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# Neutron activation analysis applied to arsenic determination

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NEUTRON ACTIVATION ANALYSIS  
APPLIED TO ARSENIC DETERMINATION

by

Bong Kyu Lee

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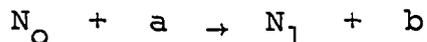
## TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. PRINCIPLES OF ACTIVATION ANALYSIS	13
III. INTERPRETATION OF GAMMA-RAY SPECTRA	31
IV. ERRORS AND LIMITATIONS OF THE TECHNIQUE	59
V. APPLICATION	86
VI. SUMMARY AND CONCLUSIONS	125
VII. LITERATURE CITED	129
VIII. ACKNOWLEDGMENTS	144

## I. INTRODUCTION

## A. Activation Analysis as an Analytical Tool

Activation analysis is a very sensitive technique for the identification and determination of elements of interest in which nuclei are bombarded with nuclear particles, and the resultant radiations are measured by means of a radiation detector. A general scheme for the nuclear transformation is given by the equation



where

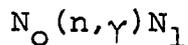
$N_0$  = the target nuclei,

$a$  = the bombarding particle,

$N_1$  = the transformed radioactive nuclei,

$b$  = the outcoming particle.

When the bombarding particles are neutrons, and the activation products emit gamma rays, the process is generally called neutron activation analysis. The scheme is often written as



If the half-life of  $N_1$  is reasonably long and the production is sufficient to allow the measurement of radioactivity, gamma rays from the product,  $N_1$  can be measured, and the intensity gives an indication of the concentration of  $N_1$  in the sample, providing that no other interference reactions occur.

The selection of activation analysis as the appropriate technique for the determination of the composition of a sample may be based on its sensitivity, speed, economy, and convenience, or on the absence of other suitable methods. In general, the mechanism involved in activation analysis consists of the following sequence of considerations and operations: (a) the selection of the optimum nuclear reaction, (b) the choice of a suitable irradiation facility, (c) the preparation of samples for irradiation, (d) the irradiation, (e) the post-irradiation assays, and (f) the evaluation of the experimental data.

The selection of the optimum nuclear reaction as the appropriate technique is, in general, based on the physical, chemical, and nuclear properties of the matrix and trace elements, and on their activation products. A trace element can be measured with the nuclear properties which determine the sensitivity. Consideration must be given to possible interfering reactions or competing activation products, and also to the practicality of providing a sample suitable for irradiation.

The choice of a suitable irradiation facility is based primarily on the type of nuclear particle and energy required. A wide selection of nuclear reactors, accelerators, and radioisotopes is available for irradiations. Important criteria for the selection of a particular facility are the flux

intensity required to achieve the desired sensitivity, the energy of the neutrons required, the physical properties of the specimen, the location of the facility, the availability of the facility, and the cost of the irradiation.

The physical, chemical, and nuclear properties limit the preparation of samples for irradiation because of safety consideration. Depending on the particular facility irradiation of powders, liquids, volatiles, or easily decomposed solids may be restricted. The mass of samples may also be limited in a particular irradiation facility. Any chemical or physical treatment of the sample prior to irradiation must be carried out in a manner which will avoid contamination.

There are two general irradiation and analytical techniques which apply to quantitative neutron activation analysis: the absolute assay technique and the comparative assay technique. The absolute assay technique requires that (a) the activation be carried out in a neutron flux of known intensity, (b) the pertinent nuclear data be known accurately, and (c) the radiometric assay be quantitative. The comparative assay technique requires standard samples of the elements being evaluated. The standard must be irradiated simultaneously with the samples and treated under the same laboratory conditions. This technique is limited to relative measurement only, and therefore does not require certain accurate nuclear data. This technique yields more accurate analytical results

with greater convenience than does the absolute assay technique. However, if no information is available with the sample, the absolute assay technique is the first choice.

The post-irradiation assay must be provided for each combination of matrix and trace elements. In many cases, chemical separations of the trace elements from the matrix and from each other are required. The extent of chemical separations depends on (a) the relative activation of the constituents, (b) the chemical properties of the activation products, and (c) the half-lives of the trace elements of interest. In cases where the major constituents are only slightly activated due to small activation cross section or low neutron energy, gross beta or gamma counting, or gamma spectrometry may suffice. Modern gamma scintillation spectrometry permits instrumental neutron activation analysis in which no chemical separation is applied.

The decay of radioisotopes or activation products is a statistical phenomenon and may be expressed by an exponential function. The evaluation of the experimental data allows the analyst to assign a reliability to the assay. Possible errors must be considered in such an evaluation. The general error sources are nuclear and analytical. A detailed discussion of these sources is given in Chapter IV.

#### B. Review of Literature

The value of activation analysis as a research tool was

recognized almost immediately upon the discovery of artificial radioactivity by the famous Frederic and Irene Curie-Joliet, in 1933. The first activation analysis experiment was carried out in 1936 by the Nobel prize-winning G. Hevesy, and H. Levi (53), when they bombarded impure yttrium with neutrons in order to activate and measure the contaminant, a small quantity of dysprosium. Since then activation analysis has caught on rather slowly, awaiting developments in the two basic components in any activation analysis facility, namely, the radiation source and the gamma-counting equipment. In 1938, the same workers (54) detected traces of europium in gadolinium. Seaborg and Livingood (133) demonstrated and presented for the first time in the United States the technique in which charged particle activation could be applied to analytical problems by determining trace quantities of gallium in high purity iron. These pioneers stimulated substantial interest in this new technique.

With the coming of the nuclear reactor in 1942, and the development of neutron generators, a source of high neutron fluxes became available, and the gamma-ray counting technique was advanced. The work at Oak Ridge National Laboratory stimulated the development of the technique and owed much of its success to the interest and encouragement of G. E. Boyd, who published his war-time researches (20), and to the early USAEC program begun by Overman and Clark (111). After

the establishment of an exploratory service group at Oak Ridge by the effort of Boyd in 1949, Ledicotte headed the Activation Analysis Group of the Analytical Chemistry Division, at Oak Ridge National Laboratory, and to him must go a great share of the credit for the success of the Oak Ridge Program, which is responsible for much of the early development of neutron activation analysis. By 1952, several review papers (20, 23, 44, 45, 82, 124, 146, 147, 148, 149) presented the basic principles of the method and the applications, including experimental data.

The International Conference on the Peaceful Uses of Atomic Energy in 1955 showed that the increasing application of radionuclei and nuclear chemistry to analytical problems led to a rapid growth of activation analysis as an established laboratory technique. By this time applications had taken a further step to special fields such as ion exchange (21, 28), gamma spectrometry (27, 105), nuclear emulsion detectors (92, 93), limitations and sources of errors (118), use of low-level neutron source (97), comparison with other analytical methods (96, 98, 136), archeology (130), biological systems, dating of minerals (52, 103), and film exposure (15, 16).

By 1958 Leddicotte (80, 84) reviewed recent developments periodically, and in 1960 Koch (78) summarized them and proceeded to present a handbook of activation analysis. Among important applications and developments of the technique were

biological and medical research (18, 33, 86), geochemical applications (123, 138, 139, 159), uses in reactor technology (71), fundamental concepts and techniques (5, 31, 40, 70, 101, 131), determination of isotopic abundances (100), interfering nuclear reactions (38), qualitative activation analysis (117), separating many elements from a single matrix (2, 17, 73, 151), use of gamma spectrometry (29, 65, 104, 128), utilization of linear accelerators (24, 90, 154), and measurement of physical properties (1, 2, 10, 11, 35, 80, 71 116, 126).

The 1961 International Conference on Modern Trends in Activation Analysis (118), held at Texas A & M University also stimulated the developing analytical technique, "activation analysis." Among important features discussed at the conference were flux monitors, automatic systems, and feedback to improve stability. Presented papers are categorized as (a) development of technique; use of multichannel pulse height analyzer, gamma ray spectrometry, and interpretation of interferences, (b) applications; determination of trace elements, metal industry, use of fast neutrons (accelerators), food industry, aerospace industry, forensic science, and medical use.

Raleigh (122) compiled a book entitled Literature Search of Activation Analysis which included 391 selected references on the use of radioactivation in a qualitative and quantitative analysis of materials through 1963. A useful index was

presented, which categorized (a) reviews and general interest, (b) analyzed materials, and (c) elements determined.

A revolutionary step was taken with the 1965 International Conference on Modern Trends in Activation Analysis, held again at Texas A & M University in memory of Dr. George Charles De Hevesey, who discovered nuclear activation analysis. Interest was shown in subjects such as (a) computer-coupled automatic system, which followed the developments of statistical interpretation of decay characteristics, computer programming, optimization of irradiation, decay, and counting times, giving the system the advantage of automation and speed; and (b) use of commercially available 14-Mev neutron generators.

The world's leading authorities on activation analysis attended the NATO Advanced Study Institute meeting in Glasgow, Scotland, in 1964 (87), and presented a comprehensive review of current practice and future prospects. Annual reviews of Analytical Chemistry (3) give total information of advancement in activation analysis. Pertinent literature (51, 78, 87, 89, 120, 121) is most helpful to every analyst in the field of activation analysis.

Arsenic, since its discovery in the early Nineteen Century, has been a significant poison, and has been administered with homicidal purposes and ingested accidentally by industrial workers. Analytical methods of arsenic have been well

reviewed (14, 99, 137). Beard (13) presented the detailed radiochemical procedures of arsenic analysis. The principal interfering element is Ge. The main methods of purifying arsenic are (a) distillation of either  $\text{AsCl}_3$  or  $\text{AsBr}_3$  (47, 66, 134, 140, 141, 142), (b) solvent extraction of  $\text{AsI}_3$  into  $\text{CHCl}_3$  or  $\text{C}_6\text{H}_6$  (77, 132), and (c) evolution of  $\text{AsH}_3$  (46, 132).

The correlation between atmospheric concentrations of various metallic elements and incidence of lung cancer is well established. The first report of cancer caused by arsenic was issued in 1887 by Hutchinson (64). In 1947, Neubauer (108) agreed that arsenic is carcinogenic by case presentation. In 1956, Hueper (63) agreed with and confirmed Neubauer's findings by compiling 23 cases of carcinoma of the lung. Satterlee (129) reported the occurrence of lung cancer associated with cigarette smoking.

"The habitual inhalation of arsenic, in minute doses, attached to irritant particles of tar may produce a suppression of respiratory metabolism and an enhancement of glycolysis that in time induces a progressive series of pathological changes in the bronchial epithelium that ultimately result in cancer cells."

In 1958, Holland et al. described a 200 to 600% increase in the arsenic content of most American cigarette tobaccos in the past 25 years. The report was that "the arsenic content of regular-sized unfiltered American cigarettes has increased from 7.5 to 30 ppm in 1932 to 1933 and 42.5 to 52.0 ppm in 1957." The chemical form of arsenic found was  $\text{As}_2\text{O}_3$ . Workers

at Veterans Administration Hospital in Dallas, Texas, (58, 59, 60) continued an investigation of arsenic content of cigarettes. The reported arsenic content in American cigarettes was 9 ppm in 1967. Bailey et al. (8) observed a level of 50 ppm in 1957, and well agreed with Holland, but Guthrie et al. (50) estimated an average level at 6 ppm in 1959. A more thorough review of arsenic in cigarettes is presented by Wynder and Hoffmann (161) in 1967.

Holland (58) states that "although the average American cigarettes contain only 9 ppm of arsenic, it is still possible for a heavy smoker (2 packages a day) to inhale 10% of this total amount, or 40 to 50  $\mu\text{g}$  a day. Although arsenic is eliminated fairly rapidly in the urine and feces (80% the first 4 days), there is still an accumulative effect of the remaining 20%." On the other hand, Lenihan (87) presented a slightly different view:

"Present levels are about 1 ppm. Even so, the smoker probably deposits appreciably increased amounts of arsenic in his lungs. It is known that about 3% of the arsenic in a cigarette is eventually deposited in the lung. The smoking of one cigarette will deposit about 0.03  $\mu\text{g}$  of arsenic in the lungs.... A simple calculation suggests that the total amount of arsenic inhaled in a day is about 1  $\mu\text{g}$  and that the total amount deposited in the lungs is about 0.03  $\mu\text{g}$ . A moderately heavy smoker may therefore increase his lung burden of arsenic quite substantially, even at today's greatly reduced concentration of this element in tobacco."

Even though Holland and Lenihan give slightly different figures for the amount of arsenic in the lungs, they confirmed

by experiments that arsenic is definitely carcinogenic to man.

However, a discussion of the relationship between the carcinoma and the lung cancer is being continued (156, 161). No tobacco chemist up to date reported on the application of neutron activation analysis to determining the arsenic amount in cigarettes. It is one of the main purposes of this work to evaluate the applicability of neutron activation analysis to cigarettes.

Moreover, the United States Department of Health, Education, and Welfare issued in its 1967 report (156), Health Consequences of Smoking, that "cigarette smoking is a health hazard of sufficient importance in the United States to warrant appropriate remedial action." The report shows a definite relationship between cigarette smoking and overall mortality, cardiovascular disease, chronic bronchopulmonary disease, and cancer. Among these and others, lung cancer is the most pronounced result of cigarette smoking.

### C. Objective of Investigation

The following work has a threefold purpose. The first part is concerned with a development of instrumental neutron activation analysis and a comparison of it with the destructive method in various aspects.

The second portion examines the applicability of the

instrumental neutron activation analysis to arsenic analysis.  
Cigarette tobacco is taken as an example of the analysis.

The final part is to determine the amount of arsenic  
contained in American cigarettes.

## II. PRINCIPLES OF ACTIVATION ANALYSIS

### A. Activation Equations

The basic concepts of the neutron activation analysis technique rely on the formation of radioactive nuclei as a result of nuclear reactions between the neutrons and nuclei of the material irradiated including the elements of interest. The nuclei are transformed into different isotopes of either the same or different elements.

Most elements become radioactive when they are irradiated with neutrons. The activity induced in an isotope of an element will be determined by the number of nuclei of the isotope in the sample, the number of neutrons per second impinging on the sample, the activation cross section of the isotope for the particular energy distribution of neutrons, the half-life of the activation products, and the time of irradiation. The rate of formation of a particular activation product,  $R$ , during the irradiation in a given sample is represented by the equation

$$R = \phi \sigma_{\text{act.}} N = \frac{\phi m N^0 f \sigma_{\text{act.}}}{M} \quad (2-1)$$

where

$\phi$  = the neutron flux (n/cm<sup>2</sup>-sec),

$\sigma_{\text{act.}}$  = the activation cross section (cm<sup>2</sup>/atom),

$N$  = the number of target atoms involved in the

activation,

$m$  = the mass of the trace element in the sample (gm),

$N^{\circ}$  = Avogadro's number (atoms/gm-atom),

$M$  = the atomic weight of the trace element (gm/  
gm-atom),

$f$  = the fractional isotopic abundance of the trace  
isotope.

The decay rate,  $D$  (atomic disintegrations per second), of the product radionuclei in the sample is given by the equation

$$D = \lambda N^* \quad (2-2)$$

where

$N^*$  = the number of atoms of the radioactive nuclide in  
the sample,

$\lambda$  = the radioactive decay constant of the nuclide  
( $\text{sec}^{-1}$ ),  $\lambda = \frac{0.693}{T_{1/2}}$ .

Therefore, the rate of change of the quantity of the activation product in the sample is represented by the equation

$$\begin{aligned} \frac{dN^*}{dt} &= R - D = \phi \sigma_{\text{act.}} N - \lambda N^* \\ &= \frac{\phi m N^{\circ} f \sigma_{\text{act.}}}{M} - \lambda N^* \end{aligned} \quad (2-3)$$

The number of radioactive atoms present after irradiation of an initially stable sample for time  $T_I$  is obtained by integration of Equation 2-3:

$$N^* = \frac{\phi \sigma_{\text{act.}} N}{\lambda} (1 - e^{-\lambda T_I}) . \quad (2-4)$$

The activity  $A_{T_I}$  in terms of disintegrations per second from the  $N^*$  atoms present after an irradiation time  $T_I$  is  $\lambda N^*$ ;

$$A_{T_I} = \lambda N^* = \phi \sigma_{\text{act.}} N (1 - e^{-\lambda T_I}) . \quad (2-5)$$

Activity for a decay time  $T_D$  after irradiation can be represented as

$$A_{T_I} = \phi \sigma_{\text{act.}} N (1 - e^{-\lambda T_I}) (e^{-\lambda T_D}) . \quad (2-6)$$

For irradiation times sufficiently long as compared to the half-life,  $e^{-\lambda T_I}$  approaches zero. Equation 2-5 becomes

$$A_{T_I} = A_{\infty} = \phi \sigma_{\text{act.}} N . \quad (2-7)$$

This is the maximum or saturation activity. If the irradiation time  $T_I$  is equal to the half-life  $T_{1/2}$ , this is one-half the activity at saturation. Therefore

$$A_{T_{1/2}} = \frac{1}{2} \phi \sigma_{\text{act.}} N . \quad (2-8)$$

For practical purposes, when the irradiation time approaches ten half-lives,  $(1 - e^{-\lambda T_I})$  becomes 0.999, and the activity becomes constant.

The saturation factor  $S$  is designated for  $(1 - e^{-\lambda T_I})$ , and

$$A_{T_I} = \phi \sigma_{act} . NS = A_{\infty} S . \quad (2-9)$$

### B. Limitations on the Activation Equations

Activation equations can be used to estimate the activation levels for the various elements in the sample under various conditions of neutron flux, irradiation time, decay time, and sample size. They can also be used to calculate the sensitivity for detection of an element under a specified set of irradiation and detection conditions by utilizing the following equation:

$$m = \frac{MA_{T_I}}{\phi N^0 f \sigma_{act} . (1 - e^{-\lambda T_I})} , \quad (2-10)$$

where  $m$  is expressed in grams, and  $A_{T_I}$  is, in this case, the minimum detectable disintegration rate for the activation product corrected for losses due to post-irradiation decay.

The activation equations as presented are based on certain assumptions and approximations. It is given in Equation 2-1 that the rate of formation of a radioactive nuclide is  $\phi \sigma_{act} . N$ . The neutron flux,  $\phi$ , and the activation cross section,  $\sigma_{act}$ , are assumed to be constant with a constant energy distribution of neutrons. However, neutron energy is not constant, and the flux and the activation cross section are functions of neutron energy. The ratio of fast neutrons to thermal neutrons depends on the place in the reactor in

which the sample is irradiated. In or near the moderator the cadmium ratio is low, but the epithermal neutrons will cause appreciable resonance activation. Therefore, the effective activation cross section will vary with the location at which the activation actually occurs.

If the values of the thermal activation cross section (78) are to be used, the activation should be done in the graphite reflector where the flux has more nearly a thermal distribution. However, the nonuniformity of energy can be overcome by the use of the standard of a known concentration similar to that of the samples. An alternative method may be adopted to correct resonance activation by using the cadmium ratio.

In deriving Equation 2-4, it is tacitly assumed that the number of target atoms  $N$  does not decrease significantly during the time of irradiation, compared to the number of atoms  $N^*$ . For isotopes of very large cross sections and long irradiation times, a correction must be made. In general, these nuclei produce long half-life isotopes, and optimum arrangement of irradiation time may overcome the large activation cross section. Moreover, it is assumed that the fraction of radioactive atoms destroyed by neutron absorption during irradiation is small, that is, an additional loss of radioactive atoms occurs. This may be corrected by adding the effective disintegration constant to term  $\phi\sigma_{act}$ . The

effective disintegration constant in the flux will be  $(\lambda + \phi\sigma_{act.}^*)$ , and the disintegration rate at saturation will then be given as

$$\frac{\phi\sigma_{act.}^* N\lambda}{\lambda + \phi\sigma_{act.}^*} .$$

If the cross sections are of the order of 10 barns, and the flux is of the order of  $10^{12}$  n/cm<sup>2</sup>-sec or more, the effect mentioned becomes insignificant. However, in cases where this effect results in a secondary reaction, a new radioisotope is formed. If this is the case, the number of secondary radioactive atoms with saturation irradiation is

$$N^{**} = \frac{\phi\sigma_{act.}^* N^*}{\lambda^{**}} , \quad (2-11)$$

and the saturation activity is

$$A^{**} = N^{**}\lambda^{**} = \phi\sigma_{act.}^* N^* . \quad (2-12)$$

If the activation cross section for the formation of the secondary radioisotopes is large, its activity may be an appreciable fraction of the total activity. An example is Au<sup>197</sup> irradiation with a neutron flux of  $1 \times 10^{12}$  n/cm<sup>2</sup>-sec, in which

$$A^* = Au^{198} = 3.0 \times 10^8 \text{ dis./sec.}$$

$$A^{**} = Au^{199} = 3.6 \times 10^6 \text{ dis./sec.}$$

However, in most cases, cross sections of secondary reactions

are much smaller than those of the main reactions.

### C. Activity During Measurement

Equations in the previous section describe the activity of a single radioactive element for an irradiation time  $T_I$ . The activity of the radioisotope decreases according to its decay constant as soon as the sample is activated. The activity at a time  $T_D$  after removal of sample from the reactor is given by the equation

$$A_{T_D} = A_{T_I} e^{-\lambda T_D} = A_{T_I} \exp\left(-\frac{0.693 T_D}{T_{1/2}}\right) \quad (2-13)$$

or

$$A_{T_D} = \phi \sigma_{act.} N (1 - e^{-\lambda T_I}) (e^{-\lambda T_D}) \quad (2-14)$$

The weight of the element in the sample is given by the equation

$$m = \frac{A_{T_D} M}{(6.023 \times 10^{23}) \phi \sigma_{act.} S e^{-\lambda T_D}} \quad (2-15)$$

If  $\phi$ ,  $\sigma_{act.}$ ,  $S$ ,  $A_{T_D}$ , and  $M$  are known,  $m$  can be calculated.

While the activity of the sample is measured, it continues to decay further. The activity is evaluated as a total count during the time interval, not at a given time. As the activity is measured during the time interval  $T_{D1}$

and  $T_{D_2}$  ( $T_{D_2} > T_{D_1}$ ), the number of radioactive atoms at the beginning of the count is

$$N_{T_{D_1}}^* = N_{T_I}^* e^{-\lambda T_{D_1}}, \quad (2-16)$$

and that at the end of the count is

$$N_{T_{D_2}}^* = N_{T_I}^* e^{-\lambda T_{D_2}} \quad (2-17)$$

The number of disintegrations during the time interval is given by the equation

$$\begin{aligned} N_{T_{D_1}}^* - N_{T_{D_2}}^* &= N_{T_I}^* (e^{-\lambda T_{D_1}}) (1 - e^{-\lambda (T_{D_2} - T_{D_1})}) \\ &= \frac{\phi \sigma_{\text{act.}} N S T_{1/2}}{0.693} \left( \exp\left(-\frac{0.693 T_{D_1}}{T_{1/2}}\right) \right) \left( 1 - \exp\left(-\frac{0.693 (T_{D_2} - T_{D_1})}{T_{1/2}}\right) \right) \quad (2-18) \end{aligned}$$

or

$$\begin{aligned} m &= \frac{(N_{T_{D_1}}^* - N_{T_{D_2}}^*) (M) (0.693)}{(6.023 \times 10^{23}) (T_{1/2}) (\phi \sigma_{\text{act.}} \lambda S) \left( \exp\left(-\frac{0.693 T_{D_1}}{T_{1/2}}\right) \right) \left( 1 - \exp\left(-\frac{0.693 (T_{D_2} - T_{D_1})}{T_{1/2}}\right) \right)}. \quad (2-19) \end{aligned}$$

If there is a way to determine the term

$$(N_{T_{D_1}} - N_{T_{D_2}})$$

in Equation 2-19, the weight of the element in the sample can be obtained.

