, 1/2-inch closer to the starting point. Accordingly, the corresponding portion of the sample strip was removed and irradiated. Analysis of the irradiated paper section showed a definite photopeak at 16.7 Kev, having a half-life of 6.7 minutes. The section of the chromatographed strip next adjacent to that containing the solvent front was irradiated and analyzed. A much smaller niobium x-ray photopeak resulted. The remainder of the strip showed essentially no trace of a niobium peak following irradiation.

Although the pre-irradiation separation of niobium by paper chromatography was not investigated thoroughly, it appears to offer a rather clean separation of niobium from contaminating activities in high yield. The determination of yield may offer some problems, but in view of the difficulties experienced in post-irradiation separations of niobium, further development of the methods appears to be worthwhile. The total time involved in the chromatographic separation amounted to approximately two hours. However, several separations can be made simultaneously with relatively simple apparatus, such that several determinations could be completed in one day.

CHAPTER VIII

FURTHER INVESTIGATIONS

The importance of short-lived isotopes in activation analysis is just beginning to be realized (109). Because of this, only a few of these isotopes have been investigated for their possible use in activation determination. An examination of the graphs of neutron activation cross-sections (131) or sensitivity charts for neutron activation analysis (127) shows that there are approximately 30 isotopes with daughters having half-lives between 10 seconds and 10 minutes. Of these, somewhat less than one-fourth have been investigated thoroughly and for even fewer have rapid separations been developed.

Many of the stable isotopes having short-lived daughters have cross-sections for activation which are too low to be of much use in activation by the (n,γ) reaction. However, some of these short-lived isotopes can be produced by (n,p) or (n,α) reactions in a neutron flux of high neutron energy, that is, several Mev. Charged particle reactions which produce these activities might also prove to be of use for activation determinations.

Another field for investigation closely related to activation analysis by means of short-lived isotopes is that of instrumentation. With the recent appearance on the market of magnetic tape units into which the information stored in the memory circuits of a multichannel analyzer can be transferred in a matter of milliseconds, activation determinations by means of isotopes with half-lives of the order of seconds appears within reach. Such determinations would require rapid means of transporting samples to and from the radiation detector within seconds of leaving the reactor or other particle source. With isotopes having such short half-lives, no transfer from one pneumatic tube to another, such as reported in Chapter III, would be possible.

In addition to the above investigations, further work on the rapid separation of niobium is indicated by the results reported in Chapter VII. In view of recent experiments (108) with a 3/32-inch by 3-inch (diameter) sodium iodide(thallium) detector involving the non-destructive determination of niobium in stainless steel and in thermocouple wire, it would appear that a crystal of these dimensions could be used to detect the niobium x-ray without detecting gamma photons with energies above 100 Kev. A crystal of this thickness presents several half-thicknesses to a low energy x-ray, but only a fraction of the half-thickness for more energetic radiations. In cases where there is interference from low energy radiation from other isotopes present in the sample, a separation would then have to be performed. For such separations, especially those involving minute amounts of niobium, a reagent is necessary which reacts with niobium rapidly and quantitatively, forming an easily filterable precipitate.

