DEPARTMENT OF CHEMISTRY

UNIVERSITY OF MICHIGAN

ANN ARBOR, MICHIGAN

---

# • ACTIVATION ANALYSIS
# • NUCLEAR CHEMICAL RESEARCH
# • RADIOCHEMICAL SEPARATIONS

---

PROGRESS REPORT 9

November 1, 1960

Supported by

DEPARTMENT OF CHEMISTRY

MICHIGAN MEMORIAL-PHOENIX PROJECT

UNITED STATES ATOMIC ENERGY COMMISSION
PROJECT NO. 7, CONTRACT NO. AT(11-1)-70

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
Ann Arbor, Michigan

# PROGRESS REPORT 9

November 1959 - October 1960

## ACTIVATION ANALYSIS
## NUCLEAR CHEMICAL RESEARCH
## RADIOCHEMICAL SEPARATIONS

Edited by
R. S. Maddock
and
W. W. Meinke, (Project Director)

November 1, 1960

Supported by
Department of Chemistry
Michigan-Memorial Phoenix Project
Project No. 7 Contract No. AT(11-1)-70
U. S. Atomic Energy Commission

The following is a report of the work completed on Project No. 7, Contract No. AT(11-1)-70 during the year of November 1, 1959 to October 31, 1960.

Previous progress reports are listed below:

| | |
|---|---|
| Progress Report 1 | November 1952 |
| Progress Report 2 | November 1953 |
| Progress Report 3 | November 1954 |
| Progress Report 4 (AECU-3116) | November 1955 |
| Progress Report 5 (AECU-3375) | November 1956 |
| Progress Report 6 (AECU-3641) | November 1957 |
| Progress Report 7 (AECU-3887) | November 1958 |
| Progress Report 8 (AECU-4438) | November 1959 |

# FOREWARD

A word is perhaps in order about the philosophy of these progress reports which are issued yearly from our laboratories. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication--yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment etc., which often require months to perfect and yet all too often must be covered in only a line or two of a journal article.

Thus our progress report endeavors to present this information which we have struggled to obtain and which we feel might be of some help to others. Certain areas which it appears will not be treated fully in regular publications are considered in some detail here. Other results which are being written up for publication in literature are often covered in a more abbreviated form.

(W. W. Meinke)

## TABLE OF CONTENTS

TABLE OF CONTENTS (cont'd)

## TABLE OF CONTENTS (cont'd)

TABLE OF CONTENTS (cont'd)

## LIST OF FIGURES

## LIST OF FIGURES (cont'd)

## LIST OF TABLES

# I FACILITIES

## A. Michigan Reactor and Pneumatic Tube System

The Ford Nuclear Reactor has operated routinely at a power of 1 megawatt (flux of $\sim 10^{13}$ n $cm^{-2}$ $sec^{-1}$ in the core) for the past year on an average of two to three 8-hour days a week, with the exception of a four-week shut down in the latter part of August and early September due to control rod troubles and annual maintenance. Of the total number of operating hours the Nuclear Chemistry Group has used ~1000 hours of 1 megawatt power obtaining 1075 irradiations. Of these, 25 irradiations were "in pool" while 1050 were made through the pneumatic tubes. There were ~690 hours of reactor time used for the "in pool" irradiations and 310 hours for the pneumatic tube runs. The "in pool" irradiations included several samples for analysis as well as for producing tracers of tin, chromium, tellurium, arsenic, copper and lanthanum.

The pneumatic tube system has been in full operation almost continuously during the past year. There were several occasions when a rabbit failed to return for some unexplained reason but it was always possible to get the rabbit out within a day or two at the most. The tube system was completely checked over by the supplier (Air-Matic) in the early part of the year and has not given trouble since.

None of the rabbits have come apart or broken in the tubes during the past year. We have continued to use polyethylene as material and the quarter turn lock feature for the rabbits but have changed the design to eliminate as much of the felt as possible

(1). Figure 1 shows our new design which has only one piece of felt, a bumper, which hits the end of the pneumatic tube in the reactor. Polyethylene "riders" now replace felt as gaskets. The body and the riders are now machined directly from polyethylene rod as one unit.

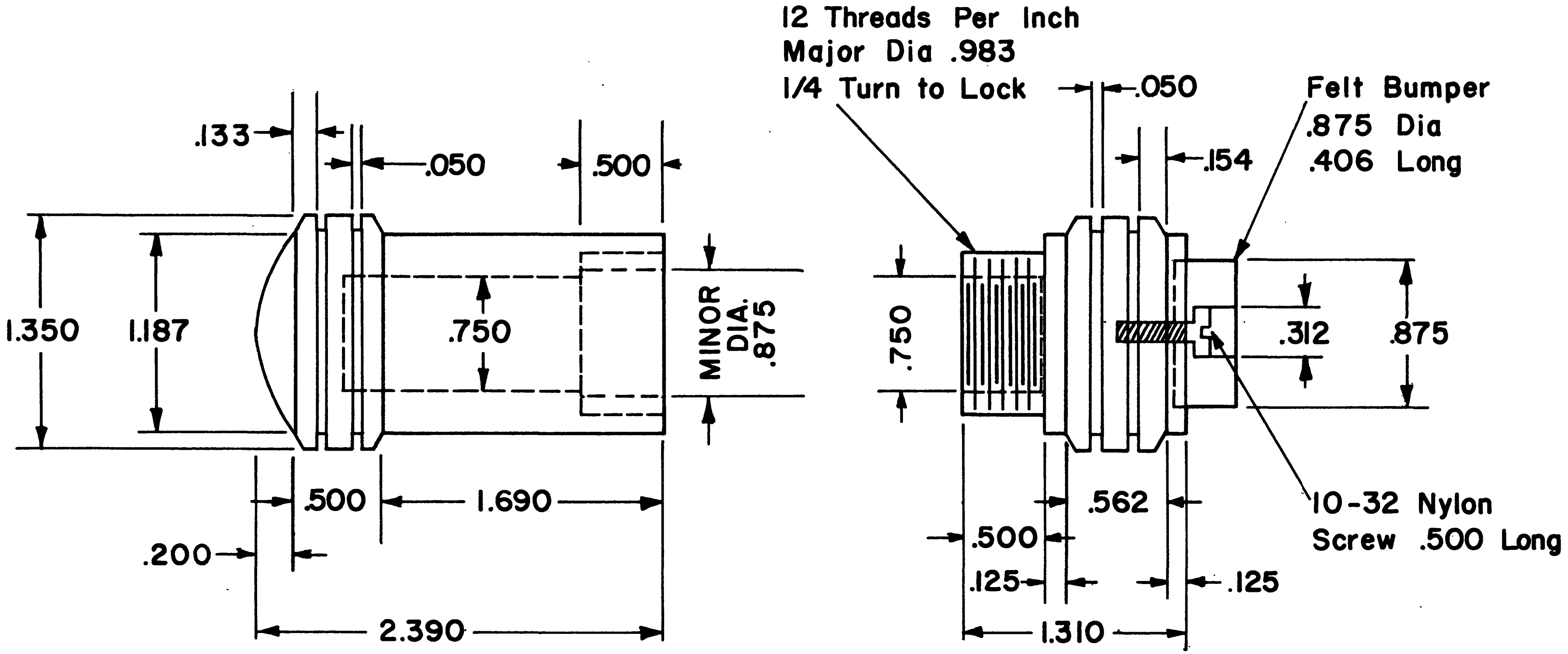
This new design has speeded the transit time of the rabbit from core to hood to 2.5 seconds and has cut in half the dosage rate from the rabbit itself (Table I) since the felt contributed a major fraction of the post irradiation dose.

Table I. Dose Rates from Rabbits.

| Irradiation Time | Surface Dose Rates* (mr/hr)<br>Nylon (2) | Polyethylene Design 1 (1) | Polyethylene Design 2 |
|---|---|---|---|
| 15 sec. | 30 | 35 | 15 |
| 1 min. | 100 | 140 | 80 |
| 2.5 min. | 200 | 260 | 148 |
| 5 min. | 250 | 310 | 177 |

*Measurements were made 3 seconds after irradiation at 1 Mw.

Almost all of the thousand pneumatic tube irradiations were handled routinely as described in the last progress report without problem of radiation hazard. In a few cases, however, finger film tabs indicated that the laboratory worker had received somewhat more than tolerance levels during a series of irradiations on a particularly "hot" sample. Investigations showed that sometimes



BODY & CAP – POLYETHYLENE
SCREW – NYLON
BUMPER – FELT

Fig. 1. New quick opening rabbit design. Features include one quarter turn lock.

the size of the original sample could be reduced to stay well within tolerance limits. Where this was not possible a simple "catcher" shown in Fig. 2 was used for the rabbit.

In any case our experience has shown that it is possible to make many irradiations per day and still stay well below radiation tolerance levels using simple rapid manipulations either with the hands directly or with simple extensions. No complicated automatic equipment is necessary at this flux level--nor do we believe it is necessary at flux levels 10 or even 100 times higher given the proper simple manual manipulators.

## 1. Thermal Flux and Cadmium Ratios in Pneumatic Tubes

During the past year we have experienced several variations in flux due to a change of fuel elements and core

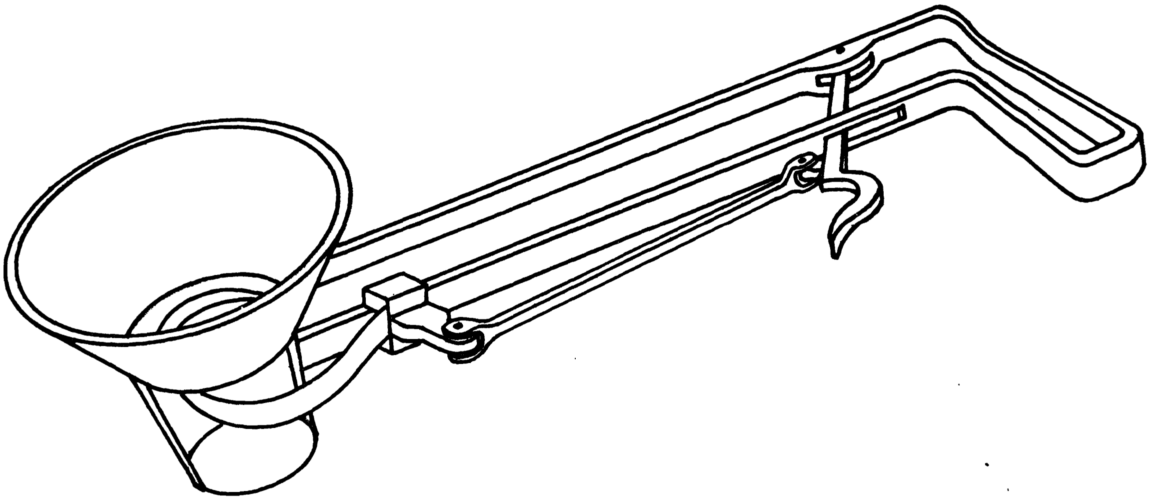


Fig. 2. Mechanical catcher. Strap holds rabbit secure while the sample is being removed.

configuration. The flux in PL-2 and PL-3 [tube numbers 2 and 3 of Progress Report 8 (1)] remained essentially the same as reported in Progress Report 8 (1) until mid-June 1960 when two new fuel elements were placed next to the pneumatic tube terminals. The thermal neutron flux increased to $\sim 2 \times 10^{12}$ in PL-2 and $1.5 \times 10^{12}$ in PL-3. In August, however, the reactor had control rod difficulties and when the reactor was put back into operation the new fuel elements were moved to the center of the core to increase the total value of the new control rods. Now the thermal neutron flux in PL-2 is $1 \times 10^{12}$ and in PL-3, $6.4 \times 10^{11}$. The cadmium ratio for PL-2 is $\sim$14:1 while that for PL-3 is 15:1. The flux values are summarized in Table II.

Table II. Neutron Flux in Pneumatic Tubes. ($n\ cm^{-2}\ sec^{-1}$)

| | 1959 | August 1960 | October 1960 |
|---|---|---|---|
| PL-2 | $1.24 \times 10^{12}$ | $2 \times 10^{12}$ | $1 \times 10^{12}$ |
| PL-3 | $0.92 \times 10^{12}$ | $1.5 \times 10^{12}$ | $0.64 \times 10^{12}$ |
| PL-1 | $1.76 \times 10^{12}$ | (No longer located in Chemistry Laboratory) | |

The measurements were made using 1 mil gold foils weighing $\nless 1.5$ mg to give counting rates within the useful range of the scintillation well counter.

The calculated thermal neutron flux was based on a cross-section (2200 m/s) of 98 for $Au^{197}$. Since the purpose of the flux monitoring program has been to detect variations in available flux, no corrections for self shielding and flux depression of the sample have been made. The precision of each individual measurement should be better than 3% based on known errors in foil weight, positioning in the rabbit, and counting of the sample. (H. Nass)

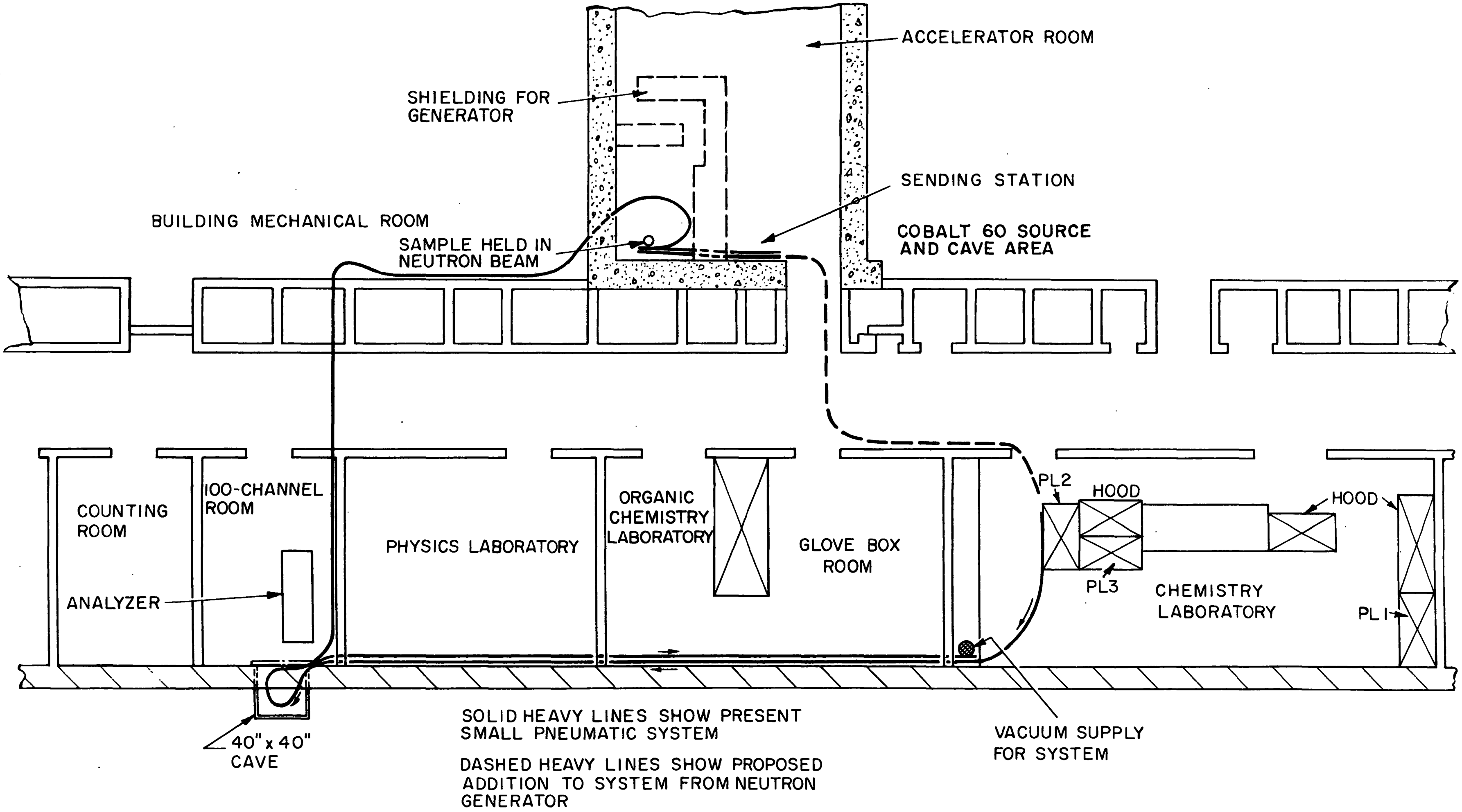
## B. "Bunny Rabbit" System

The "bunny" rabbit system has been extended as was mentioned in Progress Report 8 (1) so that samples may be sent from the neutron generator to the 40" x 40" x 40" detector cave and from there to the hot laboratory. This extension is shown in Fig. 3 along with additional extensions planned to take a sample from the generator to the hood in the chemistry laboratory. The controls for the run from the accelerator room are still temporary but do operate satisfactorily. Arrangements at the accelerator are described more fully in a later section.

The "bunny" tube in the cave (Fig. 4) is now arranged so that there is a non-operating position well out of the way of ordinary detector measurement procedures. This position places the tube against the door and up towards the ceiling. When the tube is to be used it is merely swung into position in front of the 3" detector. (H. Nass, R. Shideler)

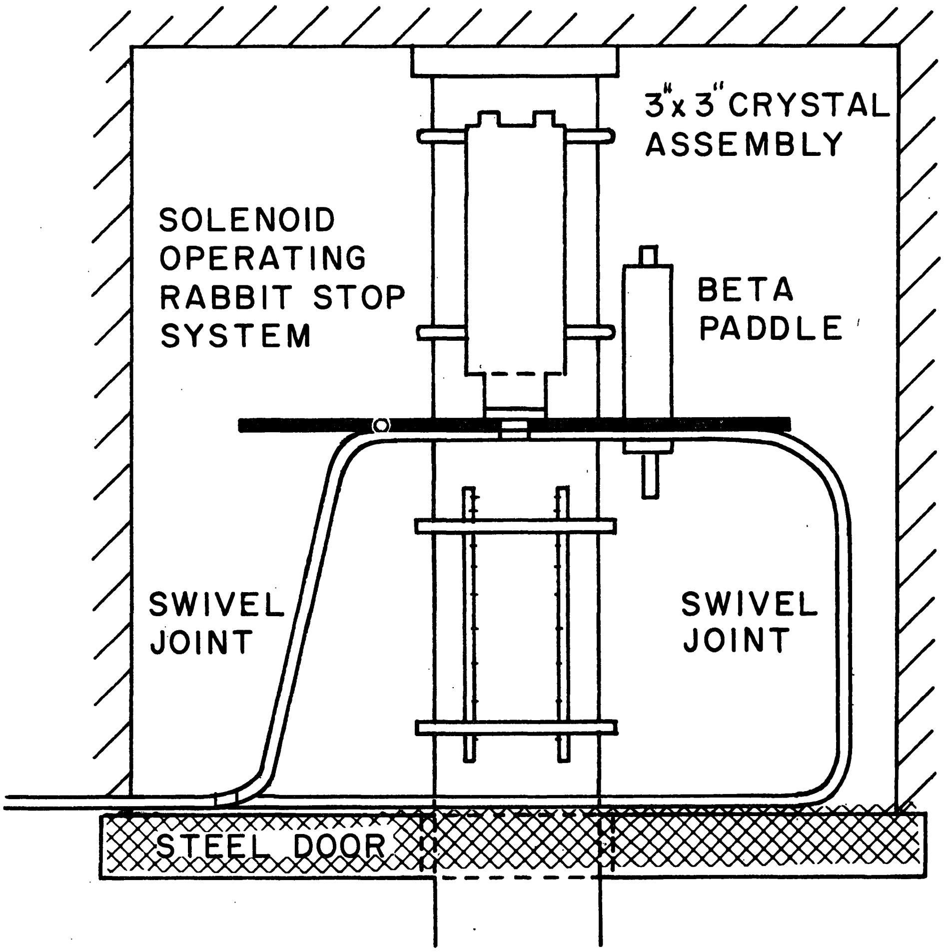
## C. Phoenix Laboratory Counting Room

The 100-channel analyzer room of the Phoenix Memorial Laboratory



FIRST LEVEL FLOOR PLAN PHOENIX LABORATORY

Fig. 3 Floor plan of Phoenix Laboratory showing the installed "bunny" system both from the generator and the chemistry hot laboratory to the 3-inch detector. It is also proposed to run a line directly from the generator to the hood in the chemistry hot lab.



THE BUNNY TUBE MAY BE ROTATED UPWARD TO BE OUT OF THE WAY OR DOWNWARD TO THE COUNTING POSITION

BUNNY TUBE SYSTEM

Fig. 4. Schematic layout of cave interior showing the "bunny" tube system (looking from above).

has been rearranged somewhat from that described and pictured in previous progress reports (1, 2). The rack containing the X-ray proportional counter was dismantled and individual units fitted into and on top of the three racks holding the 100-channel analyzer. In addition, the proportional flow counter and its methane tank were moved away from the door to the outside wall as a safety precaution so as not to block the exit should the gas cylinder break loose.

This one 12' x 15' room continues to serve most of the measurement needs for persons in our group working in the Phoenix Laboratory. It contains the dual-memory 100-channel pulse analyzer with a number of detectors ranging from a 3" x 3" NaI(Tl) crystal through several smaller scintillation flat and well detectors to a krypton-filled X-ray proportional counter. In addition there are a flow proportional counter and a scintillation well counter for gross radioactivity measurements. Sufficient room remains for an electronic repair bench, a desk, a filing cabinet and a number of wall cupboards. The room is compact, and sometimes crowded, but with our emphasis on short lived activities does not see the continuous measurement on any one sample that characterizes so many counting rooms. Occasionally a counter in a neighboring room is used to supplement the equipment.

## D. Neutron Generator

### 1. Introduction

It is our firm conviction that activation analysis will not come into general use in the analytical laboratory until it is possible to complete an analysis in the matter of minutes or at the most an hour or so rather than days, and until there is some type of neutron source which will enable a group to use the technique in their own laboratory without having to send samples to an outside reactor. Our program of studying the use of short-lived isotopes in activation analysis has proved that many elements can be determined on a short time scale using rapid radiochemical procedures. We are now also looking into the evaluation of neutron generators for activation analysis.

Few laboratories can afford a reactor just for analytical work--and even a so-called low price research reactor requires a special building, and of even more importance, has to be licensed by the Atomic Energy Commission. A few large companies have set up laboratories for activation analysis using large Van de Graaff machines at a cost of about $100,000 for the machine plus cost of the building but this price is much too high for the average laboratory. Besides, most of these machines are "physics" machines which require trained personnel to run and keep in operation.

I believe that what is needed for a good laboratory source of neutrons is a portable unit which requires no building modification and which is essentially a "black box" of neutrons with an on-off switch to control the neutrons. The price should not be above about $20,000 which is the same order of magnitude as other specialized analytical equipment such as the emission spectrograph. Finally, I think the unit should give fluxes approaching $10^8 - 10^9$ thermal neutrons $cm^{-2}$ $sec^{-1}$. This unit would not give the ultra-sensitivity so often referred to as the primary advantage of activation analysis, but it would be able for example to analyze for microgram amounts of vanadium in oil samples and somewhat larger amounts of a number of other elements. It would thus bring the technique of activation analysis within reach of a large number of laboratories.

As of the present date there are three machines which come close to satisfying these requirements. These are a Cockroft-Walton machine of Texas Nuclear Corporation, Box 9267, Allandale Station, Austin 17, Texas; a Van de Graaff machine of High Voltage Engineering Corporation of Burlington, Massachusetts; and another type of electrostatic machine manufactured by the SAMES Company, P. O. Box 150, Grenoble, (Isere) France. Each of these three machines costs about $20,000; each is about the same physical size; and each can deliver a current of about 1-2 milliamperes of deuterons to a target. (Other generators are being developed by a number of companies but to date these have not developed a sufficient beam for them to be very useful in thermal neutron activation analysis.)

We are interested in comparing for activation analysis purposes a neutron generator source of thermal neutrons with our reactor-pneumatic tube facility at the University of Michigan. The following sections describe our preliminary work with one of the machines mentioned above which I believe

applications of the fast neutron flux would be studied.

a. <u>Shielding and Installation</u>

Prior to the installation of the machine, it was decided to utilize solid concrete blocks in the construction of a portable shield room built against two walls of an already existing shielded room of large proportions. The blocks used were common concrete construction blocks (15-3/4" x 7-1/2" x 4") each weighing approximately 32 pounds. These were chosen because of their general availability and relatively low cost. The blocks were stacked in a horizontal interlocking pattern so that no vertical cracks could occur. The wall was stacked to a height of seven feet and a length of sixteen feet, leaving an open area seven feet wide.

Twenty-one "T" irons, 3" x 1-1/2", were laid inverted and parallel across to an 8"-"I" beam supported by two 6"-"H" beam pillars. Concrete blocks to a thickness of 1-1/2 feet were then added on top of the "T" beams, forming a roof. The end wall was left incomplete until after the installation of the accelerator. Figure 6 shows the partially completed room before the end was closed off. The generator has been swung away from its operating position for the picture.

A concrete block maze entrance was constructed to finish off the end of the room as shown in the scale drawing of Fig. 7. The complete accelerator shield room used approximately 2700 blocks or just under 50 tons of concrete with about 12 tons on the roof. The steel supporting members in this design could handle about 25 tons at safe design limits, therefore,

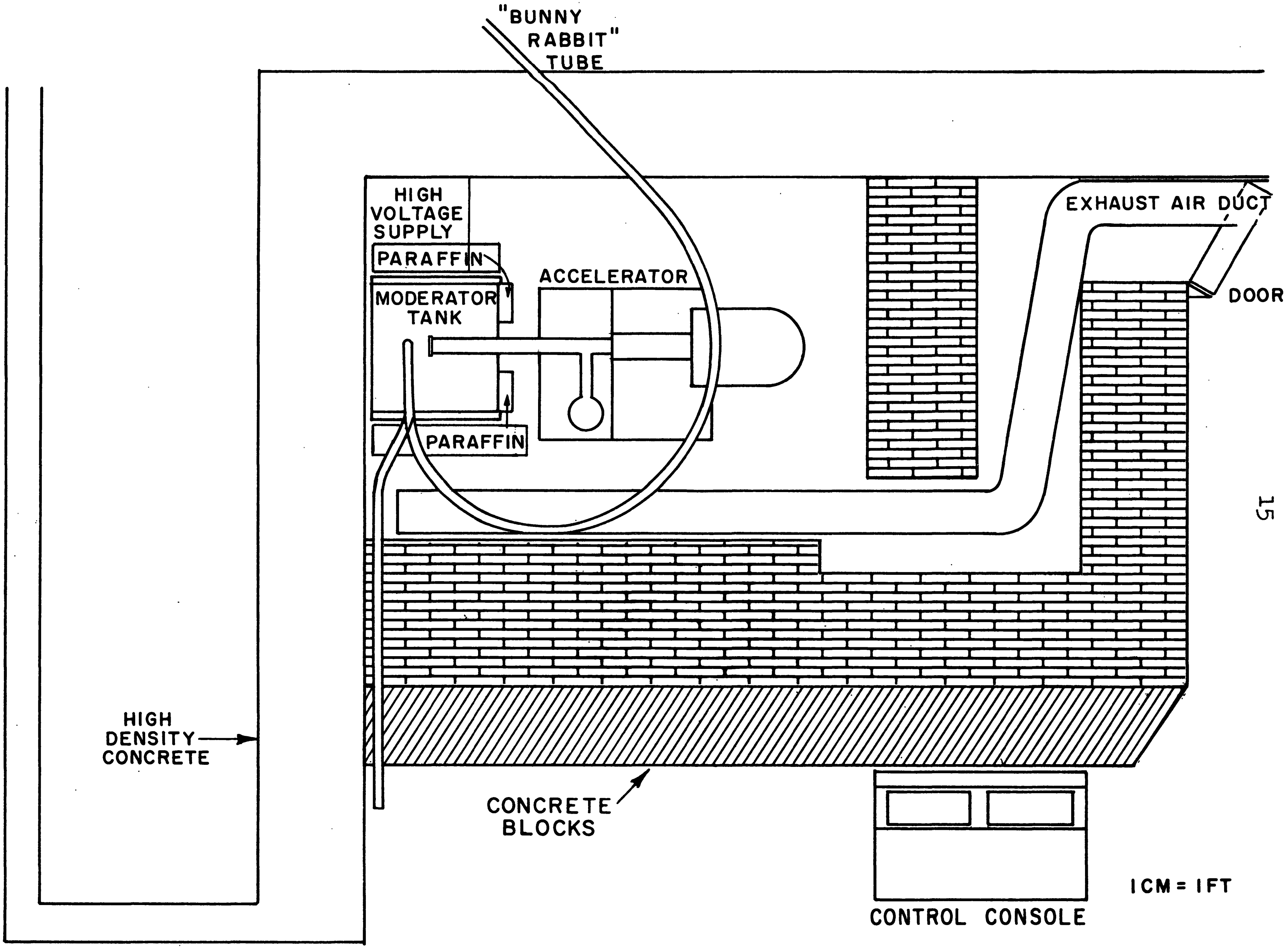


Fig. 7. Floor plan of neutron generator room showing shielding.

event tritium gas is lost off the target during operation.