In the case that the counting time is much shorter than the half-life

$$(T_{D_2} - T_{D_1} \ll T_{1/2}) ,$$

Equation 2-18 can be simplified:

$$N_{T_{D_1}}^* - N_{T_{D_2}}^* = N_{T_I}^* e^{-\lambda(T_{D_1} - T_{D_2})/2} \lambda(T_{D_2} - T_{D_1}) . \quad (2-20)$$

The average number of disintegrations in a unit time interval is represented in the equation

$$\frac{N_{T_{D_1}} - N_{T_{D_2}}}{T_{D_2} - T_{D_1}} = \lambda N_{T_I}^* e^{-\lambda(T_{D_1} - T_{D_2})/2} . \quad (2-21)$$

If the counting time is equal to or near the half-life

$$(T_{D_2} - T_{D_1} = T_{1/2}) ,$$

the effective time corresponding to the measured activity must be weighted somewhat toward the time  $T_{D_1}$ . Taking the first equation of Equation 2-18 and dividing by  $(T_{D_2} - T_{D_1})$  to get the average activity, one obtains

$$\frac{N_{T_{D_1}}^* - N_{T_{D_2}}^*}{T_{D_2} - T_{D_1}} = \frac{N_{T_I}^* e^{-\lambda T_{D_1}} (1 - e^{-\lambda(T_{D_2} - T_{D_1})})}{T_{D_2} - T_{D_1}} . \quad (2-22)$$

Actual activity corresponding to the effective time  $T_{\text{eff}}$ . may be given by the equation

$$\frac{N_{T_{D_1}}^* - N_{T_{D_2}}^*}{T_{D_2} - T_{D_1}} = \lambda N_{T_I}^* e^{-\lambda T_{\text{eff}}} . \quad (2-23)$$

From Equations 2-22 and 2-23, the left side of equations are eliminated to form

$$T_{\text{eff.}} = T_{D_1} + \frac{1}{\lambda} \ln \frac{\lambda(T_{D_2} - T_{D_1})}{(1 - e^{-\lambda(T_{D_2} - T_{D_1})})} . \quad (2-24)$$

In the case where  $T_{D_2} \gg T_{1/2}$  ,

$$T_{\text{eff.}} = T_{D_1} + \frac{T_{1/2}}{0.693} \ln \frac{0.693(T_{D_2} - T_{D_1})}{T_{1/2}} . \quad (2-25)$$

If

$$T_{D_2} - T_{D_1} = T_{1/2}$$

$$T_{\text{eff.}} = T_{D_1} + \frac{\pi/2}{0.693} \ln \frac{0.693}{0.5} = T_{D_1} + 0.47 T_{1/2}$$

$$< \frac{T_{D_1} + T_{D_2}}{2} . \quad (2-26)$$

The effective time is, in this case, slightly less than the middle of the counting period.

#### D. Optimization of Irradiation and Decay Times (67)

Equation 2-6 gives the activity of the activation product with irradiation time,  $T_I$  and decay time,  $T_D$ . The ratio of activity of element  $j$  to that of total in the mixture is given by

$$R_j = \frac{A'_j}{N \sum_{i=1} A'_i}$$

$$= \frac{N_j \phi_j \sigma_j (1 - e^{-\lambda_j T_I}) e^{-\lambda_j T_D}}{N \sum_{i=1} N_i \phi_i \sigma_i (1 - e^{-\lambda_i T_I}) e^{-\lambda_i T_D}} \quad (2-27)$$

The greatest selectivity for isotope  $j$  will be obtained when  $R_j$  is a maximum. As a consequence, two partial equations result:

$$\left( \frac{\partial R_j}{\partial T_D} \right)_{T_I} = 0 \quad (2-28)$$

and

$$\left( \frac{\partial R_j}{\partial T_I} \right)_{T_D} = 0 \quad (2-29)$$

Rearranging the two equations, one obtains the equations

$$\sum_{i=1}^N K_i (\lambda_i - \lambda_j) (1 - e^{-\lambda_i T_I}) e^{-\lambda_i T_D} = 0 \quad (2-30)$$

and

$$\sum_{i=1}^N K_i [\lambda_j e^{-\lambda_j T_I} (1 - e^{-\lambda_i T_I}) - \lambda_i e^{-\lambda_i T_I} (1 - e^{-\lambda_j T_I})] e^{-\lambda_j T_D} = 0 \quad (2-31)$$

where

$$K_i = N_i \phi_i \sigma_i .$$

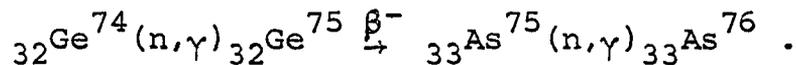
Equations 2-30 and 2-31 must be solved simultaneously to evaluate  $T_I$  and  $T_D$ . The resultant  $T_I$  and  $T_D$  are the optimized irradiation and decay times.

#### E. The (n, $\gamma$ ) Reaction

Neutrons are electrically neutral and have no Coulomb barrier surrounding them. Therefore, it is possible for a neutron of even very low kinetic energy to enter into the target nuclei and cause a nuclear reaction. The reaction scheme will depend on the neutron energy (158). Indeed, slow neutrons can induce nuclear reactions with a cross section far exceeding that of any other particles (41). Thermal neutron reactions proceed through the formation of a compound nucleus. Since the excitation energy of the compound nucleus formed in the capture of a slow neutron by a target nucleus is only a little greater than the binding energy of the

captured neutrons, it takes a relatively long time for a fluctuation which concentrates the escape energy back on a neutron to occur. There is a greater probability that the excitation energy will be emitted as gamma rays; thus the main reaction with thermal neutrons is the  $(n,\gamma)$  reaction.

Although the  $(n,\gamma)$  reaction is the most important one for thermal neutrons, it is also occasionally possible to have  $(n,p)$  and  $(n,\alpha)$  reactions (38). Particularly with targets of low  $Z$ , for which the Coulomb barrier is not so high as to hinder the emission of charged particles. A well-known and important  $(n,p)$  reaction with thermal neutrons is that with  $N^{14}$  which produces  $C^{14}$ . The  $(n,\alpha)$  reaction of  $B^{10}$  is of great value in the detection of neutrons. Another example of a reaction with  $Z-1$  and  $Z-2$  elements which disturbs the main reaction is



#### F. Irradiation Facilities (Neutron Sources)

Neutrons from radioisotopes, accelerating machines, and nuclear reactors are at present being used in neutron activation analysis associated with research, teaching, and industrial fields. There is undoubtedly a wide potential application for neutron sources, providing they satisfy the criteria of a high output of neutron flux at a low cost.

Neutrons are produced by bombarding a target nuclide with charged particles or with gamma radiation. The produced neutrons may be grouped according to their origin; radioisotopic neutron sources, particle accelerators as neutron sources, and nuclear reactors.

### 1. Radioisotopic neutron source

The radioisotopic neutron source is very favorable because of its steady output and easiness of operation. However, most of the sources developed to date have a low yield, less than  $10^8$  n/sec, and neutron energy which is too low for some of the more useful reactions. Furthermore, the source cannot be turned off, and thus requires shielding at all times.

In most cases,  $\text{Be}^9$  has been used as the target element, since it has the low neutron binding energy, 1.7 Mev, and produces a relatively high neutron yield, in which an alpha particle or a gamma ray emitter and beryllium are combined. Typical radioisotopic neutron sources are shown in Table 2-1.

The energy spectra of neutrons formed by sources of the  $(\alpha, n)$  type are complex. For example,  $\text{Po}^{210}\text{-Be}^9$  source emits neutrons of energies up to 13 Mev, having broad peaks at 3.5 Mev and 5.5 Mev. Various energy losses from sources of the  $(\gamma, n)$  type, such as  $\text{Sb}^{124}\text{-Be}^9$ , is caused by scattering in the beryllium target, which has the neutron energy of 25 kev. Although the maximum possible neutron output is required,

Table 2-1. Radioisotopic neutron sources

Sources	Reaction type	Half-life
Pb <sup>210</sup> -Be <sup>9</sup>	$\alpha, n$	22 y.
Ac <sup>227</sup> -Be <sup>9</sup>	$\alpha, n$	22 y.
Ra <sup>226</sup> -Be <sup>9</sup>	$\alpha, n$	1622 y.
Po <sup>210</sup> -Be <sup>9</sup>	$\alpha, n$	138 d.
Th <sup>228</sup> -Be <sup>9</sup>	$\alpha, n$	1.9 y.
Sb <sup>124</sup> -Be <sup>9</sup>	$\gamma, n$	60 d.

the problems are the size of shield needed to absorb intense gamma ray emission from the source, the difficulty of obtaining the required quantity of radioactive material, and the hazard associated with handling of the sources.

Among the sources in the table, Sb<sup>124</sup>-Be<sup>9</sup> has the highest neutron intensity. This has a half-life of only 60 days, but can be reactivated in a reactor and used again. However, because of the short half-life, two or more sources are suggested, one being reactivated in a reactor while the other is in use. Methods of laboratory analysis using radioisotopic neutron sources have been developed extensively in recent years (43, 97).

## 2. Accelerators as neutron sources

The accelerating machines include cyclotrons, Van de Graaffs, and Cockroft-Waltons. The Cockroft-Walton is a low energy accelerator and produces 14 Mev neutrons by bombarding tritium with deuterium. However, it has disadvantages such as its large physical size and the presence of the tritium hazard resulting from the need to change tritium-loaded targets.

The choice of activating particles naturally depends on the particular samples to be analyzed. In activation analysis one has a choice among several incident activating particles:

(a) Neutrons of thermal energy or fast neutrons from the (d,t) reaction at 14 Mev. Neutrons of intermediate energies may also be used in special cases.

(b) Charged particles, usually of moderate energies, such as protons, deuterons, tritons, alpha particles, and  $\text{He}^3$  nuclei.

(c) High-energy photons for photonuclear activation analysis through the  $(\gamma, n)$  and  $(\gamma, p)$  reactions, and occasionally through the  $(\gamma, \gamma')$  excitation reactions.

Although thermal-neutron activation analysis is possible, fast-neutron activation is more favorable in some cases by using neutrons from accelerators. A number of different nuclear reactions can be induced by fast-neutron bombardment. They are characterized as  $(n, p)$ ,  $(n, 2n)$ ,  $(n, \alpha)$ ,

(n, $\gamma$ ) reactions. Naturally the fast-neutron activation technique is more complex than thermal activation in which a stable nuclide can be transmuted to a number of different radioactive isotopes. Conversely, several different elemental species can yield the same product. Nevertheless, these complications can often be overcome by the skilled analyst by selecting a particular gamma emission not obscured by other activities (55, 56, 160).

The electron Van de Graaff or linear accelerator can be made to produce neutrons via photo-disintegration reactions. The electron beam from the accelerator is made to produce high energy X rays by interaction with a high atomic number target such as gold, and the X rays, in turn, produce neutrons by causing the photo-disintegration of a secondary target of Be (1.66 Mev threshold) or uranium (9 Mev threshold). These reactions produce neutrons of 1-2 Mev mean energy, and therefore tend to be used as means of producing thermal neutrons because they can be moderated fairly easily.

Neutrons, in a number of different energy ranges, are readily obtainable from Van de Graaff positive accelerators. Suitable reactions and targets are  $\text{Be}^9(d,n)\text{B}^{10}$ ,  $\text{T}^3(d,n)\text{He}^4$ ,  $\text{T}^3(p,n)\text{He}^3$ ,  $\text{D}^2(d,n)\text{He}^3$ ,  $\text{Li}^6(d,n)\text{Be}^7$ , and  $\text{C}^{12}(d,n)\text{N}^{13}$ . The most versatile and useful high-energy neutrons (14 Mev) are produced by the  $\text{T}^3(d,n)\text{He}^4$  reaction. Neutrons yield up to  $2.6 \times 10^8$  n/sec are obtained when tritiated

targets are bombarded with 0.8 Mev deuterons. The corresponding fast flux is  $8 \times 10^8$  n/cm<sup>2</sup>-sec, two centimeters from the target at a 150  $\mu$ a beam current (55, 56).

### 3. Nuclear reactors

Nuclear reactors are the most powerful type of neutron source, and have provided the greatest versatility and sensitivity for laboratories. Neutron activation analysis of most element is possible with nuclear reactor fluxes of  $10^{12}$  to  $10^{14}$  n/cm<sup>2</sup>-sec. The main disadvantages of a nuclear reactor are its large size and high cost. Present day nuclear reactors are, in general, thermal neutron sources. There are some elements which cannot be analyzed with thermal neutrons, because they do not activate by means of (n, $\gamma$ ) reactions. Oxygen, nitrogen, iron, and beryllium, for example, can be best analyzed with fast neutrons. They can be used in many different ways, such as thermal-neutron activation, fast-neutron activation, and pulsed-neutron activation. The detailed descriptions of nuclear reactors as neutron sources or irradiation facilities are presented in appropriate sections.

### III. INTERPRETATION OF GAMMA-RAY SPECTRA

#### A. Scintillation Method for Gamma-Ray Detection

One of the earliest methods of nuclear-radiation detection involved the counting of the scintillations produced in a phosphor screen. It is well known that Rutherford and his collaborators employed this technique in their famous study of alpha-particle scattering by nuclei. Although the basic principles remain the same, the technique has changed greatly. The scintillation method eventually gave way to electrical counters. The scope of applications of the modern scintillation detector has broadened greatly over that of the early type.

Modern scintillation counters were followed closely the development of high gain photomultiplier tubes (25). Combining various scintillating materials with a multiplier to count the scintillations produced by alpha, beta, and gamma radiations has resulted in the most versatile detector available for nuclear research. This device has come into wide-scale use, meeting demands for detectors capable of high counting rates and shorter resolving times than were possible with the existing instruments, and also making possible gamma-ray spectrometry.

A most important contribution of the modern scintillation technique has been made in the field of gamma-ray detection.

The much higher density of solid gamma-ray scintillators gives them a stopping power for photons far greater than gas-filled counters. It is feasible to prepare scintillating crystals large enough to stop completely a sizable fraction of incident gamma rays. It is possible to obtain not only gamma events, but energy spectra and gamma-ray intensities as well.

In order to be effective for gamma-ray detection, a scintillator should be of high density and high atomic number. These requirements are best satisfied by inorganic scintillators. Among many scintillating inorganic materials only the activated alkali halides can be grown in single crystals of sufficient size and yet possess the required transparency to their emitted lights (119).

Sodium iodide activated with 0.1% Tl is the only alkali halide scintillator in routine use. It has the high density of the alkali halides and a moderately high effective atomic number. The light output in NaI(Tl) per Mev is the largest of any known scintillator, and is about twice that of anthracene (135). Large single crystals of NaI(Tl) are readily obtainable and highly transparent to their own fluorescent light, which is emitted in a band about 800 Å wide, centered at 4100 Å.

Because of its higher effective atomic number, thallium-activated cesium iodide has been investigated as a gamma-ray scintillator. At present, crystals of CsI(Tl) are far more

expensive to manufacture than crystals of NaI(Tl). Furthermore, although moderate pulse-height resolution can be obtained, the usable light output is only about 40-50% that of NaI(Tl) (39). This lower apparent output may arise because the fluorescent light is emitted at longer wave lengths, namely 4200-5700 Å, and consequently cannot be measured efficiently by most commercially available photomultiplier tubes.

Mounting NaI(Tl) crystals larger than three inches in diameter calls for a more elaborate technique, although NaI(Tl) crystals of five inches in diameter are available commercially. The response of a large crystal is not sensitive to scattering from the container well as are the smaller crystals, for which the mass ratio of NaI(Tl) to cladding material is much less favorable (51).

Whenever gamma-emitting nuclei are used in radiochemistry, some variation of the versatile NaI(Tl) scintillation counter is nearly always used. Perhaps the most generally useful configuration is the well counter. Although, for example, a 3" x 3" crystal is popular among crystals, the efficiency of this detector is less than that of a well crystal of 2" x 2" with a 3/4" diameter well and 1 1/4" deep, but it can have a large sample volume.

One of the most important applications of the NaI(Tl) scintillation detector is in the field of gamma-ray spectrometry. It is possible to make a spectrometer which will

not only measure the energies of gamma rays to high precision, but will also yield their intensities. Much of the popularity of the NaI(Tl) scintillation spectrometer in radiochemistry lies in its ability to differentiate between various gamma-ray emitting components; hence, the presence of a particular nuclide in the spectrum of a mixture can be established by the characteristic energies observed, and the amount of the nuclei can be determined quantitatively from the appropriate gamma-ray intensities.

#### B. Interaction of Gamma Rays in NaI(Tl)

It should be recalled that gamma rays, as such, are not detected, but rather it is the secondary electrons produced by the interaction between the gamma rays and the crystal which give rise to the fluorescent light. In order to understand the gamma-ray spectra, the response of a scintillation detector and a knowledge of the nuclear physics with respect to the basic processes by which photons interact with matter, in terms of their effects on the response of the scintillation spectrometer, is essential.

Although many processes are involved in the events which finally produce electrical impulses at the output of the photomultiplier, the major features of the differential pulse-height spectrum resulting from the detection of the gamma rays may be interpreted in terms of the basic inter-

actions which occur in the detector; these are (a) photoelectric effect, (b) Compton effect, and (c) pair production. However, an entirely logical separation of variables which affect the production of an electrical pulse in a scintillation spectrometer is difficult. Even for fundamental aspects of a detector system it is virtually impossible to observe many of the variables separately. Although the detecting medium, NaI(Tl) crystal, may remain the same for many applications, the processes associated with the absorption of radiation will vary with different radioactive sources. Besides the type of emission of radiation, the response of the detector will also vary with the other decay scheme variables.

#### 1. Photoelectric effects and escape peaks

The process of photoelectric absorption is the most important process occurring in NaI(Tl) crystal. In this process a gamma ray imparts all of its energy to an electron, which is called a photoelectron. The energy of the ejected electron is equal to the difference between the energy of the incident photon and the binding energy of the shell from which the electron was ejected. However, some of the energy is absorbed by the recoil of the gamma ray and the photoelectron. That is, about 80% of the photoelectric interactions take place in the K-shell, and a large part of the remaining 20%

takes place in the L-shell (51, 109, 110). These short-range photoelectrons are stopped in the crystal and give up almost all of their energy to the crystal; this results in a total absorption or photoelectric peak. These peaks are the characteristic photopeak which make gamma-ray spectrometry a useful tool.

The resultant photoelectron leaves a vacancy in the iodine atom as a result of this process, which then emits a characteristic iodine X ray of 28 kev. If the interaction takes place near the surface of the crystal, the iodine X ray has a chance of leaving the crystal without being detected. Another important characteristic of the photoelectric effect in a scintillation detector is the monoenergetic-electron energy distribution within the volume of the detector.

This phenomenon may be best illustrated by Figure 3-1, which shows a pulse-height distribution for a 470 day- $\text{Cd}^{109}$  source. The peak of 88 kev is the total absorption peak. The peak at 22 kev is due to the total absorption of Ag X rays resulting from  $\text{Cd}^{109}$ . A small peak between these two is due to the escape of the iodine X ray. The phenomenon of iodine X ray escape diminishes as the energy of gamma rays increases, since the photons penetrate more deeply into the crystal before they undergo photoelectric absorption.

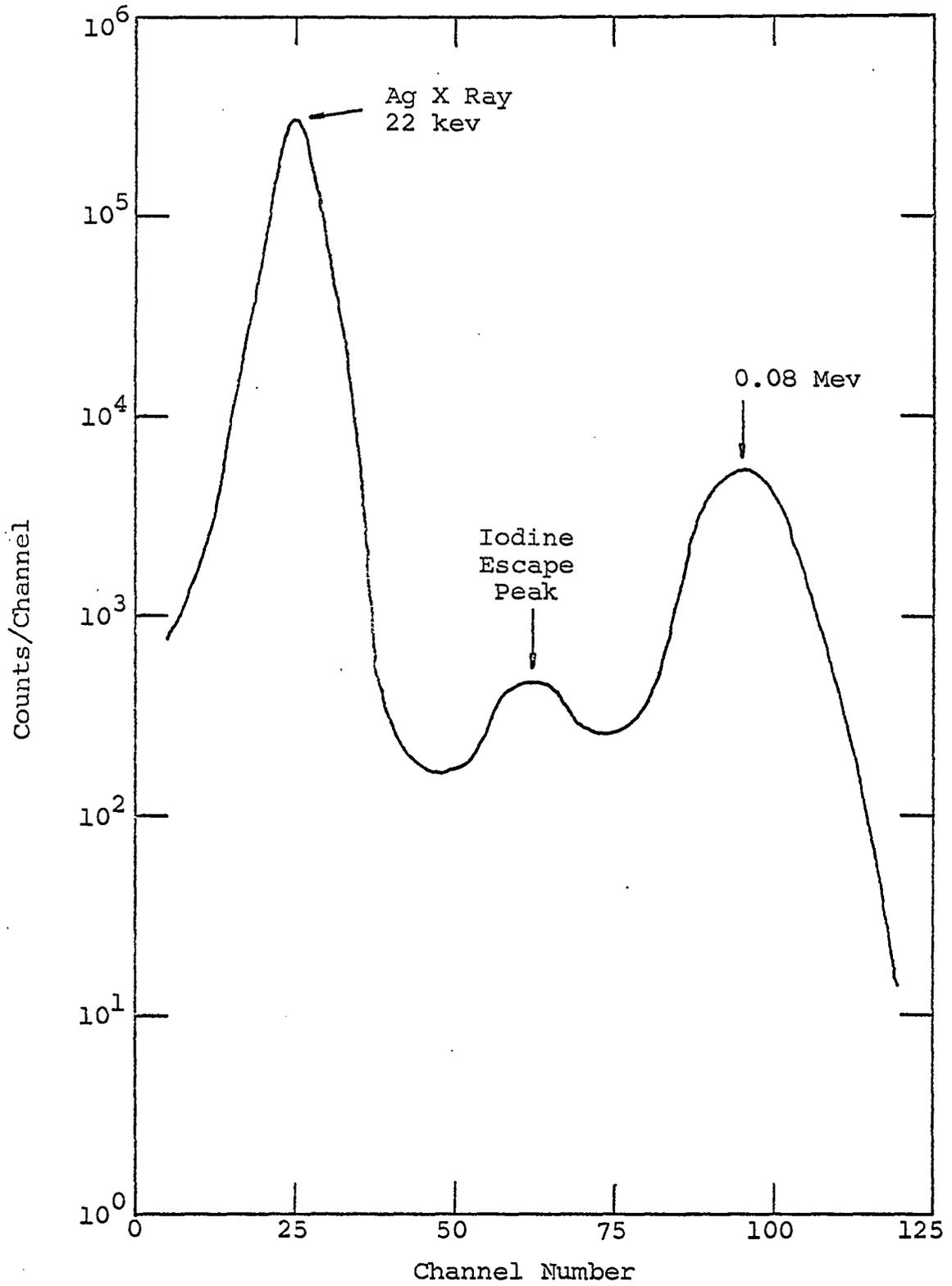


Figure 3-1. Gamma-ray spectrum of  $\text{Cd}^{109}$  (51)

Reactions of this type predominate when a gamma ray incident on sodium iodine has an energy of below about 0.2 Mev. If this were the only process for energy loss, the response of a detector capable of indicating energy of these individual photoelectrons would be quite simple.

## 2. Compton scattering phenomena

In the Compton process the incoming photons are scattered by electrons with a partial energy loss. In general, the scattering process occurs with electrons being considered free, and the energy of the incoming photon being shared between the electron and the scattered quantum.

At low energies a gamma ray may be scattered from a bound electron with the atom remaining in its initial state, in which case there is negligible energy loss and only a change in direction. Since this process does not result in an energy change, it is an important consideration in the calculation of the efficiency of a detector. The energy of the scattered photon then extends from the original photon energy down to a minimum value, which is always less than  $mc^2/2$  (0.257 Mev).

Figure 3-2 shows the total and partial absorption coefficients in NaI(Tl) for gamma rays as a function of energy. At energies below about 300 kev, the photoelectric process is most predominant, but the Compton effect dominates in the intermediate energy region approximately 0.3 Mev to 5.0 Mev.