APPENDIX I

CONSTRUCTION OF SAMPLE HOLDER CARRIAGE AND DETECTOR MOUNTING

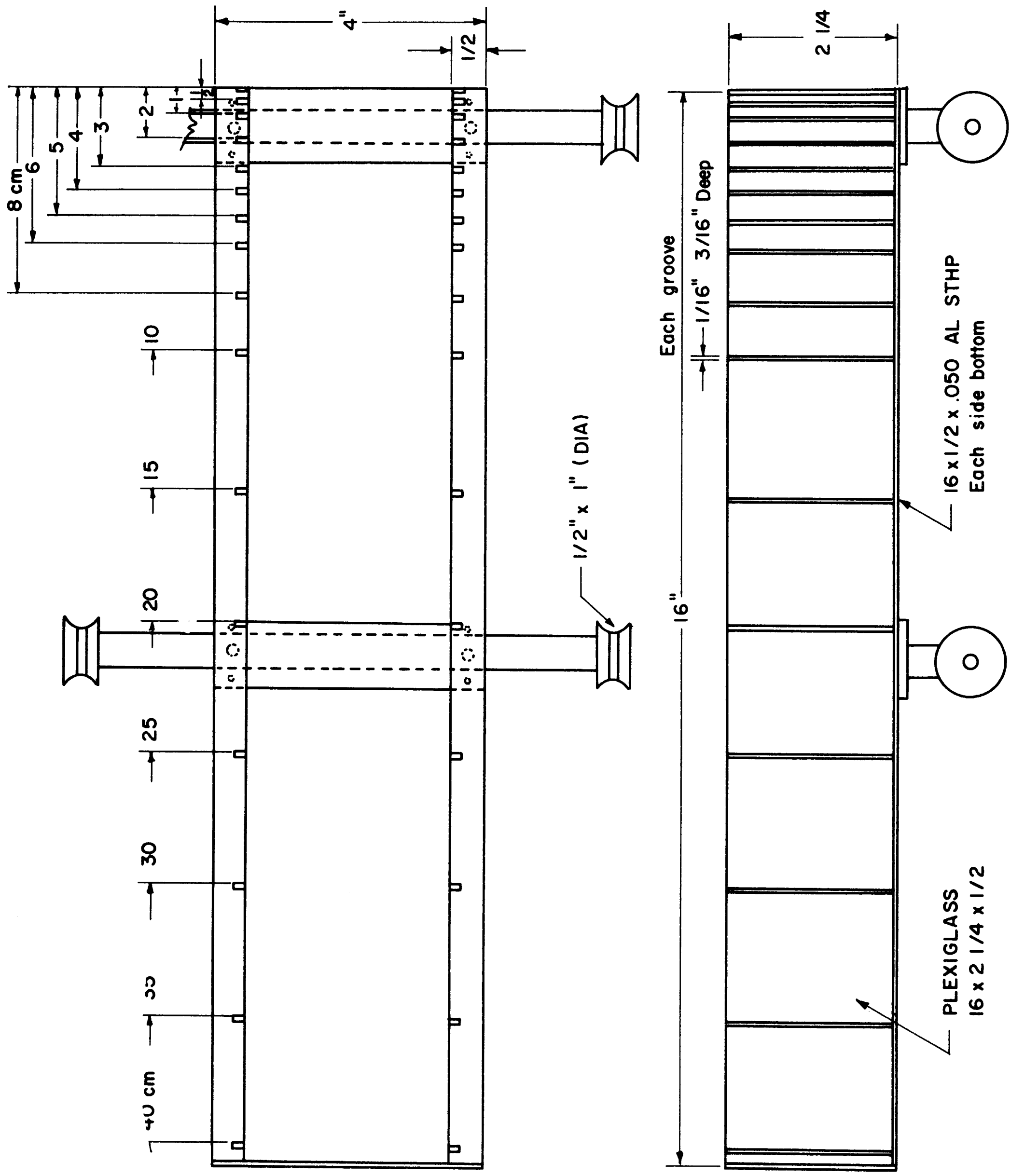


Figure 52. Sample Holder Carriage.