The door at the entrance to the maze is four inches thick and made of plywood, filled with commercial grade boric acid crystals. A lock insures that the door can be opened only by key from the outside but at any time from the inside. Since the door is interlocked electrically to the accelerator, the machine cannot be run with the door open and shuts down immediately if the door is opened during operation. The machine is also interlocked to a warning light system, Fig. 8. If the door is shut, a 60 w red blinker light provides warning to any position in the room. Another warning light is located over the door and indicates the machine is running with the high voltage on. In addition an intercom from inside to outside the shield is available and is used chiefly during maintenance and test runs. (R. Shideler)

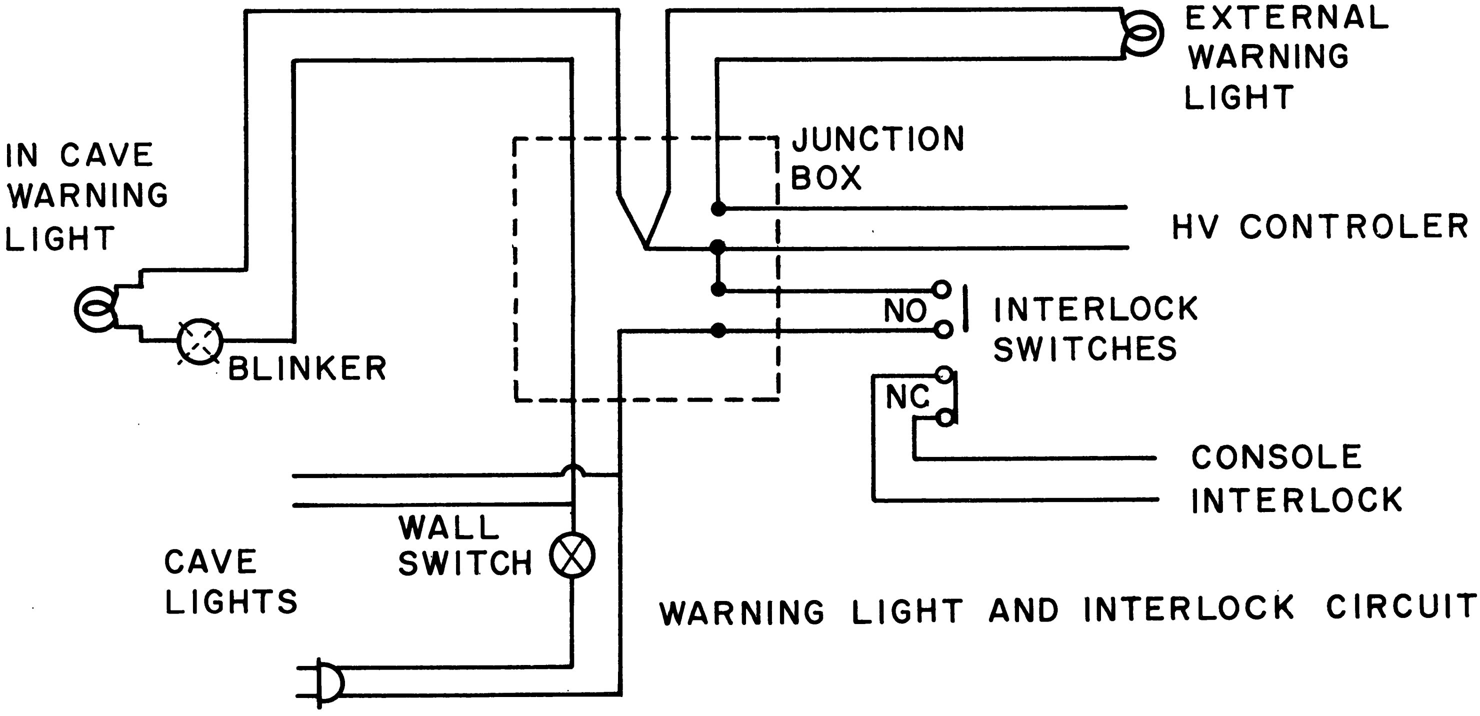


Fig. 8. Warning light and interlock schematic.

b. Moderator

The design of an efficient moderator to be used with the neutron generator was undertaken almost as a separate project. Since the neutrons leave the target with high energy (14.3 Mev) they must be slowed down considerably before they are useful for thermal neutron activation work. Reviewing the properties of various materials useful in the moderating of neutrons it was decided that water would be not only the least expensive moderator but also very effective for our purpose.

Since the neutrons leave the target at a $4\pi$ solid angle the fast flux density drops off as the square of the radius (the $r^2$ law). Therefore it is necessary and desirable to get the sample as close to the target as possible. Since a hydrogen atom has a mass of 1, closest to that of a neutron, the energy transferred per collision (energy lost by the neutron) is the highest and therefore requires the least average number of collisions (approximately 21) for thermalization. Hydrogen does have a considerably higher capture cross-section ( $\sigma$ = 330 mb) for neutrons than does deuterium ( $\sigma$ = 0.5 mb) but this disadvantage is balanced by the slowing down power of hydrogen, 1.14 for water versus 0.18 for deuterium oxide. The higher cross-section for thermal neutrons in water would cause an even more rapid drop off in thermal flux than $r^2$ would indicate if it were not for the fact that at small distances from the target the slowing down density still has a relatively high energy and the production of thermal neutrons from fast neutrons continues on until a distance such that a thermal equilibrium is reached. This being the case hydrogen seems to be a good moderator in the "point source" situation and materials having the highest hydrogen content were considered.

Long chain hydrocarbons such as paraffin are very good from this standpoint but due to the low density of paraffin the overall effectiveness of water should be ≈ 10% better. Another advantage of water (besides being non-inflamable) is that modification of experimental geometry can be altered at any time and with greater ease--a point that is important if variation of energy distribution is desirable.

The final design of the moderator tank provided for more water than was absolutely necessary as a moderator in order to provide an added measure of shielding around the target. The tank was made 30" square and 30" deep with a round bottom (Fig. 9). The tank was prefabricated out of 16-gage galvanized sheet iron and assembled inside the cave. Two rectangular steel frames provide support by means of 1" steel straps under the belly of the tank. (R. Shideler)

### c. Generator components

The neutron generator as supplied by Texas Nuclear Corporation consists of three separate units: the accelerator with vacuum system, a high voltage power supply, and a control console. These units, interconnected by cables, are capable of producing neutrons immediately upon installation with no further equipment necessary except for mounting a tritium target in the target holder and bombarding with

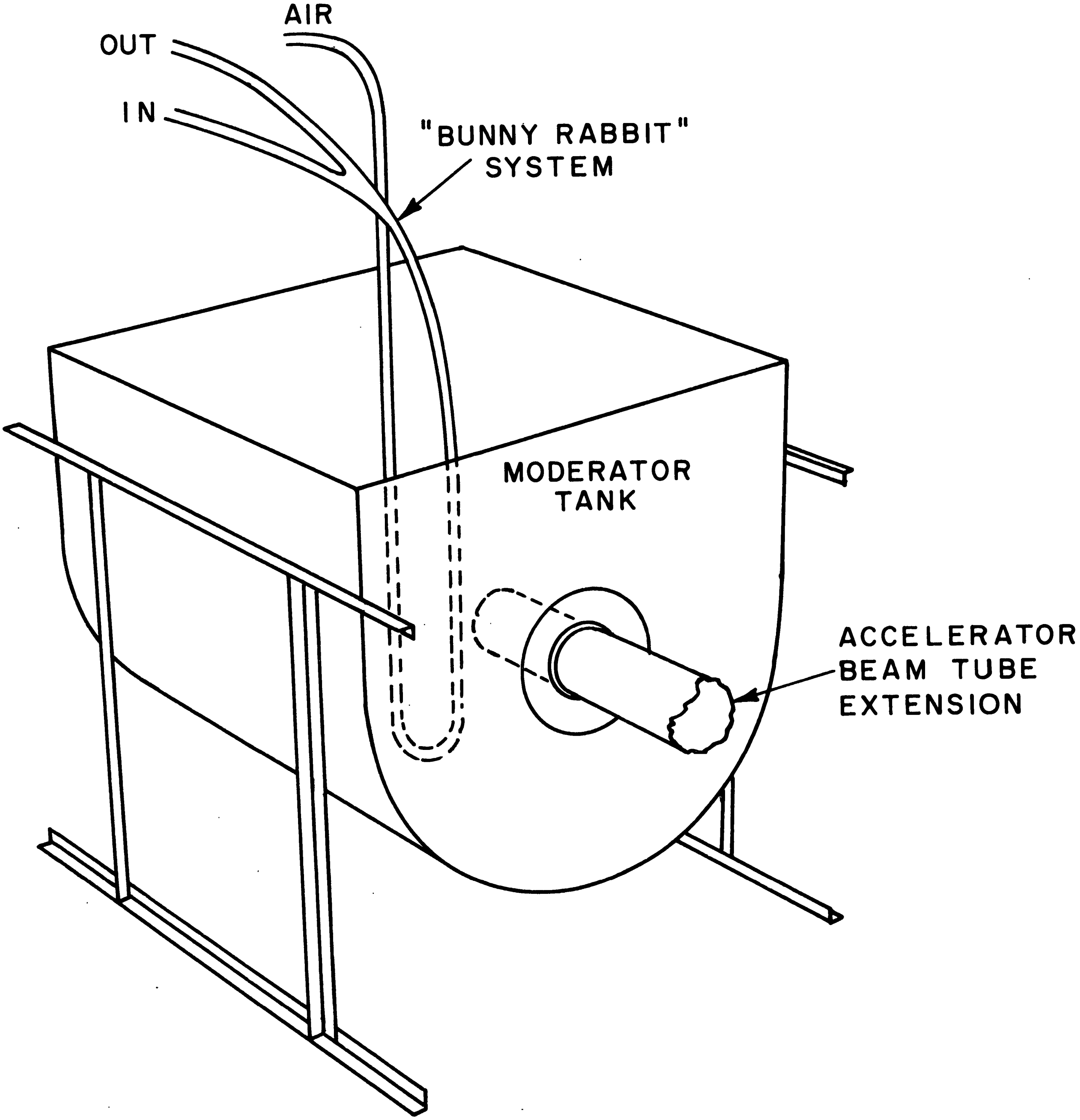


Fig. 9. Water moderator tank (30" x 30" x 30").

deuterium gas. Hydrogen is normally used for the initial "tuning up".

The accelerator beam tube, vacuum system, and associated electrical components are all mounted on a four wheeled chassis (Fig.10) of sturdy steel channel construction.

The vacuum system consists of a forepump (Fig. 10A), four-inch oil diffusion pump (Fig. 10B), cold water baffle (Fig. 10C) and a two liter cold trap (Fig. 10C,D). All parts are made of stainless steel with "O" ring seals at each flange, and two 2" gate valves (Fig. 10E,F) are provided to isolate the beam tube from the vacuum pumping system and the target end from the beam tube. An extended range Phillips type vacuum gage (Fig. 10G) is located near the cold trap. Two stainless steel flexible bellows are in the system to relieve undue stress and to provide a means of centering the beam on the target.

The beam accelerating tube itself (Fig. 10H) is bolted directly to the heavy aluminum faceplate and consists of eleven cylindrical ceramic rings bonded, sandwich style, directly to the disc-shaped accelerating electrodes. The electrostatic lens assembly is situated at the end, and the ion source bottle [inside terminal (Fig. 10J)] is coupled directly to it. On the other side of the faceplate, the drift tube connected also to the vacuum pumping system, is aligned with the accelerator beam tube and connects to the drift tube extension and target holder (Fig. 10K) completing the vacuum system.

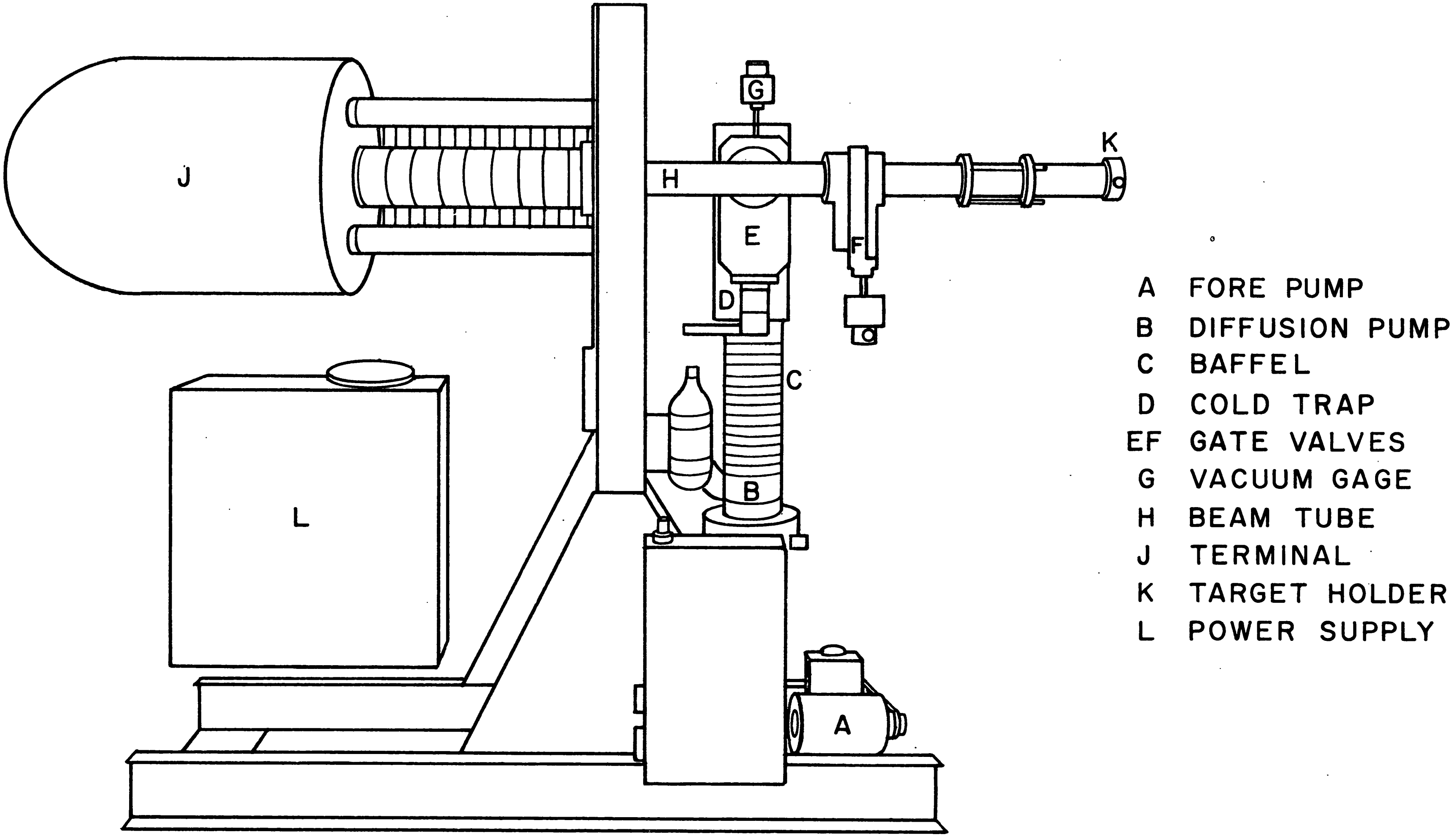


Fig. 10. Diagram of neutron generator components.

Electrically the machine consists of the terminal dome charged to a +100 kv potential by the power supply (Fig. 10L) with a divider string of 20, 5 meg resisters tapped off every other one to provide 10 kv steps of potential to the accelerating beam tube (Fig. 11).

An isolation transformer also situated in the high voltage power supply provides 117 volts AC terminal power. Operated by this are two small variable high voltage supplies, one 0-15 kv for the focus electrode, a 0- +5 kv supply for the extraction electrode, a very low voltage DC power supply for the ion source solenoid and a variable AC powerstat for the palladium leak heater. Each of these variable controls are operated by means of an insulating nylon shaft connected to control servo mechanisms on the main frame. Another rod operates a beam switch controlling power to the RF power oscillator. Controls for each of these functions are on the operators console (Fig. 12) which also contains the control panel for the high voltage power supply on the right as well as the vacuum gage panel control and a beam current meter. The vacuum gage instrument also contains a safety device which turns off power to the diffusion pump heater in the event of a vacuum leak causing loss of vacuum greater than a preset limit. (R. Shideler)

### d. Operating Procedure

Operation of the generator is basically as follows: Hydrogen or deuterium is admitted into the ion source bottle through the palladium leak. The palladium diaphragm is

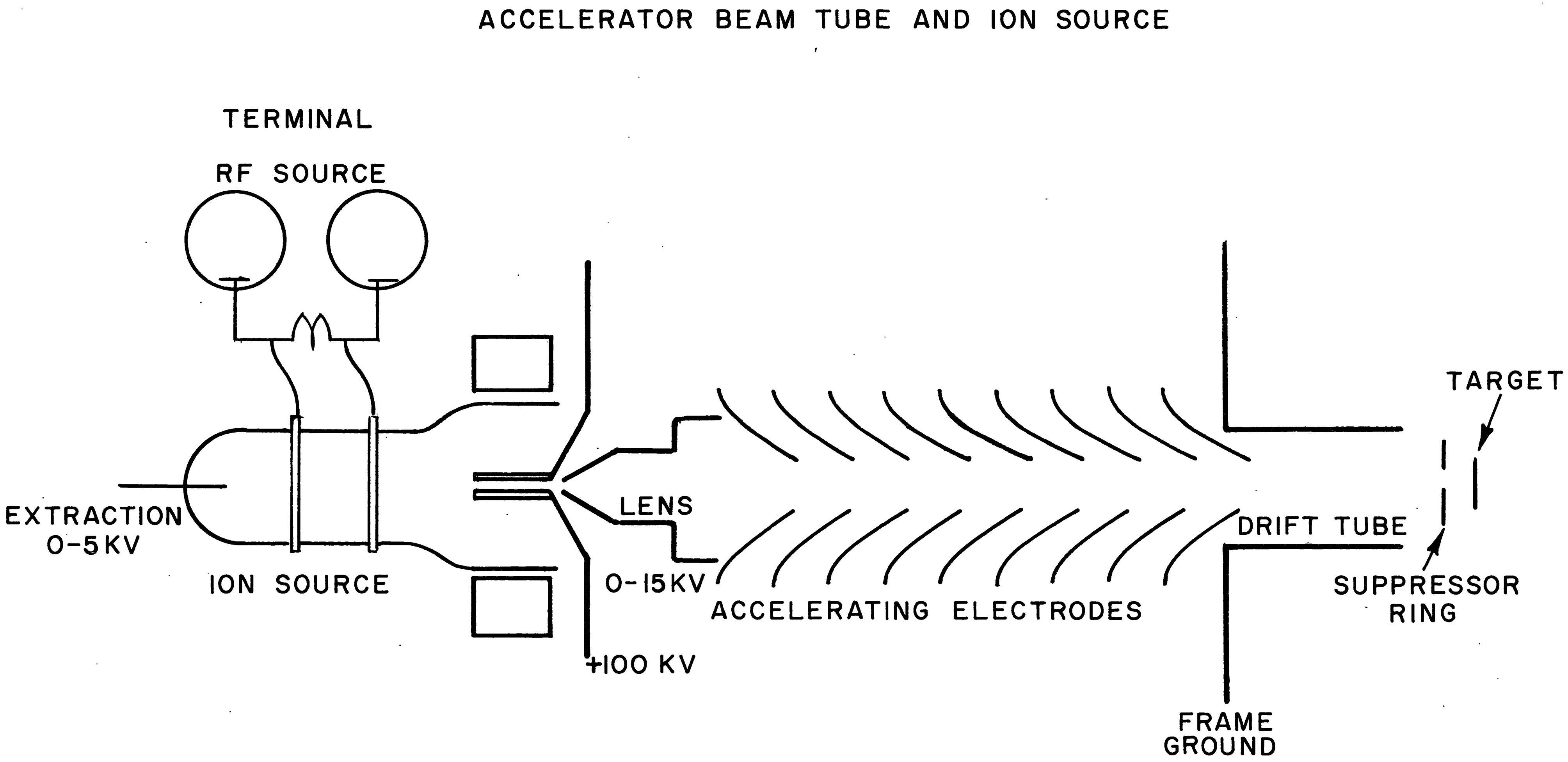


Fig. 11. Schematic diagram of accelerator beam tube and ion source.

permeable to these gases to a degree determined by its temperature. This is varied by electrical control from the operator's console. The RF power oscillator couples energy into the gas by means of two electrodes around the ion source bottle ionizing the gas. This action is further enhanced by the magnetic field produced in this region by the solenoid. Ions thus produced are accelerated toward the canal by application of a positive voltage impressed on the extraction electrode. This ion plasma is compressed by the magnetic field of the solenoid and directed further by the electrostatic field shaped by the quartz lens over the end of the canal. Ions passing through the end of the canal are focused and accelerated by the focusing electrode and then enter the beam tube for acceleration. After being accelerated they pass through the field-free region of the drift tube until they strike the target. The suppressor ring near the target is charged to -90 v to return to the target any electrons that might be emitted due to ion bombardment. If these electrons were permitted to accelerate back up the tube they could cause intense X-rays and excessive damage to the electrode structures.

Neutrons are produced when deuterons accelerated by 100 kv impinge on a tritium loaded target, $H^3(d,n)He^4$ +17 Mev. The $He^4$ comes off with 3 Mev energy and the neutron with approximately 14 Mev.

Normal operation of the neutron generator is quite simple and easily carried out. The first preparation for an irradiation is to ascertain that the vacuum system is tight and the vacuum is sufficiently good, better than $10^{-5}$ mm Hg. Enough liquid nitrogen is added to the cold trap for the duration of the run. With the target in place the target cooling water is turned on and the gate valves are checked to be sure that they are open. Making sure that no foreign object is near enough to the terminal to cause arcing the operator leaves the accelerator room and closes the door.

Terminal power is then turned on and the machine allowed to warm up one minute before the beam switch is turned on. With the terminal power on the servo controls on the console are now energized. Also if all interlocks are closed a green high voltage ready light will be seen on the panel. After a few minutes wait the vacuum gage should read approximately $2 \times 10^{-5}$ mm Hg; if not the deuterium control is adjusted accordingly.

With the sample to be irradiated in place the machine can now be brought up to power. The high voltage "on" button is pushed and a red "High Voltage On" light comes on. The voltage control knob is rotated slowly clockwise until the panel meter reads 100 kv. (The high voltage is internally protected against overvoltage or overload and if the voltage is set too high the power supply will shut itself off with an indicator light denoting the cause. With the voltage set at 100 kv the output current will read 1 ma even though no beam has been formed due to the current drain of the bleeder resistors.) Selecting the desired range of the beam current meter 0-100 $\mu$a, 0-1000 $\mu$a or 10 $\mu$a the focus control is set at about 15 turns. If a high beam current is to be used the solenoid will be turned up all the way. Now the extraction control is turned up until the desired current is reached. If maximum current output is required it is necessary to peak the current by varying the controls for extraction, focus, and deuterium pressure. (R. Shideler)

## 3. Experimental Results

The following sections give a chronological discussion of experiments done with our generator. Most of the problems encountered early in our work have subsequently been corrected by change of design of this machine. They are described here to give the reader a better perspective of the machine which has finally emerged to date and whose present characteristics are summarized at the end of this section. These points necessarily refer to the Cockroft-Walton machine we have used but can certainly be generalized to apply to each of the two types of electrostatic generators mentioned above--which in addition would have moving parts inside the vacuum system.

Our purpose in this work has been to evaluate a method and a technique and not a particular machine. Thus most of our observations are pertinent to any machine which can deliver 1-2 milliamperes of 100 kv deuterons to a tritium target, and we hope that their publication will accelerate the coming of the "ideal" neutron generator.

### a. Preliminary setting up

Operation of the accelerator for the first weeks after its initial installation was confined to hydrogen gas with a blank aluminum target so as to not produce neutrons. This was done to provide personnel with an adequate feeling for operation of the machine and also to allow time for completion of the shielding and other necessary associated equipment.

During this "shakedown" some troubles were experienced with the vacuum system. A severe leak developed due to a poor epoxy bond in the accelerator beam tube. Several other leaks that developed were quickly taken care of including one improperly assembled valve.

Operation at high beam currents proved to be difficult due to instability of the ion source and ocassional severe outgassing. A series of experiments to determine the best operating conditions for the machine was begun--adjustment of lens, RF electrode, and solenoid position as well as tabulations of lens voltage versus beam diameter and gas pressure versus beam current. Since so many variables are of first order importance no hard and fast set of rules was discovered.

Briefly some of the findings were as follows: The solenoid control is set at maximum for high beam currents. If beam currents lower than 2 or 3 hundred $\mu$a are desired the solenoid may peak at some lower setting, permitting lower extraction settings, etc. The extraction control is turned up at the beginning of a run until the desired beam current is reached. This may have to be readjusted for changes in gas pressure and if maximum output is required a peak will occur. Ion source stability is affected, being more stable below the extraction control peak and less stable at higher settings. Originally the focus setting was simply turned up to an arbitrarily prescribed limit of 15 turns, increased settings beyond this increased the beam current only slightly, 2 or 3%. The focusing lens and power supply have since been revised radically changing its performance (Fig. 13) such that more care in its adjustment is required.