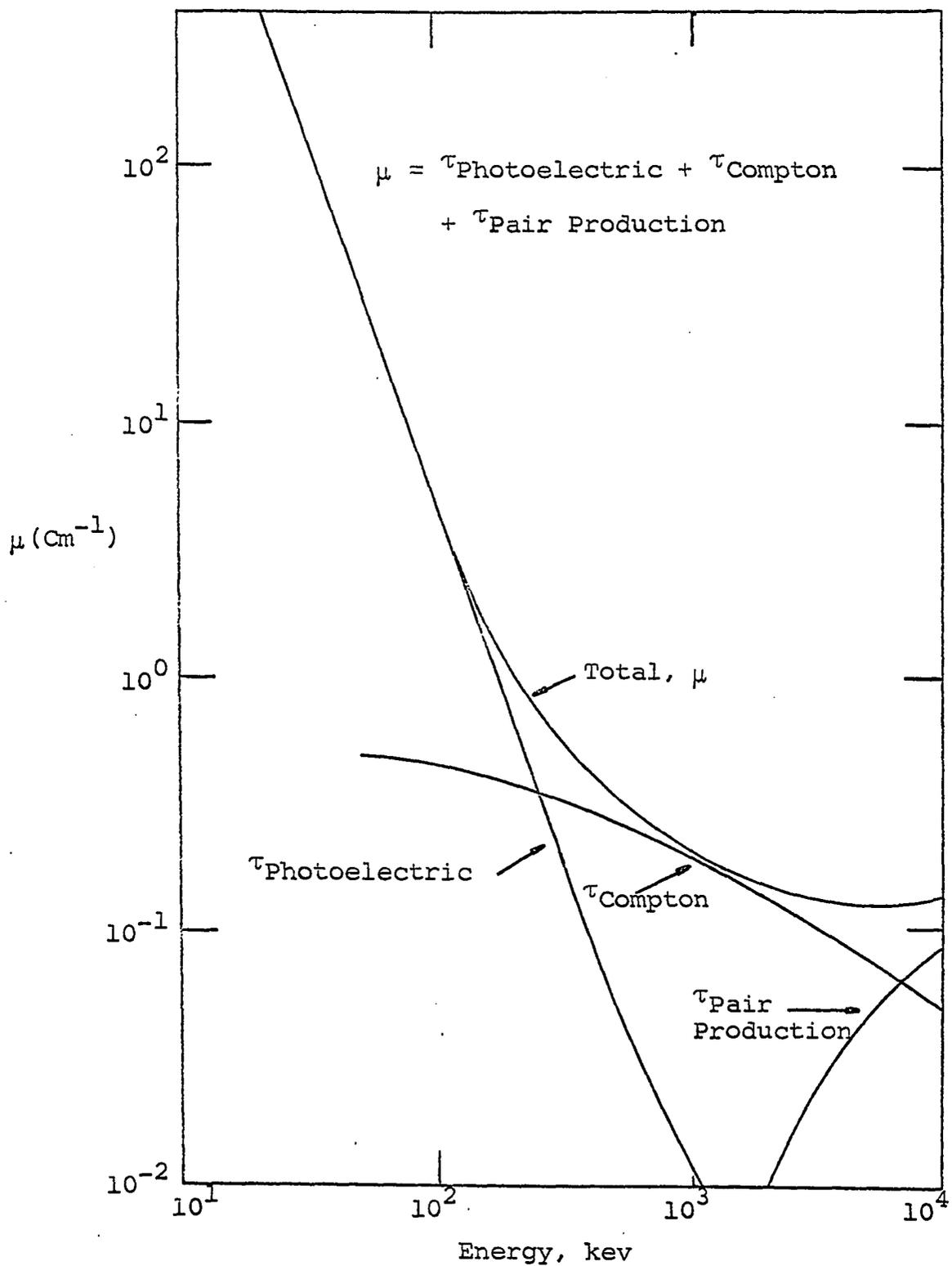


Figure 3-2. Gamma-ray absorption coefficients in NaI(Tl) for various gamma-ray energies (135)

The Compton effect is the interaction which occurs when the incident gamma ray strikes an electron of an atom and shares part of its energy. The resultant electron and degraded gamma ray recoil from the atom. The energy of recoiling electrons will have values from essentially zero up to a maximum cut-off point called the Compton edge, which represents the maximum energy transfer between the photon and a recoil electron. This point in a gamma-ray spectrum is given by the equation

$$E_c = \frac{E_r}{1 + (0.511/2E_r)} \quad (3-1)$$

where  $E_c$  is the energy of the Compton edge, and  $E_r$  is the energy of the incident photon energy in Mev. The  $2\pi$  Compton process causes a characteristic spectral feature called the backscatter peak, which looks quite like a photopeak at an energy of about 200 kev. This effect is found in Figure 3-3. The energy of the backscatter peak is given by the equation

$$E_b = \frac{E_r}{1 + (2 E_r/0.511)} \quad (3-2)$$

The magnitude of the backscatter peak may be reduced by increasing the distance from the shield to the detector. For spectrometer shields with large central cavities, one may achieve spectra with essentially no backscatter peak. However, the light generated in the crystal by each of the

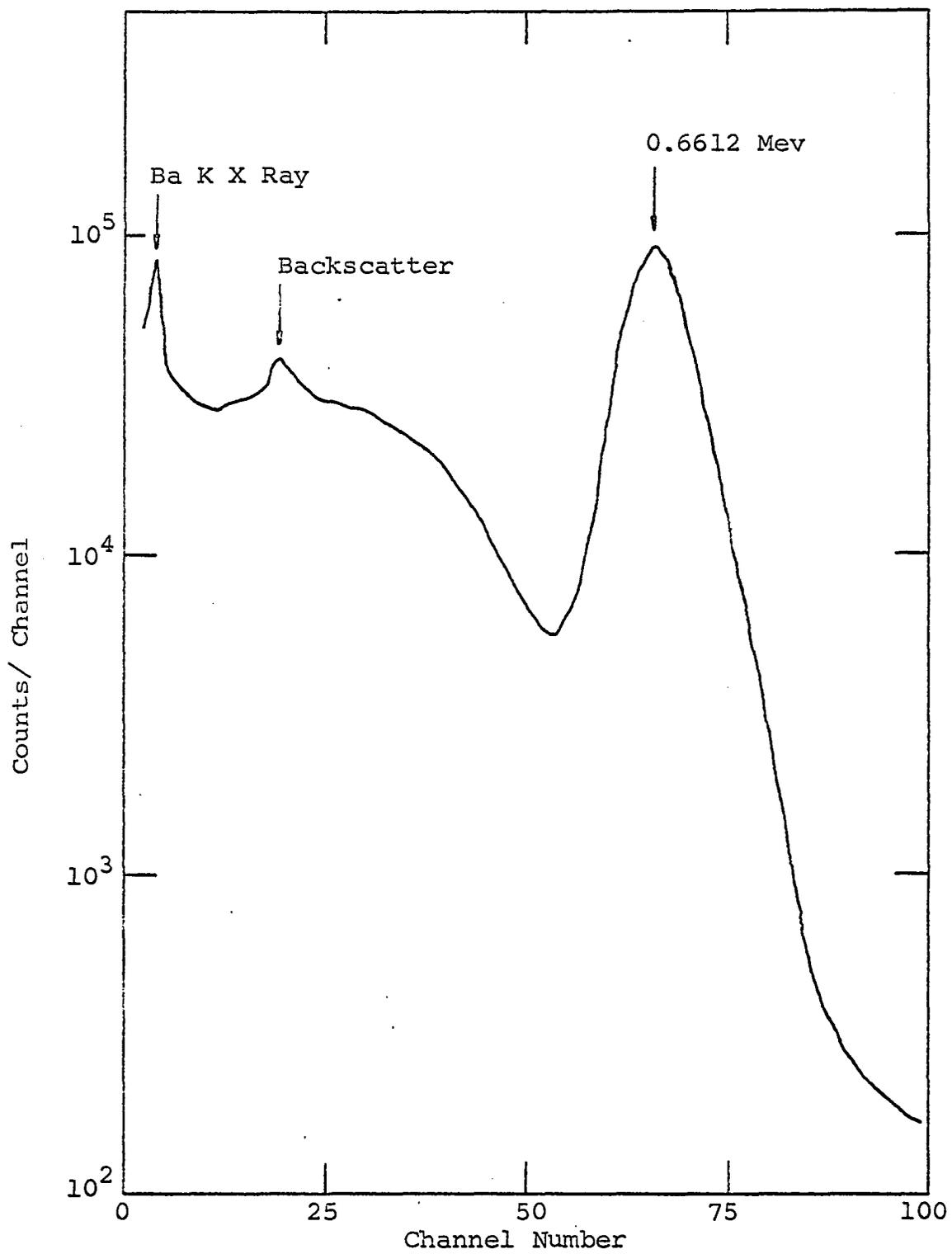


Figure 3-3. Gamma-ray spectrum of  $^{137}\text{Cs}$

individual events is summed as though they were coincident. This is because the interaction events occur in a much shorter time than does the generation or decay of the scintillation light pulse. Therefore, the full energy peak efficiency in a scintillation crystal is greater than expected from the photoelectric cross section alone, when appreciable numbers of Compton interactions are occurring in the detector.

### 3. Pair production and escape peaks

The pair production process has a threshold energy at 1.02 Mev. If the incident photon has an energy in excess of the rest mass of a positron-electron pair (1.02 Mev), pair production is possible. In this process, which occurs in the presence of the Coulomb field of a nucleus, the gamma ray disappears, and a positron-electron pair is created. The total energy of the pair of particles will be equal to the energy of the primary photon, and their kinetic energy will be equal to the total energy minus the rest energy of the two particles ( $2mc^2$ ). Interaction by the pair process in a detector will therefore result in an energy loss equal to the primary photon energy minus 1.02 Mev.

Even though the pair process has a threshold energy at 1.02 Mev, the effect of this process is not evident below about 1.5 Mev. This process occurs when a photon interacts with the nucleus of an atom and gives all of its energy in

the production of an electron-positron pair. The resultant positron is usually annihilated in the crystal, producing two 0.511 Mev photons, which are emitted in opposite directions.

The possibility also exists of detecting one or both of the annihilation quanta by either the photoelectric or the Compton process. If one of these photons escapes the crystal without interaction, a peak called the single-escape peak is produced. If both photons escape being undetected, a double-escape peak arises. The energy of the single-escape peak is found to be 0.511 Mev below the total-absorption peak, and the double escape peak is found to be 1.02 Mev below the total-absorption peak.

This may be illustrated by Figure 3-4, which shows the gamma spectrum of  $\text{Na}^{24}$ . Sodium-24 emits gamma rays of 2.75 and 1.368 Mev. The single-escape peak at 2.25 Mev and the double-escape peak at 1.74 Mev can be seen. There is no detectable escape peak due to the 1.368 Mev gamma ray.

The total possibility of the detection of a gamma ray can be expressed as the sum of the total absorption coefficient of photoelectric effect, the Compton scattering, and the pair production. The total absorption coefficient for NaI(Tl) and the contribution from the three main processes are illustrated in Figure 3-2.

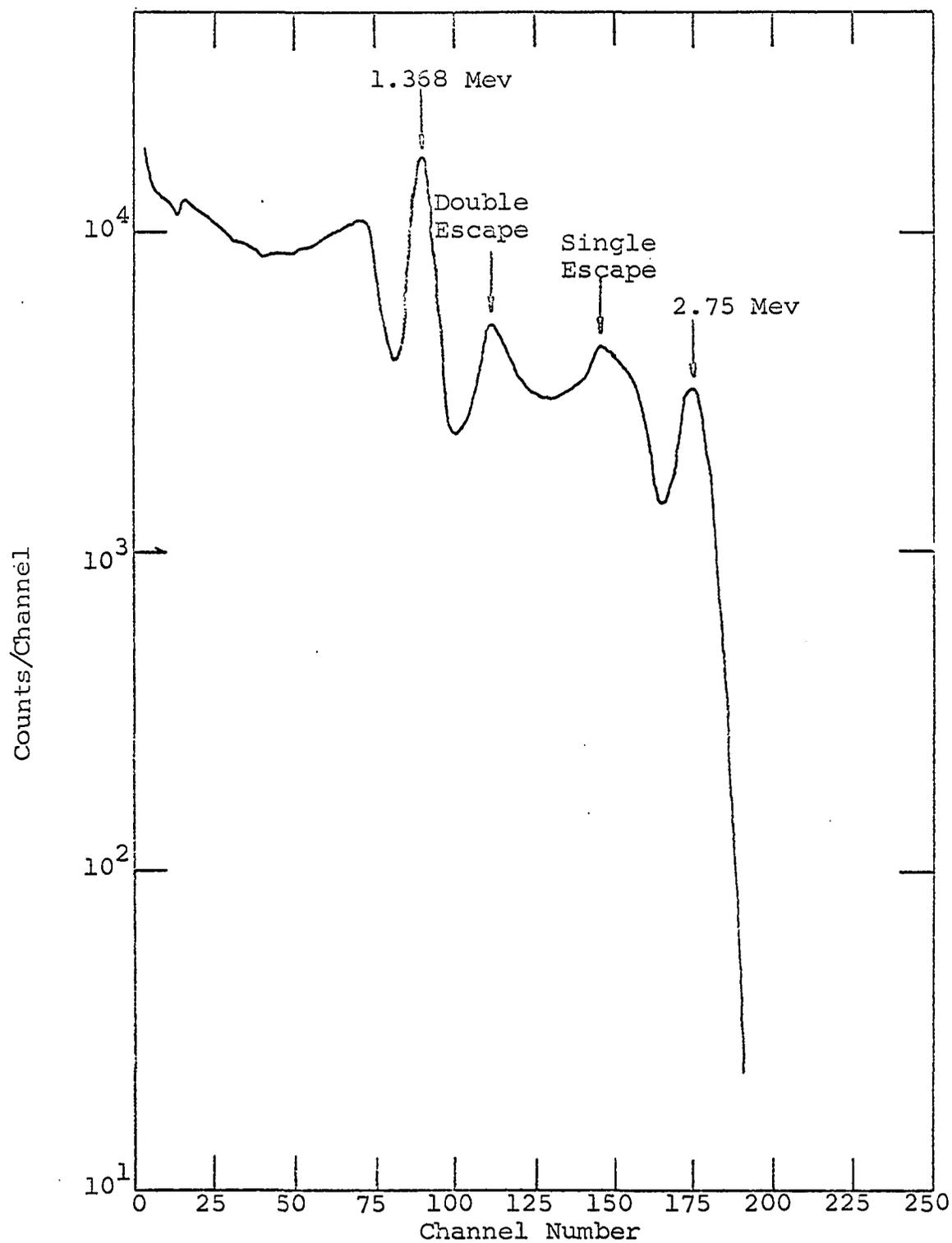


Figure 3-4. Gamma-ray spectrum of  $\text{Na}^{24}$

#### 4. Shielding effects

If the sample to be detected and the scintillation detector could be isolated from all surrounding material, the interpretation of the gamma-ray spectrum would be dependent only on the energy of the gamma ray, the nuclear and physical properties of source and detector, and the geometrical relationship between the two. Of course, this is the ideal case. Unfortunately, however, this can hardly be established in a laboratory. In practice, the shape of the observed gamma-ray spectrum will be influenced by several factors related to the experimental environment. Therefore, the response of a detector environment must be considered prior to any attempt to analyze a gamma-ray spectrum.

In a scintillation crystal, difficulty is often created by the crystal and source surroundings in getting precise measurements. As a result, a different spectrum can be obtained from a source enclosed by matter as compared with the same source, free from scattering material.

As discussed in the previous section, one aspect which complicates gamma-ray spectrum interpretation is the production of lead X ray in the usual lead shield wall by a photoelectric interaction. This X ray arises from the same type of process as on iodine escape. The lead X ray causes a peak to appear in the environmental spectrum at 72 kev. Since this peak arises from the shield material and not from

the source, it is desirable to remove this contribution. This may be accomplished by the use of a graded linear lead for the spectrometer shield.

Scattering from the surroundings of the crystal can appreciably raise the counting rate in the Compton region, and scattering peaks can confuse the identification and analysis of spectra. Extra counts are added in the Compton region of the spectrum when the crystal is in the presence of surrounding materials. These extra counts originate from several sources; (a) gamma rays which are completely absorbed in surrounding materials cause fluorescent X rays from the material to enter the crystal, (b) gamma rays which strike the surroundings such as a lead shield enter the crystal with decreased energy after a Compton scattering event, and (c) gamma rays which scatter out of the crystal enter the surrounding material and backscatter into the crystal at a low energy.

Gamma rays in the energy region below 200 keV are detected almost entirely by the photoelectric processes. As previously discussed, the ejection of a photo-electric electron from the K shell of an atom is followed by the emission of characteristic X rays. If the interaction occurs near the surface of the detector, iodine K X rays may escape without further interaction. When this occurs, the energy of the X ray (28 keV) will be lost and an additional peak will appear

in the spectrum at 28 kev less than the photopeak. Axel (6) and McGowan (95) calculate the escape peak intensities for various configurations. Heath (51) compares their calculated values with his empirical values.

In order to reduce the level of background radiation, it is usually necessary to put the NaI(Tl) detector inside a shielded enclosure. The shield is the major source of scattered radiation, but may also come from the source holder, the material used to prepare the source, beta absorbers, and the packing material surrounding the NaI(Tl) crystal.

If one examines the region of the gamma-ray spectrum which results from the Compton electrons, one can see a definite peak superimposed upon the otherwise flat energy distribution of electrons. This peak is termed the backscatter peak, as discussed previously, and arises from Compton scattering of gamma rays in the wall of the shield surrounding the detector.

Heath (51) states that for scattering angles greater than  $120^\circ$ , the energy of the scattered photon is relatively independent of the angle and the energy of the primary photon. For an angle of less than  $120^\circ$ , the scattered photon energy decreases with the increase of the gamma-ray energy. The nature of the exponent decrease is evident for the higher (greater than 1 Mev) primary photon energies. However, for low energies of the primary photon, the evidence is much

reduced. Heath also shows three examples of the 6" x 6" Fe shield, 6" x 6" Pb shield, and 32" x 32" Pb shield. The height of the backscatter peak is reduced in the order of the above configurations.

The relative magnitude of the scattered spectrum will also depend upon the source-detector geometry. Analogously to the escape of iodine gamma rays from the surface of the detector following a photoelectric event, another photo event occurring at the surface of the wall of the detector shield can result in the production of characteristic Pb X rays. The probability of detecting these gamma rays can be reduced by the use of critical absorption techniques, i.e., the use of a graded Pb shield.

The decay of the most radioactive sources includes the emission of charged particles, either positron or electron. Since NaI(Tl) is an efficient detector of charged particles, it is necessary to prevent their entering into the detector. The presence of these charged particles introduces several complications. This is particularly important for nuclei which have a high intensity of ground state transition. This requires the use of a beta absorber, such as polystyrene, above the source.

### 5. Sum spectrum effects

In the decay of the most radioactive nuclei, beta emission is frequently followed by the emission of two or more gamma rays in cascade. Hence, there is a finite probability that the gamma detected in this instance will correspond to the sum of the energies deposited in the detector by the gamma rays. This results in an energy distribution as high as the sum of the energies of the coincident gamma rays. The intensity of the peak in coincidence sum spectrum for two coincident gamma rays is given by (125),

$$N_{CSS} = N_0 E_1 E_2 \bar{W}(0^\circ) \quad (3-3)$$

where  $N_0$  is the number of coincident pairs of gamma rays emitted by the source,  $E_1$  and  $E_2$  are the efficiencies for the detection of gamma rays 1 and 2, and  $\bar{W}(0^\circ)$  is a factor included to account for the angular correlation of the coincident gamma rays. A typical coincidence sum spectrum appears in Figure 3-5, which also shows the annihilation and bremsstrahlung effects.

The relative intensity of the sum spectrum is seen to be highly dependent upon source-detector geometry. By utilizing Equation 3-3, one can find that the magnitude is proportional to the product of the detection efficiency for the two gamma rays. As a result, it can be concluded that the analysis of the complex spectrum will be more complicated if

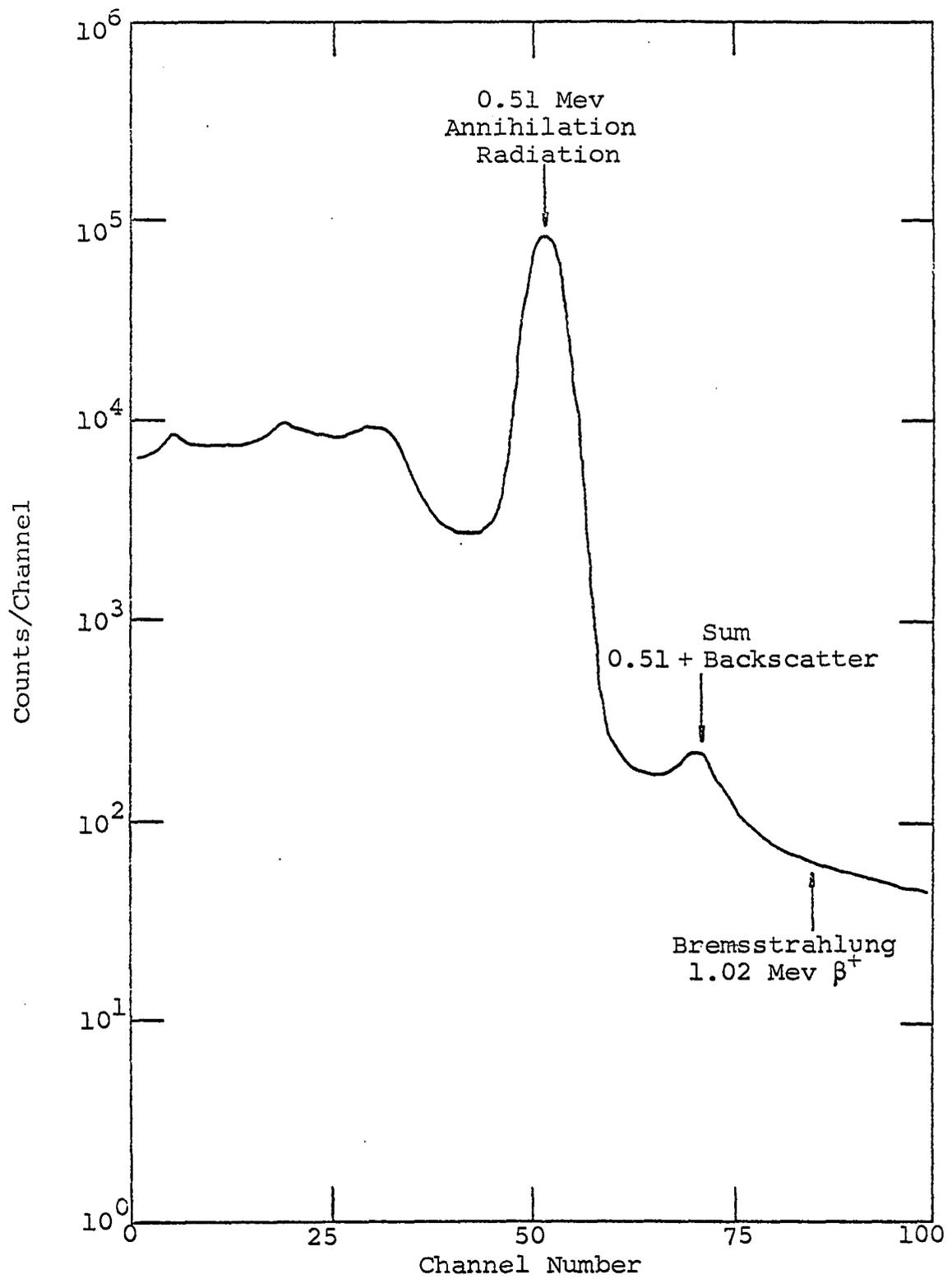


Figure 3-5. Gamma-ray spectrum of  $\text{Ti}^{45}$  (51)

the spectrum is taken under conditions of a large solid angle. On the other hand, the coincidence sum can be used to confirm coincidence relationship of two gammas and offers a means of identifying nuclei whose spectra are characterized by prominent cascades.

Sources which emit positrons present a special case for coincidence summing. It is desirable to annihilate the positrons at their source in order to ensure that the annihilation radiation will be detected in the same geometry as the other photons emitted by the source. This can be achieved by surrounding the source with an absorber of sufficient thickness to annihilate the positrons. If one of the two annihilation quanta enters into the detector, the other, which is emitted in the opposite direction, can be scattered from its surroundings.

Another sum spectrum event is due to an accidental time-coincidence between events occurring in the detector. Since the processes of radioactive decay are completely random in time, and the resolving time of the electronic system finite, pulses from two events can overlap in time, and the two events will sum in amplitude. The probability for accidental summing is given by (51) the equation

$$I_{\text{rss}} = N^2 2T \quad (3-4)$$

where  $I_{\text{rss}}$  refers to the total number of pulses appearing in

the sum spectrum occurring,  $N$  the input pulse rate, and  $T$  the resolving time.

Pulses in this sum spectrum represent the detection of photons directly incident upon the detector, and are considered as part of the energy response of the detector. As can be seen with Equation 3-4, the intensity of the random sum spectrum will vary as the square of the input pulse rate.

#### 6. Bremsstrahlung effects

The bremsstrahlung and photoelectric processes are very similar. The reverse process of the creation of a pair is the transition of an electron in the electric field of a nucleus from a positive energy state to a negative state with the emission of a photon. Bremsstrahlung differs from this process only in that both the initial and final energy states of the electron are positive.

If the energy transition of the electron in the positive energy states occurs in the electric field of a nucleus, there is a small probability of photon (bremsstrahlung) emission. The relative loss of energy is generally much less than the ionization losses. The probability of bremsstrahlung emission per atom increases with  $Z^2$  of the absorber, and decreases with the square of the mass of the incident charged particles. The latter fact makes the electron the only significant source of bremsstrahlung.

In each individual radiative interaction, the energy balance involves an electron, a nucleus, and a photon. The resulting bremsstrahlung spectrum is continuous from zero to the maximum kinetic energy of the incident electrons. All the beta transitions are sources of continuous X rays called internal bremsstrahlung. This is a result of the sudden change of charge in the nuclear electric field in all beta transitions. A radiative transition occurs with the beta emitting atoms for approximately 0.7% of the beta particle emissions.