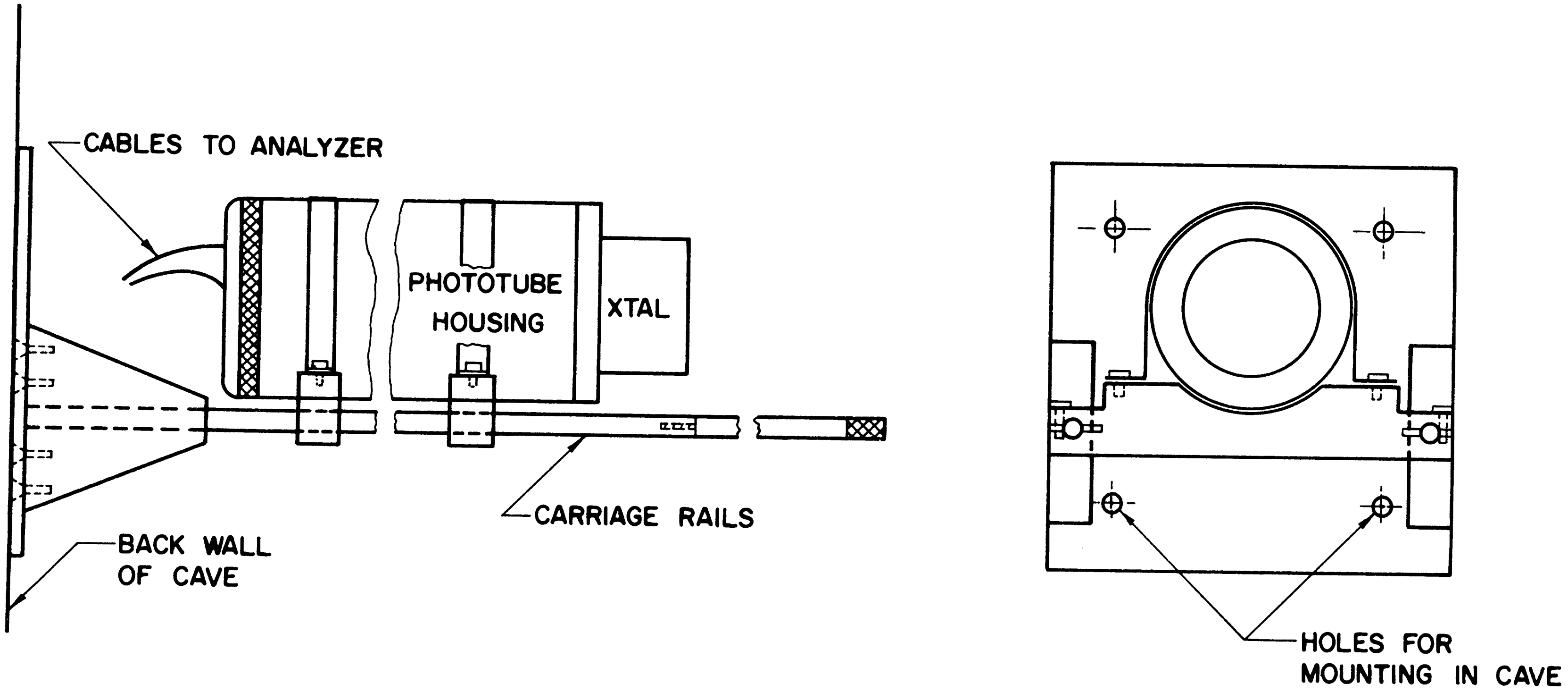


Figure 53. Detector Mounting in Cave.

APPENDIX II

OPERATING PROCEDURE FOR 100-CHANNEL ANALYZER

Before power is applied to any portion of the analyzer, the desired detector-phototube-preamplifier unit is plugged into the analyzer circuitry at the detector patch panel, section N, Figure 54. The instrument is then inspected to ascertain that the following controls are in the proper positions (in the following procedures, the letters refer to units of the analyzer as shown in Figure 54, and the numeral to the individual controls):

1. The mode selector controls J5 and 06, should be in the DISPLAY position. The READ-WAIT-STORE controls, J6 and 06, should be in the READ position.

2. Input power toggles for each individual unit should be in the OFF position (NOTE: power toggles for each unit carry the number "1" in Figure 54).