Deuterium control adjustments are rather critical. In actual operation the control is set at 19 or 20 turns while variations of one half turn or less may be used for adjustment (Fig. 14). The gas pressure in the ion source appears to be at a partial pressure of about $1.5 \times 10^{-5}$ mm Hg, i.e. $1.5 \times 10^{-5}$ greater than the absolute pressure of the system. Therefore if the pressure of the system before operation is $7.5 \times 10^{-6}$ mm Hg the best operating pressure will be $\approx 2.25 \times 10^{-5}$. Pressures below optimum will cause the beam current to drop off and the ion source passes through an oscillatory mode blinking on and off at a visible rate of 10 or 20 pulses/sec as the gas pressure gets lower. Pressures above optimum cause a slower drop off in beam current but at some higher pressures and beam currents may cause enough dispersion of the beam to cause outgassing in the system with very high load currents (5 ma and greater) of the power supply. At near maximum beam currents the pressure must be increased slightly to make up for gas used in the beam.

Some physical adjustments were made in the positioning

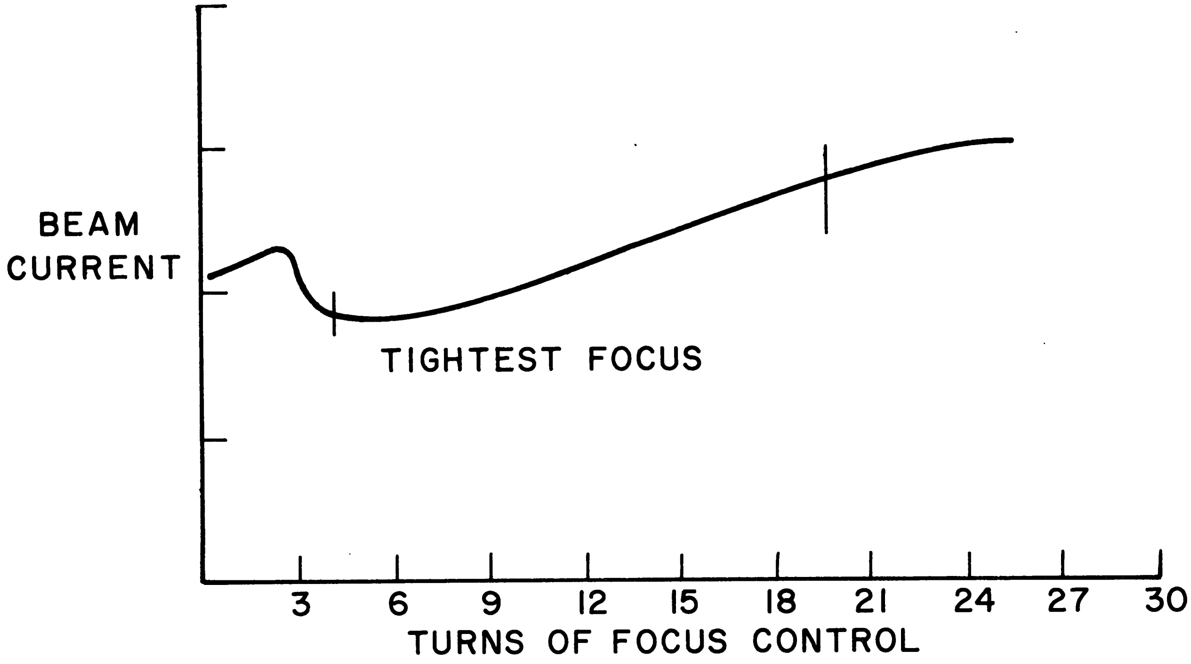


Fig. 13. Typical effect of focus control adjustment.

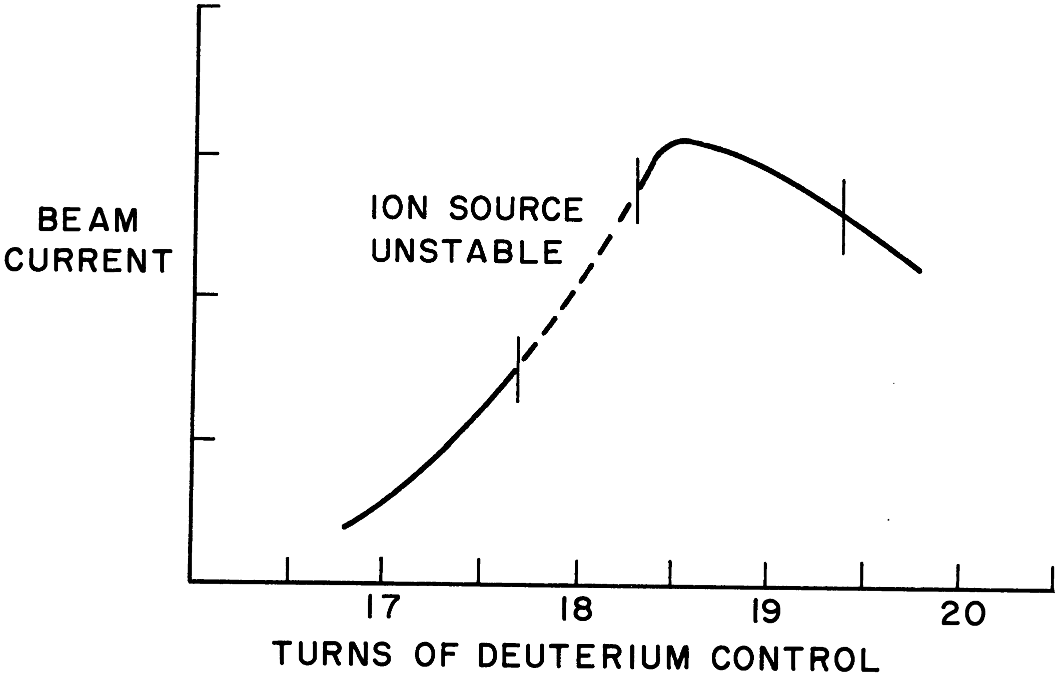


Fig. 14. Typical effect of deuterium control adjustment.

of the electrodes themselves. The ultimate beam current was varied by moving the RF electrodes back and forth on the ion source bottle with the maximum occurring when one electrode was located approximately half way down the bottle with the other electrode as close to the solenoid as possible without the RF arcing to the solenoid. This positioning however also effects the frequency of the RF oscillator and may be different under altered circumstances.

The lens electrode was also varied in position by screwing it in or out of the holder. Although higher beam currents were available (4 or 5%) when the tip was closer to the canal the criticality of the gas pressure was greatly increased. When the lens was moved away from the canal the ion source (gas pressure) was more stable and the beam more smoothly diffused. It should be said here that the beam is used as a diffused spot covering the entire target for best utilization of the target.

During the runs a rather high X-ray emission was found to be coming from the terminal end of the accelerator. These were due mainly to secondary electrons occurring when the beam struck a metal collimator plate in the drift tube. The collimator was removed but later a magnet was placed around the drift tube eliminating the problem entirely.

A few neutron runs were made using deuterium only, D(d,n)$He^3$ yielding 2.2 Mev neutrons. Since the reaction cross-section is small at 100 kv the neutron yield is relatively low. More work will be done with this reaction when a 150 kv power supply is available. Fast neutron yields on the order of $10^5$ neutrons per second $4\pi$ were detected at the target and no neutrons were observed on the outside. By this time the shield, interlock system and exhaust duct installations had been made and permission was given to run 14 Mev neutrons by the laboratory health physicists.

b. Neutron runs without water moderator tank

Near the end of January the machine was finally set up to run neutrons. The results of the first test were quite startling. Using a Nuclear Chicago Model 2112 fast neutron detector, readings were taken at various points about the shield (see Fig. 15) indicating fast neutrons at least 80 times above the tolerance value of 10 n $cm^{-2}$ $sec^{-1}$ for a full week's continuous operation. These rough readings are given in Table III for different current values.

Table III. Neutron Monitoring[a] of Work Spaces Near Accelerator. Position numbers refer to Fig. 15.

| Beam Current | 100 $\mu$a | 200 $\mu$a | 600 $\mu$a |
|---|---|---|---|
| Position 1 | 400 c/m | 1000 c/m | 2500 c/m |
| Position 2 | 2500 c/m | | 10500 c/m |
| Position 3 | 500 c/m | | |
| Position 4 | 300 c/m | | |

[a] Neutron monitor, Nuclear Chicago 2112

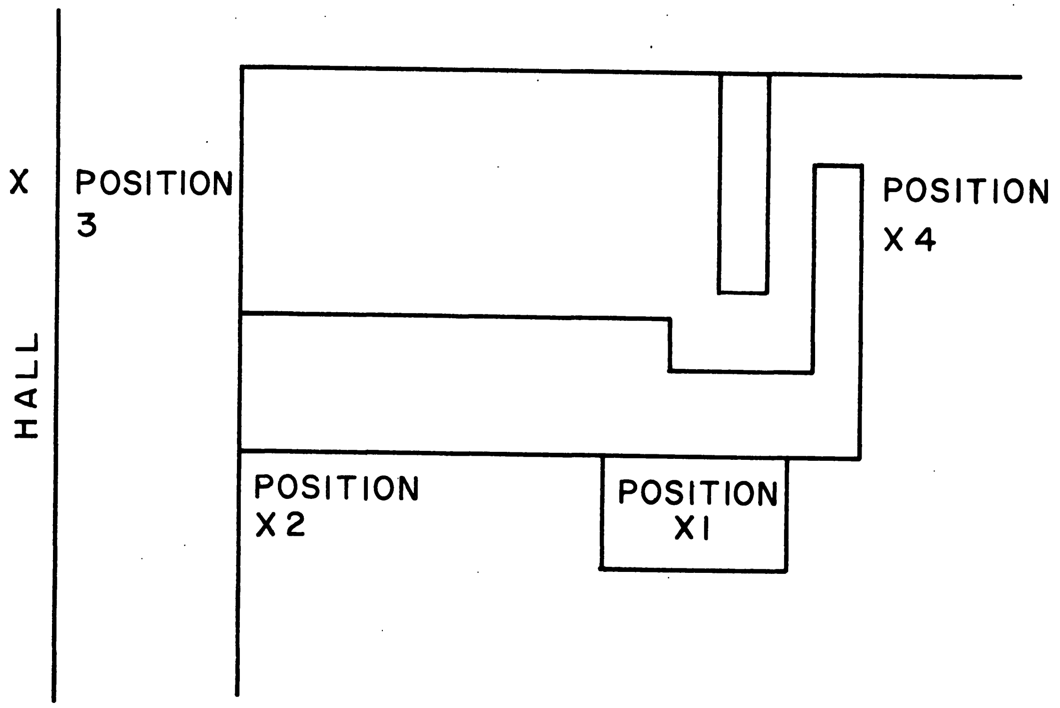


Fig. 15. **Monitoring positions outside the neutron generator shield.**

Next indium foils (both moderated in 4" paraffin blocks and unmoderated) were placed around the shield to provide a more accurate determination of flux levels outside the shield (Table IV).

Table IV. Neutron Monitoring by Indium Foil Activation. (Beam current, 750 $\mu$a for 30 minute irradiations.)

| | Moderated<br>4" Paraffin | Unmoderated |
|---|---|---|
| Position 1 | 7.5 x $10^3$ c/m | 6.3 x $10^3$ c/m |
| Position 2 | 21.2 x $10^3$ c/m | 18.0 x $10^3$ c/m |
| Position 3 | 4.2 x $10^3$ c/m | 2.5 x $10^3$ c/m |
| Position 4 | 3.0 x $10^3$ c/m | 2.0 x $10^3$ c/m |

Another run using these foils was made at the same beam current with the target area completely surrounded by $\approx$ 1 foot of paraffin wax. This reduced the thermal neutrons by a factor of $\approx$ 2 and the fast neutrons by a factor of between 3 and 4 (Table V). The flux at the target, measured by gold foils inside a 4" cube of paraffin was approximately $2 \times 10^6$ n $cm^{-2}$ $sec^{-1}$ or equal to a $4\pi$ production rate of $\approx 5.5 \times 10^8$ neutrons per second.

Table V. Neutron Monitoring by Indium Foil Activation. (Beam current, 750 $\mu$a for 30 minute irradiations and with $\approx$ 1 foot of paraffin around target.

| | Moderated 4" Paraffin | Unmoderated |
|---|---|---|
| Position 1 | $3.6 \times 10^3$ c/m | $3.2 \times 10^3$ c/m |
| Position 2 | $6.4 \times 10^3$ c/m | $5.5 \times 10^3$ c/m |
| Position 3 | $1.3 \times 10^3$ c/m | $0.98 \times 10^3$ c/m |
| Position 4 | $1.5 \times 10^3$ c/m | $1.0 \times 10^3$ c/m |

### c. Neutron runs with 7" water moderator

Permission to operate the machine was suspended by the laboratory health physists on the grounds that it was a health hazard until shielding could be improved to provide a safe level of neutrons external to the shield. A plastic garbage can was purchased and a hole cut in the side to permit the target end to protrude into its center. A polyethylene bag, sealed to the edges of the hole allowed the vessel to be filled with water surrounding the target area with a minimum of 7" of water moderator. The results of tests using this arrangement are shown in Table VI. The reduction of the fast flux using the water moderator was between 3 and 10 times which was quite encouraging.

Table VI. Neutron Monitoring[a] of Work Spaces Near Accelerator. Position numbers refer to Fig. 15.

| Beam Current | 1 ma with 7" water moderator | 100 μa unmoderated |
|---|---|---|
| Position 1 | 1100 c/m | 400 c/m |
| Position 2 | 3000 c/m | 2500 c/m |
| Position 3 | 400 c/m | 500 c/m |
| Position 4 | 400 c/m | 300 c/m |

[a] Neutron monitor, Nuclear Chicago 2112

On the basis of these tests a large tank 30" x 30" x 30" (Fig. 9) and discussed in Section 2b above, was constructed to serve the dual purpose of moderator and shield. A hole in the side permitted the beam tube (now increased in length to 14") to be situated at the center of the tank. Sealing the beam tube in the tank was done by seating a 2" "O" ring on the glass of the beam tube extension in a flange sealed to the tank. When the tank was first filled with water the beam current meter indicated a reading of greater than 100 μa. This current was attributed to electrolytic action on the target holder even though the entire inside of the tank was painted with Amercoat paint. The electrolytic effect had been noted before in the plastic can but was considered tolerable. The problem was taken care of temporarily by coating the target holder carefully with Amercoat which reduced the current to less than a μa.

### d. Approach to routine operation

At about the time serious scheduled operation was to commence, the accumulation of further data was curtailed due to a series of mishaps and failures. First, a temporary target cooling water line parted, causing a flood with water getting into the mechanical forepump. The mechanical forepump was restored to operation after several flushings with new pump oil. A curious failure next occurred when a vacuum leak occurred coincident to the failure of the vacuum gage, counteracting the effect and making it appear as though the vacuum was normal for operation. Although the vacuum appeared to be normal, the operation of the machine seemed peculiar. Something was wrong, but it was not possible to ascertain just what.

The solution of this dilemma was first brought to light when a leak was discovered using a vacuum leak detector inside the bottom of the cold trap. The machine again was operated, only to have a vacuum leak develop at the seam of the drift tube flange. Again, the mechanical forepump failed, probably due to the previous time when water got into it. The forepump was subsequently replaced. The Texas Nuclear

Corporation, concerned by the apparent difficulties we were having with this early model of their unit, had their Toronto representatives call on us at this time. It was decided that, although the machine was again ready to operate, Texas Nuclear would supply us with a complete new beam tube assembly. Also replaced were the power supplies for the lens and extraction controls. These, being of new design, would correct the difficulties we had been experiencing with the ion source stability. Upon completion of this work, the machine was found to run more smoothly than ever before with all instability of the ion source eliminated!

### e. Shielding survey

With the machine once again in operating condition, a neutron mapping program was carried out under the direction of the University Radiation Control Service for purposes of determining neutron health hazard in areas near the machine under severe conditions.

Shielding of the target was altered between runs to show effects of additional moderating material. First, the machine was run with the water tank filled. Another run was made with one foot of paraffin added to the sides of the moderator tank and four inches at the front of the tank. These runs showed that the addition of the paraffin reduces the neutron flux external to the shield by about a factor of 2 at the operator's console. To reduce this even farther it was decided to increase the thickness of the concrete wall by adding another layer of concrete block. The decrease in flux due to the additional concrete shielding was later shown to also be approximately a factor of 2.

Our present shielding arrangement for the neutron generator is shown in Figure 16 and the experimental information on neutron hazards is summarized in Table VII. It should be kept in mind that the value of 10 n $cm^{-2}$ $sec^{-1}$ mentioned as a tolerance value is based on continued exposure for a 40 hour week. These generators are not adaptable to this type of continuous operation and instead will be used generally for numerous short irradiations of 5 or 10 minutes at the most.

Table VII. Neutron Monitoring of Area Around Portable Generator. (n $cm^{-2}$ $sec^{-1}$)

| Position | Concrete Only | Water Moderator Added | Paraffin Added Without Water Moderator | Paraffin Added With Water Moderator |
|---|---|---|---|---|
| A Console | 200-300 | ~25-30 | 125-175 | 15 |
| B Hallway | ~100 | ~10-20 | ~100 | ~10 |
| C X-Ray Room | ~100 | ~15 | 50-100 | <10 |

Height to floor above generator: 15'
Shielding: 2' concrete + ~8" floor
Dosage: at floor level above: 1-2 n $cm^{-2}$ $sec^{-1}$

These hazard values are of course dependent upon the flux of neutrons being generated at any given moment which, we will point out below, varies from hour to hour with the present machine. However, we feel that with proper arrange-

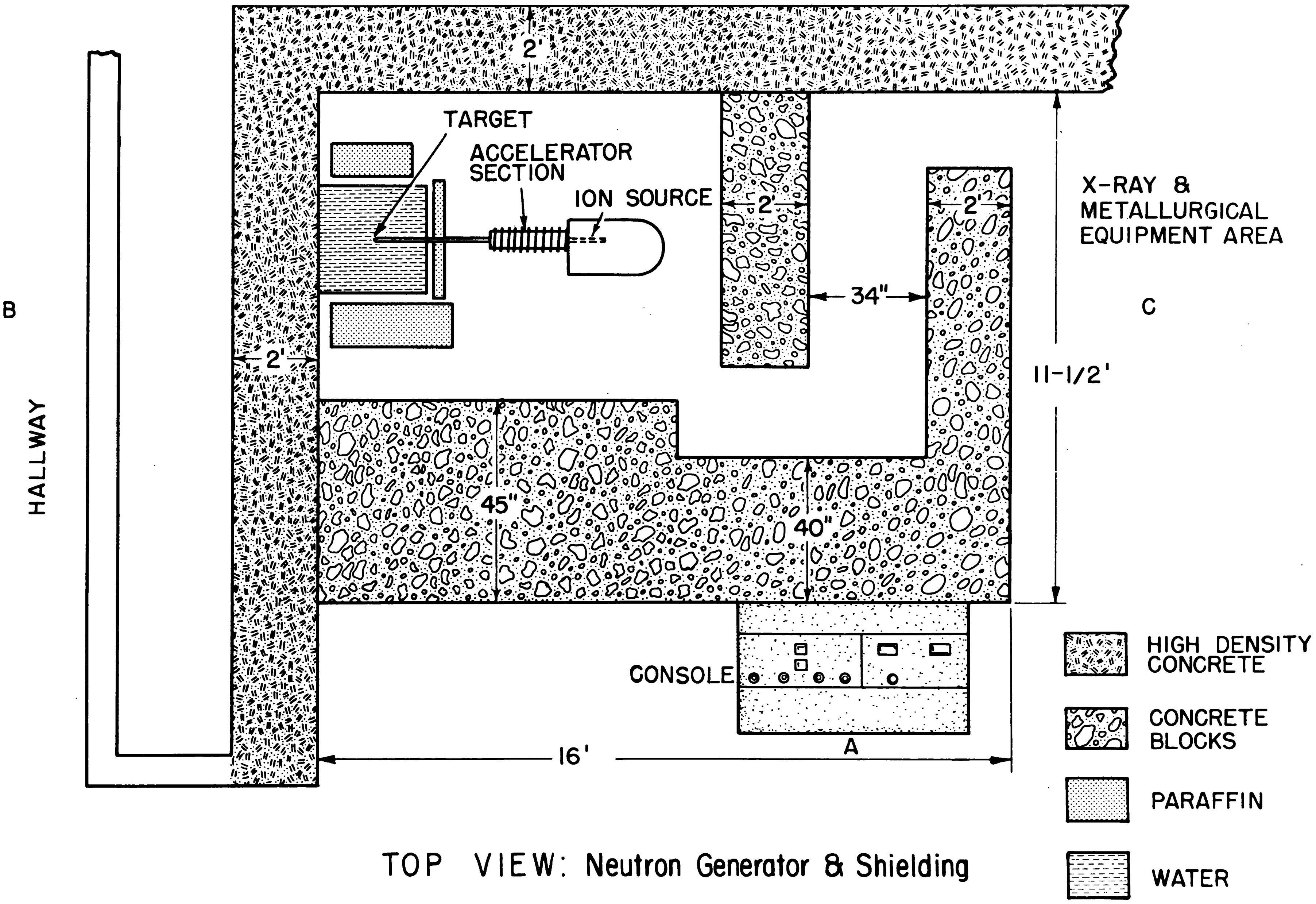


Fig. 16. Shielding arrangement for neutron generator.

ment of portable shielding we can handle safely on an intermittent basis optimum thermal fluxes of between $10^8$ and $10^9$ n $cm^{-2}$ $sec^{-1}$. Hazard measurements are taken periodically during operation and everyone associated with the project wears a neutron film badge. (R. Shideler, M. Wahlgren, W. W. Meinke)

### f. Experimental evaluation of target and moderator system (I)

Work proceeded now to determine optimum geometry of the sample position in the moderator and to establish the useful target life at high beam current operation. The newly installed "bunny rabbit" system, connected to the bunny system in use between the hot lab and the counting room (Fig. 3) was used to transport gold samples in some of the tests from their irradiation position in the moderator to the counting room. Other tests using small gold foils taped to a plastic rod served to map the thermal neutron flux in the moderator as shown in the next section.

Experiments determining tritium target burn-up rate at various beam currents were also performed (Fig. 17) showing that the target when new at beam currents less than one milliampere produced more than five times as many neutrons as it did after the first milliampere hour and then proceeded to fall off at a rate of about 50% per milliampere hour for a total of about five hours when the supply of tritium was exhausted. At beam currents higher than this or with the beam focussed to provide an area of high current density on the target, localized heating may cause loss of tritium gas,

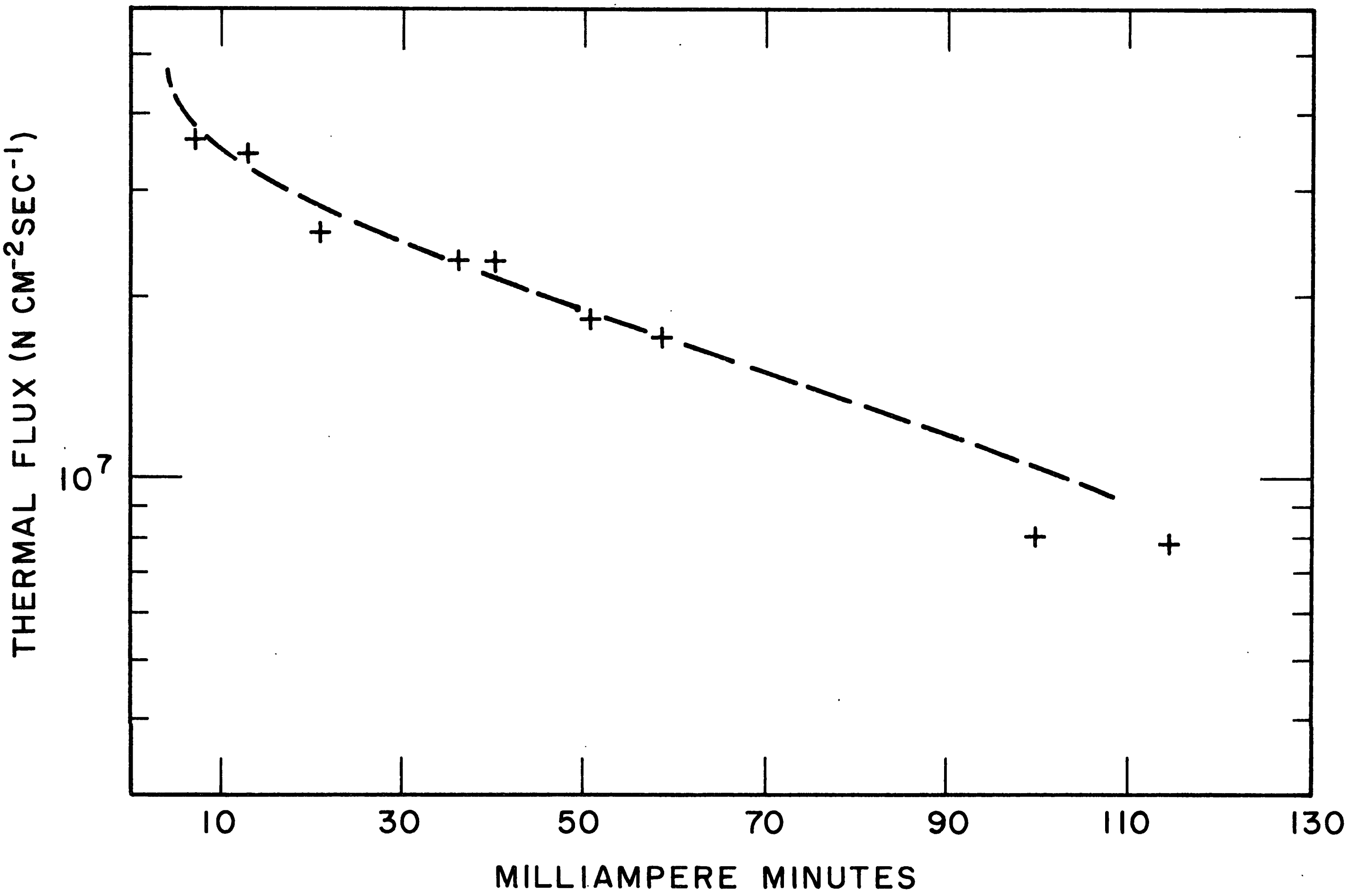


Fig. 17. Tritium target burn-up rate. This curve is very approximate and can change with conditions.

greatly reducing the target life.

While this work was carried out, a modification of the target holder was made (Fig. 18) to facilitate target replacement. Due to the length of the beam tube extension, some difficulty had been experienced in centering the beam on the target. The "electron suppresor ring" was modified to allow the beam to fall only on the target proper (Fig. 18). With this arrangement, misalignment can be detected since the current collected by the ring is a minimum when the ring is centered. This arrangement centers the beam very well but cannot provide information about the beam spot focus.