In practice, the main source of bremsstrahlung is the external interaction of electrons in thick targets. Compton and Allison (26) give an empirical formula for the energy fraction of incident monoenergetic electrons converted to bremsstrahlung in a thick target as

$$G = k(Z E) \quad (3-5)$$

where  $Z$  is the atomic number of the absorber and  $E$  is the incident electron energy in Mev. Evans (37) gives another approximate equation for the fraction of the beta energy, for a continuous beta ray spectrum, as

$$G = k_0(Z E_0) \quad (3-6)$$

where  $E_0$  is the maximum energy in Mev of the beta spectrum and  $Z$  the atomic number of absorber. Evans estimated the best values of  $k = (0.7 \pm 0.2)10^{-3} \text{ Mev}^{-1}$  and

$$k_0 = 0.33 \times 10^{-3} \text{ Mev}^{-1}.$$

The percentage of bremsstrahlung may be much higher in relation to a gamma-ray spectrum where the beta branching directly to the ground state is very high. It is virtually impossible to calculate in an actual experiment the exact shape or the intensity of the external bremsstrahlung spectrum. The relative importance of external bremsstrahlung can be estimated from a knowledge of the branching ratio and maximum energy of the beta ray.

Internal bremsstrahlung produced in a source, and external bremsstrahlung emitted when beta rays are stopped in an absorber will cause a characteristic response in a scintillation detector up to the maximum energy of the beta particles. The quantitative measurement of gamma rays in the presence of intense beta activity is difficult, and the comparative measurement of two sources may be in considerable error if one has a large quantity of beta activity present. Figure 3-6 shows the spectrum of  $Y^{91}$  which has a 1.21 Mev gamma with only 2% abundance, but 100% yield of beta particles. The contribution to the spectrum from the bremsstrahlung can be seen clearly.

For spectrometry application, it is desirable to stop beta particles or electrons from the source before they reach the detector. The use of the beta absorber should be considered. The absorber should have a sufficient surface

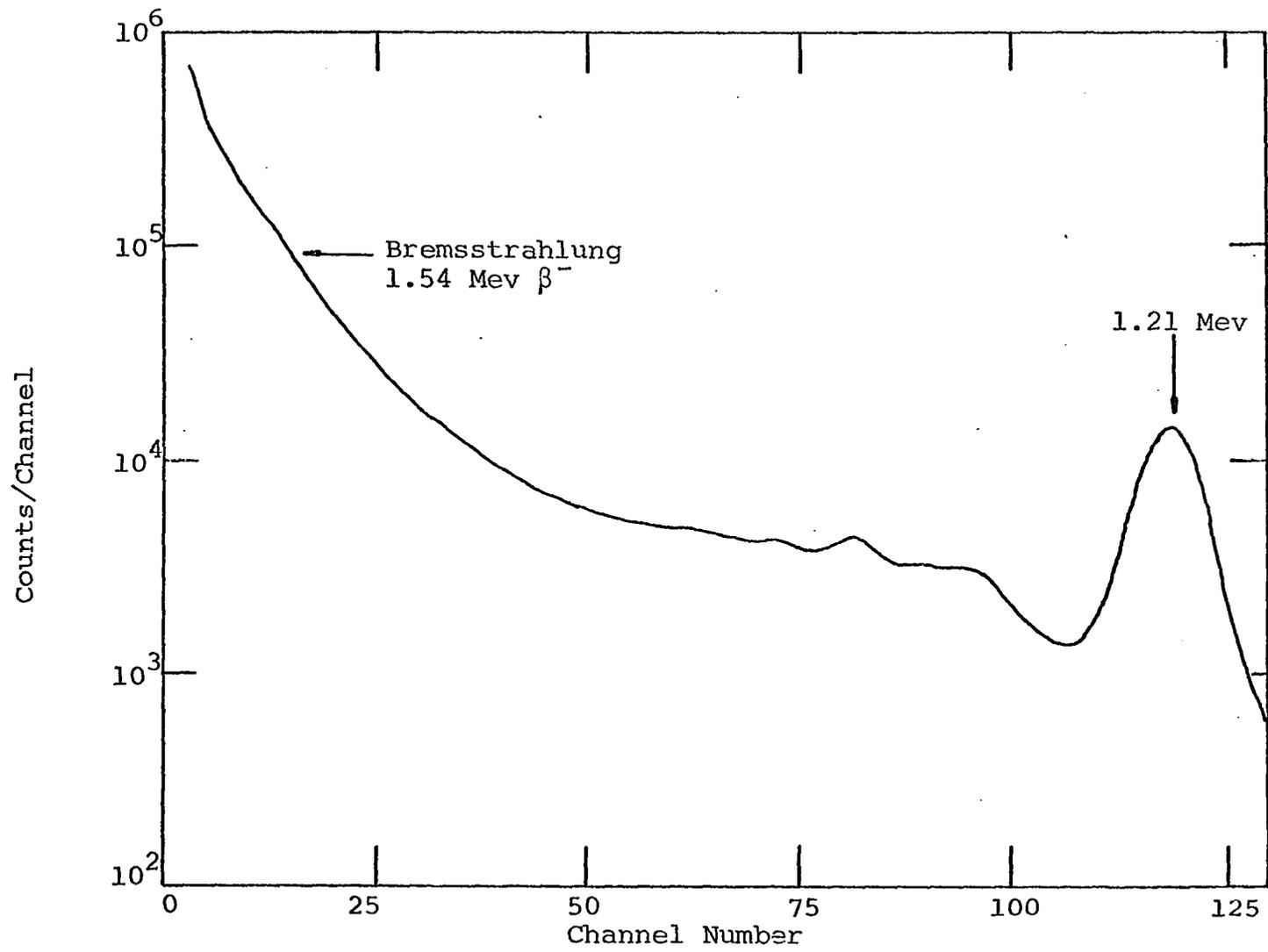


Figure 3-6. Gamma-ray spectrum of  $Y^{91}$  (51)

density of thickness to stop the most energetic beta particles from the source. For general applications, a polystyrene absorber of  $1.25 \text{ g/cm}^3$  is used. The thickness of this absorber is sufficient to stop 2.5 Mev beta particles. The absorber should be a low Z material such as beryllium, polystyrene, or aluminum, in order to keep bremsstrahlung production to a minimum. For certain precise applications, it is necessary to cover the sides of the detector with the beta absorber as well.

#### 7. Background radiation effects

Gamma radiations are always present in an environment. The scintillation detector, with its high efficiency, is very sensitive to these radiations. The probable origins of radiations in the environment are as follows:

(a) Cosmic radiation from outer space which manages to penetrate the earth's atmosphere,

(b) Radiation from mineral deposits which contain the natural radioactive isotopes of the uranium, thorium, and radium families,

(c) Radiations from such sources in construction materials used in buildings,

(d) Radiation from prepared or administered sources, present in the same room or in nearby storage.

The total result of these sources is the production of an

observed gamma-ray spectrum that has a relatively high counting rate at low energies, falling off with increasing energy. This is due to the fact that the efficiencies of crystals are highest at low energies, and gamma radiations make many interactions with surroundings such as the walls, floor, local shielding, etc. The result is that most of the background gamma rays which strike the crystal have had their initial energy decreased by one or more scattering events.

Once again, crystal size is an important factor when considering the amount and nature of the observed background.

(a) The total background counting rate of a large crystal is larger than that of a small crystal. However, if one takes the ratio of the background counting rates for a large, and then for a small crystal, and then compares the ratio of their volumes, one will find that the background ratio is smaller than the volume ratio.

(b) Large crystals, because of their efficiency, do not show as great a decrease in count rate for high-energy background as do smaller crystals.

(c) None of the high-energy background gamma rays will be absorbed in the total absorption peaks in the large crystals as they will in the small crystal.

A high-energy gamma ray may be stopped in a small crystal, and leave behind a Compton scattered electron, or may cause no reaction at all. There is always the chance that

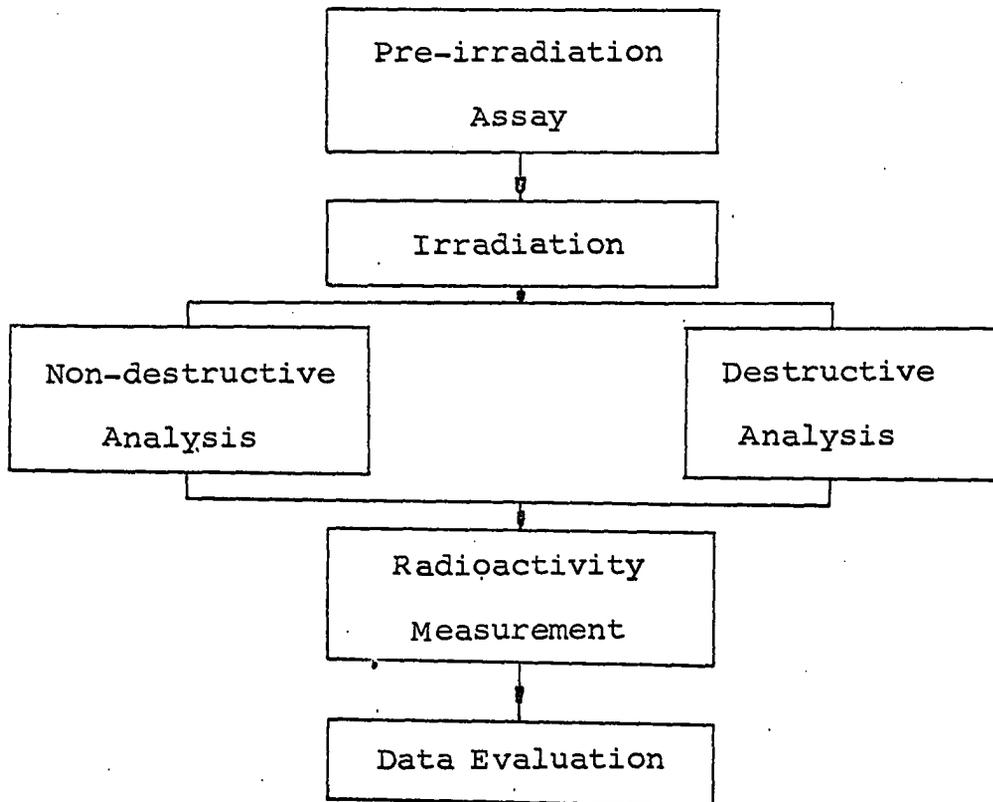
this non-reaching gamma ray will still be counted, since after escaping it may strike outside materials and scatter back one or more low-energy gamma rays which will be counted. A large crystal has better stopping power for this high-energy gamma ray, and increases the chance of a total absorption. If the detecting instrument is set to respond to only some of the lower peaks, the high-energy gamma ray which was totally absorbed will not interfere with the operation of the instrument.

## IV. ERRORS AND LIMITATIONS OF THE TECHNIQUE

In this chapter practical steps involved in neutron activation analysis are discussed, and possible error sources in the procedure are presented. Alternatives are included with advantages and disadvantages.

The evaluation of the experimental data consists primarily of an analysis of the experimental errors involved. There are, in general, two types of experimental errors: in analytical procedures and in nuclear procedures.

Block Diagram of Steps in NAA



### A. Pre-irradiation Assay

First of all, the sample to be analyzed is itself the most important factor in neutron activation analysis. Depending upon the chemical and physical properties of the sample, the analyst must select the facility to be used, and the activation reaction desired. As thoroughly discussed in the previous chapter, the sample size will decide whether it is to be irradiated by radioisotopic neutron sources, neutron generators, or nuclear reactors. The next step is to consider the chemical properties of the sample, upon which the size and shape of the sample container depend.

Possible error sources in the steps of pre-irradiation assay are (1) failure to remove surface contaminant from the sample, (2) introduction of contaminants during the sample preparation, and (3) faulty preparation of the comparator samples. Sample must be in clean form. For instance, sodium in a hair sample introduces a difficult complexity to interpret in determination of the arsenic amount in hair samples. The sodium may be removed by washing the samples with acetone. Samples must be handled at a separate laboratory or section from that in which the standard is prepared. Devices used for the preparation of standards may increase the amount of element sought in the sample, unless they are completely washed by using a carefully selected washing agent. Finished samples and standards are to be handled carefully

before irradiation. Most of these errors can be avoided or minimized by maintaining high standards for laboratory technique and for the control of contamination of chemicals.

#### B. Irradiation of Samples

Error sources in this category are largely due to transmutation effects and flux variation effects. Flux variation may result from (1) self-shielding for thermal or resonance neutrons in the sample or in the standard or monitor samples, (2) failure to detect flux gradients in the irradiating samples, (3) interferences from competing reactions, (4) interferences from primary, secondary, and second-order reactions, and (5) interferences from charged particle energy degradation during the irradiation. The transmutation effects and their minimization are discussed in the previous chapter. Several papers evaluate the flux inhomogeneity (9, 91, 118). Morzek (107) describes activation perturbation by self-absorption and flux depression in terms of the production rate of radioisotopes:

$$C_s = N \phi_0 \sigma_0 f_s \quad (4-1)$$

with

$$f_s = 1 - \frac{3}{2\sqrt{\pi}} a_0 + \frac{4}{5} a_0^2 \quad (4-2)$$

and

$$a_o = R \Sigma_a(v_o) \quad (4-3)$$

where

$C_s$  = the production rate of isotopes through self-absorption,

$N$  = the number of atoms of target element,

$\phi_o$  = the flux, where  $v_o = 2200$  m/sec,

$\sigma_o$  = the activation cross section in barn at  $v_o = 2200$  m/sec,

$f_s$  = the self-absorption factor in the thermal neutron flux without scattering,

$R$  = the radius of the sample, provided the sample is a sphere,

$\Sigma_a$  = the macroscopic absorption cross section of the sample.

Activation perturbation through flux is given by the formula

$$C_\phi = N \phi_o \sigma_o f_\phi \quad (4-4)$$

and

$$f_\phi = \frac{1}{1+\omega} \quad (4-5)$$

with

$$\omega = \frac{3}{4} \left[ \frac{L}{\lambda_{tr}} \frac{R}{R+L} \Omega_o - \Omega_1 \right] \quad (4-6)$$

and

$$\Omega_0 = 1 + \frac{1}{a} e^{-2a} - \frac{1}{2a^2} (1 - e^{-2a}), \quad a = R\Sigma_a \quad (4-7)$$

$$\Omega_1 = \frac{2}{3} + \frac{1}{a} e^{-2a} + \frac{1}{a^2} e^{-2a} - \frac{1}{2a^2} (1 - e^{-2a}) \quad (4-8)$$

where

$C_\emptyset$  = the production rate of isotopes through flux depression,

$f_\emptyset$  = the flux depression factor in the thermal neutron flux without scattering,

$L$  = the diffusion length.

If  $R \ll \lambda_{tr}$ , the diffusion theory is no longer valid. Bothe (19) calculated the following for this case:

$$f_\emptyset = \frac{1}{1+\omega} \quad (4-9)$$

with

$$\omega = 0.34 \frac{R}{\lambda_{tr}} \Omega_0 \quad (4-10)$$

where

$\lambda_{tr}$  = the transport path length in a moderator.

However, if  $R\Sigma_a \ll 1$ , Equations 4-1 and 4-4 are reduced to an unperturbed production rate,  $C = N\emptyset_0\sigma_0$ . In this case, an analyst may neglect the activation perturbation effects on the sample irradiation.

### C. Non-destructive Analysis

Non-destructive analysis is often called the instrumental neutron activation analysis, since the supporters of this technique rely entirely on instruments. In other words, no chemical separation is involved in the analysis. The only step used is the gamma-ray spectrometry for gamma emitters. Gamma ray decay characteristics are the major source of the data evaluation. In general, the method is faster than methods involving chemical separations. It is useful not only for the measurement of trace concentrations, but, because of its great speed, is also chosen for analyses of many elements at macro concentrations. The non-destructive analysis technique is especially applicable to cases in which many of the short-lived activities developed in the sample, and the element of interest has a half-life different from that of other trace elements to a great extent.

Guinn and Wagner (49) and others (4, 22, 65, 70, 85) developed a purely instrumental approach in activation analysis. This method is based entirely on gamma-ray spectrometry and half-life, and predominantly utilizes activities with half-lives in the range of minutes to hours. Guinn and Wagner established a sensitivity of about 5 ppm, and a reproducibility of about  $\pm 5$  ppm in arsenic analysis, and a sensitivity of about 10 ppm and a reproducibility of about  $\pm 10$  ppm in sodium analysis, in which 10 gm samples were irradiated

for two hours at thermal neutron flux  $5 \times 10^7$  n/cm<sup>2</sup>-sec. The probable error source appears to be the competing half-lives. This may be controlled by selecting a suitable decay time.

#### D. Destructive Analysis

In the ideal instrumental method of activation analysis, chemical techniques are unnecessary. However, in many cases, interfering or competing nuclei must be removed by chemical methods before the detecting process can begin. In the destructive analysis method, a chemical technique may be introduced in two steps: pre-irradiation assay and post-irradiation assay. In the first step, a known amount of element is added to the sample before irradiation, and is separated from the element without a carrier added (76). In the second method, the chemical separation is carried out after irradiation.

The useful chemical methods are solvent extraction, precipitation, and distillation (72, 106, 112). Steps involved in the chemical separation may be classified as follows: (1) after irradiation, dissolve the samples and standards, and add a known amount of the element being determined as carrier, which is inactive, but behaves exactly the same as the active element in the activation product, (2) let the carrier and the element in the sample be in the same chemical form, (3) carry out chemical separation by an

appropriate method to isolate the element free from all other radionuclei, (4) determine the chemical yield, (5) check the radiochemical purity of the isolated active compound.

There are two general types of errors which may enter in the chemical separation. These are incomplete chemical separations and radioactive contamination in the carrier.

The carrier added to facilitate chemical separation of the element of interest must exchange completely with the radioactive isotope of the element, and must be in the same chemical form. If one or both of these conditions is not satisfied, the chemically separated product may not contain the same ratio of active to inactive element which was in the entire system.

The chemically separated isotope must be radio-chemically pure in order for the purpose of the activity to be easily related to the amount of the particular radioactive isotope of interest. The purity can be checked by measuring the decay characteristics or the energy of the element. Thomson (152) presents a paper reviewing possible chemical methods in activation analysis.

#### E. Radioactivity Measurement

In early days, Geiger-Mueller counters were used extensively for purposes of activation analysis (79).

Scintillation detectors with the development of multi-channel pulse height analyzers are being used in almost all of activation analysis work today. The principal sources of errors in activity measurement are self-absorption, scattering, geometric errors, radioactive decay, background, and instrumental errors. The comparator technique eliminates most of these error sources. The technique requires that a standard which is as nearly identical in size and shape as possible to the element of interest in the sample is irradiated, and the activity measured under the same laboratory conditions. In this technique, counting need not be absolute or include corrections for self-absorption, scattering, and geometry errors, as long as suitable standards are treated with the sample. The only problem which may arise is the instrumental error. This error can hardly be avoided. However, establishment of an energy calibration curve for the analyzer may minimize the instrumental non-linearity.

The sample and the standard are irradiated under as nearly the same conditions as possible, which may minimize variations in the neutron flux, flux depression, self-absorption, and hardening of the flux. If the arrangement for the irradiation is such that these effects are small under any circumstances, the error from these sources will be small in the comparator method, as compared to the absolute method.

Upon irradiation the sample and the standard are counted under as nearly similar conditions as possible. Activation equations are expressed such that the unknown amount of the element in the sample can be found so that, after an appropriate post-irradiation treatment,

$$\begin{aligned} & \frac{\text{Weight of X in sample}}{\text{Weight of X in standard}} \\ &= \frac{\text{Activity from the element X in sample}}{\text{Activity from the element X in standard}} \\ &= \frac{\text{Photopeak area of X in sample}}{\text{Photopeak area of X in standard}} . \end{aligned}$$

If one has a fairly good prediction for the amount of the element sought in the sample from previous experience or the test analysis, the chances for success are greater, since the standard containing roughly the same quantity of X as in the sample will have nearly the same contributions as the possible error sources. If this is not the case, it may be advantageous to activate several standards containing different amounts of the element X, and establish a calibration curve. On the other hand, if the facilities are not suitable for irradiating the standards at the same time as the sample, another alternative is to use a boron trifluoride flux monitor foil of nearly the same nuclear properties as the element of interest for normalization of the flux for the standards and the unknowns in the sample.

## F. General Limitations

The choice of an appropriate activation reaction for a specific application is generally based on the nuclear properties of the matrix and of the trace elements of interest, and on a review of available results of experimental activation analysis. The chemical and physical properties of the matrix and trace elements are also important. Furthermore, safety criteria must be analyzed. Nuclear properties of the sample will determine the reaction type and, in turn, the irradiation facility. Detector size depends not only on the laboratory circumstance, but also on sample size. Like any other method of analysis, neutron activation analysis has its limitations, and the would-be user must be aware of them. The limitations involved in the applications of neutron activation analysis for a particular sample will be discussed.

The technical considerations require that the samples:

- (a) produce radionuclei which are retained in the sample and have appropriate half-life and decay characteristics for accurate measurements,
- (b) have optimum or sufficient sensitivities,
- (c) have no interfering reactions producing or consuming the desired activation product,
- (d) have no reactions producing competing radioactive isotopes of the same element as the activation product, and
- (e) that the requisite irradiation and post-irradiation assays are feasible (78).

### G. Selection of Useful Nuclear Reactions

A variety of nuclear reactions such as  $(n,\gamma)$ ,  $(n,p)$ ,  $(n,\alpha)$ ,  $(n,2n)$ , and  $(n,f)$  can be utilized in activation analysis. However, the feasibility of using a certain reaction depends on factors such as the type of sample matrix, activation cross section, neutron flux, nuclear and chemical properties of the activation product, and possible interferences. Each factor needs to be examined separately as well as in relation to others.

Thermal neutron reactions  $(n,\gamma)$  are by far the most useful reactions. This is mainly due to the large thermal neutron flux of reactors, and to the large thermal neutron activation cross sections exhibited by the most stable nuclei. The difficulty of performing an activation analysis depends, to a large extent, on the types and relative magnitudes of activities induced into a sample. This is particularly true if the measurements of one or more radionuclei are to be done without chemical separations. In certain cases an analysis can be facilitated by activating with resonance neutrons and suppressing the thermal neutron activation. The relative activations of two or more nuclei by resonance neutrons depend only on their resonance integrals. Since the resonance integrals of many nuclei differ appreciably, activation with resonance neutrons frequently permits one to make an analysis without chemical separations.

Although almost all elements become radioactive to some extent after irradiation, the half-lives of some activation products are too short to allow for removal of the sample from the reactor. In some cases removal is possible, but the half-life is still too short to allow for chemical separation if it necessary. In still some cases, both removal and chemical separation are possible, but the half-life is not long enough to allow for counting. Elements in these categories include He, Li, B, N, O, F, and Ne with half-lives of seconds or less. On the contrary, some elements such as Be and C give only relatively long-lived radionuclei upon activation, and the sensitivity is very low, while H and Pb have very low activation cross sections. Hence, normal activation techniques are not readily applicable to these elements.

A fast neutron activation technique has been developed by Wood (160) for troublesome elements, for which he used a neutron generator combined with an automatic mounting system which includes computer programming. Oxygen, nitrogen, beryllium, and iron are best analyzed by fast neutron activation. The conditionally best elements are P, Si, F, Se, Ti, Cr, and B. Wood states that H, C, and Li, as well as the rare gases He, Ne, and A, are well analyzed for special cases.

## H. Physical Limitations

Heat is produced to some extent in a reactor by means of neutron bombardment as well as by gamma heating, and, therefore, samples must be of such a character that they can withstand the particular temperature to which they are exposed. Moreover, they must be enclosed in such a manner that there is no danger of contaminating the reactor or other samples.

There is almost certainly some limitation in the overall size of the sample which can be irradiated. Preferable forms of samples are crystalline or metallic solids, and these should be sealed in polythene or silica and placed in a screw-topped cylindrical aluminum can or similar receptacle. If the samples are in the form of powders or liquids, they should be contained in a solid container and sealed. In cases where samples are bigger than the rabbit tube in which they are normally contained and irradiated, they must be placed in specially designed places such as thermal columns or irradiation caves. Exceptionally large samples may be irradiated by rotating them outside the reactor or neutron generators, if safety criteria can be met. In this case, samples are normally irradiated at a low neutron flux.