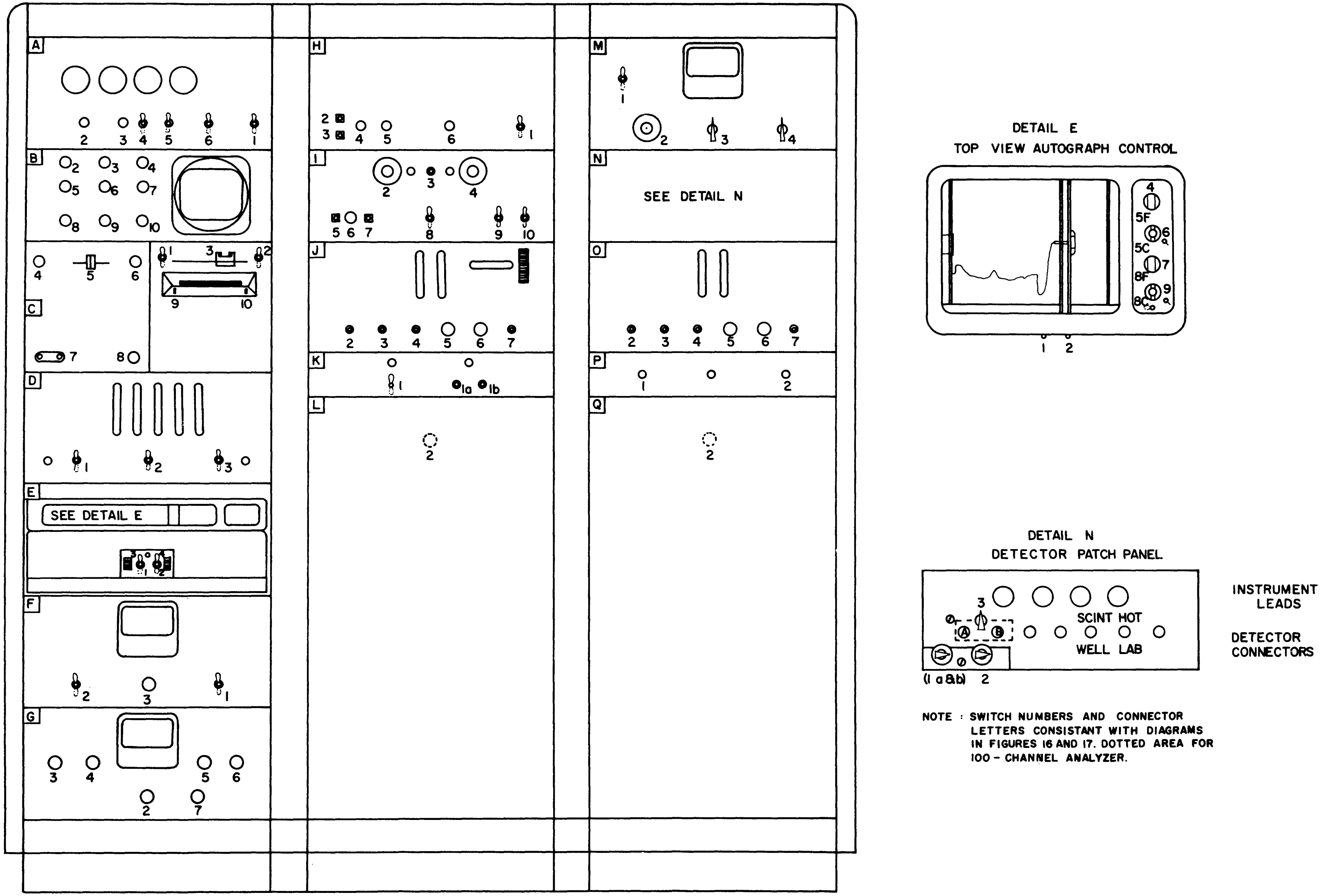
<u>To Turn Power ON</u>:

1. Turn INPUT POWER toggle K1, to the ON position; <u>wait at least thirty seconds</u>.

2. Depress D. C. POWER pushbotton, K1b (red).

3. Proceed with routine observations as outlined in the Operators Test Chekclist, Appendix III.

4. Place CONVERTER POWER toggle, F1, to the ON



NOTE : SWITCH NUMBERS AND CONNECTOR LETTERS CONSISTANT WITH DIAGRAMS IN FIGURES 16 AND 17. DOTTED AREA FOR 100 - CHANNEL ANALYZER.

Figure 54. Components and Controls of the 100-Channel Analyzer.

position and allow voltages to attain proper values (see checklist, Appendix III). In order to check voltages, toggle F2 must be in the VOLTMETER position.

5. Turn on power for each individual unit, observing any effects on voltages, etc.

6. If TOGGLE 1 and/or TOGGLE 2 pilot lamps (chassis I) are not lighted, depress RESET button, I3, until both pilots are lighted.