At present writing, an optical system for remote viewing of the target is being prepared to enable the operator to

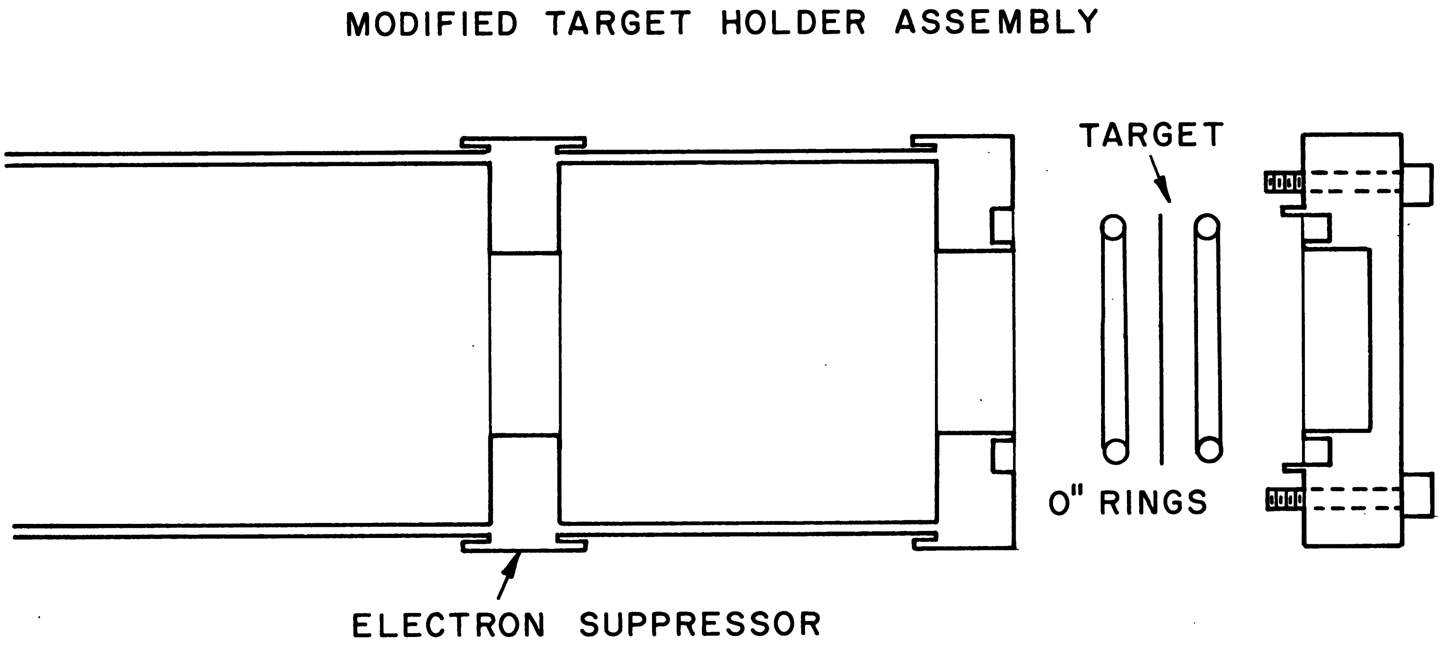


Fig. 18. Modified target holder assembly for Ti:$H^3$ target.

determine exactly how and where the beam strikes the target. (R. Shideler, M. Wahlgren)

### g. Experimental Evaluation of Target and Moderator System (II)

In view of the proposed flexibility of the system for either fast neutron (n,$\alpha$; n,p; n,2n) or thermal neutron (n,$\gamma$) activations, experimental data have been obtained for a number of useful parameters of the target-moderator system. Some of these such as target life and maximum flux may be revised on the basis of further experience.

#### 1.) Target

The targets used have been the standard commercially available type of ~1 curie/in$^2$ of $H^3$ adsorbed in a 700 Å layer of titanium on a 2 mil stainless steel backing foil, cooled by 300-500 ml/min of tap water. The rate of decrease of neutron flux has been 50% per 50-60 milliampere minutes of running time at normal beam currents of 600-800 microamperes (see previous section). This exponential decrease is consistent with a postulated tritium displacement, corresponding to a rate of tritium loss close to one half of the rate at which the beam adds deuterons to the target ($6.3 \times 10^{15}$ sec$^{-1}$). Because of uncertainty as to beam spot size on the target and as to variation from target to target, the effect of surface heating on tritium loss due to the high beam current has not been established. If the displacement hypothesis is correct, the slope of neutron output versus milliampere minutes would be unchanged but the line displaced upward for lower beam currents, corresponding to a higher $H^3$:Ti ratio stable at the lower surface temperature.

## 2.) Neutron output

The neutron output was determined by irradiation of several Cu foils at varying distances from the target and counting the 9.9 min $Cu^{62}$ activity from the n,2n reaction on $Cu^{63}$. The total $4\pi$ neutron output from new targets has been $\sim 1.5 \times 10^{10}$ $sec^{-1}$ using an (n,2n) cross-section of 550 mb. This corresponds to a 14 Mev neutron flux of $3 \times 10^8$ n $cm^{-2}$ $sec^{-1}$ at the fast neutron irradiation position located at $\sim 2$ cm from the target foil.

## 3.) Thermal neutron flux

The $(n,\gamma)$ activation of gold foils versus distance from the target foil in the water moderator (in the forward direction) is shown in Fig. 19. At the target holder a considerable amount of $Au^{196}$ is also formed. The thermal flux obtained with relatively new targets has been about $4 \times 10^7$ n $cm^{-2}$ $sec^{-1}$ at the position of maximum flux. The 14 Mev flux versus distance in the moderator is shown in Fig. 20, measured using the (n,2n) reaction of $Cu^{63}$. Thermal neutron irradiations are made at 5 cm from the target foil, where the thermal flux is still relatively high but the primary neutron flux diminished by distance and moderation. The Cd ratio at this position for 1 mil gold foils is 9 which is somewhat lower than the 15 observed at the reactor irradiation stations.

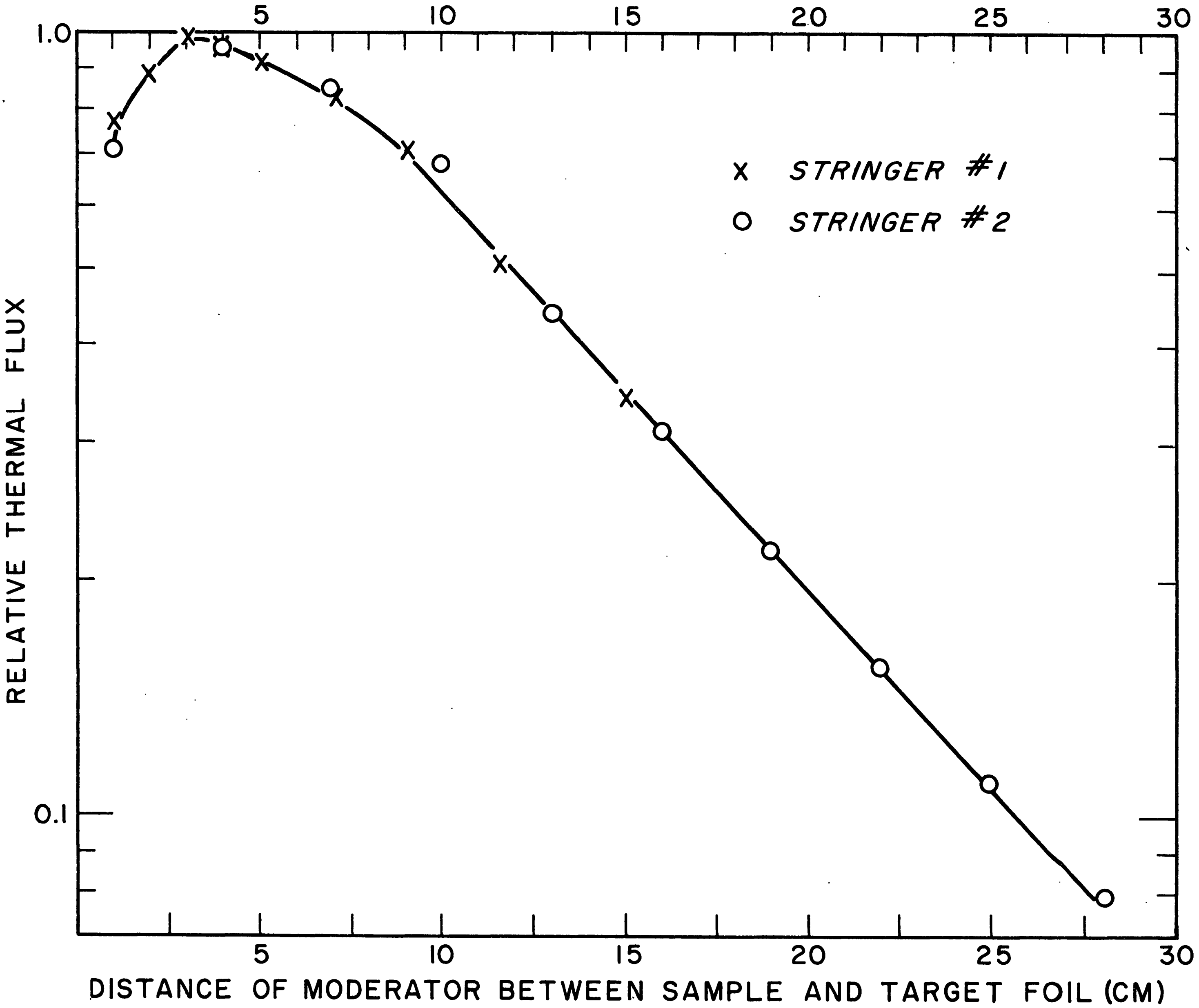


Fig. 19. Distribution of thermal neutron flux from neutron generator.

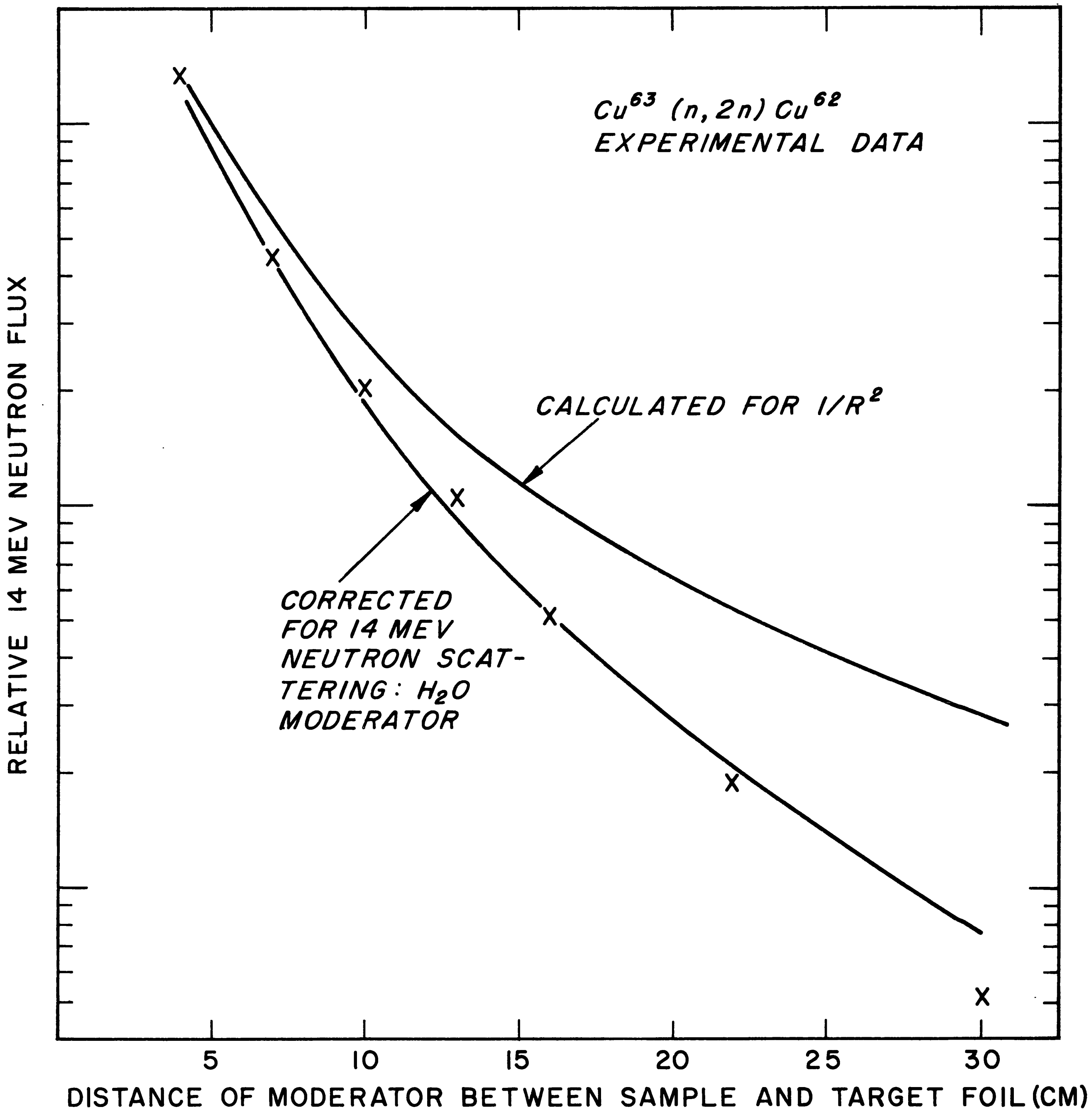


Fig. 20. Distribution of fast neutron flux from neutron generator.

## 4.) Conclusion

The data obtained up to this point indicate at least the lower limit of the thermal and fast neutron fluxes available with this system. These data also point out a difficulty inherent in the system from the standpoint of thermal fluxes e.g., the low scattering cross-section of hydrogen for 14 Mev neutrons. The scattering half-thickness in water for these primary neutrons is ~15 cm and consequently only a small fraction of the neutron output is moderated to thermal energy in a useful distance.

To study any correlation between the thermal conductivity of the target backing material and the target life with this system, a target of Ti on 5 mil Cu has been obtained. The initial neutron output was the same as from stainless backed targets. The Cu backed target will be run for an extended period after more data have been accumulated on the stainless steel backed targets.

Among future experiments will be one to determine the effect on thermal flux of replacing part of the water moderator with concentrated aqueous solutions of elements with higher scattering cross-sections for 14 Mev neutrons, and utilizing neutron multiplication and wavelength shift by the (n,2n) reaction. (M. Wahlgren, R. Shideler)

## 4. Summary of Experience to Date

How well does this generator satisfy the criteria we set up earlier? It is portable and new modifications in designs of several of the machines will make them even smaller.

No building modification is required for installation and safe operation--only a relatively large room on a ground floor which is capable of holding the weight of the shielding is necessary.

The three units considered are still not in the category of "black box" sources of neutrons although the revised unit we have been working with for the past few months has given us little trouble. There are still occassional vacuum line problems but introduction of VacIon pumps in place of the oil diffusion pumps with resultant simplification of the vacuum system should reduce these. Eventually a completely enclosed generator tube would be ideal but to date fluxes from this type of tube are much too low.

The three units mentioned all sell for about $20,000 and apparently they will stay at about this level because of competition, even while being improved. The fluxes obtainable are still short of that desired but it appears that with our machine we should be able to approach $10^8$ n $cm^{-2}$ $sec^{-1}$ regularly. With present target design though, $10^9$ n $cm^{-2}$ $sec^{-1}$ seems unlikely. The target lasts for only a few hours but actually this still means that many 5 or 10 minute irradiations can be made--and a new target costs only about $50.

Thus it appears that any of these three generators can be useful to many laboratories at the present time as an intermediate level source of neutrons and I feel that within the next year or two developments in target and generator design should bring them close to the "ideal". (W. W. Meinke)

# II INSTRUMENTATION

## A. 100-channel Pulse Height Analyzer

The 100-channel analyzer has been in operation all year with only a few major failures. The analyzer has been drifting 2-3 channels over a 24-hour period due primarily to the amplifier and phototube circuits. It drifts ~1/4 of a channel due to a base line shift over 24 hours. The analyzer is linear except for about the first 10 channels.

The analyzer has been used about 1800 hours this past year. There have been encountered the normal number of tube, resistor and diode failures with a few of the more critical trigger circuits becoming more sensitive to tube replacement indicating age and heavy usage.

The purchase of the second printer unit as mentioned in Progress Report 8 (1), has cut down the inoperative periods due to print wheel jamming and locking failures. Each print unit runs about five months or ~800 hours before it is necessary to be overhauled. The analyzer has been inoperative about 45 hours this year giving about 95% "up time". Most of the down time was caused by a tube failure, minor resistor replacement, or a readjustment.

There were, however, several breakdowns which put the analyzer out of use for 4 hours or more. In December 1959 a multi-resistor burn-up in "toggel 2's" circuit shut down the converter. This breakdown took ~ 4 hours before the trouble was located and repairs made. About March an unusual trouble kept appearing. The printer would not print out numbers above 999 for A unit. Before the cause of the difficulty was found, about 8 hours were lost. The failure was traced to a heat sensitive circuit in A's address advance control. In early August 1960 the live timer became erratic, counting correctly for A unit but not for B unit and vice versa. The analyzer was down about 8 hours before the trouble was located. A redesigning of the power supply for the +300, +400, and +450 volt power supplies corrected the difficulty. Previous to this, the power supply contained a double full wave germanium rectifier circuit and the voltages were low by ~20 v. This was replaced by a silicon double bridge using M-500 rectifiers which brought the voltages back to their specified range. About 4 full days have been lost due to failure of the room air-conditioner--complete shut down of the analyzer was necessary to prevent damage by overheating. The failures are becoming more and more those encountered with resistor aging, wire insulation cracking, and changing circuit values. (H. Nass)

## B. Analyzer Live Time Test

A malfunction of the analyzer live time circuitry was indicated early this year by some anomalous experimental results. Since live time corrections are frequently necessary when working with short-lived activities, a simple experimental test was set up to establish whether the circuit is working properly or not. The photopeak area of a $Cs^{137}$ standard of low count rate ($>95\%$ live time) is measured, and then with the $Cs^{137}$ sample in the same geometry, an active source of low energy pulses ($P^{32}$ bremstrahlung for example) is added, and the composite sample counted. Live timer malfunctions then show up on comparison of the $Cs^{137}$ photopeak areas of the two samples. (M. Wahlgren, H. Nass)

## C. 3" x 3" NaI(Tl) Crystal

The resolution of the 3" x 3" NaI(Tl) crystal obtained in June 1957 became poorer with loss of gain (Fig. 21). The crystal did not appear to be defective. Checks showed that an A. C. ripple of ~1.5 v on our signal cable could be reducing the gain and resolution. The ripple was corrected but the resolution improved very little. A D. C. filament supply and several new 3" photomultiplier tubes were tried but the loss in the resolution and gain continued to exist.

A careful inspection of the 3" x 3" crystal was made using a high radiation field of $Co^{60}$ to determine if any diffraction planes had developed within the crystal--none had. At this time the crystal was viewed under a fluorescent light fixture and an extremely yellow coating around the crystal was disclosed. (Only a faint yellow tint could be observed under normal filament light bulbs.) Consultation with Harshaw confirmed our belief that an air leak had occurred and the crystal was deteriorating.

The reactor shut down for several weeks in August and September; therefore the faulty crystal was sent to Harshaw to be repotted and put into an integral line assembly. The resolution of the repotted crystal using a D. C. filament supply and running the phototube voltage at 970 v was 7.0-7.2% for $Cs^{137}$ with a peak to valley ratio of ~10 - 1 with the $Co^{60}$ peaks.

The resolution of the repackaged crystal and that obtained for the corresponding gamma rays with the same crystal in 1957-1958 are shown in Fig. 21. The improvement of resolution versus gamma ray energy is plotted in Fig. 22. The precision of the data over the energy range for which comparison data is available is sufficient that the slope of the line is real but probably not exact. The slope of this line seems opposite in direction to that to be expected for a series of statistical processes.

The improved resolution at higher gamma ray energies is of special interest in this laboratory for the study of short-lived fission products and in future capture gamma ray experiments.

A second integral line assembly has been ordered from Harshaw and it is planned to mount the two 3" crystal assemblies opposite each other to approach as close as possible a $4\pi$ arrangement to increase the measurement efficiency available. (H. Nass, M. Wahlgren)

## D. 80 Mil Thick NaI(Tl) Crystal

An 80-mil thick, two inch diameter, NaI(Tl) crystal with a 1-mil aluminum window was purchased from Harshaw Chemical Co. in May 1960. This crystal is used to measure the spectra of X-rays and $\gamma$-rays with energies up to $\sim$ 80 kev without interference from higher energy $\gamma$-rays. The crystal has proved to be very useful especially in the region from 10 to 40 kev. Figure 23 shows a spectrum of irradiated Te metal taken with the gamma ray spectrometer using the 3" x 3" crystal and the 80-mil crystal. (H. Nass)

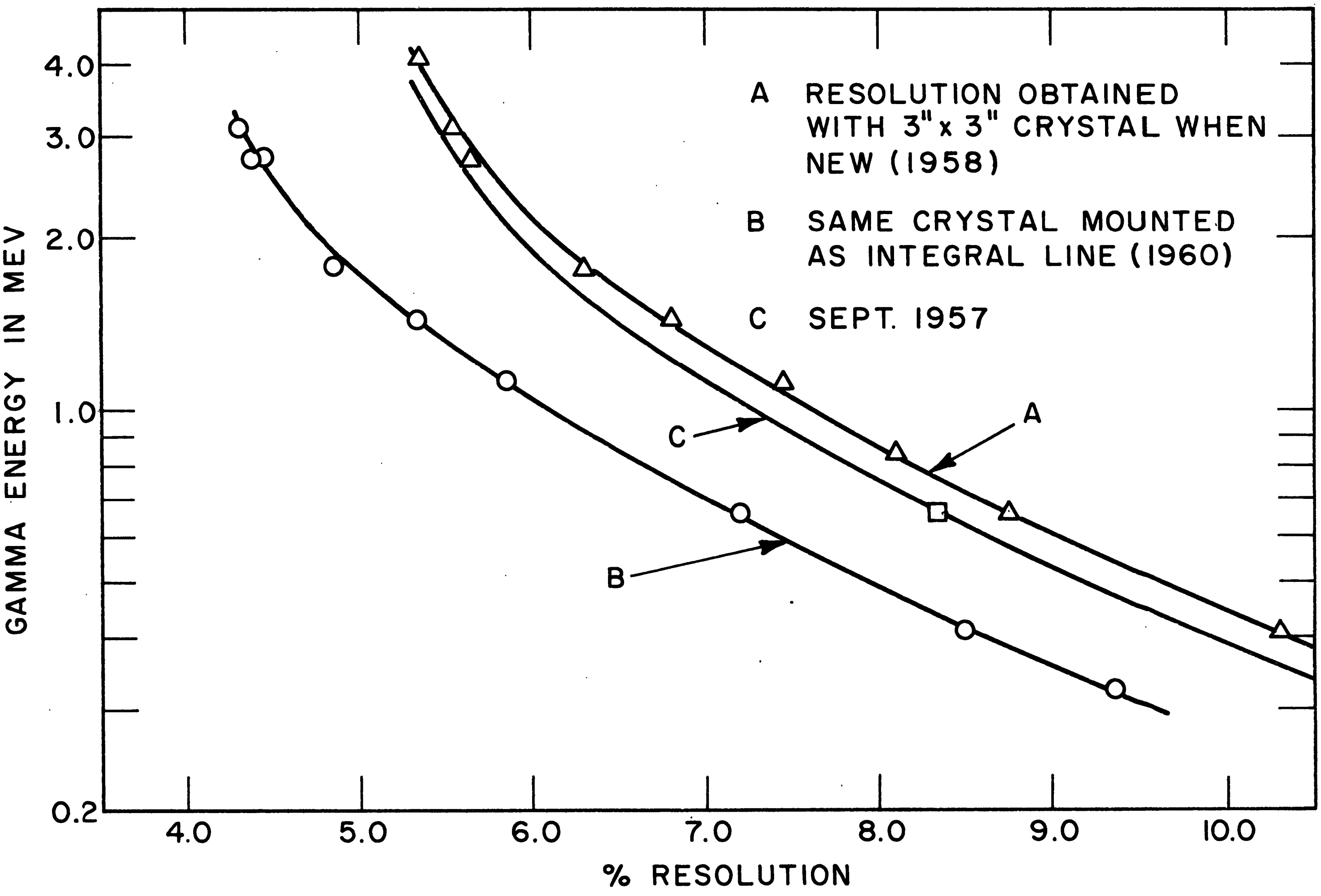


Fig. 21. 3" crystal resolution for $Cs^{137}$.

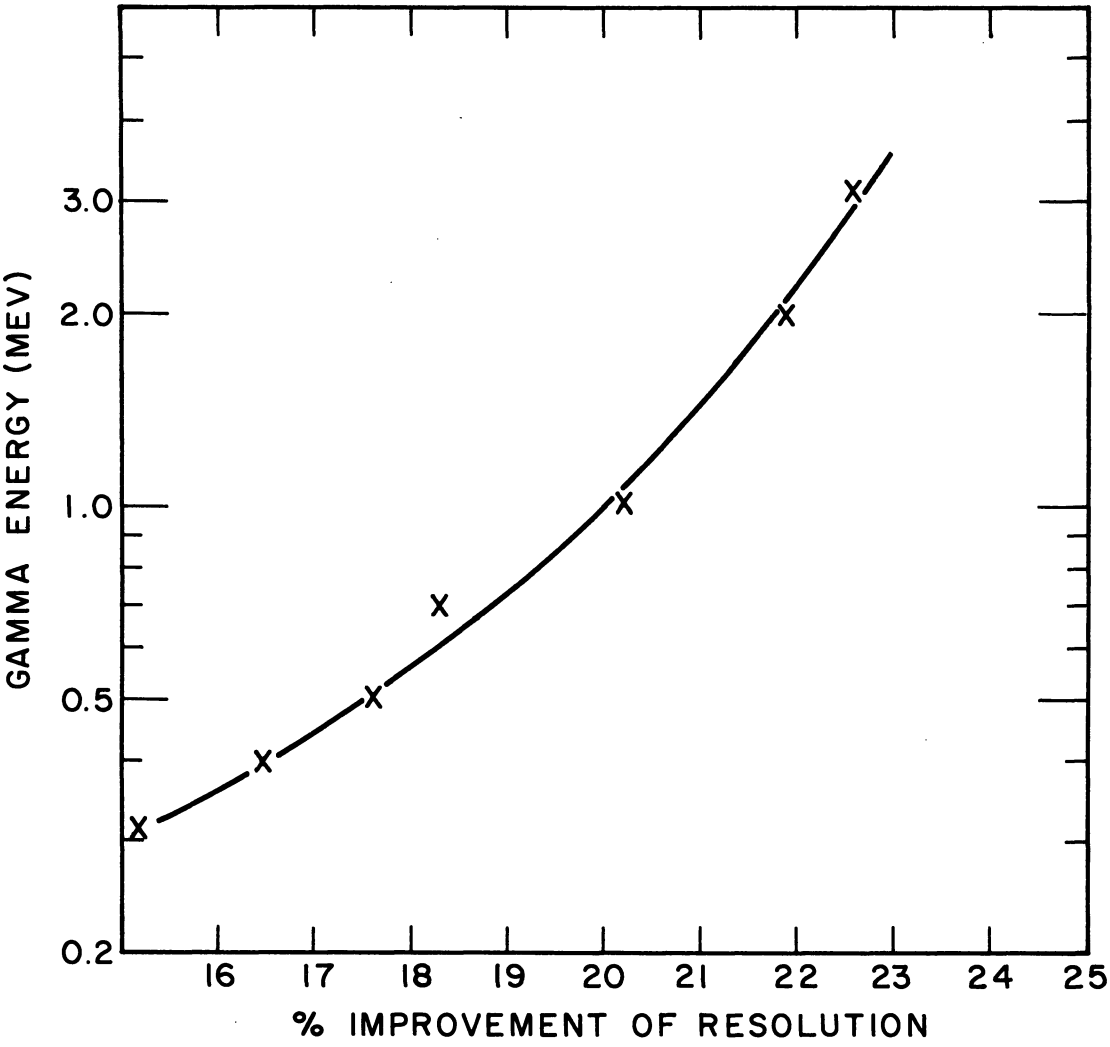


Fig. 22. Improvement of resolution in repotted 3" crystal.