## I. Chemical Limitations

Structural damage and decomposition may be introduced under irradiation, if it is extended over a considerable

amount of time. Silica and polythene are normally used for containing samples in the rabbit tube. Silica becomes almost black, and polythene becomes brittle with a tendency to crack after a few days' irradiation (137). Therefore, long irradiations of samples must not be carried out in such manner.

Furthermore, many substances decompose during irradiation, some with evolution of gas. Furthermore, the pressure build-up of such gas can cause the breakage of sealed containers.

Chemical separations, if used, must be efficient. The isolated material must not contain any significant amount of radioactivity due to any other elements. If the carrier is used, the carrier and the irradiated elements should be brought into the same chemical form, and should behave qualitatively alike. For instance, the arsenic in biological material (141) might be present as  $\text{AsO}_2^-$ ,  $\text{AsO}_3^-$ ,  $\text{As}^{+3}$ ,  $\text{As}^{+5}$ , or as an organic compound, while the carrier solution contained arsenic in the form of  $\text{AsO}_2^-$ . This problem may be overcome by mineralizing the organic material, and then oxidizing it under alkaline conditions so that all types of arsenic, both in the irradiated samples and the carrier, can be present as arsenate before proceeding with separations.

#### J. Nuclear Limitations

Self-absorption is one of the major limitations of the technique. Samples containing elements of interest which

have a very large absorption cross section of neutrons may be such that the neutron flux in the neighborhood is seriously affected. When this happens, the neutron flux may fall off progressively throughout the thickness of the sample. In a sample of finite thickness, the neutron flux becomes smaller toward the center than at the outside, due to the absorption of neutrons by the sample. If this happens to a different degree in the sample and in the standard, then the analysis will obviously be in error. Providing that the sample and the standard behave in exactly the same way, this argument is no longer a problem. However, it is, in general, more satisfactory for the sample weight and volume to be restricted to a suitable minimum so that the neutron flux will not be seriously affected by self-absorption effects.

The thermal-neutron activation cross sections of the elements are listed in pertinent literature (78). This, however, may be misleading. As a matter of fact, as in most nuclear reactors, the energy spectrum at the site of irradiation covers a wide range of energy, and at some energies resonance absorption may occur where the value of the thermal-activation cross section listed may be much higher than for mere thermal neutrons. The contribution of neutrons of intermediate energy can, in many cases, introduce considerable self-absorption effects. Even so, it is possible to minimize this difficulty by the simultaneous irradiation of a number

of samples of different weights or dilutions, or by ensuring that only thermal neutrons are used for the irradiation. This can also be done by employing the reactor thermal column or irradiation cave as the irradiation site.

Another consideration is the half-life of the activation product as briefly discussed previously. The half-life of the activation product must be consistent with the time required for checking by the health physicist, transportation from the irradiation facility, and performance of the post-irradiation assay, including chemical separations if required, and the counting activity.

The suitability of other decay characteristics depends on the reactivity measuring equipment available to the analyst and on the relative activation of other isotopes of the same element. In certain cases, the activation product may decay to a radioactive daughter which has more favorable decay properties. Moreover, the need for a rapid, routine analytical procedure may dictate the use of a nuclear reaction which yields an activation product with a convenient half-life which is either easily separable from the matrix, or which requires no chemical separation or complicated radioactivity measurements after irradiation.

Sensitivity is defined as the limit of detection for an element in a given analysis. For short-lived activation products, delays due to transportation or extended chemical

separations may result in reduced practical sensitivities. The sensitivity is also dependent upon the type of instrumentation used in the post-irradiation assay. Interfering reactions may limit the duration or intensity of the irradiation or the size of the sample, and further reduce the sensitivity. The dimensions of the irradiation location or of the large irradiation capsule may also limit the size of the sample.

#### K. Interfering Reactions

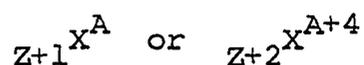
The major nuclear limitation is the interfering reactions occurring with the main  $(n,\gamma)$  reaction by thermal neutrons, as well as reactions with fast neutrons and gamma rays. Examples of reactions which interfere with the more commonly used activation reactions may be shown in Table 4-1 where

A = the mass of the target and activation product nuclei,

Z = the atomic number of the target and activation product nuclei of interest.

##### 1. Primary interferences

Reactions of primary interference are induced in sample constituents with



by  $(n,p)$  or  $(n,\alpha)$  reactions, respectively. The reaction

Table 4-1. Interfering reactions

Reactions	Examples
1. Principal reaction	
${}_Z X^A (n, \gamma) {}_Z X^{A+1}$	${}_{33} \text{As}^{75} (n, \gamma) {}_{33} \text{As}^{76}$
	${}_{15} \text{P}^{31} (n, \gamma) {}_{15} \text{P}^{32}$
3. Primary interferences	
${}_{Z+1} X^A (n, p) {}_Z X^{A+1}$	${}_{34} \text{Se}^{76} (n, p) {}_{33} \text{As}^{76}$
${}_{Z+2} X^{A+4} (n, \alpha) {}_Z X^{A+1}$	${}_{35} \text{Br}^{79} (n, \alpha) {}_{33} \text{As}^{76}$

Table 4-1 (Continued)

Reactions	Examples
3. Secondary interferences	
${}_{Z+2}X^{A+1}(n,p) {}_{Z+1}X^{A+1} \xrightarrow{\beta^+} {}_Z X^{A+1}$	
${}_{Z+1}X^{A+4}(n,\alpha) {}_{Z-1}X^{A+1} \xrightarrow{\beta^-} {}_Z X^{A+1}$	
4. Second-order interferences	
${}_{Z-1}X^{A-1}(n,\gamma) {}_{Z-1}X^A \xrightarrow{\beta^-} {}_Z X^A(n,\gamma) {}_Z X^{A+1}$	${}_{32}\text{Ge}^{74}(n,\gamma) {}_{32}\text{Ge}^{75} \xrightarrow{\beta^-} {}_{33}\text{As}^{75}(n,\gamma) {}_{33}\text{As}^{76}$
	${}_{14}\text{Si}^{30}(n,\gamma) {}_{14}\text{Si}^{31} \xrightarrow{\beta^-} {}_{15}\text{P}^{31}(n,\gamma) {}_{15}\text{P}^{32}$
${}_Z X^A(n,\gamma) {}_Z X^{A+1}(n,\gamma) {}_Z X^{A+2}$	
${}_{Z+1}X^{A+1}(\gamma,p) {}_Z X^A(n,\gamma) {}_Z X^{A+1}$	${}_{34}\text{Se}^{76}(\gamma,p) {}_{33}\text{As}^{75}(n,\gamma) {}_{33}\text{As}^{76}$
${}_{Z+1}X^{A+2}(\gamma,p) {}_Z X^{A+1}$	${}_{34}\text{Se}^{77}(\gamma,p) {}_{33}\text{As}^{76}$

products are the same nuclei as the principal activation reaction. These reactions are mostly induced by fast neutrons. The probability of the reaction is the function of the relative concentrations of the target nuclei in the matrix, the ratio of their activation cross sections, and the ratio of fast to thermal-neutron fluxes. In general, the primary interfering reactions are important only if the element to be assayed is present in extremely low concentrations. The factors relating to the fast flux are less significant, because the effective fluxes and cross sections for fast neutrons are usually much less than those for thermal neutrons.

## 2. Secondary interferences

The importance of secondary reactions depends upon the composition and size of the sample, the energy of the incident particles, and the ratio of the cross sections for the primary and secondary reactions. However, the secondary interfering reactions are less significant than the primary, because photons and alpha particles created by reactor neutrons have either too low an energy or too low an abundance to be significant.

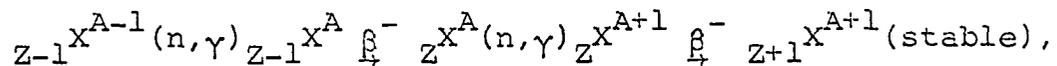
## 3. Second-order interferences

There are two types of second-order interferences, one of which increases the concentration of the principal activation product, while the other decreases its concentration.

The first type of reaction occurs when the element of interest and the trace element have adjacent atomic numbers. The first, third, and fourth reactions are included in the category of the first type of reaction, while the second type of reaction includes the second reaction in the table. Continued irradiation may decrease the concentration of the principal activation product significantly, since this reaction is the continuation of the principal reaction. An increase in the concentration of the principal activation depends upon the amount of the adjacent trace elements. In general, the degree of the second-order interferences depends on the concentrations of the two elements, their activation cross sections, and the half-life of the intermediate radioactive nuclide. In order to avoid an appreciable interference of this type, it is necessary to limit the neutron flux and energy, or to limit the duration of irradiation. There is little, if any, error introduced into the analysis if the comparator method is used, since the second-order reaction also occurs in the comparator.

#### 4. Mathematical treatments of the second-order reactions

The first reaction is the most significant among the second-order reactions listed. Since this type of reaction,



increases the concentration of  ${}_Z X^{A+1}$ , the amount of  ${}_Z X^{A+1}$  created by this reaction must be corrected. One may establish the following sets of equations (73):

$$\frac{dN_1}{dt} = N_0 \phi \sigma_1 - N_1 \lambda_1 \quad (4-11)$$

$$\frac{dN_2}{dt} = N_1 \lambda_1 - N_2 \phi \sigma_2 \quad (4-12)$$

$$\frac{dN_3}{dt} = N_2 \phi \sigma_2 - N_3 \lambda_2 \quad (4-13)$$

$$\frac{dN_4}{dt} = N_3 \lambda_2 \quad (4-14)$$

where  $N$  stands for the concentration,  $\sigma$  the activation cross section,  $\lambda$  for the decay constant,  $\phi$  the thermal flux,  $t$  the irradiation time, and subscript  $o$  for  ${}_{Z-1} X^{A-1}$ ,

1 for  ${}_{Z-1} X^A$ ,

2 for  ${}_Z X^A$ ,

3 for  ${}_Z X^{A-1}$ , and

4 for  ${}_{Z+1} X^{A+1}$ .

The equation for  $N_4$  will be disregarded in the further calculation, since  $N_4$  is stable and is not of interest. The quantity to look for is  $N_3 \lambda_2$ , the activity of  ${}_Z X^{A+1}$ . Initial conditions are  $N_1 = N_2 = N_3 = 0$  at  $t = 0$ . The solution is

represented in the formula

$$N_3 \lambda_2 = N_0 \phi \sigma_1 \left( \frac{\phi \sigma_2}{\lambda_2} \right) (\lambda_2 t + e^{-\lambda_2 t} - 1) \quad (4-15)$$

provided

$$t \ll \frac{1}{\phi \sigma_2}, \frac{1}{\lambda_2} \gg \frac{1}{\lambda_1} \gg \frac{\phi \sigma_2}{\lambda_1 \lambda_2}, \text{ and } t \gg \frac{1}{\lambda_1} .$$

#### L. Contamination and Safety Considerations

Once the sample has been irradiated, the determination of an element in neutron activation analysis depends on the measurement of a radioisotope. Contamination can occur in any method. However, one of the greatest advantages of the activation method is that any contamination of the sample will be completely immaterial. If chemical separation is not involved in the analysis, the activation analysis is theoretically contamination free. Nevertheless, contamination may possibly occur in the laboratory when the sample is prepared. Another concept of contamination is the radiation contamination, which the analyst should bear in mind in the laboratory.

A possible contamination of the comparator on the sample, which increases the concentration of the element sought, occurs when the sample is prepared. Therefore, comparators and samples must be handled separately in steps of weighing, capsuling, and storing. The analyst should wash and change

to some degree the devices used before he proceeds from the preparation of comparators to the preparation of samples, as well as from the post irradiation assay to the irradiation assay. If the contamination occurs due to radionuclei of some elements other than the one being determined, this will become apparent when the radiochemical purity is checked. The duration of a series of irradiations sometimes causes a serious contamination and makes the analysis complex, if the half-life of the element of interest is relatively short. The analyst must avoid this possibility. However, it is, in most cases, possible very readily to monitor equipment, apparatus, and reagent solutions, etc. before proceeding with a particular experiment, in order to make sure that significant contamination is absent. This is possible because of the availability of sensitive methods of detecting radioactivity. The general aim is to avoid cross-contamination, first of all by careful work, and secondly by handling, in any one batch of experiments, similar activity levels of the particular element concerned.

Generally, the safety consideration is highly related to contamination problems. However, three types of safety must be pointed out and paid attention to by the analyst. These are reactor safety, radiation safety, and poison safety. Certain samples cannot be accepted for reactor irradiation, as they may endanger the safety of the reactor. For example,

these are volatile liquids which may decompose under the action of the intense gamma and neutron bombardment, and may build up dangerous pressure in the sealed sample container. If this is the case, the irradiation procedure must be altered from the normal procedure as did Smales (142) in his seawater experiment. Certain matrices become highly radioactive upon irradiation, and emit highly penetrating radiations when they possess an exceptionally high activation cross section. Therefore, the irradiated samples must first be checked by a health physicist, and facilities in a laboratory suitable for handling relatively high levels of radioactive materials are required. Some elements, such as beryllium, plutonium, polonium, and arsenic, which are interesting to analysts in activation analysis, are definitely poisonous. An analyst must avoid inhaling the poisonous material, and must provide a special hood, sealing it completely if possible.

#### M. Experimental Feasibility

The experimental feasibility of irradiation depends on the physical, chemical, and nuclear properties of the matrix and trace elements. As discussed before, some samples may not be permitted in some irradiation facilities because of high macroscopic cross sections, dimensional considerations, or because they are combustible, volatile, or liquid in form.

The feasibility of the post-irradiation assay depends

on the chemical properties, decay characteristics of the activation products, and on the radiation detecting and counting equipment available. The need for a routine analytical technique may eliminate those activation reactions which do not yield activation products with convenient half-lives, or which require difficult or extended assay procedures. Another consideration extends to the availability or location of a suitable irradiation facility, and the cost of its use.

There are few reports that demonstrate the accuracy and the precision of activation analysis. This is understandable, because the determination of accuracy requires that the activation technique be applied to samples whose content of the element of interest is known in most cases with confidence. Smales (137) states that the accuracy level of  $\pm 10\%$  is adequate in many cases of trace element determination.

## V. APPLICATION

## A. Sample Preparation

1. Samples and the standard

## Samples

Fifty-two kinds of cigarettes in thirty-three brands were purchased from the open markets at Ames, Iowa, during the months of July and August, 1967.

## The standard

Five grams of arsenic powder (99.999% in purity) were purchased from Alfa Inorganics, Inc., Beverly, Massachusetts, in early 1967.

2. Chemical, physical, and nuclear properties of samples and the standarda. Physical and chemical properties of arsenic (12, 113)

Color: steel gray

State: semi-metallic

Outer electronic configuration:  $4S^2 4P^3$

Molecular state of gas:  $As_4$   $\rightleftharpoons$   $As_2$

Atomic volume: 13.13 ml (metal)

Melting point:  $814.5^{\circ}C$  (36 atm),  $450.0^{\circ}C$  (Sublimes)

Boiling point:  $610.0^{\circ}C$  (Sublimes)

Density: 5.7 gm/cc (metal), 3.9 gm/cc (yellow)

Radius: Covalent,  $1.21 \overset{\circ}{\text{A}}$

Radius: Crystal,  $\overset{\circ}{\text{As}}^{-3}$  2.22 Å;  $\overset{\circ}{\text{As}}^{+3}$  0.69 Å;  $\overset{\circ}{\text{As}}^{+5}(\text{AsO}_3)$   
0.47 Å

Ionization potential: ~ 10 ev

Electronegativity: 2.0 on the Pauling scale

Principal oxidation states: -3, +3, +5

$E^\circ$ :  $\text{As} + 3\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_3 + 3\text{H}^+ + 3\text{e}^-$ , -0.25 v ( $\text{HAsO}_2$ )

$\text{AsO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^-$ , -0.559 v.

Heat capacity: 0.082 cal/gram

Solubility: Soluble in carbon disulfide

Structure: Covalent layer structure

Representative compounds:

+5;  $\text{As}_2\text{O}_5$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{AsCl}_5$

+3;  $\text{As}_4\text{O}_6$ ,  $\text{H}_3\text{AsO}_3$ ,  $\text{AsCl}_3$ ,  $\text{As}_2\text{O}_3$

0; As

-3;  $\text{AsH}_3$

b. Nuclear properties of  $\text{As}^{75}$  (78)

Abundance (percent): 100

Absorption cross section (thermal neutron):  $4.3 \pm 0.2$  b.

Activation cross section (thermal neutron):  $5.4 \pm 1.0$  b.

Resonance integral (activation): 36.8 b.

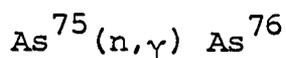
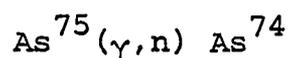
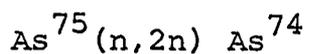
Possible reactions with  $\text{As}^{75}$ :

$\text{As}^{75}(n,p)\text{Ge}^{75}$

$\text{As}^{75}(p,n)\text{Se}^{75}$

$\text{As}^{75}(n,\alpha)\text{Ga}^{72}$

$\text{As}^{75}(p,pn)\text{As}^{74}$



c. Nuclear properties of As<sup>76</sup>

(1). Half-life

26.4 h. (62, 78)

26.5 h. (12, 34, 102, 144)

26.1 h. (7)

26.3 h. (102)

26.8 h. (102)

27.0 h. (150)

(2). Beta ray energies (Mev)

2.97 (56%), 2.41 (31%) (144)

2.98, 2.40, 1.76 (150)

2.965 (53%), 2.405 (35%), 1.748 (6.9%) (12)

(3). Gamma ray energies (Mev)

0.559 (71%), 0.658 (6%), 1.127 (16%) (12)

0.55, 0.64, 1.20 (150)

0.56 (45%), 0.66 (6%), 1.21 (6%) (144)

(4). Isotopes of arsenic (12, 144)

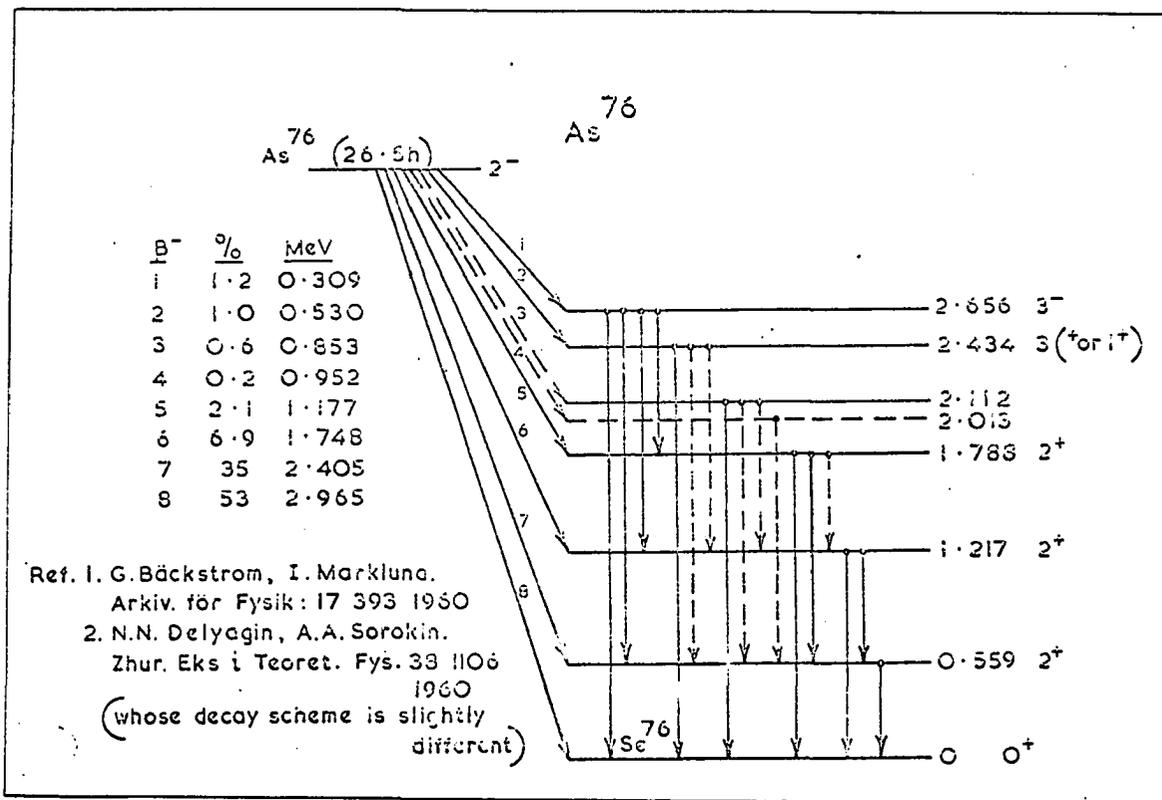
Isotopes Half-lives Methods of preparation

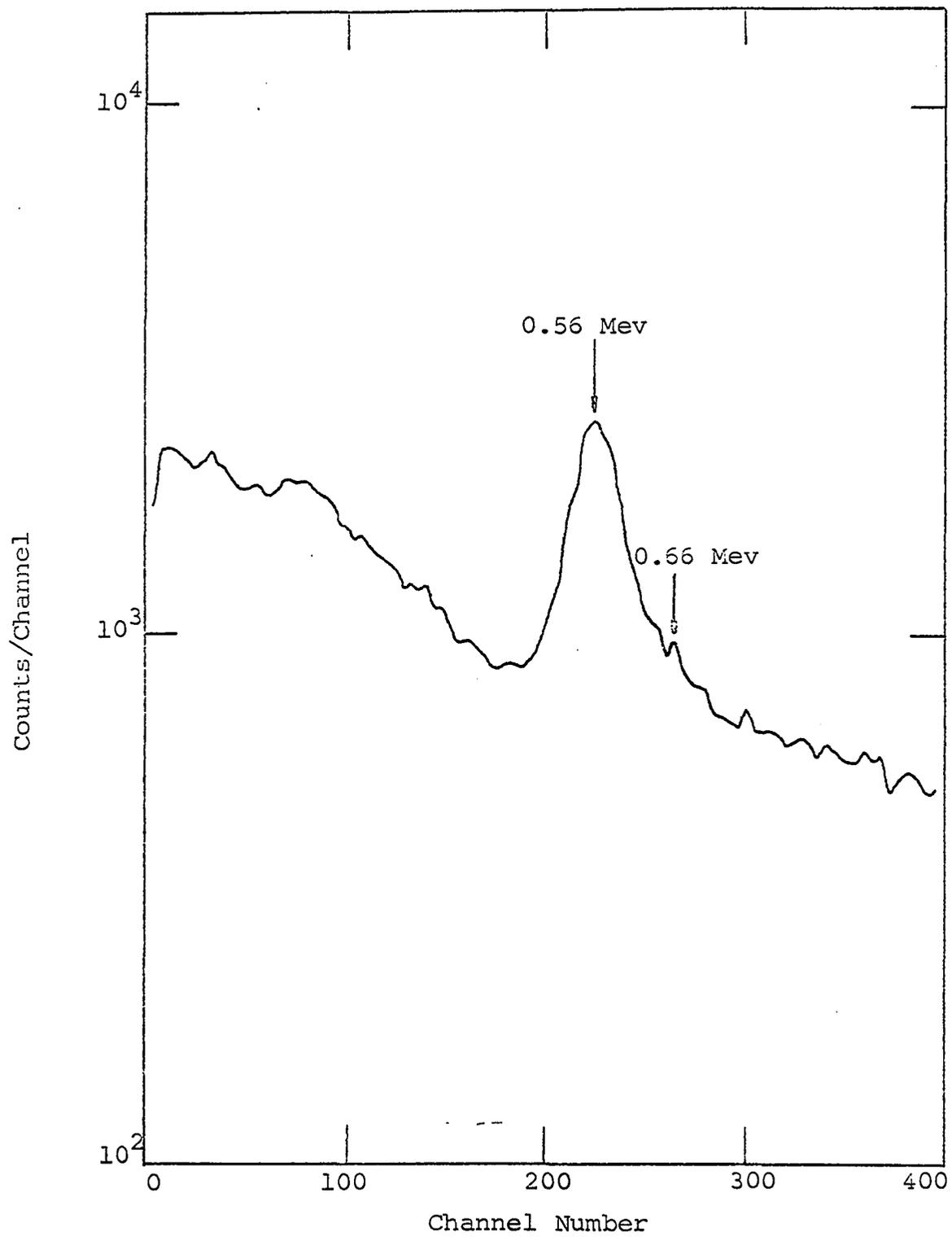
As<sup>68</sup> 7 m. Ge<sup>70</sup> (p, 3n)As<sup>68</sup>