7. Check and adjust, if necessary, UPPER LEVEL and LOWER LEVEL controls, I2 and I4. This is accomplished as follows: Turn H4 to the P. G. position, and J6 to the STORE position. Channel lights on the Address Control Unit (J) should indicate 49-50. If not, adjust the LOWER LEVEL control, I4, until 49-50 are lighted. Now turn H4 to the P. G./2 position. Channel lights should now indicate 24-25. If not, adjust I4 very slightly until 24-25 are lighted. Turn H4 back to the P. G. position, and check to see that 49-50 are lighted. Make any minor adjustment necessary, then return H4 to the AMP. position.

8. The UPPER LEVEL, I2, should be set between 950 and 1000.

9. Place a cesium-137 source in the sample carriage and push into cave.

10. Place GAIN COARSE, H6, on the "1/4" position, and GAIN FINE, H5, at about mid-scale.

11. Turn H. V. SELECTOR, M3, to the POSITIVE position, with the H. V. COARSE control M4, at position A and H. V. FINE, M2, at zero.

12. Set timer unit, A, for some long time interval by adjusting A2 and A3. Depress TIME-AUTO-RESET switch A6, to RESET position, return to AUTO position.

13. Depress MEMORY pushbutton, J2, to clear "A" memory. Place J6 in the STORE position.

14. Adjust H. V. COARSE, M4, until a spectrum appears on the oscilloscope. Adjust M4 and H. V. Fine, M2, until the cesium-137 photopeak appears in or near channel 66. Small changes in peak position can then be made with the amplifier GAIN FINE, H5. The scope display is cleared while adjusting the high voltage by momentarily placing J6 in the READ position, depressing J2, and returning J6 to the STORE position. When the proper high voltage settings have been determined, J6 is returned to the READ position. Table XIII gives the approximate energy ranges analyzed for various settings of the amplifier GAIN COARSE, H6, when the instrument is calibrated in this manner.

Once the high voltage has been adjusted, calibration within each energy range should be performed according to section 3 for accurate energy determinations.

TABLE XIII

ENERGY RANGES ANALYZED FOR VARIOUS AMPLIFIER COARSE GAINS

Gain, Coarse	Energy Range, Mev.
1	0 - 0.25
1/2	0 - 0.50
1/4	0 - 1.0
1/8	0 - 2.0
1/16	0 - 4.0

To Place in Overnight Standby Operation:

1. Turn M2 to the OFF position.

2. Place J5 and O5 in the TEST 1 position, and J6 in the READ position.

3. Set PRESET TIME controls, A2 and A3, for ten minutes. Place toggle A4 in the CLOCK-TIMER position, and toggle A5 in the RECYCLE position.

4. Place switch A6 in the TIME position.

5. Decrease scope illimination by rotating the INTENSITY control, B9, counterclockwise until the scope presentation is no longer visible.

6. Turn power toggles C1, D1, E1, and E2 to the OFF position.

To Remove from Standby Operation:

1. Turn J5 and 05 to the DISPLAY position.

2. Depress switch A6 to the RESET position; return to the AUTO position.

3. Place power toggles C1, D1 and E1 in the ON position.

4. Turn H. V. SELECTOR, M3, to the POSITIVE position.

5. Perform observations outlined in paragraphs 2, 3 and 4 of the Analyzer Operator's Daily Checklist (Appendix III). The instrument is now ready for use.

A. Single Spectrum Operation

1. Place the sample in the carriage and push into the cave.

2. Select proper position of H6 from Table XIII for the energy range of interest.

3. Select preset counting period by adjusting A2 and A3 (units x multiplier = preset count time in minutes).

4. Depress switch A6 to the RESET position; return to the AUTO position.

5. Set toggle A4 to CLOCK-TIMER or LIVE-TIMER, as desired. In the LIVE-TIMER position, instrument coincidence losses are corrected automatically. Reset clock timer on Address Control unit, J, to zero.

6. Depress J2 to clear "A" memory. J6 must be in the READ position.

7. Turn J6 to the STORE position. Data will begin to appear on the oscilloscope.

8. Rotate DISPLAY SCALE, B10, to the smallest numerical position which will allow an undistorted picture of the stored data to appear. Data will continue to accumulate until the end of the preset time interval, when the instrument will automatically cease to store, and the spectrum will be displayed on the scope.