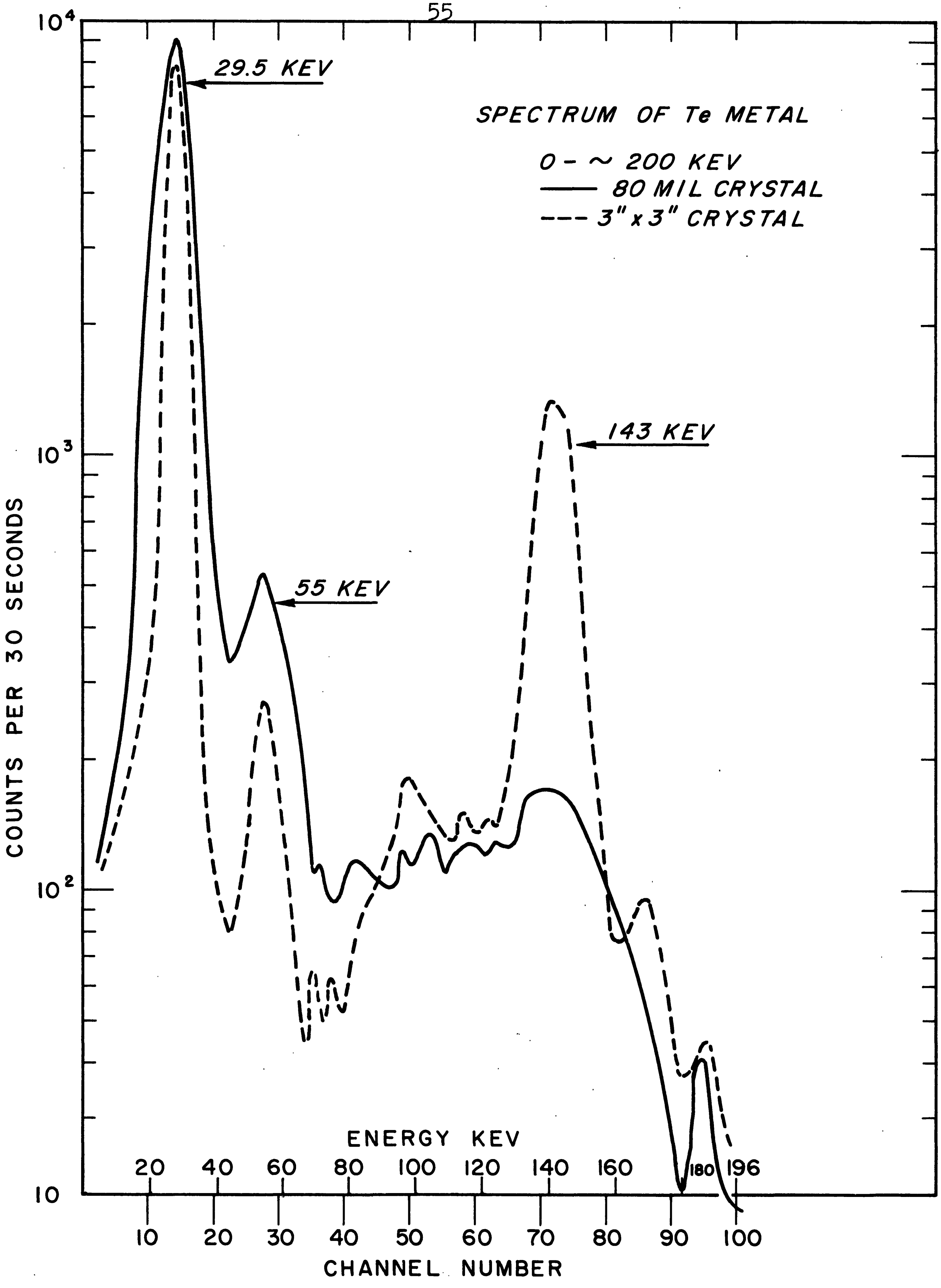


Fig. 23. Spectra of irradiated tellurium taken with thin and thick crystals.

## E. The Case for the Non-linear Amplifier

In the experiments on short-lived fission products, involving gamma rays of up to ~5 Mev and short (~30 seconds) recycle times useful in following decay and growth of several activities, the resolution of the pulse analyzer seriously limits the quality of spectral data at lower energies. For example, two gamma rays of ~200 kev energy are resolved by the crystal (width at half maximum ~25 kev) but not in the pulse analyzer (channel width 50 kev). This effect obviously decreases with increasing energy, and the crystal resolution becomes the limiting factor. On the same energy scale, a 4 Mev photopeak has a channel width of 3.4 channels.

In practice two approaches are taken to the problem. In the first case a series of similar samples is run over several energy ranges using the 100 channels, while in the second a larger number of channels (200, 256, 400, etc.) can be used. The first case has the disadvantage of being time consuming and requiring repeated handling of active samples, while in the second case the print-out time of the extra channels seriously limits the minimum recycle time.

An alternative approach to this problem would be the use of a suitably non-linear amplifier. In this system the ~200 kev photopeaks are at ~ channel No. 20, rather than channel No. 4 as in the original case, and have widths at half maximum of ~25 channels. The 4 Mev photopeak now will appear relatively unchanged, at ~ channel 85, versus channel 80 in the original example.

The analyzer dead time would be somewhat increased with this system, and more energy calibration points required. However this approach would utilize more effectively the inherent resolving capabilities of the system. (M. Wahlgren)

# III NUCLEAR CHEMISTRY

This year again the emphasis in our work has been on the Michigan reactor and little contact has been made with the cyclotron.

## A. Absolute (d, alpha) Reaction Cross-Sections and Excitation Functions

No further experimental results have been obtained in this area during the past year. The early work of Anders (2,3) has been accepted for publication in The Physical Review as an article entitled "Absolute (d, alpha) Reaction Cross-Sections of Zirconium, Molybdenum, Titanium and Sulphur". It will appear in the December 15, 1960 issue of Physical Review. The following is an abstract of the article.

> "Absolute cross-sections for 7.8 Mev deuterons were measured for the following reactions: $Zr^{94}$(d,alpha)$Y^{92*}$; $Zr^{92}$(d,alpha)$Y^{90*}$; $Zr^{90}$(d,alpha)$Y^{88*}$; $Mo^{97}$(d,alpha)$Nb^{95*}$; $Mo^{97}$(d,alpha)$Nb^{95m}$; $Mo^{98}$(d,alpha)$Nb^{96}$; $Mo^{92}$(d,alpha)$Nb^{90}$; $Ti^{46}$(d,alpha)$Sc^{44}$; $Ti^{48}$(d,alpha)$Sc^{46}$ and $S^{34}$(d,alpha)$P^{32*}$. Excitation functions were also determined for the reactions indicated with an $^*$. Beam intensity was determined with a Faraday cage coupled to a current integrator able to measure the current with less than 1% error. The reaction products from the thin targets were chemically purified by carrier-free separations. The absolute disintegration rates were determined by $4\pi$ beta counting and coincidence gamma counting. Carrier-free tracer techniques were used to establish yields of chemical purification steps." (O. U. Anders)

## B. Short-Lived Fission Gases

This work as outlined in the previous progress report (1) has gone about as far as practicable with the techniques and equipment available, and is being written up for publication. As the sampling and handling techniques improved with time, the crystal resolution unfortunately became progressively poorer leading to appreciable uncertainties in photopeak area measurements.

With the unexpected availabliity of the higher-resolution detector, it is planned to make a number of re-runs to check the earlier data.

The procedure of computing the parent disintegration rate from the photopeak area of its well-characterized daughter has given reasonable and self-consistent gamma-ray abundances. Nine-minute $Cs^{139}$ can be added to the isotopes reported in the last progress report having a gamma-ray at 1280 kev of ~16% abundance.

If the data taken previously are confirmed in the re-runs, it will be possible to determine decay energies for at least $Kr^{89}$, $Kr^{90}$, and $Cs^{139}$ and these will be included in the final report.

(M. Wahlgren)

## C. Independent Fission Yields

Preliminary experiments indicate that the rapid fission gas separation previously described (1) can be used to obtain experimental data for the determination of independent fission yields for the chains of mass number 87 (17-second $Se^{87}$, 56-second $Br^{87}$, 78-minute $Kr^{87}$) and 88 (16-second $Br^{88}$, 2.8-hour $Kr^{88}$).

In the first experiment, gas samples were taken from a freshly irradiated fission product sample at 20-second intervals and the half-lives of the precursors of $Kr^{85m}$, $Kr^{87}$, $Kr^{88}$, and $Kr^{89}$ checked. This was intended primarily to be an experimental verification of the technique rather than a measurement of half-lives of the Br precursors.

The second experiment involved irradiation of a series of samples for 15 seconds, with sampling times of 20, 60, 120, and 240 seconds after the end of irradiation. A typical series of gamma ray spectra is shown in Fig. 24. The measurement then requires only that the relative energy response of the detector be known and that each of the Kr isotopes have a resolvable gamma-ray photopeak.

For the Kr isotopes $Kr^{89}$ is a convenient chemical yield and flux monitor since the 4.5-second $Br^{89}$ precursor has a half-life short compared to the decay time and since the $Kr^{89}$ activity at the end of irradiation can be readily computed from the photopeak area of its 15-minute daughter, $Rb^{89}$.

The data will be verified by further runs utilizing the higher-resolution crystal which will permit more accurate measurement of photopeak areas and then will be submitted for publication.

(M. Wahlgren)

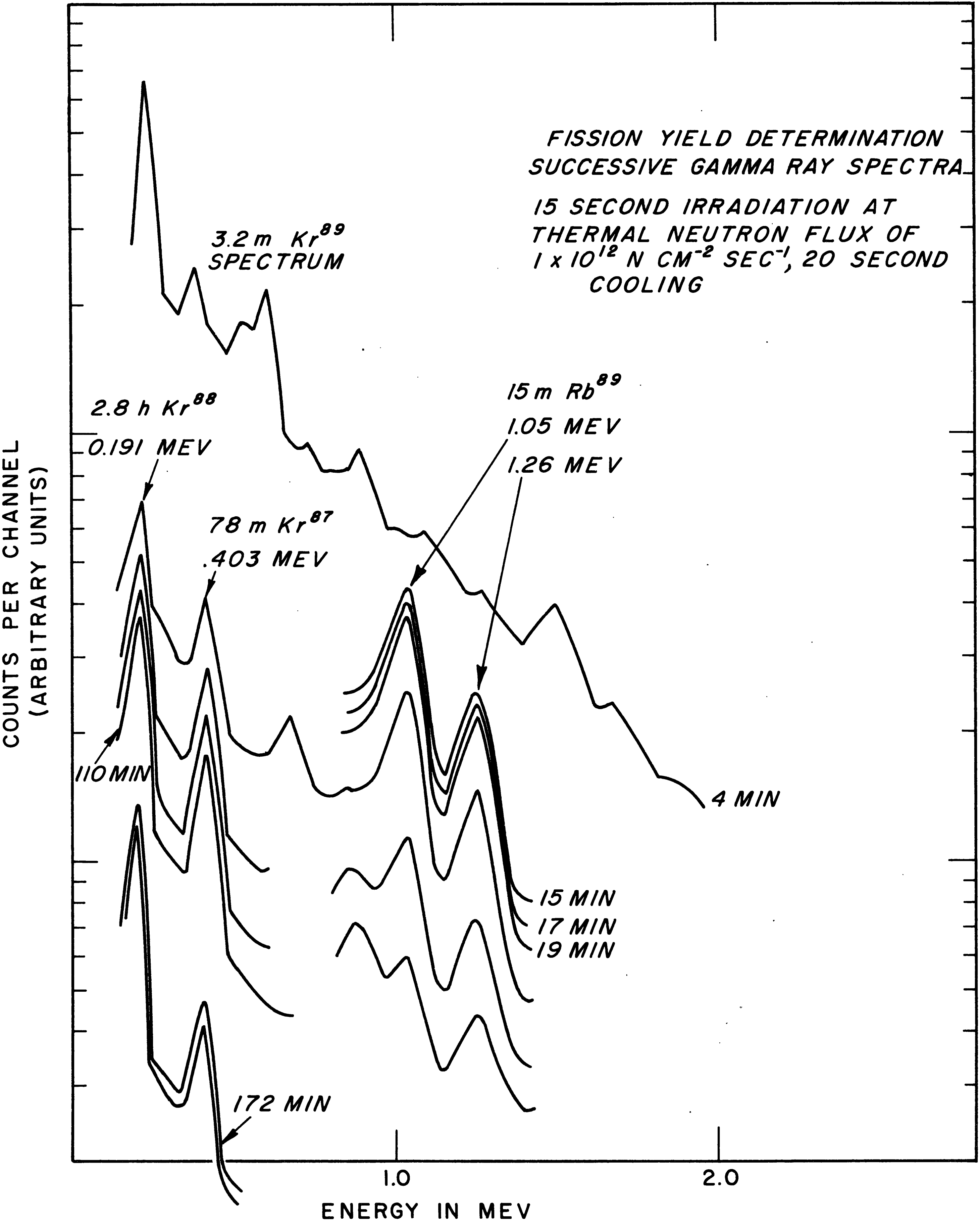


Fig. 24. Sucessive gamma-ray spectra, fission yield determination.

# IV RADIOCHEMICAL SEPARATIONS

Some additional experimental work was done in this area during the year particularly in the area of the amalgam exchange separation but much of the effort has gone into writing. Again considerable of the director's time has been taken up as Chairman of the Subcommittee on Radiochemistry, of the Committee on Nuclear Science of the National Research Council. This Subcommittee has had three meetings during the year and has concerned itself with such things as low level contamination in materials, radiochemically pure reagents, teaching experiments in radiochemistry, monographs on radiochemistry of the elements, and a source booklet for radiochemistry. These items are covered in detail in the minutes of the meetings of this Subcommittee.

## A. Subcommittee on Radiochemistry Program

### 1. Pamphlet on "Source Material for Radiochemistry"

Two printings of the first edition of this booklet have been distributed and a revised edition is about ready for distribution. In this revision the format has been rearranged considerably to group the references according to areas of interest. In addition the number of references included has been expanded several fold. Information as to availability as well as a short description is still included for most references. The revised edition will be available in November, 1960, free of charge from the Division of Physical Sciences, National Research Council, 2101 Constitution Avenue, Washington 25, D. C.

(W. W. Meinke)

## 2. Radiochemistry Monographs

The monograph program described a year ago (1), which is being coordinated and edited by the undersigned, has gotten well underway during the current year. A total of 57 monographs have been assigned in this series on the Radiochemistry of the Elements. These include reports on all the elements except hydrogen, helium, lithium, and boron. (Some monographs include discussions of several related elements). Fourteen of these monographs have already appeared in print and many of the rest of them will be submitted for printing by the end of the year.

The monographs are being issued by the Technical Information Service of the United States Atomic Energy Commission, are printed at Oak Ridge, and are now available for sale from the Office of Technical Services, Washington 25, D. C. at a price approximating 1 cent per page. The monographs average about 50 pages and have been given document numbers such as NAS-NS-3001, NAS-NS-3002, etc.

An additional series of monographs on "Techniques of Radiochemistry" is also being planned and to date seven monographs in this series are being prepared. These include such subjects as thin films, low level radiochemistry, rapid radiochemical separations, etc. (W. W. Meinke)

## 3. Teaching Experiments in Radiochemistry

The Subcommittee has been collecting information on radiochemical experiments available both in printed books and in documents. Lists of these experiments are being prepared and cross referenced by subject, and will then be issued as a monograph. This study should point out blank spots in the coverage of such experiments. The Subcommittee will then encourage persons to devise experiments to fill these blank spots. It is hoped that the net result of this "clearing house" for experiments will be to exapnd the uses of radioisotopes in the colleges and universities, particularly at the undergraduate level. (W. W. Meinke)

## 4. Low Level Contamination in Materials

During the year Dr. James DeVoe has been working for the Subcommittee under another AEC contract on this problem. He has visited more than 50 laboratories around the country discussing with interested persons the question of contamination and collecting information. He has learned of many types of materials which are at present slightly contaminated and has also discovered some materials which are available with low contamination levels. He has discussed the production of contamination-free materials as well as the possible stockpiling of uncontaminated materials.

Dr. DeVoe is at present compiling this information into a report. This report will then form the basis for a special conference on this subject which will be held on January 30 and 31, 1961 in Washington. This report, with an endorsement by the Subcommittee, will be made generally available after the conference. The purpose of the report was to collect in one place as much factual information on this subject as possible so that it could be used as a starting point for further work. As a result of the report and the conference, recommendations will be forewarded to the National Academy as to what steps should be taken in regard to this problem. (J. R. DeVoe, W. W. Meinke)

### 5. Radiochemically Pure Reagents

Dr. DeVoe has also collected information on this problem during his visits and will be including some of this in his report. Representatives of the Subcommittee have met with the Committee on Analytical Reagents of the American Chemical Society and have been assured of their interest in this problem and their willingness to consider recommendations of specific tests which could be incorporated into their standard analytical testing procedures.

The Subcommittee will recommend a gross gamma counting assembly to the chemical reagent companies for use in measurement of all analytically pure reagents. This gross gamma assay value would then be put on the label of the reagent along with the results of their other chemical and physical tests.

(J. R. DeVoe, W. W. Meinke)

## B. Preparation of Radiochemistry Monographs

Because of the work of this project during the past few years in evaluating and developing radiochemical procedures, current or former members of the group were asked to prepare monographs in their specialties. Thus J. R. DeVoe has prepared monograph NAS-NS-3001 on "The Radiochemistry of Cadmium", D. N. Sunderman has co-authored monographs NAS-NS-3010 on "The Radiochemistry of Barium, Calcium, and Strontium", and NAS-NS-3014 on "The Radiochemistry of Indium." Other monographs in preparation here include "The Radiochemistry of Vanadium", "The Radiochemistry of Thallium", "The Radiochemistry of Titanium", and "Rapid Radiochemical Separations."

## C. Radiochemical Separations by Amalgam Exchange

### 1. Cadmium

The following is an abstract of a paper entitled "Radiochemical Separations By Amalgam Exchange: Cadmium" presented before the Analytical Chemistry Division of the American Chemical Society in New York in September, 1960.

> "A selective radiochemical separation procedure has been developed with the use of amalgam exchange. The separation of the radioisotope takes place by virtue of the rapid exchange which is known to occur between an element in the form of a dilute amalgam and its ions in solution. If there are more inactive atoms of the element in the amalgam than there are of its radioisotope in solution, the amalgam exchange will result in most of the activity being present in the amalgam.
>
> The separation technique that has been studied uses the exchange of cadmium amalgam in the extraction step, which is then followed by a back-extraction with thallous ion to selectively remove the cadmium from the contaminant in the mercury. This technique resulted in decontamination factors of at least $10^3$ with a cadmium yield of 80% for 18 elements which are representative of groupings in the periodic table. Indium, thallium, and tin comtaminate the separation. The introduction of an indium amalgam scavenger before the extraction step improved the separation from most elements by at least a factor of 10 (the decontamination factor of tin was increased to $10^4$), but did not appreciably improve the separation from

> indium and thallium. Nitric, hydrochloric, and perchloric acid concentrations of 1 M do not affect the cadmium amalgam exchange at room temperature. Oxidizing agents such $U^{+6}$, $Ce^{+4}$, etc., must be avoided to prevent removal of the cadmium from the amalgam. The extraction separation step can be carried out in 5 minutes and should have practical application in the separation of short-lived nuclear reaction products where separation from many different contaminating elements is not required."

A technique using this exchange reaction has been worked out for separating Cd from fission products. The paper on the above work will be submitted to Analytical Chemistry for publication in 1961. (J. R. DeVoe, H. W. Nass)

## 2. Selective Elution

It is of interest to know if a selective elution of the desired element could be accomplished by affecting the heterogeneous exchange so that the radioactivity will transfer from the amalgam into the aqueous phase. The two step separation process can be represented in the following reactions.

$$\text{(I)} \qquad \underset{0.1\ \text{mg/cc}}{\text{Cd(Hg)}} + \underset{10^{-4}\ \text{mg/cc}}{\overset{*}{\text{Cd}}{}^{+2}_{(aq)}} = \overset{*}{\text{Cd}}{}^{+2}(\text{Hg}) + \text{Cd}^{+2}_{(aq)}$$

$$\text{(II)} \qquad \underset{0.1\ \text{mg/cc}}{\overset{*}{\text{Cd}}(\text{Hg})} + \underset{10\ \text{mg/cc}}{\text{Cd}^{+2}_{(aq)}} = \text{Cd(Hg)} + \overset{*}{\text{Cd}}{}^{+2}_{(aq)}$$

An asterisk indicates the radioactive atoms. In most of these experiments a volume ratio (aq/Hg) of 40 with a 2 ml aqueous volume was used. The theoretical yields at equilibrium for step I and with the concentrations indicated are:

$Y_I = \frac{n}{n+N}$ where $N$ = cadmium atoms in aqueous phase

$n$ = cadmium atoms in Hg phase.

$$= \frac{0.1 \times 100}{0.1 + 10^{-4} \times 40} = 96\%$$

$$Y_{11} = \frac{N}{n+N} = \frac{10 \times 40 \times 100}{10 \times 40 + 0.1} = 99.9$$

The overall yield for both steps is $Y_I \times Y_{II} \cong 96\%$. The combination of these steps would result in good selectivity since step I would separate Cd isotopes from all elements above Cd in the electromotive series, and step II would separate cadmium from all elements below cadmium in the electromotive series. The only interference which might result is the oxidation of trace quantities of the contaminant in the mercury phase by hydrogen ion. This is not believed to be a serious problem.

Of considerable detriment to the procedure is the fact that the time required to reach equilibrium in step II is much longer than that in step I. S. Fronaeus (Acta Chem Scand. 8 , 412-19 (1954) ) has calculated that in a system similiar to that used here; the rate of exchange is proportional to the concentration of cadmium in the aqueous phase and independent of that in the amalgam phase. Using this information he derives the following expression for the rate of activity change in the amalgam phase

$$\frac{dq_a}{dt} = h' \left( \frac{C_a}{c} - \frac{q_a}{q} \right)$$

where $h' = \frac{S_o}{M_o} h$ = constant;

$S_o$ = surface area of amalgam;

$M_o$ = weight of amalgam;

$h$ = rate of exchange = $KC$;

where $K$ = constant

$q_a$ = concentration of active Cd in amalgam phase;

$C_a$ = concentration of active Cd in aqueous phase.
q = total concentration of Cd in amalgam phase.
C = total concentration of Cd in aqueous phase.

From this equation it can be seen that increasing the total concentration of cadmium in the aqueous phase will increase the time required to reach equilibrium. We have found that a 10 minute back exchange results in less than 40% of the equilibrium amount of activity in the aqueous phase. At this rate, equilibrium would be reached in about an hour. This is considered to be too long for most radiochemical applications.

An alternate approach to this problem is to use carrier-free or trace amounts of activity in the mercury phase. By contacting the mercury phase with an aqueous solution of the most electropositive element present in the mercury, isotopic exchange should result in rapid removal of the activity into the aqueous phase. In the event that there are elements in the mercury phase that are above the most electropositive exchangeable ion it will be necessary to rid the mercury phase of these with a selective oxidant (one that will oxidize all elements above the exchangeable element in the electromotive series). We are now making a study of this technique. (J. DeVoe, I. Quershi)

### 3. Separation of Indium by Amalgam Exchange

Previous work indicated that indium will exchange between its amalgam and an aqueous solution. Several neutral (pH 6.5) salt solutions (KI, $KNO_3$, KCl) did not allow rapid exchange; however, 0.5 M acids improved the exchange. Optimum exchange was found with HBr. Measurement of the exchange with concentration of HBr at 3-minute contact times and the exchange at 1M HBr with time of contact are shown in figure 25 and 26 respectively. It is evident that the absence of a significant plateau (within 0.2%) plateau on either curve restricts its applicability. It is possible that reduction of hydrogen ion by the In amalgam is causing this difficulty. The concentration of bromide ion is important as evidenced by less exchange below 1M HBr. Therefore, it may prove useful to maintain moderate acidity while increasing the bromide ion concentration.

Use of thallous ion as a selective oxidant for indium is not practical because their oxidation potentials are too close together. Cobaltous ion will oxidize the In from the mercury, and still retain selectivity. No tracer experiments have yet been made to determine the efficiency of this technique.

(J. R. DeVoe, G. Weiss)

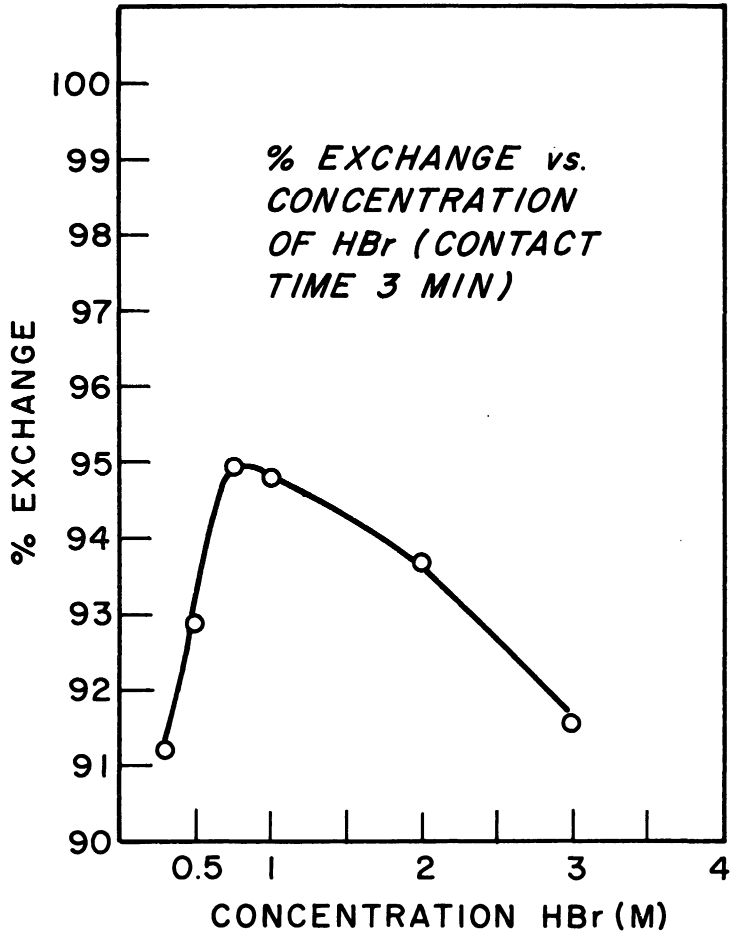


Fig. 25. Variation of amalgam exchange separation of indium with HBr concentration.