As<sup>69</sup> 15 m. Ge<sup>70</sup> (p, 2n)As<sup>69</sup>

Isotopes Half-lives Methods of preparation

As <sup>70</sup>	52 m.	Ge <sup>70</sup> (d,2n)As <sup>70</sup>
As <sup>71</sup>	62 h.	Ge <sup>70</sup> (d,n)As <sup>71</sup>
As <sup>72</sup>	26 h.	Ga <sup>69</sup> (α,n)As <sup>72</sup> , Ge <sup>72</sup> (p,n)As <sup>72</sup> , Ge <sup>72</sup> (d,2n)As <sup>72</sup>
As <sup>73</sup>	76 h.	Ge <sup>72</sup> (d,n)As <sup>73</sup>
As <sup>74</sup>	17.5 d.	Ga <sup>71</sup> (α,n)As <sup>74</sup> , Ge <sup>74</sup> (p,n)As <sup>74</sup> , Ge <sup>74</sup> (d,2n)As <sup>74</sup> , As <sup>75</sup> (n,2n)As <sup>74</sup>
As <sup>75</sup>	Stable	100% natural abundance
As <sup>76</sup>	26.5 h.	As <sup>75</sup> (n,γ)As <sup>76</sup> , As <sup>75</sup> (d,p)As <sup>76</sup> , Br <sup>79</sup> (n,α)As <sup>76</sup> , Se <sup>76</sup> (n,p)As <sup>76</sup>
As <sup>77</sup>	39 h.	Ge <sup>76</sup> (d,n)As <sup>77</sup> , Fission
As <sup>78</sup>	91 m.	Br <sup>81</sup> (n,α)As <sup>78</sup> , Se <sup>78</sup> (n,p)As <sup>78</sup> , Fission
As <sup>79</sup>	9 m.	Se <sup>80</sup> (γ,p)As <sup>79</sup> , Se <sup>80</sup> (n,pn)As <sup>79</sup> , Se <sup>82</sup> (d,αn)As <sup>79</sup>
As <sup>80</sup>	15.3 s.	Se <sup>80</sup> (n,p)As <sup>80</sup>
As <sup>81</sup>	31 s.	Se <sup>82</sup> (γ,p)As <sup>81</sup>

(5). Decay scheme of As<sup>76</sup> (7, 12, 144, 145, 155)

(6). Gamma ray spectrum of As<sup>76</sup>



										38																			
										Sr	Sr 80	Sr 81	Sr 82	Sr 83	Sr 84	Sr 85	Sr 86	Sr 87	Sr 88	Sr 89	Sr 90	Sr 91							
										87.62	1.7h	29m	25d	33h	0.56	64d	9.86	2.8h	7.02	82.56	50.4d	28y	97h						
										σ 1.3	σ 7.58	σ 1.1	σ 1.75, 395.040	σ 1.15, 8.1	σ 1.23	σ 1.11	σ 1.008	σ 1.000	σ 1.146										
											Rb 79	Rb 80	Rb 81	Rb 82	Rb 83	Rb 84	Rb 85	Rb 86	Rb 87	Rb 88	Rb 89	Rb 90							
											21m	34s	32m	47h	5.3h	7.5s	83d	20m	10m	1.67h	27.5s	18m	29m						
										σ 7.3	σ 1.1	σ 1.1	σ 1.1	σ 1.1	σ 1.1	σ 1.1	σ 1.1	σ 1.1	σ 1.1	σ 1.1	σ 1.1	σ 1.1							
											Kr 74	Kr 75	Kr 76	Kr 77	Kr 78	Kr 79	Kr 80	Kr 81	Kr 82	Kr 83	Kr 84	Kr 85	Kr 86	Kr 87	Kr 88	Kr 89			
											15m	5m	14.8h	12h	0.35	55s	34h	13s	11.56	186h	11.56	4.4h	10.76y	17.37	76m	2.8h	3.2m		
										σ 24	σ 41	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85	σ 1.040-85			
Br											Br < 74	Br 74	Br 75	Br 76	Br 77	Br 78	Br 79	Br 80	Br 81	Br 82	Br 83	Br 84	Br 85	Br 86	Br 87	Br 88			
79.909											4m	42m	16h	16.5h	42m	58h	48s	3.7h	3.7h	3.7h	6m	2.4h	3.0m	3.0m	3.0m	3.0m	16s		
σ 6.7											σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7	σ 6.7		
Se											Se 70	Se 71	Se 72	Se 73	Se 74	Se 75	Se 76	Se 77	Se 78	Se 79	Se 80	Se 81	Se 82	Se 83	Se 84	Se 85	Se 87?		
78.96											44m	5m	8.4d	44m	11h	9.02	120d	18s	17.5h	23.52	49.62	57m	9.19	69s	1.25m	3m	35s	16s	
σ 12											σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12	σ 12
As	As 68	As 69	As 70	As 71	As 72	As 73	As 74	As 75	As 76	As 77	As 78	As 79	As 80	As 81															
74.926	~7m	15m	50m	62h	26h	81	18d	100	26.5h	39h	5m	9m	9m	33s															
σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5	σ 4.5															

d. Chemical composition of a tobacco product (75, 161)

<u>Material</u>	<u>Weight (mg/cigarette)</u>	<u>Weight of total effluent (%)</u>
Particular matter	40.6	8.2
Nitrogen (67.2 vol. %)	295.4	59.0
Oxygen (13.3 vol. %)	66.8	13.4
Carbon dioxide (9.8 vol. %)	68.1	13.6
Carbon monoxide (3.7 vol. %)	16.2	3.2
Hydrogen (2.2 vol. %)	0.7	0.1
Argon (0.8 vol. %)	5.0	1.0
Methane (0.5 vol. %)	1.3	0.3
Water vapor (relative humidity)	5.8	1.2
C <sub>2</sub> -C <sub>6</sub> hydrocarbons	2.5	0.5
Carbonyle	1.9	0.4
Hydrogen cyanide	0.3	0.1
Other known gaseous material	1.0	0.2
Total	505.6	101.2
Measured total effluent	500	100

3. Preparation of samples and standards

Standards

Forty standards were prepared. Each contained 1 mg of As<sup>75</sup>. They were put in individual plastic containers and sealed. The container had a 10/16" outside diameter, 9/16" inside diameter, and was 3 3/16" height.

## Samples

Cigarettes were dried for one week in a storage cabinet at room temperature to eliminate most of the moisture contained in tobacco. Tobacco from two cigarettes was weighed and put in a container which was then sealed.

The arsenic standards were prepared while the tobacco samples were being stored in the cabinet. All equipment used in the preparation of standards was cleaned with alcohol or acetone and kept in another clean cabinet.

### B. Sample Irradiation and Data Analysis

The cigarette sample coded 17-102 was irradiated at a thermal neutron flux of  $3 \times 10^9$  n/cm<sup>2</sup>-sec for 10 minutes in the UTR-10 reactor at Iowa State University. Sample 32-101 was irradiated at  $\phi = 1.2 \times 10^{10}$  n/cm<sup>2</sup>-sec for 10 minutes. Sample 32-102 was irradiated at  $\phi = 6 \times 10^{10}$  n/cm<sup>2</sup>-sec for one hour. Sample 32-100 was irradiated at  $\phi = 3 \times 10^{10}$  n/cm<sup>2</sup>-sec for two hours. Sample 27-101 was irradiated at  $\phi = 6 \times 10^{10}$  n/cm<sup>2</sup>-sec for one hour. The above five samples were first analyzed for the identification of arsenic in the cigarette tobacco samples and for the optimization of decay time.

Samples coded 1 through 33 were irradiated separately at  $\phi = 6 \times 10^{10}$  n/cm<sup>2</sup>-sec for one hour, two samples and one arsenic standard, side by side, at each reactor run. The

irradiated samples were stored in a lead cave for about one and a half days because of their high activity. They were then moved to the sample storage cabinet before being counted.

Samples were placed in a NaI(Tl) well crystal of 1 3/4" diameter x 2" height, and their activity was counted by means of a PIP-400 multichannel pulse height analyzer. The detection and counting system is shown in Figure 5-10. The outgoing results were obtained in three ways: Polaroid photographs of the CRT display, a punch-tape, and a teletypewriter print-out. A typical photograph of sample 17 is shown in Figure 5-6. Gamma-ray spectra of sample 19 were plotted from the print-out data, which is shown in Figure 5-7.

A scintillation detector was employed for the purpose of gamma ray detection. The detector is composed of a canned NaI(Tl) well type crystal, an RCA type-6655A photomultiplier, a mu-metal shield, a lead shield, and a preamplifier. The crystal and photomultiplier tube form an optical plug-in unit which is light tight and magnetically shielded. The analyzer and all necessary equipment were calibrated prior to the sample counting. Monitors such as Cs<sup>137</sup>, Au<sup>198</sup>, Mn<sup>56</sup>, Na<sup>24</sup>, and Co<sup>60</sup> were used for the analyzer calibration.

The net weight of the cigarette samples in each container was, on the average, 1810.4 mg, ranging from 2278.5 mg to 1386.1 mg. The tobacco of each cigarette sample was obtained from two cigarettes.

The samples and standards were counted at every half integer of the arsenic half-life ( $T_{1/2} = 26.5$  hours) for a series of about ten counts. Eliminating the activity of other components in cigarettes, the average amount of arsenic was obtained by averaging the three values obtained at  $3T_{1/2}$ ,  $3.5T_{1/2}$ , and  $4T_{1/2}$ . The results are shown in Tables 5-1 and 5-2.

### C. Discussion

In this section the fitness of samples and standards will be presented in terms of their physical, chemical, and nuclear properties, and limitations discussed in Chapter IV. A comparison is made with the results of other analysts and also included are methods which investigators have yet utilized. The procedure of experimental data analysis and the results are discussed.

#### 1. Experimental feasibility

a. Arsenic standard ( $\text{As}^{75}$ )      Because of the significance of arsenic analysis in terms of forensic science, and because of the importance of arsenic as a possible cause of lung cancer, arsenic must be examined in order to determine whether it can be well analyzed by neutron activation analysis. First of all, arsenic must be thoroughly considered whether it does overcome limitations on the technique. The properties of known arsenic isotopes are presented in the