To Subtract Background Automatically:

1. Follow the steps outlined under Section A (Single Spectrum Operation).

2. Following step 8, complement spectrum by depressing button J7. The mirror image of the spectrum now appears on the oscilloscope.

3. Remove the sample from the sample carriage, and push the empty carriage back into the cave.

Depress A6 to the RESET position. The background is now added (negatively) to the complemented spectrum. The complemented spectrum appearing at the end of the counting period is now corrected for background activity, and may be printed without complementing a second time.

To Print and Graph Spectrum:

1. Complement spectrum by depressing button J7. Spectrum must be complemented in order to print and graph the data.

2. Turn J6 to the WAIT position and J5 to the PRINT position. J6 <u>must</u> be in the WAIT position each time J5 is changed.

3. Turn J6 to the READ position.

4. Clear address to channel zero by depressing CLEAR ADDRESS button, J3.

5. Turn RECORD toggle, C2, to the ON position.

6. Place graph paper on the recording table of the Autograf. Turn SERVO toggle, E2, to the ON position.

7. From the scope DISPLAY SCALE, B10, select the proper range for the ANALOG OUTPUT SELECTOR, C3 (3-2-1 for a maximum count of 999, 4-3-2 for a maximum count of 9999, etc.).

8. Place switch C5 in the GALV. ZERO position, and adjust the recorder pen to y-zero by rotating the Y ZERO control, E4. The Y-RANGE, E5c, should be set for 10-volts or 50-volts.

9. Place C5 in CALIBRATE position and adjust maximum travel of recorder in the y-direction by means of E5f. Return C5 to the OPERATE position.

10. Adjust the x-zero by means of E7. X-RANGE E8c, should be set for 1-volt. The maximum travel of the recorder in the x-direction is adjusted by means of E8f.

11. Place switch E3 in the DOWN position to lower pen onto paper.

12. Check to be certain that D3 is in the COUNT position. Depress D2 to RESET, then place in the PRINT position. Data is printed in digital form on tape and graphed on paper. Stop print-graph cycle by depressing D2 to RESET, and return to AUTOMATIC.

13. Return J5 to DISPLAY and J6 to READ. Depress J2 and A6. Memory is now cleared, the timer reset, and the analyzer is ready for another run.

B. Recycle Operation

1. Perform steps 1-8, section A, above. Toggle A5 must be in the RECYCLE position.

2. Place J5 in the AUTO. PRINT position.

3. Depress button 02 to clear "B" memory.

4. Perform steps 13, 14, 16-19 (section A, above). When the counting interval is very short, these can be performed before step 1.

5. Check to ascertain that D3 is in the COUNT position and C5 is in the OPERATE position.

6. From the scope DISPLAY SCALE, B10, select the proper range for the Analog Output Selector, C3, just prior to the end of the initial count cycle.

7. When the initial count cycle is finished, the data will be printed and plotted automatically. Immediately as the print-graph cycle begins, turn 05 to

the AUTO-PRINT position. Data may now be recorded automatically for as many intervals as desired.

8. At the end of the run, turn toggle E2 to OFF, E3 to Up, J5 and O5 to DISPLAY, and J6 to READ. Depress J2 and A6. The instrument is now ready for a future run.

C. Automatic Start-Recycle Operation

1. Check to ascertain that both "bunny" system control panels (see schematic Fig. 9) are connected to an A. C. outlet. The System toggle should be in the ON position, and the Motor toggle in the vertical position on the master unit in the radiochemistry laboratory.

2. Perform steps 2-5 (section A, above); place J5 in the READ position.

3. Depress button P1 (red) and hold. Place J6 in the STORE position. Release P1. The pilot lamp on panel P, Figure 19, should be lighted.

4. Place J5 in the AUTO-PRINT position.

5. Depress button O2 to clear "B" memory. Place O5 in the AUTO-PRINT position.

6. Depress button O3 (red) to clear "B" address to zero.

7. Estimate the proper position of C3.

8. Perform steps 13 and 14 (section A, above).

9. Perform steps 16-19 (section A, above).

10. Check to ascertain that D3 is in the COUNT position.

The analyzer is now ready for the automatic start by means of the bunny system. When a sample is sent to the room housing the analyzer and cave, it will automatically start the analyzer in recycle operation. In the event that the type of sample is such as to preclude use of the bunny system, and must be transported to the analyzer room on foot, the analyzer can be started by depressing button P2 (black) when the analyzer is set up as above.