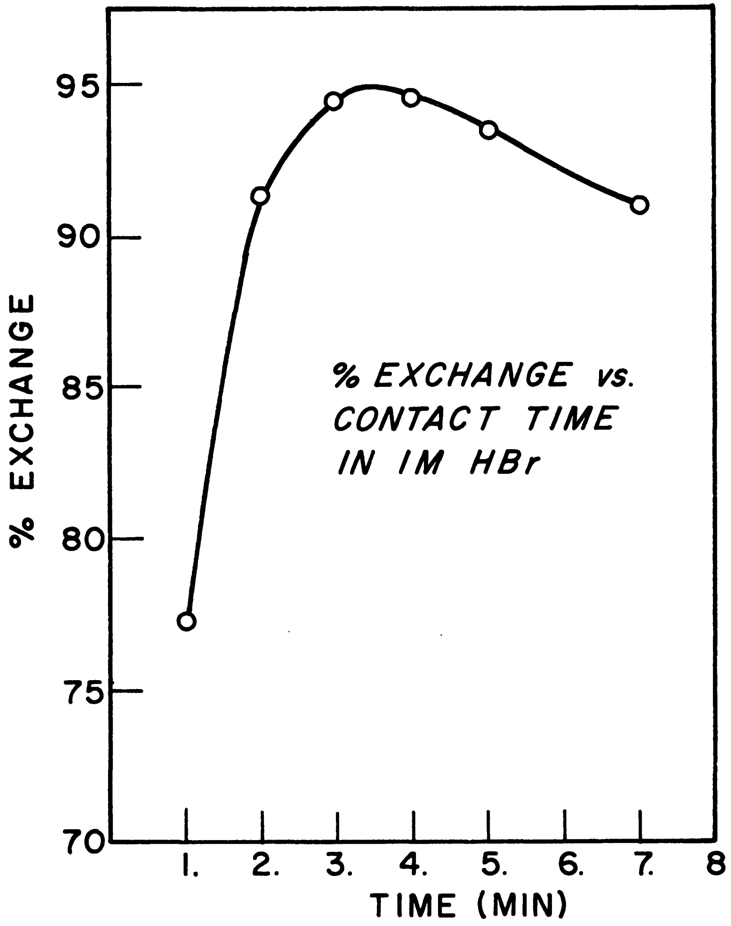


Fig. 26. Variation of amalgam exchange separation of indium with time.

## D. Considerations on General Rapid Chemical Separation

The time which is consumed for a chemical separation is a very important factor in activation analysis using short-lived radioisotopes or in the nuclear chemical characterization of a nuclide. It is essential that the time necessary for these separations be not longer than several half-lives of the isotope to be studied.

Using certain assumptions it is possible to estimate roughly the time required for chemical separations.

From the considerations on all the procedures which have been worked out by our group in the Phoenix Laboratory, the time consumed for each step in the rapid chemical procedure was estimated and the results are shown in Table VIII.

Table VIII. Time Consumed for Each Step in Rapid Chemical Separation in Activation Analysis

| Step | Time (minutes) |
|---|---|
| Fusion by $Na_2O_2$ | 1.5 |
| Wet dissolution for biological ash | 0.5 |
| Wet dissolution for rock | 5.0 |
| Dissolution for $Na_2O_2$ melt | 1.5 |
| Solvent extraction | 2.0 |
| Back extraction | 2.0 |
| Washing of extract | 2.0 |

Table VIII. (continued)

| Step | Time (minutes) |
|---|---|
| Boiling off of solvent (ether, $CHCl_3$, etc.) from aqueous solution | 3.0 |
| Precipitation (rapid formation) | 1.0 |
| Neutralization | 1.0 |
| pH adjustment | 1.0 |
| Acidification | 0.3 |
| Alkalinization | 0.3 |
| Oxidation | 0.5 |
| Reduction | 0.5 |
| Dilution | 0.3 |
| Evaporation | 1.0/ 5 ml |
| Filtration (~ 150 ml) | 1.0 (medium funnel)* |
| (~ 150 ml) | 2.5 (fine funnel) |
| (~ 50 ml ) | 0.5 (medium funnel) |
| Ion exchange (5-15 ml) | 10.0 |
| (15-30 ml) | 20.0 |
| Drying counting sample by alcohol, acetone, or air | 0.5 |
| Mounting of counting sample | 0.5 |

* Filtration through filter paper on filter discs belongs to this category.

From these values and the procedures described in previous Progress Reports (1,2,3) the time consumed for the separation can be estimated and compared with the reported times. These values are summarized in Table IX.

Table IX. Comparison Between Estimated and Reported Time For Rapid Separation Procedures

| Element | Estimated Value (minutes) | Experimental Value (minutes) | Investigator | Progress Report |
|---|---|---|---|---|
| Vanadium | 10 | ~10 | Fukai | 1958 |
| Vanadium | 3 | ~ 4 | Fukai | 1958 |
| Arsenic | 27 | ~30 | Fukai | 1958 |
| Rhodium | 11 | 9 | Schindewolf | 1958 |
| Silver | 7 | 5 | Schindewolf-Wahlgren | 1958 |
| Cadmium | 26 | 25 | DeVoe | 1958 |
| Indium | 32 | 30 | Schindewolf-Wahlgren | 1958 |
| Vanadium | 9 | 10 | Brownlee | 1959 |
| Vanadium | 8 | ~ 5 | Kaiser | 1959 |
| Cobalt | 11 | ~15 | Kaiser | 1959 |
| Copper | 10 | 8 | Kaiser | 1959 |
| Niobium | 7 | 10 | Brownlee | 1959 |
| Technetium | 32 | 30 | Fukai | 1959 |
| Tungsten | 28 | 30 ~ 40 | Fukai | 1959 |
| Rhenium | 32 | 30 | Fukai | 1959 |
| Gold | 24 | 30 | Fukai | 1959 |
| Thallium | 13 | 9 | Kim | 1959 |
| Titanium | 11 | <9 | Kim | 1960 |

Table IX. (continued)

| Element | Estimated Value (minutes) | Experimental Value (minutes) | Investigator | Progress Report |
|---|---|---|---|---|
| Uranium | 20 | $<30$ | Das | 1960 |
| Rhodium | 6 | 7 | Steele | 1960 |
| Silver | 5 | 5 | Kusaka | 1960 |
| Silver | 8 | 6 | Kusaka | 1960 |
| Silver | 7 | 7 | Kusaka | 11960 |

Many assumptions are of course included in these estimations. However, from the rather close correlation of Table IX, it appears that the times reported in Table VIII for different separation steps may be useful in planning separation procedures.

(Y. Kusaka)

# V ACTIVATION ANALYSIS

Our program of studying the application of short half-lived radioisotopes to activation analysis has continued throughout the year, using the Michigan reactor and associated pneumatic tube facilities. The neutron generator is also about to the point where it can be used routinely in this type of study.

## A. Review Articles and Data Correlation Summaries

### 1. Calculated Sensitivity Charts

Existing charts of sensitivity (4) have been designed for Geiger counter measurement and often emphasize the longer half-lived isotopes. Much of our recent experimental work on the other hand involves gamma-ray spectrometry and emphasizes isotopes with half lives of a few minutes or less. Application of complement subtraction techniques to certain isotopes with half lives shorter than a minute also appears to make possible non-destructive analyses. The 24-second silver-110 isotope appears to be particularly conductive to such a measurement.

Thus a graph of calculated relative sensitivities for gamma rays of elements has been prepared. This graph is based on an irradiation of 24 seconds (to optimize the $Ag^{110}$) and an immediate count. It is presented in Fig. 27 inserted at the end of this report. The plot gives relative sensitivities (in units of weight--i.e. grams--rather than moles) versus the gamma ray energy and also records the half life of the radioisotope involved. Thus it is possible from the graph to see for a short irradiation which contaminants would be expected at a given γ-ray energy. A similar graph is being prepared to optimize the 3.76-minute $V^{52}$ isotope and involves calculations using a 4-minute irradiation and a 4-minute decay before measurement.

It should be pointed out again that these are calculated sensitivities. Decay schemes have been evaluated from information available in the Sullivan chart (5) and from Strominger, Hollander, and Seaborg (6) and corrections for efficiency of counting in a 3" NaI(Tl) crystal, time of irradiation, etc., have been included. About two dozen isotopes including the high sensitivity $Hf^{179m}$ have not been included on this graph because no information was available on their cross sections.

Thus this graph can serve a dual purpose--it can give at a glance a feeling for possible contaminants in short irradiations, and through comparisons with experimentally determined sensitivities it can help point out nuclear constants which are lacking to date in the literature. The next step of course is to modify this graph to make it a graph of experimentally determined sensitivities and we are in the process of doing this now. Since relative sensitivities are plotted in the graph it is equally applicable to any source of neutrons. (W. W. Meinke)

## 2. Review of Fundamental Developments in Nucleonics

This biannaul review was completed in December 1959 and covered late 1957 to late 1959 without overlapping the previous review (7). The new paper published in the April 1960 issue of Analytical Chemistry (8) contains 1059 references including a considerably larger number of Russian papers than the previous two reviews (7, 9).

One point of interest regarding these reviews is the number of papers on activation analysis included. In 1954-55 (9) there were 60 papers in this field while in 1956-57 (7) there were 85 and in 1958-59 there were 125. At least 95% of these papers were still on the simple techniques of thermal neutron activation.

## B. Activation Analysis of Vanadium, Thallium and Niobium

The work on these three elements reported previously (1, 2) has been completed and incorporated into a thesis (10) which will also be made available as an AEC document. An abstract of this thesis follows.

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

and evaluated for the analysis of the beta and gamma radiation of counting samples.

"Determinations were made of the amount of vanadium, as 3.7-minute vanadium-52, in a series of petroleum process stream samples which included distillation residues and condensates. Samples from various refinery streams were sealed in polyethylene tubing for irradiation in the reactor. It was found that the vanadium in these samples could be determined non-destructively by gamma spectrometry of the irradiated gross samples. Determinations of vanadium in samples of petroleum cracking catalyst required chemical separation of the vanadium prior to gamma spectrometry because of interference from the photopeak of aluminum-28. A rapid separation of vanadium from aluminum and silicon was developed, employing solvent extraction of vanadium cupferrate into chloroform. This extraction followed fusion of the sample with sodium peroxide and removal of aluminum with 8-hydroxyquinoline. The chloroform solution of vanadium cupferrate was used for gamma analysis. This separation, requiring approximately 9-1/2 minutes, has been used to separate vanadium from several types of samples.

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

"Determination of thallium, as 4.2-minute thallium-206, was performed on rock and mineral samples. Thallium-206, being a pure beta emitter, was determined by decay curve resolution on separated thallium fractions. Several procedures were investigated for the chemical separation of thallium. Fusion, and extraction of bromothallic acid into isopropyl ether were common to all procedures. Following extraction and evaporation of the ether, thallium(I) was precipitated as the iodide, the tetraphenylboron salt, or as the thionalide complex. These procedures were evaluated and used in the determination of microgram amounts of thallium in rock samples. Results show that amounts of thallium down to the order of $10^{-7}$ grams can be determined as thallium-206.

"Niobium was investigated by means of its K x-ray, emitted in the decay of 6.6-minute niobium-94m. Detection was achieved by means of a sodium iodide (thallium) scintillation detector, a krypton-filled x-ray proportional counter having proved to be of little use for quantitative work.

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

Papers on each of these methods are being prepared for publication. (J. L. Brownlee)

## C. Activation Analysis Using 4.2-minute Thallium-206

A paper was presented on this subject at the New York meeting of the Analytical Chemistry Division of the American Chemical Society in September 1960. The abstract presented here supplements some of the information given above in section B.

> "Neutron activation determinations of thallium, as the 4.2-minute thallium-206, have been performed on various rock and mineral samples. Thallium-206, a pure beta emitter, was determined by resolution of the gross beta decay curve of a separated thallium fraction. In the development of separation procedures gamma spectra of the separated thallium fractions were measured simultaneously with measurement of the decay curves in order to determine the type and extent of gamma-emitting contaminants. Beta spectra were also analyzed simultaneously with decay curve measurement for many samples and compared with a thallium-206 standard in order to obtain evidence, in addition to the 4.2-minute half life, for the presence of thallium-206 in the counting sample.
>
> "Samples for thallium determinations were irradiated for 10 minutes at a thermal neutron flux of about $10^{12}$ n $cm^{-2}$ $sec^{-1}$ and the thallium separated radiochemically. The irradiated samples were fused with sodium peroxide or digested quickly with a mixture of sulfuric and hydrofluoric acids.

Thallium was separated by extraction into isopropyl ether from hydrobromic acid solution with subsequent precipitation as thallous iodide or the thallous-thionalide complex.

"Determinations have been made in microcline and lepidolite samples to a standard deviation of less than 10% of amounts of the order of 70 parts per million. Other results indicate that approximately $10^{-7}$ grams of thallium can be determined by this method. The procedure developed should be equally applicable to biological and other types of samples." (J. L. Brownlee, C. K. Kim)

## D. Activation Analysis Using 5.8-minute Titanium-51

Colorimetric determinations for titanium are simple, fast and sensitive to about $4 \times 10^{-6}$ grams of titanium. However in any method of trace analysis problems of contamination from reagents can be troublesome and can be eliminated by activation analysis techniques. Thus it was of interest to us to study the application of the 5.8-minute titanium-51 to the determination of trace amounts of titanium.

Samples varying from biological and botanical materials, to rocks and minerals and alloys were studied. The sample was irradiated in a gelatin capsule and was then put in solution either by digesting with nitric acid or by fusion with sodium peroxide. In biological samples where iodine might be present, special decontamination steps such as fuming and $CCl_4$ extraction were included. This was necessary since the radiations of $I^{128}$ interfere with the 0.32 Mev gamma ray used to measure the titanium.

The titanium was then extracted with cupferron into isopropyl ether from hydrochloric acid solution. Contaminants were back extracted with NaOH solution, or washed out with a 10% HCl wash and the solution counted. Such a procedure could be completed in about 9 minutes with a titanium yield of about 70%. Samples with considerable amounts of rare earths, copper, vanadium and manganese required additional steps such as an oxine precipitation which reduced the yield of titanium and increased the time of separation.

The chemical yield of the separation was generally determined colorimetrically. Activity measurements were made using the 0.32 Mev titanium photopeak on the 100-channel scintillation spectrometer.

With this procedure the practical lower limit of detection at a thermal neutron flux of $10^{12}$ n $cm^{-2}$ $sec^{-1}$ seems to be about $6 \times 10^{-7}$ grams of titanium. Thus although on sensitivity charts (see section VA1) the titanium shows a very poor sensitivity, it is possible in many practical samples to couple activation analysis with a simple radiochemical procedure to yield good results. This activation method is as fast and simple as the colorimetric determination, gives about 7 times higher sensitivity with our flux level, and eliminates the problems of reagent contamination.

This work is presently being written up in more detail for publication. (C. K. Kim)

## E. Activation Analysis of Uranium Using Short-Lived $U^{239}$

We have carried out a program of study on the trace analysis of uranium. The importance of the determination of trace concentrations of uranium in the fields of geology and geochronology, reactor technology and health physics has been reviewed along with the methods available for its determination. The advantages and limitations of various radionuclides for the assay of uranium in neutron activation analysis have also been compared.

Experiments were then run to determine the applicability of the short-lived $U^{239}$ to activation analysis. Following a 20 minute irradiation of a sample in a flux of $\sim 1 \times 10^{12}$ n $cm^{-2}$ $sec^{-1}$, the 23.5-minute $U^{239}$ isotope formed by the $(n,\gamma)$ reaction on $U^{238}$ was chemically separated from the associated elements using natural uranium as carrier. Depending upon the nature of the sample several conventional methods of dissolving the sample and purification of uranium have been adopted. The final purification of uranium was based on its selective extraction as hydroxyquinolinate into chloroform in the presence of EDTA which is used to complex most of the associated impurities. The uranium was finally back extracted into acid and precipitated as the hydroxyquinolinate in which form it was counted.

The radiochemical purity of the separated $U^{239}$ was checked both by its $\beta^-$ decay using a gas flow proportional counter and by $\gamma$ spectrometry using a 3" x 3" NaI(Tl) activated crystal coupled to our RIDL dual memory 100-channel analyzer.

The method has been applied for the determination of traces ($\sim$0.1 to 10 ppm) of uranium in vanadinite, ilmenite, granites, thorium nitrate, seaweed and fish bones. The gross beta decay of the separated samples is shown in Fig. 28 and a calibration curve is given in Fig. 29. The precision of an individual deter-

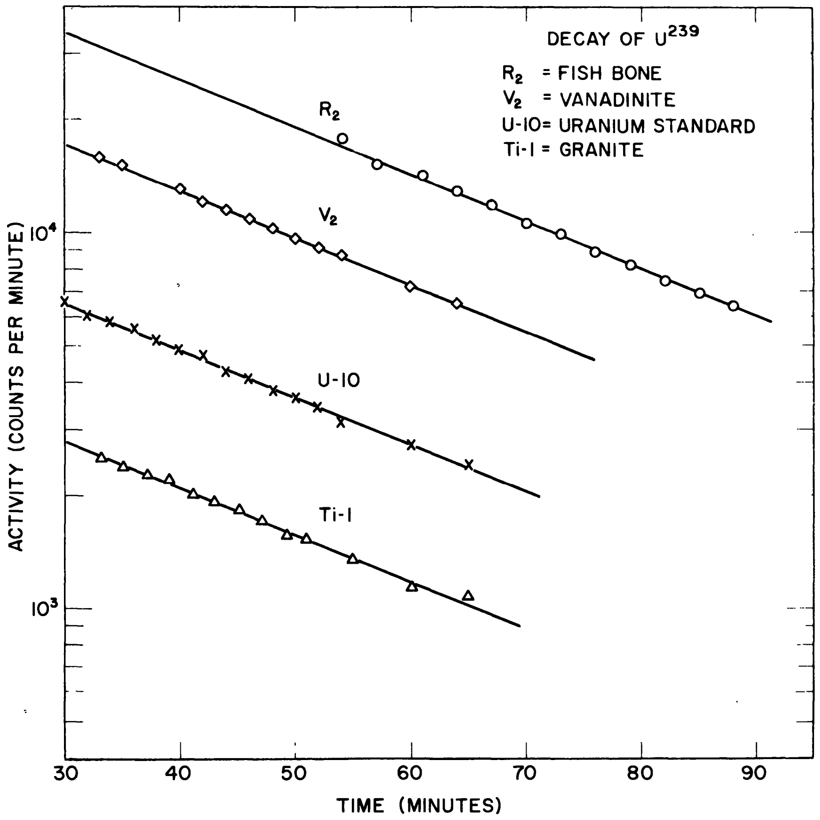


Fig. 28. Gross beta decay of uranium samples separated in activation analysis.

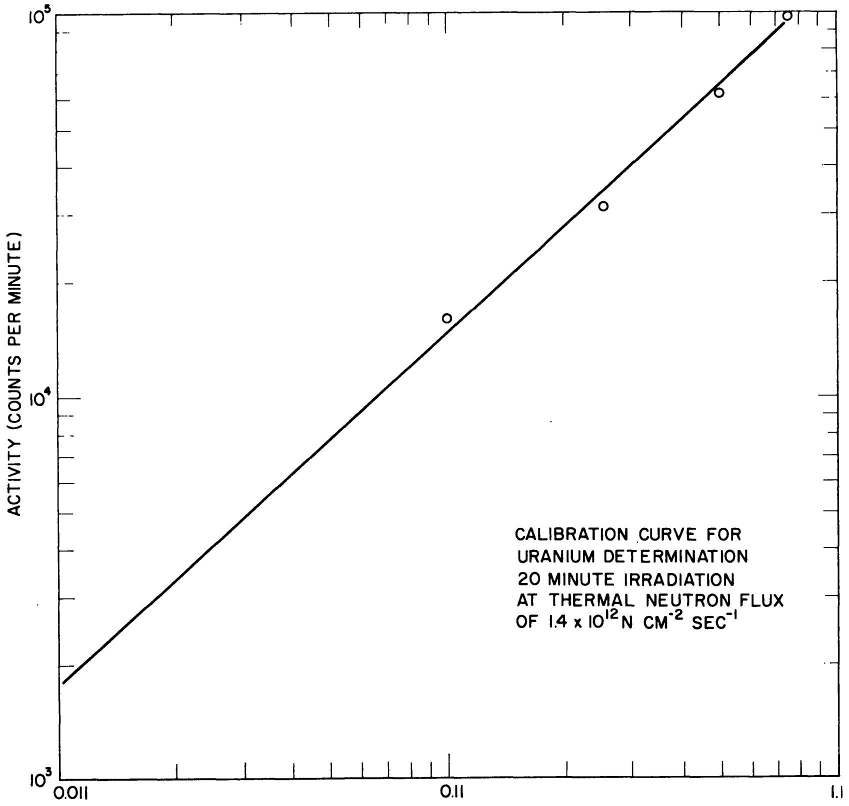


Fig. 29. Calibration curve for activation analysis of uranium using the 23.5-minute U-239.

mination has been found to be better than 10% in the analysis of the rock "standards" G-1 and W-1.

The program will be discussed in detail in a paper which is in preparation. (S. Das)

## F. Activation Analysis of Rhodium

Rhodium occurs in nature as the stable $Rh^{103}$ isotope to the extent of 0.2-0.3 $g/10^6$ g of silicon. Since the element is widely distributed in the earth's crust, it was deemed advisable to investigate activation analysis as a possible method for the determination of trace quantities of rhodium in a variety of samples.

When exposed to a source of thermal neutrons $Rh^{103}$ becomes radioactive by neutron absorption in a $(n,\gamma)$ reaction forming $Rh^{104}$ and $Rh^{104m}$. The reaction cross-sections are 138 barns and 12 barns, respectively. The $Rh^{104}$ decays by beta and gamma emission with a half-life of 42 seconds while $Rh^{104m}$ decays first to $Rh^{104}$ by I.T. with a half-life of 4.4 minutes. Hence, the analyst can use the short-lived isomer in a non-destructive method or take advantage of the transient equilibrium between the two isomers to chemically separate rhodium from its matrix.

Non-Destructive Method - Samples containing varying amounts of rhodium ($RhCl_3$ in 1 N HCl) were irradiated in a thermal neutron flux of approximately $10^{12}$ n $cm^{-2}$ $sec^{-1}$ for 42 seconds and analyzed with the dual 100-channel gamma spectrometer. Rhodium was quantitatively determined by measuring the counts in the 550 kev gamma peak. Figure 30 shows the calibration curve obtained with this method. Quantities as small as 0.01 $\mu$g of rhodium can be determined in the absence of interfering materials. Table X lists the results of analysis of several synthetic samples containing rhodium in a matrix of silica and alumina.

Table X. Analytical Results of Standard Rhodium Samples by Activation Analysis.

| Sample | Irradiation Time | Matrix | Chemical Separation | $\mu$g Rh Added | $\mu$g Rh Found |
|---|---|---|---|---|---|
| 1 | 42 sec | $H_2O$-HCl | None | 0.01 | 0.011 |
| 2 | 42 sec | $H_2O$-HCl | None | 0.10 | 0.095 |
| 3 | 42 sec | $H_2O$-HCl | None | 0.25 | 0.24 |
| 4 | 42 sec | $H_2O$-HCl | None | 0.50 | 0.50 |
| 5 | 42 sec | $SiO_2$-$Al_2O_3$ | None | 0.50 | 0.53 |
| 6 | 42 sec | $H_2O$-HCl | None | 0.75 | 0.74 |
| 7 | 42 sec | $SiO_2$-$Al_2O_3$ | None | 0.75 | 0.77 |
| 8 | 42 sec | $SiO_2$-$Al_2O_3$ | None | 1.00 | 1.02 |
| 9 | 5 min | $H_2O$-HCl | Pyridine Extraction | 0.10 | 0.09 |
| 10 | 5 min | $H_2O$-HCl | Pyridine Extraction | 0.50 | 0.48 |
| 11 | 5 min | $H_2O$-HCl | Pyridine Extraction | 1.00 | 1.01 |
| 12 | 5 min | $SiO_2$-$Al_2O_3$ | Pyridine Extraction | 1.00 | 1.04 |

Destructive Method - Samples containing varying amounts of rhodium were irradiated for 5 minutes in a thermal neutron flux of approximately $10^{12}$ n cm$^{-2}$ sec$^{-1}$ then fused with ten times their weight of $Na_2O_2$. The melt was dissolved in concentrated HCl. Carrier rhodium, tartaric acid and pyridine were added and the solution filtered into a separatory funnel. The pyridine was separated from the aqueous phase by the addition of 12 N NaOH and the pyridine-rhodium complex followed the organic phase. The pyridine layer was transfered to a counting tube which was then measured in the 100-channel analyzer. Chemical yields were determined by measuring the absorption of the complex at 420 mμ with a Beckman DU spectrophotometer. A detailed description of the separation procedure is given in the section on chemical separations.

Other techniques which were investigated for rhodium separations were ion exchange and precipitation of the potassium-rhodium-nitrite complex. For the ion exchange technique, the rhodium solution was adjusted to 0.2 N HCl and run through a small column of Dowex-50 resin. After washing with 0.2 N HCl the rhodium was removed with 2 N HCl. By this procedure rhodium is separated pure enough to isolate the 550 kev peak for gamma spectroscopy but the time involved is prohibitively long.

The nitrite precipitation described in a previous report (2) is much faster than ion exchange, but the chemical yield determinations require considerably more time than the extraction method.

The calibration curve for rhodium determination by extraction with pyridine is given in Figure 31. It appears from this curve and the results listed in Table X, that quantities as small as 0.10 μg of rhodium can be determined by this method at a flux level of $10^{12}$ n $cm^{-2}$ $sec^{-1}$. (E. Steele)

## G. Preliminary Experiments for the Activation Analysis of Silver

There is some interest at the present time in the activation

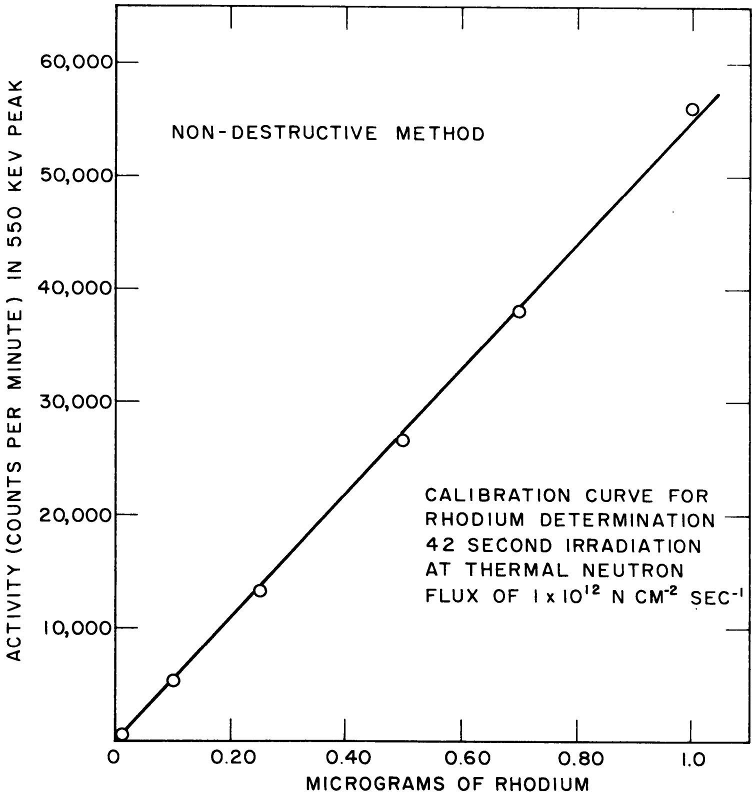


Fig. 30. Calibration curve for activation analysis of rhodium--non destructive.