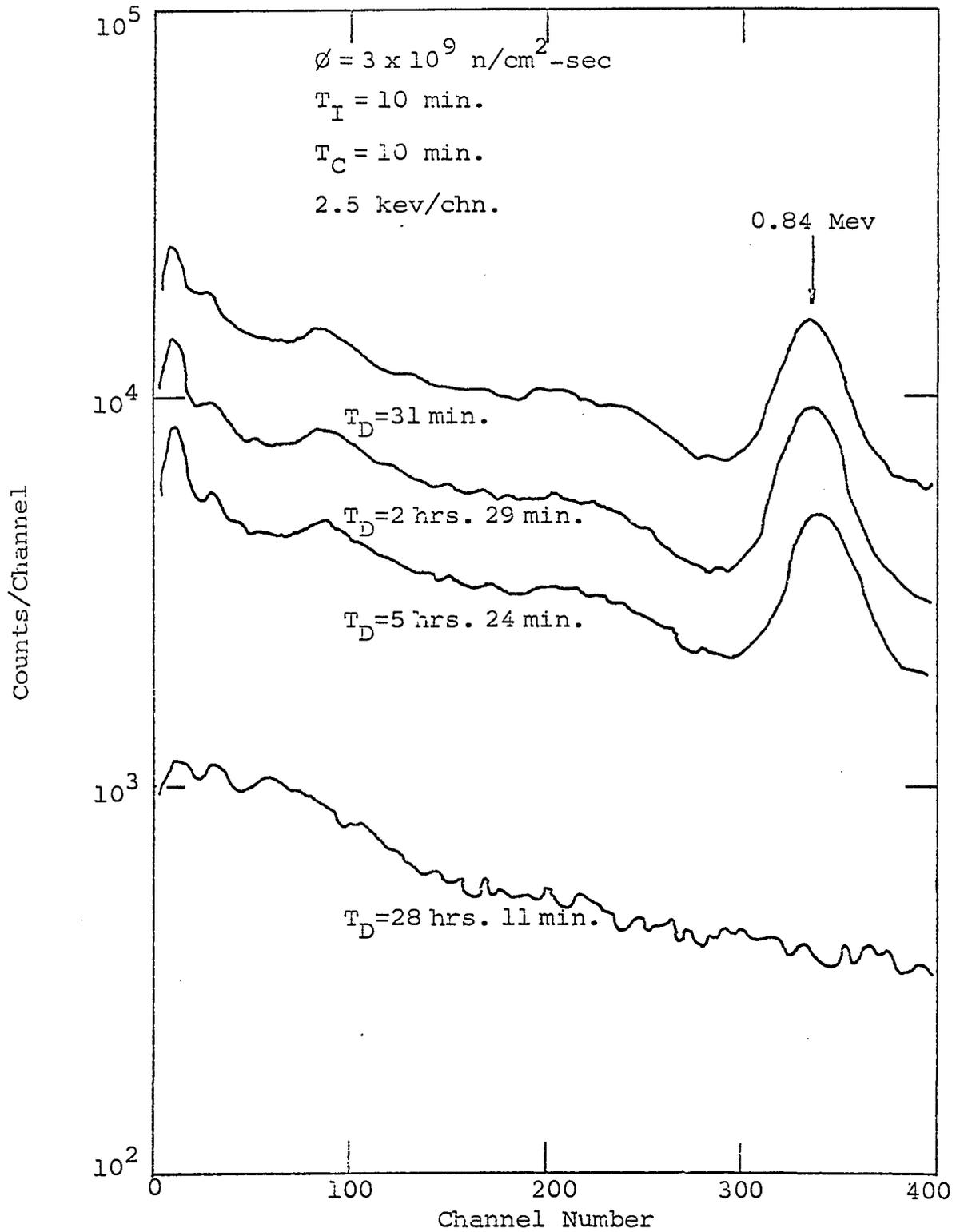


Figure 5-1. Gamma-ray spectrum of sample 17-102

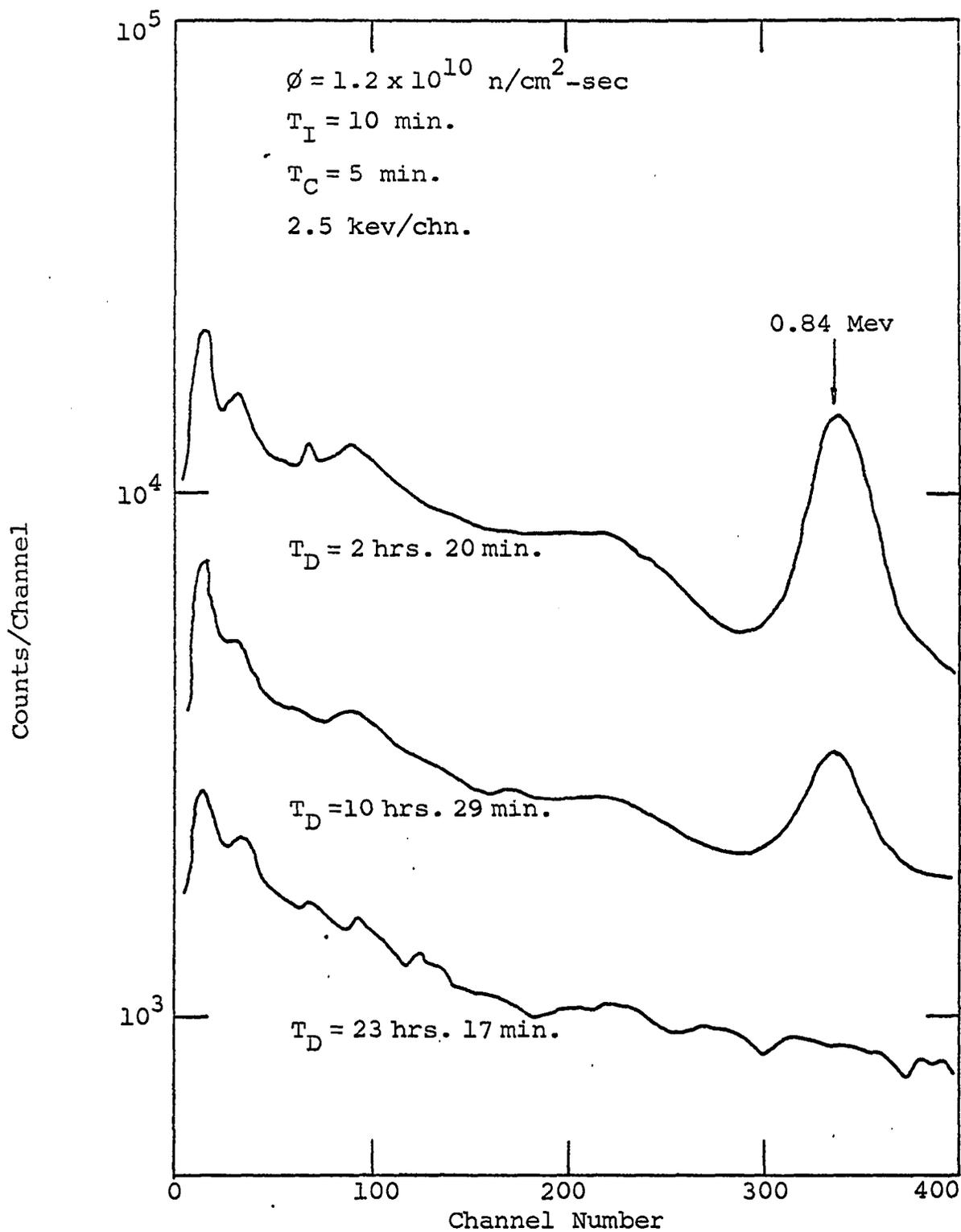


Figure 5-2. Gamma-ray spectra of sample 32-101

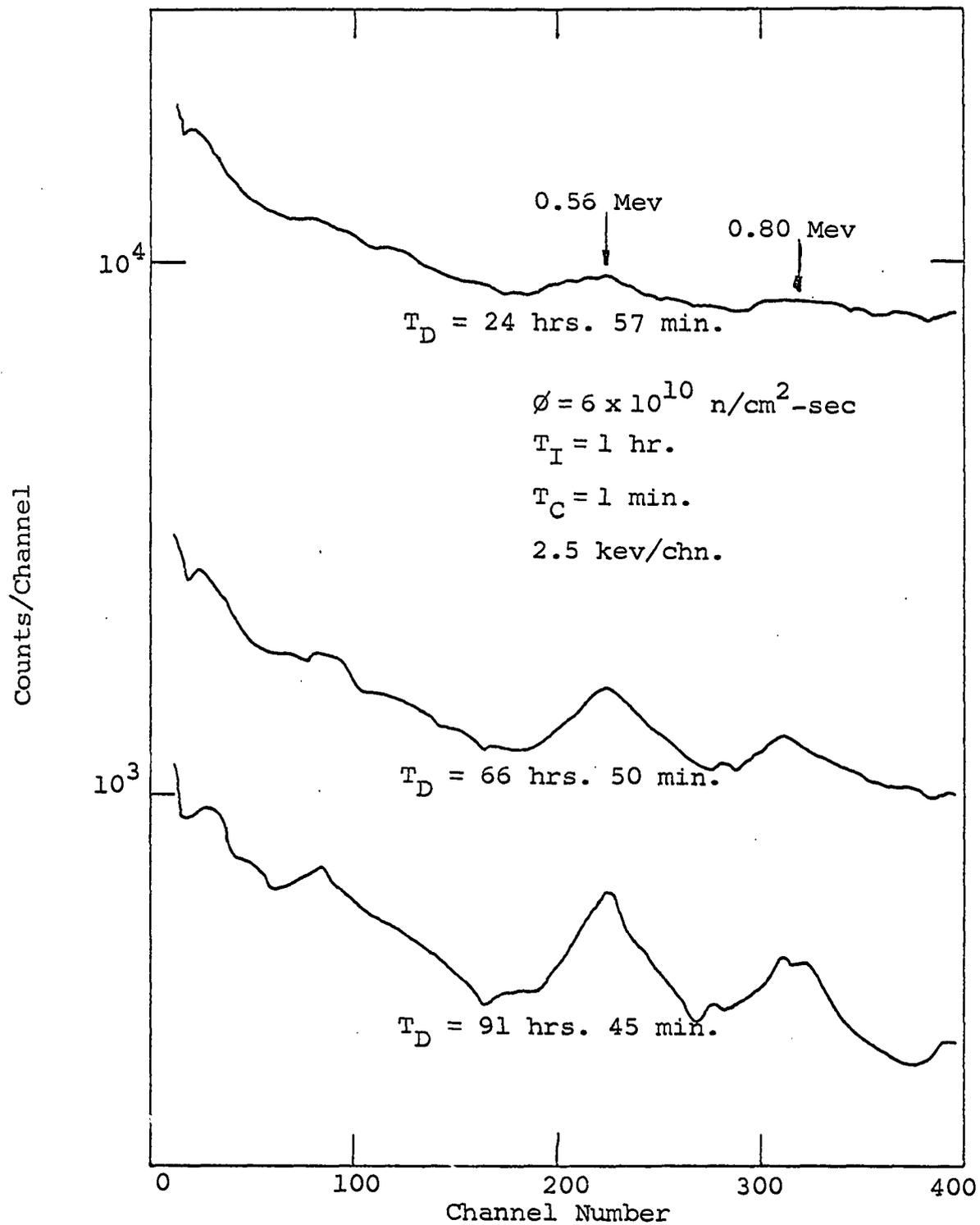


Figure 5-3. Gamma-ray spectra of sample 32-102

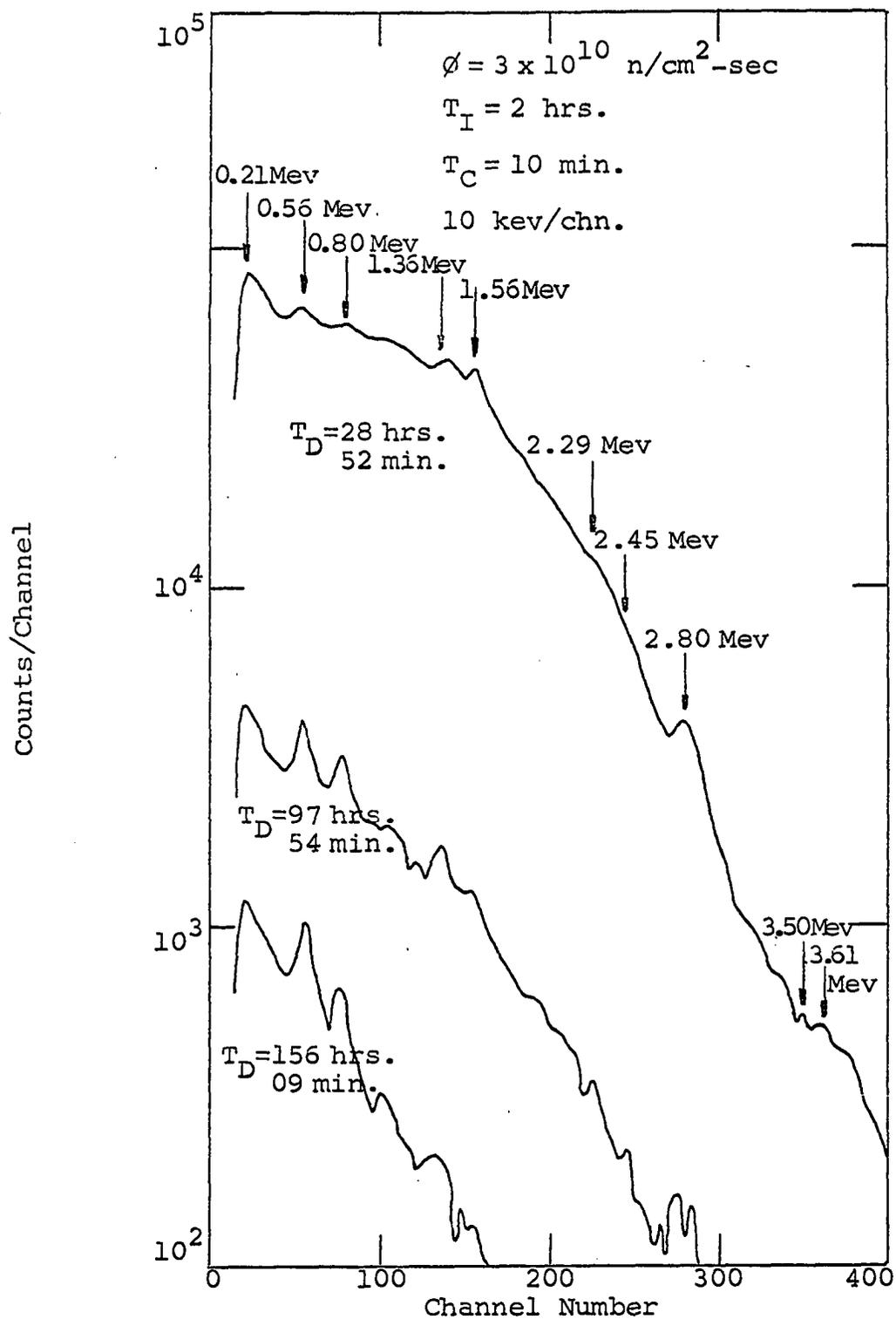


Figure 5-4. Gamma-ray spectra of sample 32-100

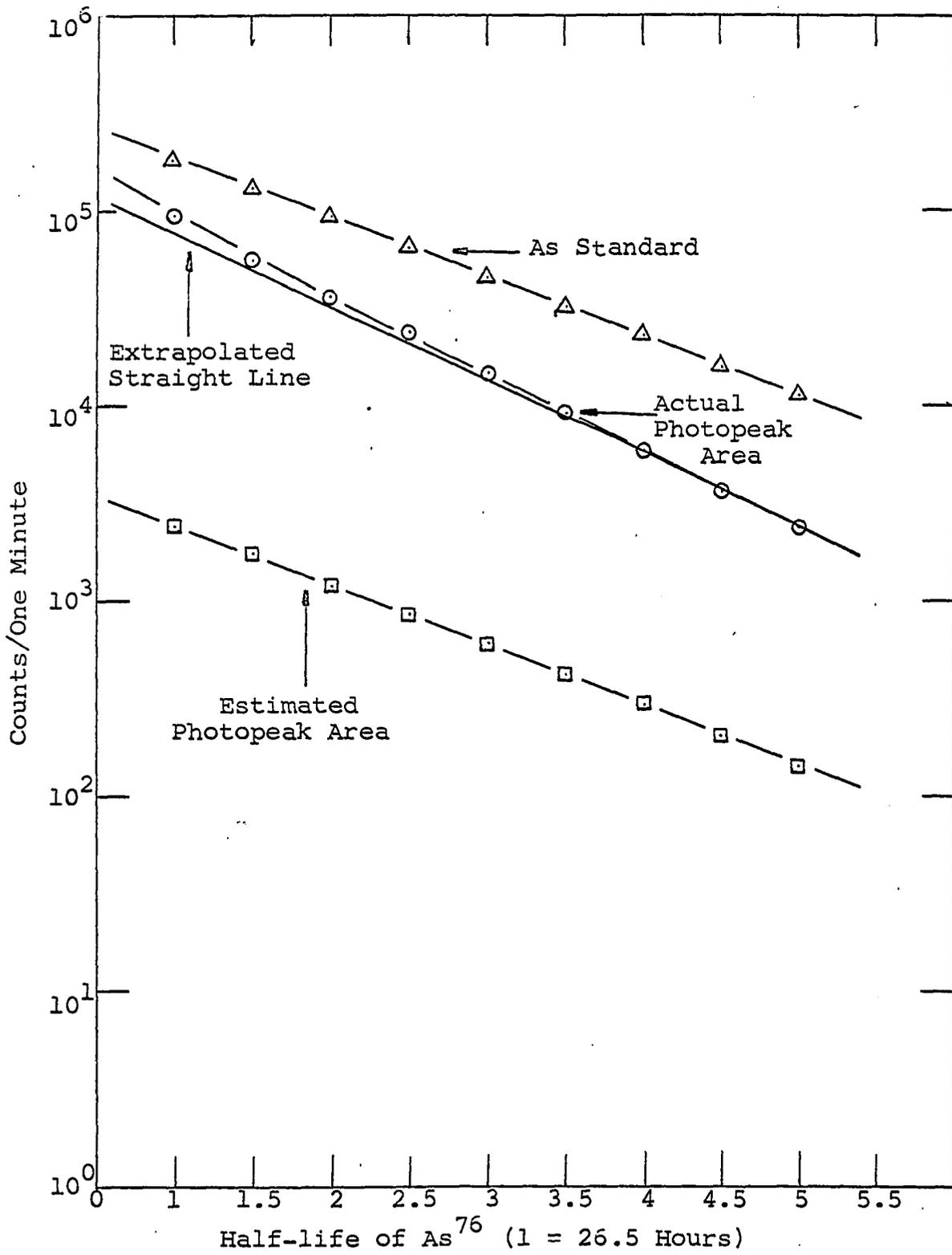


Figure 5-5. Determination of half-life of  $\text{As}^{76}$  found in sample 27-101 and optimization of decay time

Figure 5-6. Gamma-ray spectra of sample 20-1 and arsenic standard 17



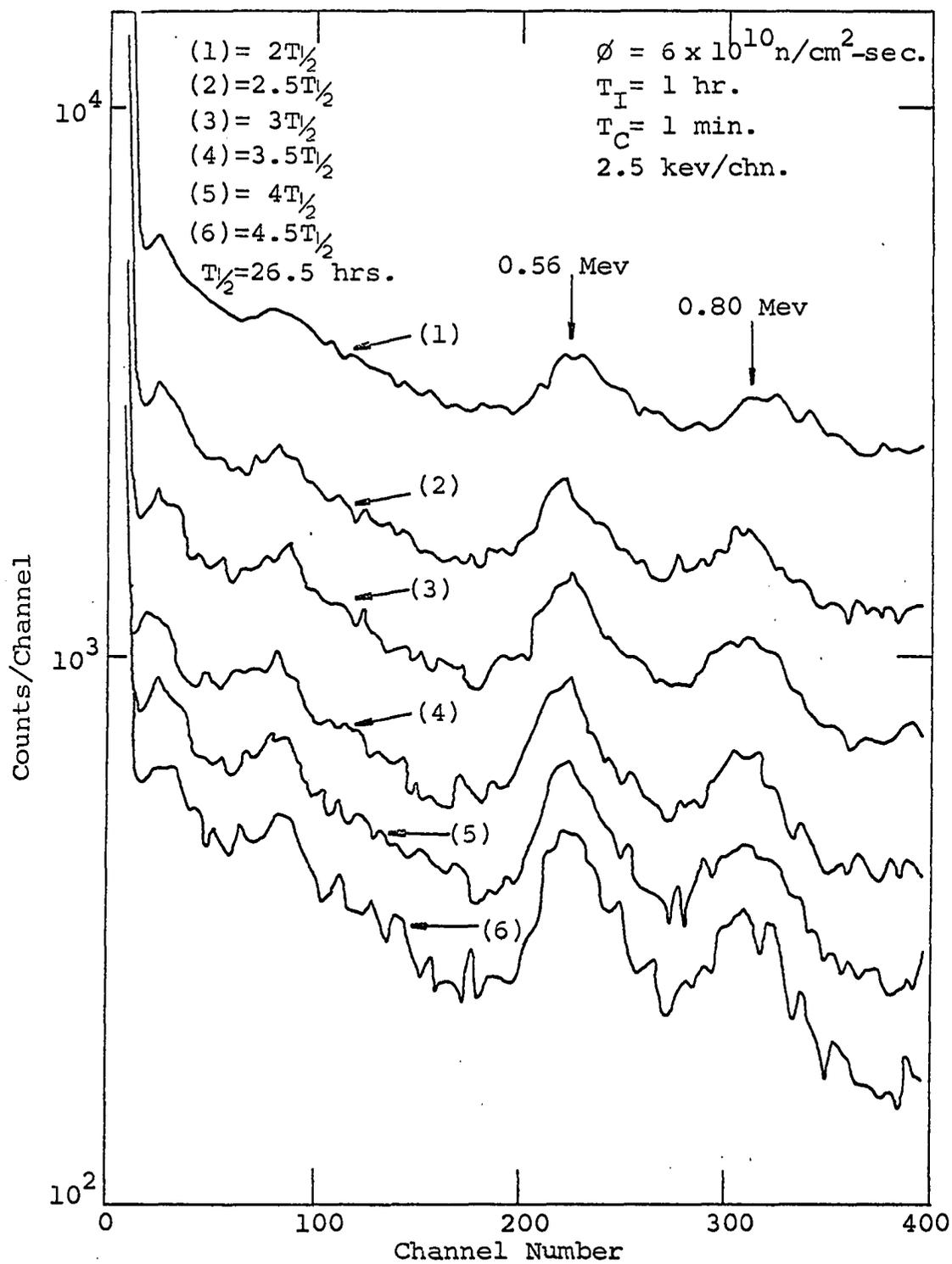


Figure 5-7. Gamma-ray spectra of sample 19

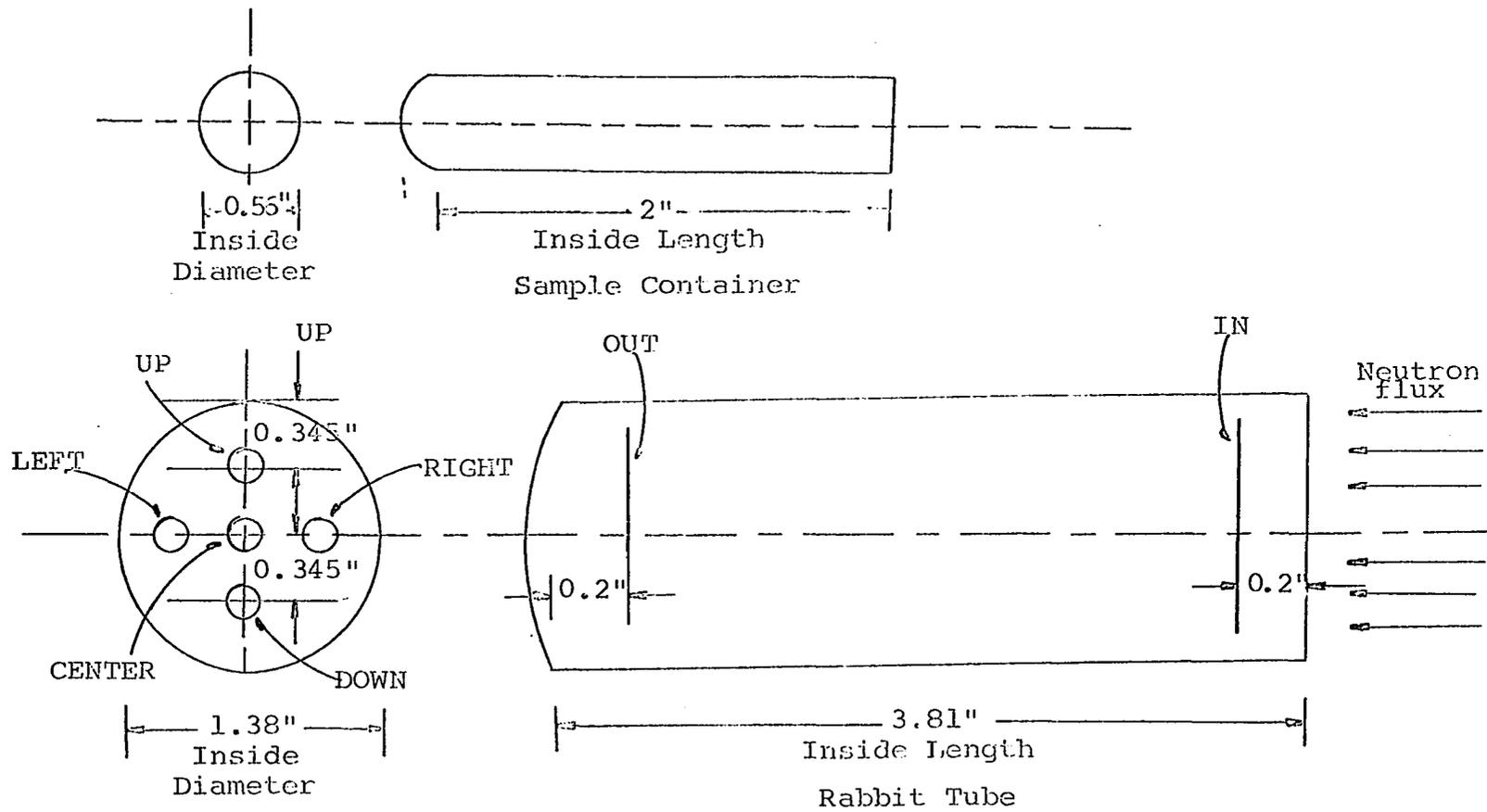


Figure 5-8. Rabbit tube and sample container

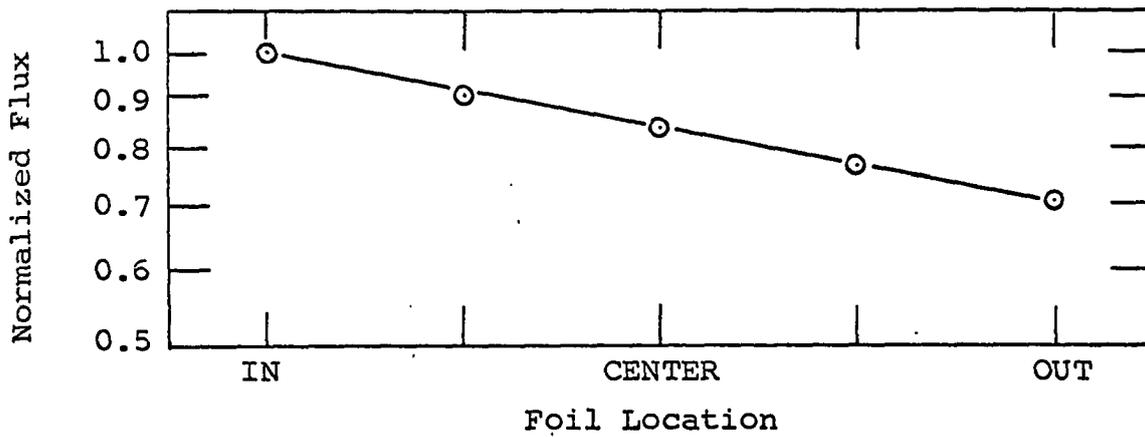
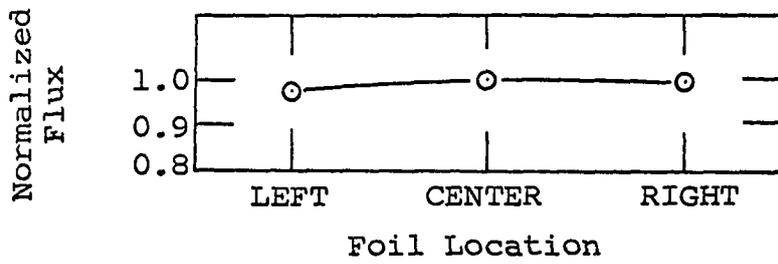
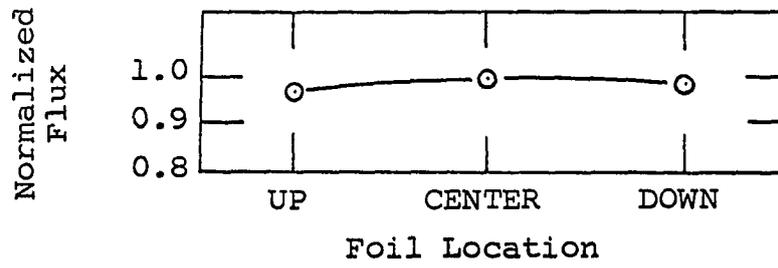


Figure 5-9. Flux configuration inside rabbit tube with plexiglass

Figure 5-10. Detection and counting system

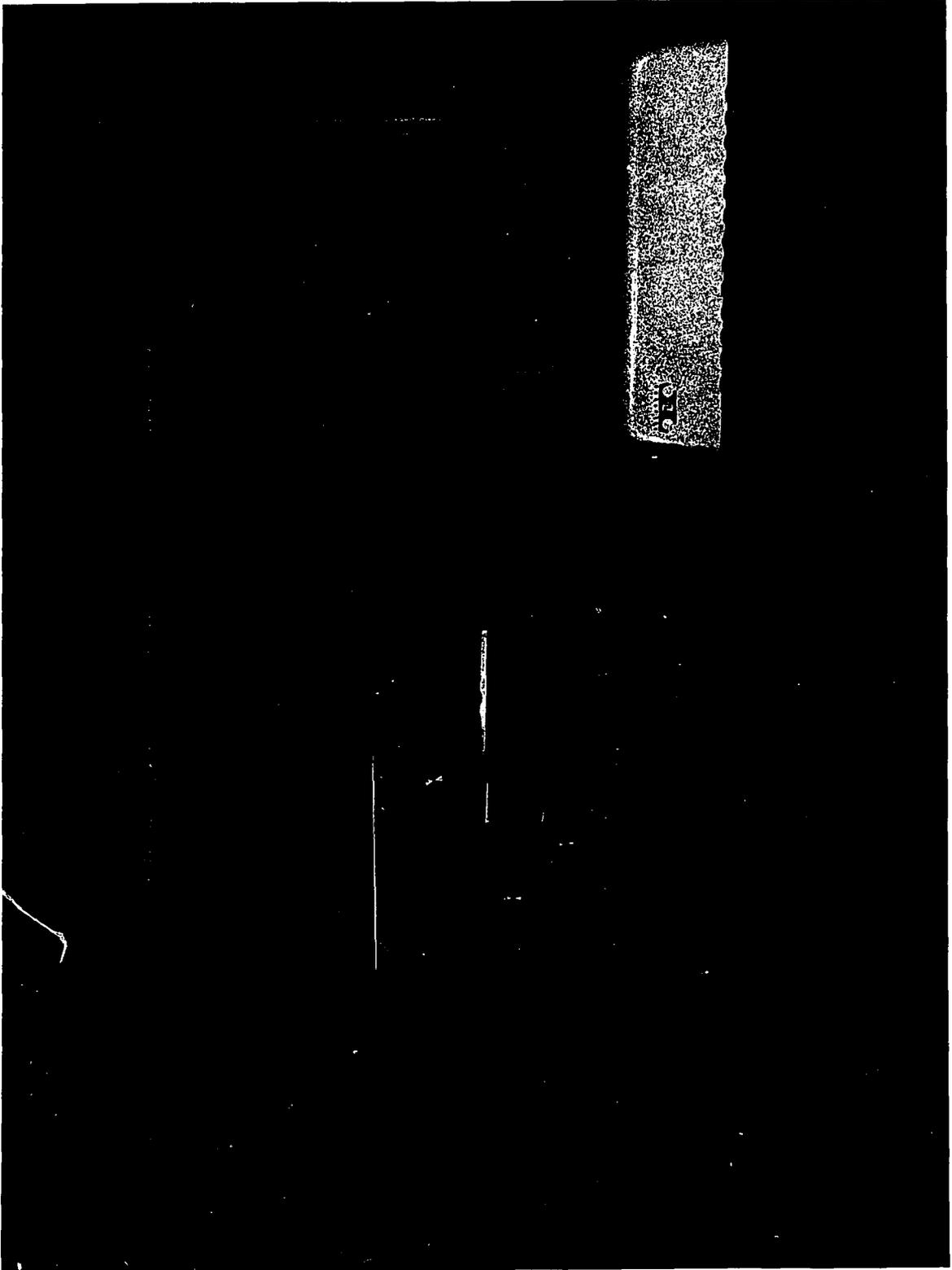
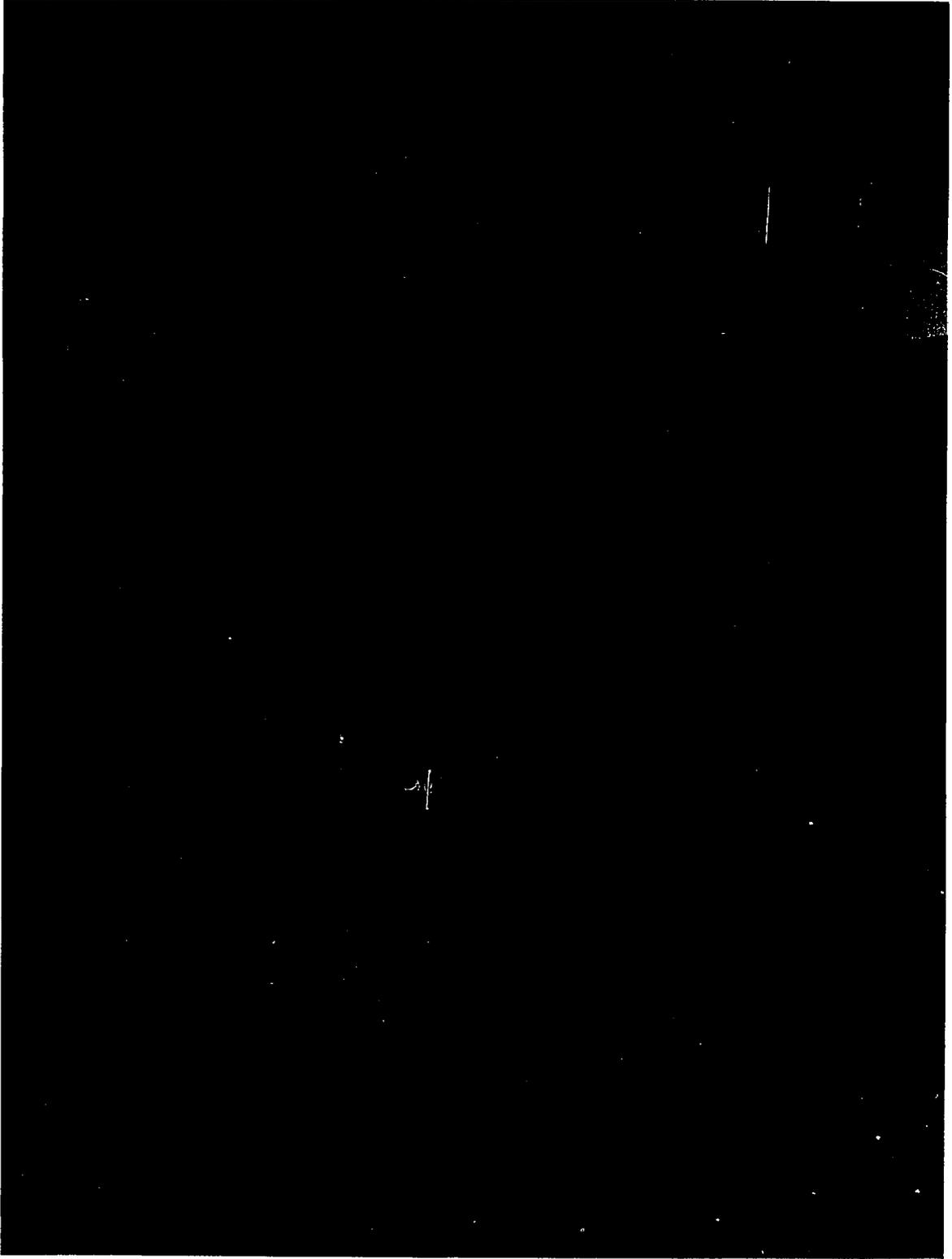