In the case that a recycle time of less than approximately 24 seconds is required, it may be necessary to adjust LOWER level, I4, since at recycle times of less than 24 seconds the entire one hundred channels cannot be printed. This is accomplished by taking a standard source having a gamma photopeak close to that of the short-lived isotope of interest, and adjusting I4 so that this peak falls within the first 30-40 channels. The energy range analyzed is not affected by this procedure; the base line is affected, however, so that channel zero will no longer correspond to zero energy, but to some energy greater than zero.

APPENDIX III

ANALYZER OPERATOR'S DAILY CHECKLIST

1. After turning the Analyzer on, check the Memory Power Supply with selector G2. These voltages should read:

-150: 95% of full scale, ± 5%
-100: 95% of full scale, ± 5%
- 15: Not used
+ 5: 50% of full scale, ± 10%
+100: 95% of full scale, ± 5%
+150: 95% of full scale, ± 5%
+300: Past full scale, not adjustable.

There will be small variations from the normal voltage values when power is first turned on, but these will stabilize after approximately 30 minutes of operation. Tolerances are wide enough so that the ± 5% figure will indicate no probable failure. However, all the variation should be in the same direction. A departure of one value from normal could indicate failure of some component. To adjust the voltages to their proper values, use a screw driver on controls G3-G7. The +5 voltage should function down to 10% and as high as 75% of full scale. Failure to function properly in the upper range indicates impending failure in the Arithmetic panel.

2. Check the Converter Power Supply. For this check, toggle F2 must be in the VOLTMETER position. The voltage values should read:

+450: 75% of full scale
+300: Full scale
+200: 66% of full scale
-150: 50% of full scale
-300: Full scale

These values are all preset and are not adjustable. Significant differences should be noted and compared with previous readings. Deviations of 1 or 2 divisions on the meter scale indicate service is required.

3. All pilot lights should be on. If not, check for a burned out pilot bulb or a POWER switch in the OFF position. If TOGGLE 1 and 2 indicator lights (located to left and right of I3) are not on, depress RESET button, I3.

4. If the scaler lights on the Address and Control front panel are not lighted, or are lighted but do not read zero, depress CLEAR ADDRESS button, J3. Switch J6 from WAIT to READ and observe the display. The trace should appear as an unbroken line with each of the 100 channel spots distinct. If nothing appears on the Display except a single spot, again depress J3.

5. Depress COMPLEMENT button, J7. The spectrum should move to the top of the display and be uniform. Depress COMPLEMENT again and the trace will move to the bottom of the display. The display cathode ray tube and complementing procedure can often tell the operator whether the analyzer is operating properly. It is therefore advisable to comple-

ment several times throughout each position of the FULL SCALE selector, B10.

6. With the controls on DISPLAY and WAIT, switch J5 from DISPLAY to RECORD, J6 from WAIT to READ and depress CLEAR ADDRESS button, J3. Observe the address indicator lights on the Address and Control panel, J. They should show a uniform advance of 1 channel per second (2 channels per second on some models).

7. Switch J6 to WAIT, J5 from RECORD to TEST 1, then J6 from WAIT to READ. The trace on the Display should, on a series of alternate depressions of J2 and J7, clear to zero and then complement throughout each position of the DISPLAY SCALE selector without loss of a single channel as evidenced by a spot displacement. NOTE: The trace will move vertically at a rate depending upon the setting of the DISPLAY SCALE selector, C9.

8. Switch J6 to WAIT, J5 from TEST 1 to TEST 2, and then J6 from WAIT to READ. Observe the address indicator lights and the spot on the display. There should be a uniform progression of the spot on the Display from channel 0 to 99, resetting back to 0 and repeating the cycle as long as the controls are in READ and TEST 2. Note particularly any skipping of the lights which would indicate Address Scaler failure.

9. The same check may be made with the controls in RECORD and READ with the same results except that the action

of the address lights and the Display spot is much slower, advancing one channel per second (2 channels per second on some models).

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