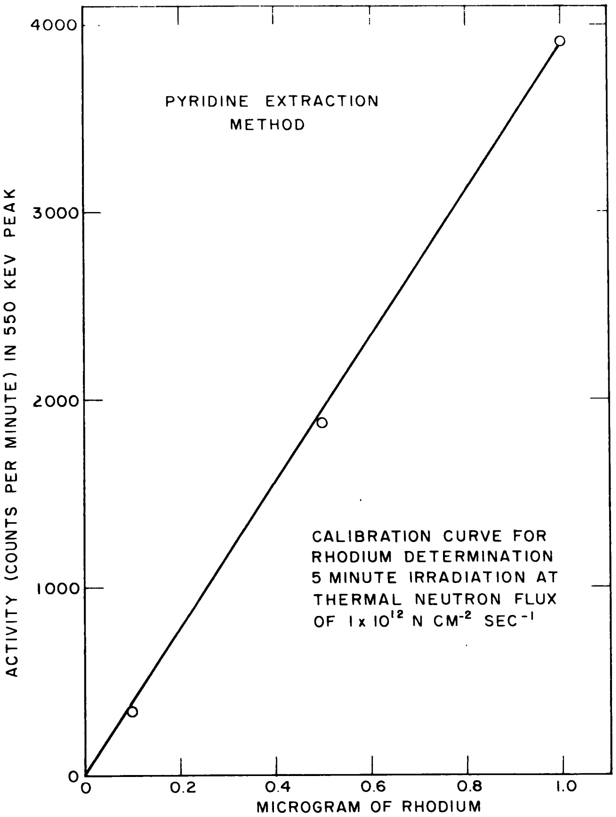


Fig. 31. Calibration curve for activation analysis of rhodium--with chemical separation.

analysis by $\gamma$-spectrometry of $Ag^{108}$ (2.3-minute half-life) or $Ag^{110}$ (24.2-second half-life) because of their high cross-section values for thermal neutrons. For the case of $Ag^{108}$ a rapid radiochemical separation is necessary while in the measurement of $Ag^{110}$ the non-destructive method would be of interest. We have initiated studies of both methods.

Several rapid radiochemical separations for silver have been studied; detailed procedures for two of these are given in the last section of this report. One of these procedures makes use of an interesting new rapid chemical separation technique. A hot acid ($HNO_3$) solution containing the sample and 40 mg of silver carrier is filtered through two Buchner funnels in tandem as shown in Fig. 32. The top funnel contains only filter paper and is used to filter out solids such as silica which tend to adsorb considerable contamination. A $PbCl_2$ precipitate layer containing about 1.5 g of Pb is put in the lower funnel on a filter paper. The filtering action is speeded up with an aspirator or vacuum pump.

During filtration the hot acid solution dissolves some of the lead precipitate freeing chloride ions which in turn react with the silver ions to form AgCl. At the end of the filtration the lead chloride can be easily flaked off the paper while most of the AgCl sticks to the paper. Only about 10% of the total silver is lost during this flaking while ~90% remains on the paper which can now be mounted for counting. This procedure is rapid and simple and is now being applied to practical samples.

In actual runs using G-1 rock samples, the chloride radioactivity from the gelatine capsule used as a container contaminates the AgCl sample. Thus it is recommended that the sample be irradiated in a sealed polyethylene tube and that after the irradiation the sample only be transferred to the peroxide melt. (Y. Kusaka)

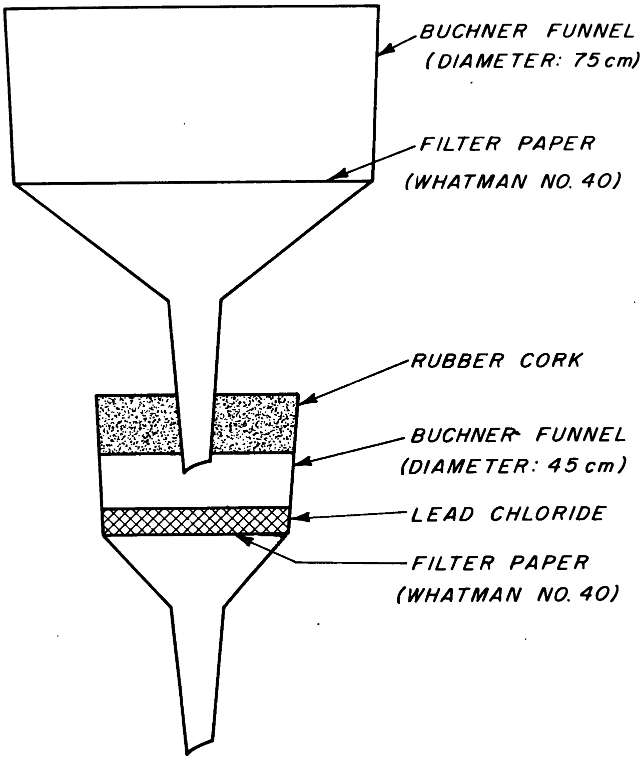


Fig. 32. Filtration apparatus for silver separation.

## H. Activation Analysis of Trace Vanadium in Cadmium

Samples of cadmium containing submicrogram amounts of vanadium along with samples of the pure cadmium rod from which the cadmium-vanadium mixture (alloy) was made were available. The estimated amount of vanadium present in the mixture was $<2$ ppm. The problem was to determine the amount of vanadium in the mixture, or to set some lower limit of detection.

Irradiations were made in the pneumatic tube system of the

Ford Nuclear Reactor at a flux of ~1.4 x $10^{12}$ n $cm^{-2}$ $sec^{-1}$. The samples were analyzed on the dual 100-channel analyzer and associated circuits.

Several preliminary irradiations were made on both the stock cadmium and the cadmium-vanadium alloy. These irradiations showed a high Bremsstrahlung underlying the photopeaks and a high abundance $\gamma$-ray at 1.3 Mev which would interfere with the 1.43-Mev vanadium $\gamma$-ray. The 1.3-Mev $\gamma$-ray was due to 50-minute $Cd^{117}$ and the Bremsstrahlung, mostly from 54-hour $Cd^{115}$. The above problems were overcome by using a beta paddle and spreading out the scanned area to show 0.5 - 2.5 Mev instead of the normal 0 - 2 Mev.

A more serious problem was one of flux depression due to the 27000 barn cross-section of $Cd^{113}$ on the vanadium with its 1.43 barn cross-section. It was felt that although the flux depression could not be avoided the effect could be lessened if the samples were dissolved and the solutions irradiated, thus spreading the sample and taking advantage of a larger surface area. The preliminary analysis showed no trace of vanadium and a more thorough examination was made.

Because there was no indication of vanadium present in the alloy a series of standard cadmium-vanadium solutions were made to determine a detection limit. An amount of the stock cadmium was dissolved in $HNO_3$ and diluted so that 1 ml of solution had 20 mg of cadmium. A vanadium standard solution was made and calibrated against a previously determined vanadium standard curve. Amounts of vanadium standard were added to constant amounts of cadmium standard so the resulting solutions gave 10 mg/ml of cadmium with varying amounts of vanadium.

The analysis procedure was to package $>$ 1 ml of the standard cadmium-vanadium solution in a 0.320" I.D. polyethylene tubing and irradiate it for 10 minutes. One ml of the irradiated solution was then transferred to a graduated tube, sealed and analyzed. The total time from the reactor core to the analyzer was no more than 90 seconds although all samples were corrected to 120 seconds. A gold foil was run along with each sample to permit correction for flux variation.

The subsequent results showed that without a chemical separation .00909 $\mu$g of vanadium can be determined in the presence of 10 mg of cadmium. This amount gave 235 c/m/photopeak area. By extrapolating the standard curve it is believed that .006 - .007 $\mu$g vanadium in 10 mg cadmium could be determined. This would give a photopeak area of ~150-200 c/m.

An amount of the cadmium-vanadium alloy was dissolved and diluted so that there was 10 mg/ml cadmium and run in the same manner as the standards. The alloy showed no decay in the 1.43 Mev region. From this, the amount of V in the cadmium-vanadium alloy appears to be $<$ 0.7 ppm.

## I. Reactor Pool Water Radioactivity

During the past year qualitative analyses have been performed on a variety of samples associated with the reactor pool water. These samples were obtained from the following sources, (a) pool floor air monitor filter, (b) primary cooling loop, (c) de-ionizer regeneration and (d) the pool floor cleaning device.

Several fission products have been observed as well as neutron-capture activities of generally indeterminate origin. Most of these activities have been observed at other swimming pool reactors. The source of fission-products is believed to be the ~1 ppm of uranium present in most cladding and structural materials.

When operating at the normal power level of 1 megawatt, water is drawn down through the core at the rate of 1000 gpm to a temporary hold-up tank, then circulated through the heat exchanger and returned to the pool through a diffuser plate at the pool floor. The primary activity observed on the pool floor air monitor during operation of the reactor was found to be 32-minute $Cs^{138}$. This activity and lesser amounts of other fission products results from diffusion of fission product xenon and krypton from the pool water in the air and subsequent decay to a filterable daughter activity. The rate of fission gas diffusion into the pool floor air rises with increasing temperature of the water returned from the primary cooling loop and may be of concern at the proposed 5-megawatt operation.

Samples taken from the primary loop showed $Mg^{27}$, $Na^{24}$, $Cu^{64}$, $F^{18}$, $W^{187}$, $Mo^{99}$ and $Cr^{51}$. The chromium apparently results from a commercial preservative treatment given the fuel elements when new.

Regeneration of the de-ionizer allowed observation of certain longer-lived activities which had built up over a period of several weeks. These were $Cr^{57}$, $Zn^{65}$ and smaller amounts of $I^{131}$, $Mn^{54}$, $La^{140}$, $Ce^{141}$ and $Ru^{106}$.

One of the periodic clean-ups of the pool bottom turned up a very interesting sample. This was a piece of silvery metal weighing 55 μg and having beta activity of over 100 mr/hr. A short irradiation of a portion of the metal eliminated a number of possible components such as aluminum. Subsequent chemical treatment of a second portion, with gamma spectrometry, proved the presence of $Zr^{95}$, $Nb^{95}$, $Ru^{106}$-$Rh^{106}$, $Cs^{137}$ and $Ce^{144}$, in quantities corresponding to ~100-day cooled fission products. The assumption was then made that the metal was either cladding or structural material. The results were within an order of magnitude of that calculated for 93% enriched uranium irradiated for the 2000 megawatt hours the FNR has been in operation. This specimen is believed to have come from an old fission plate previously present in the system. (M. Wahlgren)

## VI INDIRECT NEUTRON ABSORPTIOMETRY (11)

It is possible to utilize the absorption of neutrons for analysis just as the absorption of electromagnetic radiation is used for other methods. In the past few years, some work of this type has been reported in the literature (12-17) but in general this method has had little acceptance except for the analysis of boron.

The tendency for an element to absorb thermal neutrons is indicated by a "thermal neutron absorption cross section". Table XI lists these cross sections for the 20 elements which are the best neutron absorbers. It is interesting to note that most of these elements, particularly those with the highest cross sections, are rather exotic elements not often encountered in the majority of analytical laboratories.

The application of neutron absorptiometry to the analysis of boron appears to have filled a need for a rapid, non-destructive, and on occasion "in-line" (18,19) method for macro amounts of this element. From Table XI we see, however, that there aee several elements for which the method would be much more sensitive and for which there would be less potential interference. Indeed the element gadolinium would be some 60 times more sensitive than boron and almost 10 times better than any other element in the periodic system.

We are studying a technique for utilizing this unique neutron absorption property in the analysis of common elements such as fluorine. This technique, which we call "Indirect Neutron Absorptiometry", is analogous to radiometric analysis in that

Table XI Thermal Neutron Absorption Cross Sections (5)

| Element | Cross Section (barns) |
|---|---|
| Gadolinium | 46,000 |
| Samarium | 5,500 |
| Europium | 4,600 |
| Cadmium | 2,550 |
| Dysprosium | 1,100 |
| Boron | 750 |
| Iridium | 430 |
| Mercury | 380 |
| Indium | 190 |
| Rhodium | 150 |
| Thulium | 118 |
| Hafnium | 105 |
| Lutetium | 108 |
| Gold | 98 |
| Rhenium | 84 |
| Lithium | 71 |
| Holmium | 64 |
| Silver | 62 |
| Neodymium | 46 |
| Terbium | 44 |

neutron absorbing elements are utilized in the determination of elements which do not themselves absorb neutrons.

In a typical procedure, fluoride ions in solution are precipitated with an excess of gadolinium ions. Gadolinium ions absorbed on the precipitate are washed off or eliminated by a dissolution and reprecipitation. Neutron absorption measurements are then made either on the dissolved precipitate or on the liquid residue. The neutron absorbing gadolinium measured thus represents a stoichiometric amount of fluoride.

The sensitivity obtainable is quite dependent upon the geometry of the neutron source, sample container and neutron detector within the assembly. At present a modified Nuclear-Chicago Neutron Howitzer is being used with a 5-curie plutonium-beryllium source. This permits a bottled liquid sample to be placed between the source and the detector. We are, however, assembling a modified apparatus in which the sample solution is contained in a Marinelli-type beaker surrounding the small neutron detector tube. This should eliminate much of the scattered neutron radiation which now reaches the detector without "seeing" the sample. By improving the geometry we should also increase the sensitivity of the method.

Preliminary results indicate that the idea of indirect neutron absorptiometry is sound and that values reproducible to within a few per cent can be obtained rapidly by this technique. Even with relatively poor geometry it is possible to analyze for milligram amounts of fluoride and it should be possible to improve this sensitivity with the new apparatus being assembled. This method should also be applicable to the analysis of other ions which form insoluble compounds with gadolinium. It may even be possible to analyze for potassium as the tetraphenyl borate by this technique.

Indirect neutron absorptiometry is a non-destructive method which utilizes encapsulated sources only and does not require handling of radioactive solutions. In this respect it presents no more problems than the thousands of thickness, density and level gauges used routinely in industry at the present time. Furthermore it utilizes the same principles of absorptiometry already so familiar to the analytical chemist — only the type of radiation is different.

Work is continuing on this method to elaborate the areas of analysis in which it will be most useful. Detailed evaluation of procedures and equipment will establish limits of sensitivity, as well as point up problems of contamination, manipulation, and the like. It appears now, however, that this indirect approach to neutron absorption has considerable potential for the average analytical laboratory.

The undersigned enjoyed many fruitful discussions with G. W. Leddicotte and J. E. Strain on the general topic of neutron absorption during a leave at Oak Ridge National Laboratory in the Spring of 1960. (W. W. Meinke)

## A. Use of Gadolinium for the Determination of Fluoride

Gadolinium, as other rare earths, forms a highly insoluble fluoride. The $K_{sp}$ is $6.7 \times 10^{-17}$. It is feasible therefore that a modified gravimetric method could be devised for the determination of fluoride in which 1 mg of gadolinium would be equivalent to 0.363 mg of fluoride. Various amounts of fluoride (NaF) were precipitated in pH 2 to 3 aqueous media with excess gadolinium. After washing, two procedures were then attempted for the final measurements.

In the first procedure the $GdF_3$ was slurried with excess NaOH and heated, coverting the fluoride to the hydroxide. After sufficient washing, the hydroxide was then dissolved in dilute $HNO_3$, diluted to 100 ml and its absorption measured in the neutron flux. The second procedure involved adding a known excess amount of gadolinium to the fluoride sample, and quantitatively diluting the supernatant liquid before measurement, thus in effect measuring the gadolinium which did not precipitate.

Both the preceding two procedures gave low results from the calculated amounts of fluoride present and suffered from poor precision. This work will be pursued further with the new measurement set-up. Different variables in the process will be explored to try to optimize this indirect technique. (R. Ruch)

# VII SEPARATION PROCEDURES

## CHEMICAL SEPARATIONS

Element separated: Titanium

Procedure by: Kim

Target material: Meteorites, rocks and minerals, alloys, botanical and biological ashes

Time for sep'n: 13 min.

Equipment required: Nickel crucible with a lid, Fisher burner, centrifuge, separatory funnel

Type of bbdt: Neutron activation

Yield: $\sim$68%

Degree of purification: Mechanical contamination of $\sim 10^{-8}$g $Mn^{56}$, $V^{51}$

Advantages: Simple and fast

Procedure:

(1) Heat 5 ml $Ti^{+4}$ carrier (0.8 mg) in Ni-crucible to dryness; add 4 or 5 g $Na_2O_2$. (The amount of carrier added is dependent on the titanium content in the sample.)

(2) Fuse $\sim$0.1 g of irradiated finely ground sample for one min; swirl melt on side of crucible.

(3) Dissolve the melt in $H_2O$, boil, centrifuge and acidify the residue with either HCl or $H_2SO_4$.

(4) Add Fe-carrier and make the solution alkali with $NH_4OH$ to precipitate $TiO_2$; centrifuge.

(5) Add 20 ml of 10% $H_2SO_4$ to the residue and add 10 ml of 6% aqueous cupferron and 10 ml of isopropyl ether. $Ti^{+4}$ extracts into the organic layer. Draw off the aqueous layer (crushed ice should be used to keep the liquids cool).

(6) Add crushed ice to the ether solution; back wash with 20 ml of cooled 15% NaOH (Cu, V, Mo, W are eliminated completely).

(7) Wash ether fraction with 10% $H_2SO_4$ and transfer ether to marked tube for counting.

(8) Count 0.32 Mev $\gamma$-ray of 5.8 min $Ti^{51}$ with $\gamma$-spectrometer; determine chemical yield by measuring pertitanic acid (yellow) with Beckman spectrophotometer (420 m$\mu$).

✓

Remarks:

Depending on the type of sample, some of the steps in the separation could be skipped. For instance, unless a large amount of vanadium is contained in the sample, step 6 (NaOH backwashing) is unnecessary since most of the vanadium is eliminated as the sodium vanadate which is dissolved in water when $Na_2O_2$ melt is treated with water and centrifuged. However, if there is a large amount of vanadium in the sample, a trace of vanadium might come down with titanium and it interferes with the spectrometrical determination of titanium. Although NaOH backwashing eliminates vanadium very well, it reduces the chemical recovery of titanium appreciably by forming a titanium oxide precipitate.

The temperature should be kept cool ($\sim 10^{\circ}C$) preceeding the NaOH backwashing and the aqueous layer should be removed immediately after the shaking. A filtering step through a fine sintered glass chimney or Whatman No. 42 filter paper would be required if a large amount of sample is fused, because a limited separation time causes incomplete fusion occasionally.

Step 4 would not be necessary unless a fair amount of copper is present in sample. Copper is a rather serious contamination if it comes down with titanium since it has a 0.511 Mev annihilation peak near to the 0.32 Mev titanium peak. Step 6 eliminates copper too.

Step 7 should be done twice if possible to eliminate mechanical contamination which always accompanies solvent extraction. Care must be taken to draw the aqueous layer completely from the ether layer. Throughout the experiment, it should be borne in mind to keep the temperature considerably low ($\sim 10^{\circ}C$) so as not to destroy the cupferron. Often, the heat involved in the neutralization with NaOH will cause trouble.

If .3-.4 mg of titanium is contained in the sample, either a large amount of Ti carrier or a small amount of the sample should be taken so that colorimetric yield determination gives reproducible value. For a large amount of titanium carrier, 500 mμ would be used instead of normal 420 mμ for photometric determination.

Much practice will be required for the $Na_2O_2$ fusion. A ring clamp for holding a Ni-crucible should be one inch away from the surfaces of a burner for best results. When the crucible becomes red, a swirling motion would be recommended. Air cooling from red crucible to black makes it easy to dissolve the melt with water. A few drops of conc HCl could be used for taking out the melt which might otherwise remain on the inner surface of the crucible.

√

# CHEMICAL SEPARATIONS

Element separated: Titanium

Procedure by: Kim

Target material: Botanical and biological

Time for sep'n: 12 min

Yield: 90%

Equipment required: Normal

Degree of purification: Fairly good for γ-spectrometry

Advantages: Fast and simple

Procedure:

(1) Leach the sample with conc $HNO_3$ and heat to dryness in a 250 ml beaker. Add 72% $HClO_4$ and fume it.

(2) Add conc HCl and clarify solution by heating.

(3) Add Fe carrier and make the solution alkali with NaOH to precipitate $FeOH_3$ and $TiO_2$. Centrifuge.

(4) Dissolve the residue with 10% $H_2SO_4$.

(5) Extract $Ti^{+4}$ with 6% cupferron.

(6) Count 0.32 Mev $Ti^{51}$ with γ-spectrometry. The yield is determined by the color of $H_2TiO_3$.

Remarks:

Step 3 can be eliminated if the sample does not contain a large amount of any one element. Iodine is a rather significant problem for handling marine organisms. Fe does not carry iodine down with the titanium. A preliminary $CCl_4$ extraction can be used to eliminate much of the iodine if desired but it must be repeated at least twice for this purpose. Fuming with conc $H_2SO_4$ expells most of iodine; however, it is not advisable to use the technique because active iodine might contaminate the hood. $Na_2S_2O_3$ absorbs iodine upon filtering the solution but a trace amount is still retained in the solution.

In step 1 fusion with $Na_2S_2O_7$, $NaHSO_3$ or $KHF_2$ in a platinum crucible can be substituted for the acid leach. The melt is then dissolved in conc $H_2SO_4$ and water. Silica rocks can be fused with HF plus $H_2SO_4$ in a platinum crucible. If a large amount of vanadium is contaminated in a sample, 15% NaOH backwashing should be done after cupferron extraction instead of Step 3.

## CHEMICAL SEPARATIONS

Element separated: Niobium

Procedure by: Brownlee

Target material: Rocks and minerals

Time for sep'n: ~12 min

Type of bbdt: Neutron irradiation

Yield: ~30%

Procedure:

(1) Fuse 100-400 mg finely ground irradiated sample (removed from gelatine capsule) with ~4 g $K_2S_2O_7$ for 5 min or until clear. Cool quickly.

(2) Digest the solidified melt in 35 ml $H_2O$ containing 5 ml saturated oxalic acid and 2 drops Nb(V) carrier (10 mg Nb(V)/ml). Filter; rinse ppt with 15 ml sol n containing 1 ml saturated oxalic acid in 100 ml $H_2O$.

(3) Add 150 ml HCl to filtrate. Extract 3 times with 15 ml portions 4-methyl-2-pentanone equilibrated with 9 $\underline{M}$ HCl.

(4) Back extract Nb(V) from combined organic extracts by shaking 3 times with 15 ml portions of a solution containing 4 ml saturated oxalic acid in 100 ml $H_2O$.

(5) Boil aqueous layer briefly to expel organic material; add 100 mg Ca(II) as $Ca(NO_3)_2$, followed by a few drops $NH_4OH$.

(6) Collect ppt; wash with dilute $Ca(NO_3)_2$ solution.

(7) Mount sample; analyze from ~0-70 kev with 100-channel analyzer. Determine chemical yield with Nb-95 tracer.

## CHEMICAL SEPARATIONS

Element separated: Rhodium

Procedure by: Steele[a]

Target material: Synthetic rock samples[b]

Time for sep'n: 7 min

Type of bbdt: Neutron (in pneumatic tube) 5 min at 1 megawatt

Equipment required: Spectrophotometer

Yield: 95-100%

Degree of purification: Sufficient for $\gamma$-spectroscopy

Advantages: Rapid separation and chemical yield determination

Procedure:

(1) Irradiate sample for 5 min at 1 megawatt.

(2) Two min before end of irradiation heat 5 g $Na_2O_2$ in a Ni crucible to melting. Add sample!! ...CAUTION... and fuse for one min.

(3) Cool crucible by cautiously dipping into cold water.

(4) Dissolve melt with 20 ml conc HCl!! ...CAUTION... and add:
  (a) 5 ml $RhCl_3$ soln. (1 mg/ml in 1 N HCl)
  (b) 1 ml 10% tartaric acid
  (c) 8 ml pyridine

(5) Mix well and transfer to separatory funnel by filtering off the silica. Wash ppt with 5 ml 6 N HCl and collect this filtrate in the same separatory funnel.

(6) Add 15 ml 12 N NaOH to the separatory funnel and separate the pyridine layer (upper) for analysis with 100-channel analyzer.

Chemical yield: Determine by measuring rhodium-pyridine complex absorbance at 420 mμ.

Remarks:

(a) A combination of previously reported methods.

(b) Silica, alumina and $RhCl_3$.

## CHEMICAL SEPARATIONS

Element separated: Silver

Procedure by: Kusaka

Target material: Rock (G-1)

Time for sep'n: 5 min

Type of bbdt: Neutron (in pneumatic tube) 5 min at reactor power level of 1000 kw

Equipment required: Standard

Yield: ~60%

Degree of purification: Sufficient for γ-spectroscopy

Advantages: Simple, rapid separation

Procedure:

(1) Place 40 mg of Ag carrier and 50 mg of Mn holdback carrier in Ni crucible; dry.

(2) Place 5 g sodium peroxide in this nickel crucible and fuse for one min before the end of irradiation.

(3) Fuse 0.5 g irradiated sample for one min in this crucible.

(4) Dissolve melt in hot 100 ml of 4 N $HNO_3$ containing 5 ml of 30% $H_2O_2$.

CAUTION!!!

(5) Filter through two Buchner funnels in tandem, with $PbCl_2$ (Pb weight = 1.5 g) in lower funnel (see diagram).

(6) Remove upper funnel and wash $PbCl_2$ layer with hot 4 N $HNO_3$ and dry with acetone.

(7) Flake off most of $PbCl_2$ and count AgCl remaining on filter paper.

Chemical yield: Thiocyanate titration.

Remarks:

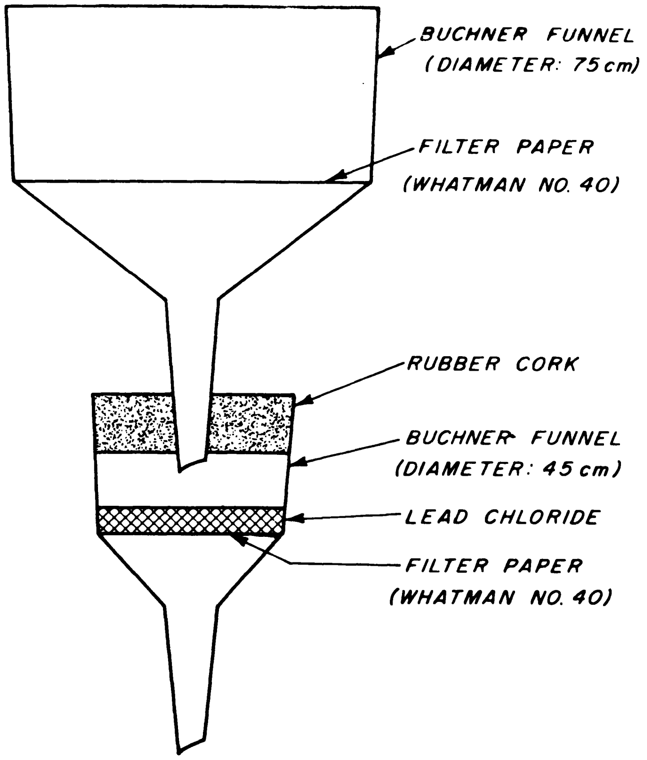
Although the counting sample in this method was contaminated with chlorine-38 activity, this activity did not interfere for with determination of silver by γ-spectrometry.