Figure 5-11. Sample storage cabinet



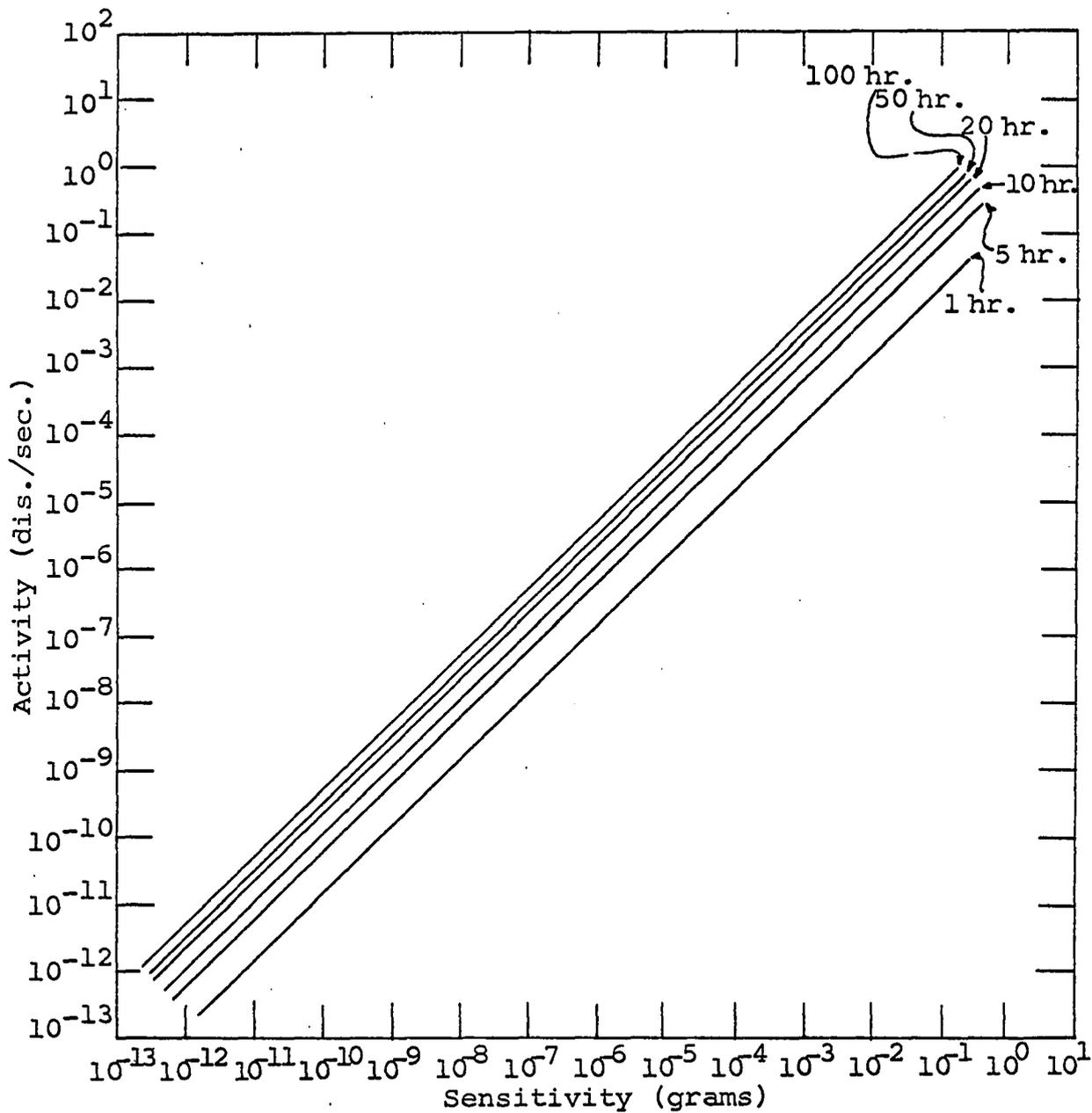


Figure 5-12. Sensitivity of  $As^{76}$

Table 5-1. Arsenic content of cigarettes

Sample code	Net sample wt. (mg)	Tobacco wt. in a cig. (mg)	As in the sample ( $\mu\text{g}$ )	As in a cigarette ( $\mu\text{g}$ )	As per gm of tobacco ( $\mu\text{g}$ )
1	1610.3	805.15	10.4	5.2	6.5
2	1538.6	769.30	11.0	5.5	7.6
3	1867.1	933.55	12.1	6.0	6.9
4	1981.1	990.55	11.4	5.7	5.8
5	1676.1	838.05	10.2	5.1	6.1
6-1	1689.9	844.95	11.5	5.7	6.8
6-2	1939.4	969.70	10.6	5.3	5.4
7-1	1601.7	800.85	10.7	5.3	6.6
7-2	1737.7	868.65	16.1	8.0	9.3
7-3	2278.5	1139.25	23.5	11.7	10.3
8	1886.4	943.20	14.6	7.3	7.7
9	1686.7	843.35	11.9	5.9	7.0
10	1799.5	899.75	12.3	6.1	6.8
11-1	1573.2	786.60	14.3	7.1	9.0
11-2	1939.9	969.95	12.4	6.2	6.4
12-1	1587.8	793.90	16.3	8.1	10.2
12-2	1843.2	921.60	10.4	5.2	5.6
13-1	1762.1	881.05	20.7	10.3	11.7
13-2	2251.5	1125.75	15.5	7.7	6.8
14	1732.1	866.05	16.0	8.0	9.2
15	1386.1	693.05	10.8	5.4	7.8
16-1	1835.5	917.75	12.7	6.3	6.9
16-2	1622.5	811.25	9.1	4.5	5.6
16-3	1959.3	979.65	14.4	7.2	7.3
17-1	1698.7	849.35	16.0	8.0	9.4
17-2	1664.7	832.35	14.6	7.3	8.9
17-3	1992.2	996.10	15.2	7.6	7.6

Table 5-1 (Continued)

Sample code	Net sample wt. (mg)	Tobacco wt. in a cig. (mg)	As in the sample ( $\mu\text{g}$ )	As in a cigarette ( $\mu\text{g}$ )	As per gm of tobacco ( $\mu\text{g}$ )
18	1693.6	846.80	15.6	7.8	9.2
19	1613.6	806.30	20.6	10.3	12.7
20	1491.4	745.70	17.9	8.9	11.7
21-1	2117.8	1058.90	14.7	7.3	6.9
21-2	2152.6	1076.30	14.6	7.3	6.7
21-3	2005.1	1002.55	12.4	6.2	6.2
22	1519.3	759.65	13.1	6.5	8.6
23-1	1719.7	859.85	12.8	6.4	7.4
23-2	2053.9	1026.95	17.3	8.6	8.2
24-1	1669.3	834.65	12.8	6.4	7.6
24-2	2077.4	1038.70	13.2	6.6	6.3
25-1	1737.4	868.70	14.0	7.0	8.0
25-2	2141.5	1070.75	10.9	5.4	5.0
26	2075.5	1037.75	20.2	10.1	9.7
27-1	1598.9	799.45	11.7	5.8	7.3
27-2	1990.0	995.00	11.2	5.6	5.6
28	1639.4	819.70	9.2	4.6	5.6
29	1800.6	900.30	12.2	6.1	6.8
30-1	1672.3	836.15	15.1	7.5	9.0
30-2	1505.4	752.70	12.8	6.4	8.5
31	1651.8	825.90	13.4	6.7	8.1
32-1	1685.4	842.70	10.6	5.3	6.3
32-2	2166.0	1083.00	15.0	7.5	6.9
32-3	2182.9	1091.45	13.5	6.7	6.2
33	2037.6	1018.80	15.4	7.7	7.5

Table 5-2. Average arsenic content of cigarettes

Manufacture code	Average As content of tobacco of a cigarette ( $\mu\text{g}$ )	Average As content per gm of tobacco ( $\mu\text{g}$ )
A	6.3	7.8
B	6.3	7.7
C	8.6	9.0
D	7.0	7.9
E	8.1	9.4
F	5.9	6.3
G	6.3	6.8

previous section. Arsenic-75 is only the naturally occurring isotope. Other isotopes are made artificially by using adjacent elements and nuclear fission.

The standard overcame the limitations presented in Chapter IV, except in some of the following respects:

- (a) The standard is a powder,
- (b) The standard is poisonous,
- (c) The standard may have interfering reactions.

Since arsenic is soluble only in carbon disulfate, it is impractical to weigh a small quantity unless it is in solution form. In order to obtain the best results, the amount of arsenic standard and arsenic in the sample must be accordingly

of the same quantity. A fairly good prediction of the quantity in the sample is most significant in the preparation of the standard. The arsenic content of cigarettes found by chemical means gives a valuable information, and was determined to be 9 ppm by Holland in 1966. The laboratory provided a balance which can weigh down to 0.1 mg. Arsenic standards used in the present investigation, however, were 1.0 mg throughout. It took the analyst at least one hour to prepare one arsenic standard. Special care was taken to ensure the poison safety of the analyst and others, and the standards were being prepared under a special hood. No significant interfering reactions were found with the standards. Therefore, it was concluded that the arsenic standards overcame the limitations fairly well.

b. Cigarette samples As stated previously, cigarettes were purchased from open markets. The cigarette samples overcame limitations described in Chapter IV, and the final consideration was given to possible trace elements. As seen in the previous section, the chemical components of tobacco are mostly nitrogen, oxygen and carbon. The small quantity of minerals present includes arsenic, Po-210, Ni, etc. Polonium-210 ( $T_{1/2} = 134.4$  days) emits the gamma rays of 0.80 Mev which appear on the gamma ray spectra displayed in Figures 5-3, 5-4, 5-6, and 5-7. However, there is no evidence of 0.37 Mev gamma rays from Ni-65.

c. Comparison with the results of other analysts (161)

<u>Analysts (or authors)</u>	<u>Amount of arsenic in ppm (year of report)</u>
Carey <u>et al.</u>	7.5-26.4, ave. 13.9 (1934)
Waltz and Hausermann	56.5 (1951), 2.7-14.4 (1958)
Holland <u>et al.</u>	7.5-30 (1932-1933), 42.5-52.0 (1957)
Weber	7-51 (1939-1957)
Cogbill and Hobbs	6-25 (1957)
Guthrie <u>et al.</u>	2.7-14.4, ave. 6.2 (1957)
Zanetti and Cutrufelli	15.1-46.2 (1961)
Hjern	2.3, 0.8, 2.5, 3.9 (1961)
Holland <u>et al.</u>	ave. 9 (1966)

The known methods for finding arsenic in cigarette tobacco include the following:

(a) Pavlu and Sula (114) applied silver diethyldithiocarbamate as a color complex-forming reagent for  $H_3As$  for the determination of trivalent arsenic in tobacco products, in which  $As^{+3}$  is reduced to  $H_3As$ .

(b) Hjern (57) used the molybdenum-blue photometric technique.

(c) Holland et al. (58) utilized the oxygen bomb for the destruction of the tobacco and release of the arsenic, and also the silver diethyldithiocarbamate technique.

Most of the investigators belonged to medical associations. Methods which have been utilized up to date have

involved chemical operations, which is a destructive technique to the best of the author's knowledge, and found arsenic as a form of  $\text{As}_2\text{O}_3$  or  $\text{H}_3\text{As}$ . However, no previous investigators have yet attempted to utilize a very sensitive method, the neutron activation analysis in arsenic research associated with cigarettes.

## 2. Discussion of results

As described in the previous chapter there are two different methods of the neutron activation analysis: the purely-instrumental method and the radiochemical separation method. Each of these methods has its own distinct areas of useful application.

The purely-instrumental technique is based upon multichannel gamma-ray spectrometry, and involves no chemical operations. After an appropriate irradiation period and an appropriate decay period, each dependent upon the half-lives of the induced activities of main interest, the activated sample is placed on a  $\text{NaI(Tl)}$  scintillation detector which is coupled with a linear amplifier and multichannel pulse height analyzer, and counted for an appropriate period of time.

The purpose of the experimental part is to determine the arsenic content of the cigarette samples. The most important information used for both quantitative and quali-

tative analyses of arsenic is the  $\text{As}^{75}(n,\gamma)\text{As}^{76}$  reaction by reactor thermal neutrons. The resultant arsenic isotope  $\text{As}^{76}$  emits gamma rays of energies 0.56 Mev, 0.66 Mev, and 1.21 Mev (144). All of the pertinent information for the identification and determination of arsenic in the samples is from the 0.56 Mev gamma rays of the samples.

The sample 17-102 was irradiated at the thermal-neutron flux time of  $nvt = 1.8 \times 10^{12} \text{ n/cm}^2$  and sample 32-101 was irradiated at  $nvt = 7.2 \times 10^{12} \text{ n/cm}^2$ . Gamma-ray spectra obtained from both samples did not show any evidence of  $\text{As}^{76}$ , i.e., 0.56 Mev gamma rays, as shown in Figures 5-1 and 5-2, respectively.

Only a peak at 0.64 Mev was seen in both cases. It was determined to be  $\text{Mn}^{56}$  produced by a reaction of  $\text{Mn}^{55}(n,\gamma)\text{Mn}^{56}$ . The activation cross section of  $\text{Mn}^{55}$  for thermal neutrons is 13.3 barns and its half-life is 2.576 hours. Even if the samples contained  $\text{Mn}^{55}$  a very small quantity, they were easily activated. However, the manganese photopeak died out completely at decay time over 25 hours, as seen in the figures, which is less than one half-life of  $\text{As}^{76}$ . Therefore, the presence of manganese would not disturb data analysis. However, there left a large amount of residual activity, possibly due to various organic components of the samples. It was impossible to justify that the samples contained arsenic. The first choice of improvement of the

results was to raise the neutron flux during irradiation and to take longer irradiation time to  $\phi = 6 \times 10^{10}$  n/cm<sup>2</sup>-sec and  $T_I =$  one hour, respectively.

The sample 32-102, which was irradiated at the thermal-neutron flux time  $nvt = 2.16 \times 10^{14}$  n/cm<sup>2</sup>, gave the photopeak at 0.56 Mev. The evidence of the presence of arsenic in the sample became more clear as the decay time increased than in the earlier decay times. This implied that the sample has impurities which produce short-lived radioisotopes. The gamma-ray spectra obtained for this sample is displayed in Figure 5-3.

Another attempt was made to compare the results of sample 32-102 and sample 32-100 by using different fluxes and irradiation times. The sample 32-100 was irradiated at the same thermal-neutron flux time as sample 32-102, but at  $\phi = 3 \times 10^6$  n/cm<sup>2</sup>-sec and  $T_I =$  two hours. This sample also showed the 0.56 Mev photopeak and confirmed the identification of As<sup>76</sup> in the irradiated samples. Gamma-ray spectra taken from sample 32-100 appears in Figure 5-4. There was no significant difference found in the results of samples 32-102 and 32-100.

In order to avoid the complicated corrections for decay characteristics for the various possible impurities, which exist in the samples, and in order to meet the operating power level of the reactor, it was optimized for all samples

to be irradiated at thermal flux of  $\phi = 6 \times 10^{10}$  n/cm<sup>2</sup>-sec for one hour. The flux is equivalent to the maximum operating power level of the UTR-10 reactor. The one hour irradiation is used to minimize possible competing, or interfering reactions, which may occur and possibly reduce or raise the concentration of As<sup>76</sup> in the sample, and to allow the irradiation of a number of samples at each reactor run.

The configurations of sample containers and the rabbit tube are displayed in Figure 5-8. A geometrical error and possible flux depression were considered by using tiny gold foils mounted by plexiglass in the tube. The plexiglass, which is a neutron-moderating material, was used for the purpose of supporting gold foils and examining the flux depression inside the tube. The flux at the IN end was normalized to one and that of the central point was depressed 16.5% and 29.1% at the OUT end. The UP end was depressed by 2.3% and 1.2% at the DOWN end. Two and half percent depression was marked at the LEFT end and 2.3% at the RIGHT end. The flux depression is displayed in Figure 5-9. To insure the least amount of error due to geometry of the samples in the tube, samples and the standards were placed side by side and as close to one another as possible while they were being irradiated.

In Figure 5-5 a series of photopeak area, i.e., total counts under the photopeak taken from sample 27-101, is

displayed. The half-life of  $\text{As}^{76}$  in the sample 27-101 was determined to be 26.7 hours and that in samples was calculated to be 27.2 hours, on the average, which agree well with the established half-life of 26.5 hours. The actual photopeak was taken at every half integer of the arsenic half-life. In order to eliminate the residual activity, which raised slightly the counting rate at the photopeak area, an extrapolated line was made by extending back from the straight line portion of the actual photopeak area. The difference between the actual photopeak area and the extrapolated straight line gave the estimated photopeak area of  $\text{As}^{76}$  in the sample. The estimated photopeak area was used in the calculation of arsenic in the sample.

A chance coincidence check was made between the counts at 0.56 Mev and 0.66 Mev, which is another gamma ray energy that  $\text{As}^{76}$  emits. The ratio of peak count at 0.56 Mev to the count at 0.66 Mev was 3.45 for samples and 3.56 for the arsenic standards, on the average. The error due to the residual activity was determined to be 3.6%, on the average, throughout the experiment. The arsenic content of the sample 27-101 was calculated, in such a manner as described above, to be 13.3 ppm and that of the samples was calculated to be 7.69 ppm, on the average.

The applicable decay time was optimized at a range of from approximately 80 to 120 hours after the irradiation.

A consideration was given to the decay time optimization for short decay times and the counting statistics for long decay times. The optimized decay time fell approximately between  $3T_{1/2}$  and  $4T_{1/2}$ , in which  $T_{1/2}$  is the half-life of  $As^{76}$ . Therefore it was decided to use data taken at  $3T_{1/2}$ ,  $3.5T_{1/2}$ , and  $4T_{1/2}$  for the quantitative determination of arsenic in samples. The optimized decay time by an experiment is in fairly good agreement with the value of 70.2 hours, calculated by Isenhour (67).

The  $As^{76}$  photopeak of the samples, and this photopeak compared with that of the  $As^{76}$  photopeak of the standard can be seen in Figure 5-6. In the figure the upper one shows the cigarette sample spectrum and the lower one shows that of the arsenic standard. In Figure 5-7, gamma spectra are shown according to the decay time of the sample 19. The estimated photopeak area was obtained in such a way described above, and the amount of arsenic was obtained by the following formula:

$$\frac{\text{Amount of } As^{75} \text{ in the sample}}{\text{Amount of } As^{75} \text{ in the standard}} = \frac{\text{Estimated photopeak area of } As^{76} \text{ in the sample}}{\text{Estimated photopeak area of } As^{76} \text{ in the standard}}$$

where the amount of  $As^{75}$  in the sample is unknown and other three terms are all known or measured. Thus the amount of  $As^{75}$  was calculated under the same laboratory conditions.

It was assumed that the activation ratio ( $\text{As}^{75}/\text{As}^{76}$ ) in the sample and the standard was the same. Therefore, the amount of  $\text{As}^{76}$  in the activated sample may represent the total amount of  $\text{As}^{75}$  in the original sample. This is another advantage of the comparator technique, which is the method in which the sample and the known amount of standard are irradiated simultaneously. Tables 5-1 and 5-2 show the arsenic content of cigarettes for different brands and for different manufactures, respectively.

In the experimental procedure of this work, only one step would cause an error. This is stripping the residual activity. Chemical operations, which might include one or more steps other than stripping the residual activity, were completely eliminated.

A repeatability is checked with six samples of sample code 32-1. The standard deviation of the arsenic content in ppm is  $\pm 6.18\%$ .

A sensitivity of  $\text{As}^{76}$  is established by utilizing Equation 2-15 with thermal neutron flux of  $\phi = 6.0 \times 10^{10}$  n/cm<sup>2</sup>-sec, at decay time of  $T_I = 79.5$  hours, which is three half-lives of  $\text{As}^{76}$ .

## VI. SUMMARY AND CONCLUSIONS

## A. Summary of Investigation

Neutron activation analysis, which is applicable to a large number of analytical problems, particularly in the analysis of trace elements, often is not suitable because of the necessity of destruction of the material being evaluated.

Instrumental neutron activation analysis, which relies entirely on instruments, is applied to the evaluation of the arsenic content of American cigarettes by utilizing the decay phenomenon of  $\text{As}^{76}$  in the samples.

## B. Conclusions

The following conclusions are drawn:

(a) The cigarette samples investigated contain on the average,  $7.69 \pm 0.48 \mu\text{g}$  of arsenic ( $\text{As}^{75}$ ) per gram of tobacco, and  $6.89 \pm 0.42 \mu\text{g}$  of arsenic ( $\text{As}^{75}$ ) per cigarette.

(b) The arsenic content of the cigarette samples differs from one manufacturer to another, ranging from  $6.33 \pm 0.39 \mu\text{g}$  to  $9.37 \pm 0.58 \mu\text{g}$  of  $\text{As}^{75}$  per gram of tobacco.

(c) Manganese-55 has been found to be a component of cigarette samples. Also found is Po-210, however, quantitative analysis of Po-210 has not been possible.

(d) A sensitivity of  $\text{As}^{76}$  is  $0.1 \mu\text{g}$  with thermal neu-

neutron flux of  $\phi = 6.0 \times 10^{10}$  n/cm<sup>2</sup>-sec, and  $T_I =$  one hour.

### C. Recommendations for Further Study

Investigators have occasionally stated that the neutron activation analysis is a well established analytical tool in a laboratory. However, this statement fails when samples do not overcome the limitations discussed in Chapter IV, though several alternative means are available to avoid or minimize the limitations. The author believes that any samples can be analyzed by the purely-instrumental method effectively, and that the limitations can be overcome if the following can be developed:

- (a) A completely automatic system,
- (b) The utilization of information other than photopeak, if it is disturbed,
- (c) The establishment of a data library,
- (d) The optimization of the sample size.

The recommended automatic system is shown in Figure 6-1. Research groups such as Kaman Nuclear, Colorado Springs, Colorado and Gulf General Atomic, San Diego, California have developed ones very similar to that shown in the figure by using a neutron generator and a TRIGA reactor, respectively.

When an analyst considers the use of neutron activation analysis, the photopeak has been his most useful information.

This is true as long as the photopeak is not disturbed in various ways. However, there is no reason for the analysis not to utilize other pertinent information. This information includes the bremsstrahlung intensity, the back scatter peak, the Compton edge, the angle and time coincidences, the sum peak, and the single and double escape peaks. To the best of the author's knowledge, these have not been utilized. Utilization of this information has been discussed in Chapter III.

A data library is necessary, first of all, for an analysis of a number of samples. Attention must be paid to the purity of the standard in establishing library data. Data for the different standards, flux times, and information mentioned above should be available to the analyst at all times.

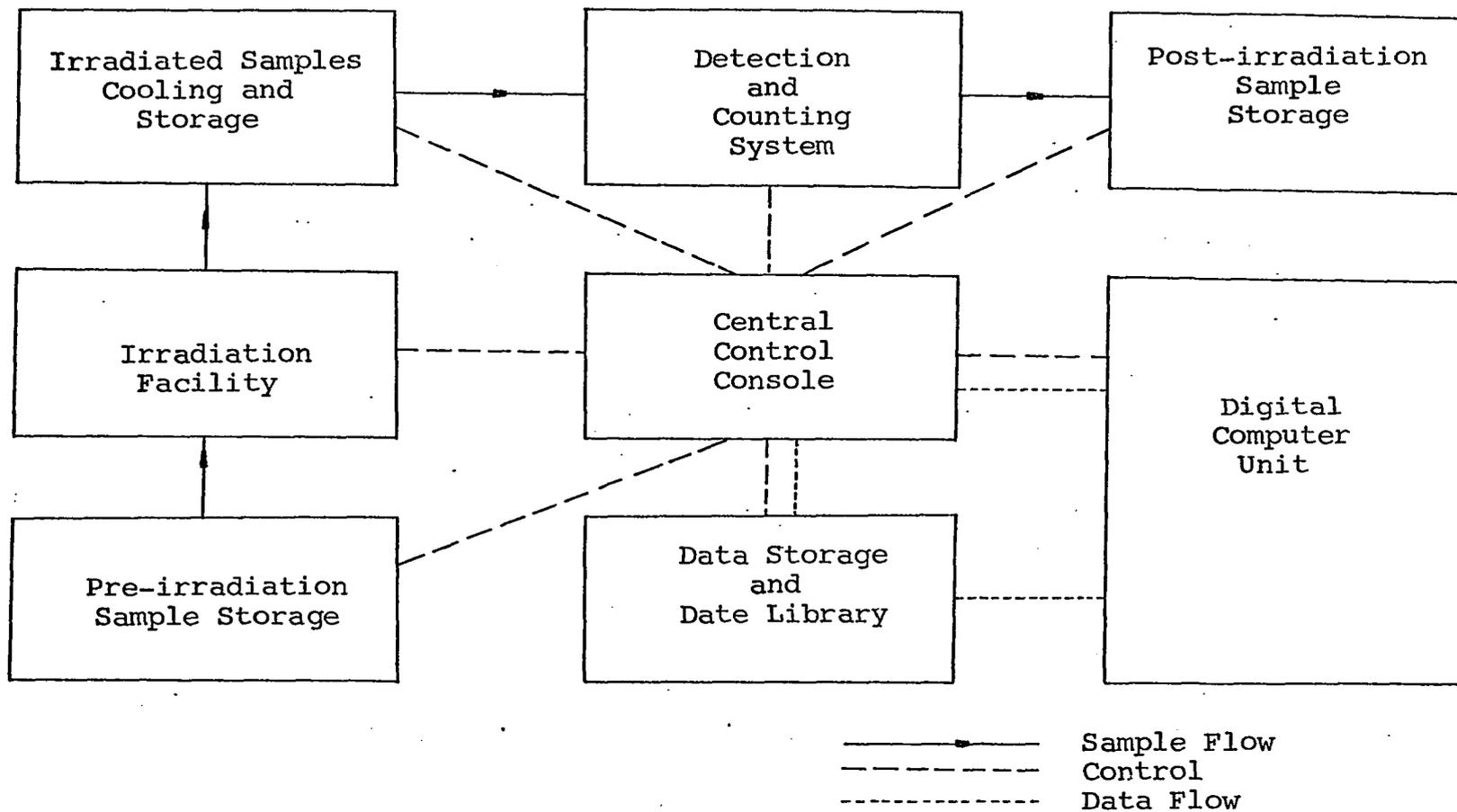


Figure 6-1. Block diagram of the proposed complete automatic system

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