The chemical yield of silver was determined as follows. The precipitate on the counting paper was dissolved by hot ammonia solution. After boiling, the solution was filtered. 1.5 g zinc

√

powder was added to the filtrate and stirred and filtered.

The precipitate was dissolved by nitric acid and titrated with standard thiocyanate solution using ferric ion.



## CHEMICAL SEPARATIONS

Element separated: Silver

Procedure by: Kusaka

Target material: Rock (G-1)

Time for sep'n: 7 min

Type of bbdt: Neutron (in pneumatic tube) 5 min at reactor power level of 1000 kw

Equipment required: Standard

Yield: ~60%

Degree of purification: Enough for $\gamma$-spectroscopy

Advantages: Rapid separation

Procedure:

(1) Place 20 mg of Ag carrier and 50 mg of Mn holdback carrier in nickel crucible; dry.

(2) Fuse 0.5 g irradiated sample, contained in gelatine capsule, with 5 g sodium peroxide for one minute. (Finely ground samples)

(3) Dissolve melt in hot solution containing 20 ml of 6N HCl, 70 ml of 6N $HNO_3$, 5 cc of 30% $H_2O_2$ and 45 ml $H_2O$.

CAUTION!!!

(4) Filter off silver chloride through 60-mm medium glass frit, wash with water.

(5) Dissolve silver chloride from glass frit with hot ammonia in bottle containing 1 g metallic zinc powder.

(6) Swirl for short time and filter through filter chimney.

(7) Wash final sample with hot dilute acid, water; dry with acetone.

Chemical yield: Thiocyanate titration

Remarks:

(1) This method is modification of Schindewolf-Wahlgren method;(2) the dissolving solution for the $Na_2O_2$ melt has been changed to reduce Ag loss by $AgCl_2$ complex formation, and the decontamination of manganese improved.

(2) The chemical yield of silver was determined as follows: The precipitate on the counting paper was dissolved by hot ammonia solution. After boiling, the solution was filtered. 1.5 g

of zinc powder was then added to the filtrate, stirred and filtered. The precipitate of silver metal was dissolved by nitric acid and titrated with standard thiocyanate solution, using ferric ion.

✓

## CHEMICAL SEPARATIONS

Element separated: Cadmium

Target material: Miscellaneous samples

Yield: ~ 80%

Procedure by: DeVoe

Time for sep'n: 7 min.

Equipment required:

Mechanical stirrer, 50 ml centrifuge tube (round bottom), 25 ml. Boston round bottle with polyethylene seal in cap.

Degree of purification: See remarks

Procedure:

(1) To a 2 ml solution of miscellaneous "carrier free" activities add 50$\lambda$ (0.675 g) of 2% (by weight) Cd(Hg). There are 14 mg of Cd in the Hg. The final acid strength of the solution should be less than 0.5 N. Elements that are not reduced by Cd(Hg) can be present in macro quantities.

(2) Stir the solution mechanically in a 50 ml centrifuge tube for 5 minutes, remove the supernate, wash carefully with 0.1 N $HNO_3$ and three times with distilled water.

(3) Transfer the amalgam to a stoppered bottle of thallous acetate solution (150 mg $Tl^{+1}$/2 ml, pH=1) which has been made $O_2$ free with $N_2$. Shake for one minute.

(4) Remove the aqueous layer containing the cadmium radioisotopes and count.

Remarks:

(1) Decontamination factors for I, Co, Sr, Y, Ir, Cs, Ba, La, Zr, Nb, Cr, Zn, and Ce-Pr are greater than $10^4$; Sb, Ru, Ag, and Hg are $10^3$; In, Tl, Sn, Se, and Te interfere with the separation. Improvement in the separation can be made by using a scavenger technique. 2% In(Hg) can be used before the Cd(Hg) separation to give decontaminations of Sn, Sb, Ru, and Hg greater than $10^4$. Separation of thallium and indium can be accomplished by sucessive extractions using Tl(Hg) and In(Hg) exchange. The Tl(Hg) exchange must be done in an inert atmosphere.

(2) Oxidizing agents such as $MnO_4^-$, $Ce^{+4}$, $UO_2^{++}$, etc. which oxidize cadmium from the mercury must be reduced before separation. Contaminating elements which oxidize Cd from the Hg must have a total concentration less than $10^{-4}$ M so that the yield is not adversely affected.

(3) Time of Separation with scavenge 14 minutes.

## CHEMICAL SEPARATIONS

Element separated: Thallium

Procedure by: Brownlee

Target material: Rocks, minerals, meteorites

Time for sep'n: 10-12 min

Type of bbdt: Neutron irradiation

Yield: 45-80%

Procedure:

(1) Fuse 200-1000 mg samples (finely ground) with 3.5-4 g $Na_2O_2$. Cool melt quickly. Digest samples with large amounts of silica, $H_2SO_4$ and HF in Pt.

(2) Dissolve peroxide melt with 20 ml 1 N HBr, followed by 20-25 ml conc HBr. Add 10 mg each of Al, Cu(II), Mn(II), K and Zn carriers, plus 5 ml $Br_2$-$H_2O$.

(3) Extract solution 2 times with 20 ml portions of isopropyl ether. Wash combined ether extracts 3 times with 15 ml portions of 1 N HBr.

(4) Evaporate ether extracts over 10 ml $H_2O$. Cool; saturate aqueous sol'n with $SO_2$ gas.

(5) Add excess saturated KI; heat to almost boiling on a hot plate.

(6) Filter, wash with water and mount between Teflon and Scotch tape for decay curve analysis.

(7) Determine chemical recovery with $Tl^{204}$ tracer or by adding carefully weighed amount of $TlNO_3$ and weighing precipitate.

## CHEMICAL SEPARATIONS

Element separated: Thallium
Procedure by: Brownlee

Target material: Rocks, minerals, meteorites
Time for sep'n: 12-14 min

Type of bbdt: Neutron irradiation

Yield: 83-100%

Procedure:

(1) Fuse 200-1000 mg samples (finely ground) with 3.5-4 g $Na_2O_2$. Cool melt quickly. For samples containing large amounts of silica, digest with $H_2SO_4$ and HF in Pt.

(2) Dissolve peroxide melt with 20 ml 1 N HBr, followed by 20-25 ml conc HBr. Add 10 mg each of Al, Cu(II), Mn(II), K and Zn carriers, plus 5 ml $Br_2$-$H_2O$.

(3) Extract solution 2 times with 20 ml portions of isopropyl ether. Wash combined ether extracts 3 times with 15 ml portions of 1 N HBr.

(4) Evaporate ether extract over 10 ml $H_2O$. Cool; saturate aqueous solution with $SO_2$ gas.

(5) Add 15 ml of 20% sodium tartrate, plus 5 drops phenolphalein indicator. Add 6 N NaOH to end point ($\sim$5-7 ml).

(6) Add 15 ml 20% KCN and 8 ml of 6 N NaOH.

(7) Add 50 mg thionalide in 10 ml acetone. Heat sol'n to boiling. Cool, adding liquid $N_2$ to beaker.

(8) Filter, wash with $H_2O$. Mount between Teflon and Scotch tape for decay curve analysis.

(9) Determine chemical yield with $Tl^{204}$ tracer.

Remarks: This is an alternate procedure.

## CHEMICAL SEPARATIONS

Element separated: Thallium    Procedure by: Kim

Target material: Silica rocks    Time for sep'n: ~14 min

Type of bbdt: Neutron irradiation

Yield: 75%

Procedure:

(1) Add 2 ml HF and 1 ml conc $H_2SO_4$ to 50 mg $TlNO_3$ in Pt crucible.

(2) Add ~0.2g finely ground irradiated sample; boil 1 min.

(3) Transfer to a 250 ml beaker; add 1 ml 1 N HBr.

(4) Extract $Tl^{+++}$ with 1 N HBr saturated isopropyl ether and back wash the ether twice.

(5) Add 10 ml water to the ether and evaporate the ether off on a hot plate. Filter.

(6) Add 2 M sodium acetate and reduce $Tl^{+++}$ by $SO_2$ gas while cooling.

(7) Add 2% $NaB(C_6H_5)_4$ until white precipitate appears.

(8) Heat; pour through filter chimney onto No. 42 filter paper. Cover sample with Teflon.

(9) Count β-rays of 4.2-minute $Tl^{206}$ in proportional counter. Determine chemical yield by weighing $TlB(C_6H_5)_4$.

## CHEMICAL SEPARATIONS

Element separated: Thallium  Procedure by: Kim

Target material: Meteorite, rocks, alloys  Time for sep'n: ~12 min

Type of bbdt: Neutron irradiation

Yield: ~70%

Procedure:

(1) Add 5 g $Na_2O_2$ to 50 mg $TlNO_3$ in Ni crucible.

(2) Add~0.2g finely ground irradiated sample; fuse 1 min.

(3) Dissolve melt in $H_2O$ and add conc HBr.

(4) Extract $Tl^{+++}$ with 1 N HBr saturated isopropyl ether and backwash the ether twice.

(5) Add 10 ml $H_2O$ to ether; evaporate ether off. Filter.

(6) Add 2 $\underline{M}$ sodium acetate to filtrate; reduce $Tl^{+++}$ with $SO_2$ gas while cooling.

(7) Add 2% $NaB(C_6H_5)_4$ until white precipitate appears.

(8) Heat; pour through filter chimney onto No. 42 filter paper. Cover sample with Teflon.

(9) Count β-rays of 4.2-minute $Tl^{206}$ in proportional counter. Determine chemical yield by weighing $TlB(C_6H_5)_4$.

## CHEMICAL SEPARATIONS

Element separated: Uranium     Procedure by: Das

Target material: Thorium nitrate     Time for sep'n: ~30 min

Type of bbdt: Neutron irradiation

Yield: 60-80%

Procedure:

(1) Transfer irradiated thorium nitrate into a 100 ml pyrex beaker containing 20 mg U carrier in 10 ml 0.1 N $HNO_3$.

(2) Transfer to separatory funnel; add 10 ml 0.25 M TTA in benzene, extract for 30 sec, wait 30 sec, collect aqueous phase in original beaker. Repeat twice.

(3) Adjust acidity of aqueous phase to 2 N with $HNO_3$ and extract again with TTA.

(4) Extract aqueous phase with an equal volume of benzene; discard benzene.

(5) Add $NH_4OH$ to aqueous phase, centrifuge, discard supernate.

(6) Dissolve ammonium diuranate in dilute $HNO_3$.

(7) Add 5 ml 0.1 M EDTA to aqueous phase and make neutral to methyl orange with $NH_4OH$.

(8) Add 10 ml 1% oxine in CHCl and extract uranium oxinate. Transfer $CHCl_3$ phase to another separatory funnel; repeat and combine $CHCl_3$ phases.

(9) Scrub uranium oxinate with 5 ml 0.02 M $(NH_4)_2$ EDTA.

(10) Back extract uranium oxinate from $CHCl_3$ into dilute acid and discard $CHCl_3$.

(11) Transfer acid extract into 150 ml beaker, boil. Add $NH_4OH$ to initiate precipitation of uranium oxinate; clear sol'n by dropwise addition of HAc, dilute to ~50 ml, complete precipitation of uranium oxinate by addition of 5 ml 20% ammonium acetate. Bring to boil.

(12) Cool, filter, wash with $H_2O$ and dry with suction. Mount and count in proportional counter. Determine chemical yield by weighing as $U_3O_8$.

✓

## CHEMICAL SEPARATIONS

Element separated: Uranium

Procedure by: Das

Target material: Biological ash

Time for sep'n: ~30 min

Type of bbdt: Neutron irradiation

Yield: ~60%

Procedure:

(1) Add ~1.0 g finely powdered irradiated sample to 20 mg U carrier and 2 ml conc $HNO_3$ in 100 ml pyrex beaker; evaporate to dryness; add 2 ml $HNO_3$ and evaporate.

(2) Dissolve in minimum amount 2 N $HNO_3$; add 1 g $Al(NO_3)_3$ and stir up into a wad with Whatman cellulose powder.

(3) Extract the wad with 3 successive portions of 20, 20, and 10 ml of ether and pass the ether through a 3" cellulose column preequilibrated with ether-0.5 N $HNO_3$, collecting the elute in a separatory funnel.

(4) Back extract the uranium with water and precipitate the uranium as diuranate; dissolve in dilute $HNO_3$.

(5) Add 5 ml 0.1 M EDTA to aqueous phase and make neutral to methyl orange with $NH_4OH$.

(6) Add 10 ml 1% oxine in $CHCl_3$ and extract uranium oxinate. Transfer $CHCl_3$ phase to another separatory funnel; repeat and combine $CHCl_3$ phases.

(7) Scrub uranium oxinate with 5 ml 0.02 M $(NH_4)_2$ EDTA.

(8) Back extract uranium oxinate from $CHCl_3$ into dilute acid and discard $CHCl_3$.

(9) Transfer acid extract into 150 ml beaker, boil. Add $NH_4OH$ to initiate precipitation of uranium oxinate; clear sol'n by dropwise addition of HAc, dilute to ~50 ml, complete precipitation of uranium oxinate by addition of 5 ml 20% ammonium acetate. Bring to boil.

(10) Cool, filter, wash with $H_2O$ and dry with suction. Mount and count in proportional counter. Determine chemical yield by weighing as $U_3O_8$.

Note:

Samples containing excessive amounts of iodine are decomposed in an enclosed system drawing off the iodine vapor through an alkaline or thiosulfate trap.

## CHEMICAL SEPARATIONS

Element separated: Uranium

Procedure by: Das

Target material: Silicate minerals

Time for sep'n: ~30 min

Type of bbdt: Neutron irradiation

Yield: 60-80%

Procedure:

(1) Fume ~.1 g of finely powdered irradiated sample in a Pt crucible containing 20 mg U carrier, ~1 ml conc $HNO_3$ and ~.5 ml 40% HF to near dryness. Repeat.

(2) Repeat 1 using $HNO_3$; dissolve residue in dilute $HNO_3$, dilute to ~30 ml; ppt with $NH_4OH$; centrifuge, discard supernate. Repeat.

(3) Dissolve ppt in 10 ml (2:10) HCl; cool in ice and transfer to separatory funnel containing 10 ml 6% cupferron; swirl funnel and extract cupferrates with 10 ml $CHCl_3$. Let stand 30 sec; discard $CHCl_3$. Repeat.

(4) Add 5 ml 0.1 M EDTA to aqueous phase and make neutral to methyl orange with $NH_4OH$.

(5) Add 10 ml 1% oxine in $CHCl_3$ and extract uranium oxinate. Transfer $CHCl_3$ phase to another separatory funnel; repeat and combine $CHCl_3$ phases.

(6) Scrub uranium oxinate with 5 ml 0.02 M $(NH_4)_2$ EDTA.

(7) Back extract uranium oxinate from $CHCl_3$ into dilute acid and discard $CHCl_3$.

(8) Transfer acid extract into 150 ml beaker, boil. Add $NH_4OH$ to initiate precipitation of uranium oxinate; clear sol'n by dropwise addition of HAc, dilute to ~50 ml, complete precipitation of uranium oxinate by addition of 5 ml 20% ammonium acetate. Bring to boil.

(9) Cool, filter, wash with $H_2O$ and dry with suction. Mount and count in proportional counter. Determine chemical yield by weighing as $U_3O_8$.

## VIII PERSONNEL, PUBLICATIONS, TALKS, MEETINGS

### A. Personnel Listing

| | |
|---|---|
| Project Director | Meinke, W. W. |
| Post Doctoral | Kusaka, Y. (Michigan Memorial Phoenix Project No. 191) |
| | Steele, E. |
| Exchange Students | Das, S.(') (India) |
| | Kim, C.(') (Korea) |
| Graduate Students | Brownlee, J.*(') |
| | De Voe, J.*(') |
| | Ruch, R. |
| | Wahlgren, M.* |
| | Weiss, G.(') |
| Staff Assistant | Maddock, R. S. |
| Assistant in Research | Nass, H. W. |
| Assistant in Research (Electronics) | Shideler, R. W. |
| Typing | Coleman, F. G.(') |
| | Hoffman, B.** |
| | Schwing, J.** |
| Undergraduate Students | Fry, E.** |
| | McQuilken, M.**(') |
| | Vogt, J.**(') |

* Half time

** Hourly

*** Hourly summer only

(') Terminated

## B. Papers and Reports Published

1. Trace Analysis of Marine Organisms: A Comparison of Activation Analysis and Conventional Methods. Rinnosuke Fukai and W. Wayne Meinke. Limnology and Oceanography 4, 398 (1959). 11 pages, 1 fig.
2. Method for the Analysis of Multicomponent Exponential Decay Curves. Donald G. Gardner, Jeanne C. Gardner, George Laush and W. W. Meinke. J. Chem. Phys. 31, 978 (1959). 9 pages, 10 figs.
3. Some Activation Analyses of Six Trace Elements in Marine Biological Ashes. R. Fukai and W. W. Meinke. Nature 184, 815 (1959). 1 page.
4. The Rhodium, Silver, and Indium Content of Some Chondritic Meteorites. U. Schindewolf and M. Wahlgren. Geochimica et Cosmochimica Acta 18, 36 (1960). 6 pages.
5. Activation Analysis of Trace Cobalt in Tissue Using 10.5-Minute Cobalt-60m. David G. Kaiser and W. W. Meinke. Talanta 3, 255 (1960). 6 pages, 1 fig.
6. Tellurium-Selenium Content in Meteorites. U. Schindewolf. Geochimica et Cosmochimica Acta 19, 134 (1960). 5 pages.
7. Nucleonics in Analysis. W. W. Meinke. Special Technical Publication No. 261 (February 1960), ASTM, Phila. 8 pages, 6 figs.
8. Isomerism of Ag-108. Morris A. Wahlgren and W. W. Meinke. Phys. Rev. 118, 181 (1960). 3 pages, 2 figs.
9. Radiochemical Separations by Amalgam Exchange. James R. DeVoe, Chong K. Kim and W. W. Meinke. Talanta 3, 298-299 (1960) 2 pages.

10. Review of Fundamental Developments in Analysis: Nucleonics. W. Wayne Meinke. Anal. Chem. 32, 104R (1960). 33 pages.

11. The Radiochemistry of Cadmium. James R. DeVoe. Nuclear Science Series Report NAS-NS-3001 (January 1960), Subcommittee on Radiochemistry, National Research Council, Washington 25, D. C. 57 pages, 6 figs.

12. Radiochemical Separations of Cadmium and the Application of Vacuum Distillation of Metals to Radiochemical Separations. James R. DeVoe. U. S. Atomic Energy Commission Unclassified Report AECU-4610. Ph.D. Thesis (December 1959). 91 pages 11 figs.

13. Activation Analysis Utilizing Fast Radiochemical Separations and Portable Neutron Generators. W. W. Meinke. Paper RICC/283, IAEA Conference on the Use of Radioisotopes in the Physical Sciences and Industry, Copenhagen, Denmark, September 1960. 24 pages, 3 figs.

14. Une Source Reservoir a Francium 223. J. Fourage and W. W. Meinke. Paper RICC/64, IAEA Conference on the Use of Radioisotopes in the Physical Sciences and Industry, Copenhagen, Denmark, September, 1960. 12 pages, 6 figs.

15. Neutron Activation Analysis by Means of Short-Lived Isotopes. James L. Brownlee, Jr. U.S. Atomic Energy Commission Unclassified Report . Ph.D. Thesis (May 1960). 208 pages, 54 figs.

16. Absolute (d,$\alpha$) - Reaction Cross Sections of Zirconium, Molybdenum, Titanium, and Sulphur. Oswald U. Anders and W. W. Meinke. Phys. Rev. (In press, December 15, 1960).

17. Indirect Neutron Absorptiometry. W. Wayne Meinke. Talanta (In press).

## C. Talks

1. J. L. Brownlee, Jr., "Activation Analysis Using Short Half-Lived Isotopes", U. of M. Chemistry Department Colloquium, Ann Arbor, November 19, 1959.
2. M. Wahlgren, "Neutron Absorptiometry", U. of M. Chemistry Department Seminar, Ann Arbor, November 11, 1959.
3. W. W. Meinke, "Activation Analysis Using Short-Lived Activities", Chemistry Division Seminar, Argonne National Laboratory, Argonne, Illinois, December 23, 1959.
4. W. W. Meinke, "Activation Analysis Using Short-Lived Activities", Oak Ridge Section, American Chemical Society, Oak Ridge, Tenn., April 21, 1960
5. W. W. Meinke, "Rapid Radiochemical Separation", Joint Seminar Chemistry and Analytical Chemistry Divisions, Oak Ridge National Laboratory, Oak Ridge, Tenn., June 6, 1960
6. W. W. Meinke, "Techniques for Fast Radiochemistry", Gordon Conference in Nuclear Chemistry, New London, New Hampshire, June 29, 1960.
7. E. Steele, "Industrial Applications of Activation Analysis", Esso Research Forum, Linden, New Jersey, July 1, 1960
8. W. W. Meinke, "Techniques for Fast Radiochemistry", Institute für Radiochemie, Kernforschungszentrum Karlsruhe, Germany, August 31, 1960
9. W. W. Meinke, "Activation Analysis Using Fast Radiochemical Separations and Portable Neutron Generators", IAEA Conference on Use of Radioisotopes in the Physical Sciences and Industry, Copenhagen, Denmark, September 12, 1960

10. J. Fourage (with W. W. Meinke), "Une Source Reservoir a Francium-223", IAEA Conference on Use of Radioisotopes in the Physical Sciences and Industry, Copenhagen, Denmark, September 13, 1960.
11. J. R. DeVoe (with H. W. Nass and W. W. Meinke),"Radiochemical Separations by Amalgam Exchange: Cadmium", Analytical Division, American Chemical Society, New York, September 16, 1960.
12. J. L. Brownlee, Jr. (with C. K. Kim and W. W. Meinke), "Activation Analysis of Thallium Using the 4.2-Minute Thallium-206.", Analytical Division, American Chemical Society, New York, September 16, 1960
13. W. W. Meinke, "Potentialities of Activation Analysis", Symposium on Recent Developments in Research Methods and Instrumentation, NIH, Bethesda, Md., October 4, 1960
14. W. W. Meinke, "Activation Analysis", Chemistry Colloquim. National Bureau of Standards, Washington, D. C., October 5, 1960.
15. W. W. Meinke, "Neutron Activation Analysis", Chemistry Department Seminar, University of Maryland, College Park, October 5, 1960
16. W. W. Meinke, "A Radiochemist in Western Europe", University of Michigan Chemistry Seminar, Ann Arbor, October 19, 1960.
17. W. W. Meinke, "Neutron Activation Analysis Using Portable Neutron Sources, a Machine Source, and the Phoenix Reactor Facilities at the University of Michigan", Detroit Anachem Conference, Detroit, October 24, 1960.

18. E. Steele, "Activation Analysis with Fast Neutrons", Analytical Research Division Seminar, Esso Research, Gulf Hills, Miss., October 24, 1960

19. W. W. Meinke, "Potentialities of Activation Analysis", Michigan State Section of American Chemical Society, East Lansing, October 26, 1960.

## D. Committee Meetings

1. W. W. Meinke, Committee on Nuclear Science, National Research Council, Washington, D. C., November 6, 1959.
2. W. W. Meinke, Subcommittee on Radiochemistry, Committee on Nuclear Science, National Research Council, Tallahassee, Florida, February 1, 1960.
3. W. W. Meinke, Subcommittee on Radiochemistry, Committee on Nuclear Science, National Research Council, Montreal, Canada, May 23, 1960.
4. W. W. Meinke, Subcommittee on Radiochemistry, Committee on Nuclear Science, National Research Council, Washington, D. C., October 31, 1960.

# IX ACKNOWLEDGEMENTS

Many thanks are due to Professor H. J. Gomberg, A. H. Emmons, C. W. Ricker and the staff of the Michigan Memorial-Phoenix Project for their help in arranging for laboratory space and reactor irradiations for this research. Part of this work was supported by Phoenix Projects Nos. 151 and 191.

The assistance of Dr. Norman Bostrum and the staff of Texas Nuclear Corporation in our work with the neutron generator is also greatly appreciated. The help of the Isotopes Division of the Oak Ridge National Laboratory in supplying a number of radioisotopes for this work is acknowledged.

It is a pleasure also to acknowledge the hospitality of Drs. George Boyd, Myron Kelley and George Leddicotte during a leave at Oak Ridge National Laboratory in the Spring of 1960.

(W. W. M.)

# X LIST OF REFERENCES

1. Meinke, W. W., "Progress Report No. 8", U. S. AEC Project No. 7, Contract No. AT(11-1)-70; AECU-4438 (November 1, 1959).
2. Meinke, W. W., "Progress Report No. 7", U. S. AEC Project No. 7, Contract No. AT(11-1)-70; AECU-3887 (November 1, 1958).
3. Meinke, W. W., "Progress Report No. 6", U. S. AEC Project No. 7, Contract No. AT(11-1)-70; AECU-3641 (November 1, 1957).
4. Meinke, W. W., "Sensitivity Charts for Neutron Activation Analysis", Anal. Chem. 31, 792 (May, 1959).
5. Sullivan, W. H., Trilinear Chart of Nuclides, 2nd Edition, U. S. Government Printing Office, Washington 25, D. C., 1957.
6. Strominger, D., Hollander, J. M. and Seaborg, G. T., Revs. Mod. Phys. 30, 683 (1958).
7. Meinke, W. W., "Review of Fundamental Developments in Analysis: Nucleonics", Anal. Chem. 30, 686 (1958).
8. Meinke, W. W., "Review of Fundamental Developments in Analysis: Nucleonics", Anal. Chem. 32, 104R (1960).
9. Meinke, W. W., "Review of Fundamental Developments in Analysis: Nucleonics", Anal. Chem. 28, 736 (1956).
10. Brownlee, J. L., Jr., "Neutron Activation Analysis by Means of Short-Lived Isotopes", Doctoral Thesis, Department of Chemistry, University of Michigan, June, 1960.
11. Meinke, W. W., "Indirect Neutron Absorptiometry", Talanta. (In press).
12. Ford, I. H. and Picciotto, E. E., Nuovo cimento, 2 (9), 141 (1952).
13. Hamlen, R. P. and Koski, W. S., Anal. Chem. 28, 1631 (1956).

## LIST OF REFERENCES (cont'd)

14. Khristianov, V. K. and Panov, G. I., Zhur. Anal. Khim. 12, 362 (1957).

15. Khristianov, V. K., Panov, G. I. and Chernova, A. A., Geokhimiya, 2, 95 (1957).

16. DeFord, D. D. and Braman, R. S., Anal. Chem. 30, 1765 (1958).

17. Kusaka, Y., Bull. Chem. Soc. Japan, 31, 917 (1958).

18. Chem. Eng. News, 35, No. 23, 52 (1957).

19. Mine Safety Appliances Co. Bulletin, "M-S-A Boron Analyzer", 210 North Braddock Ave., Pittsburgh 8, Pennsylvania.

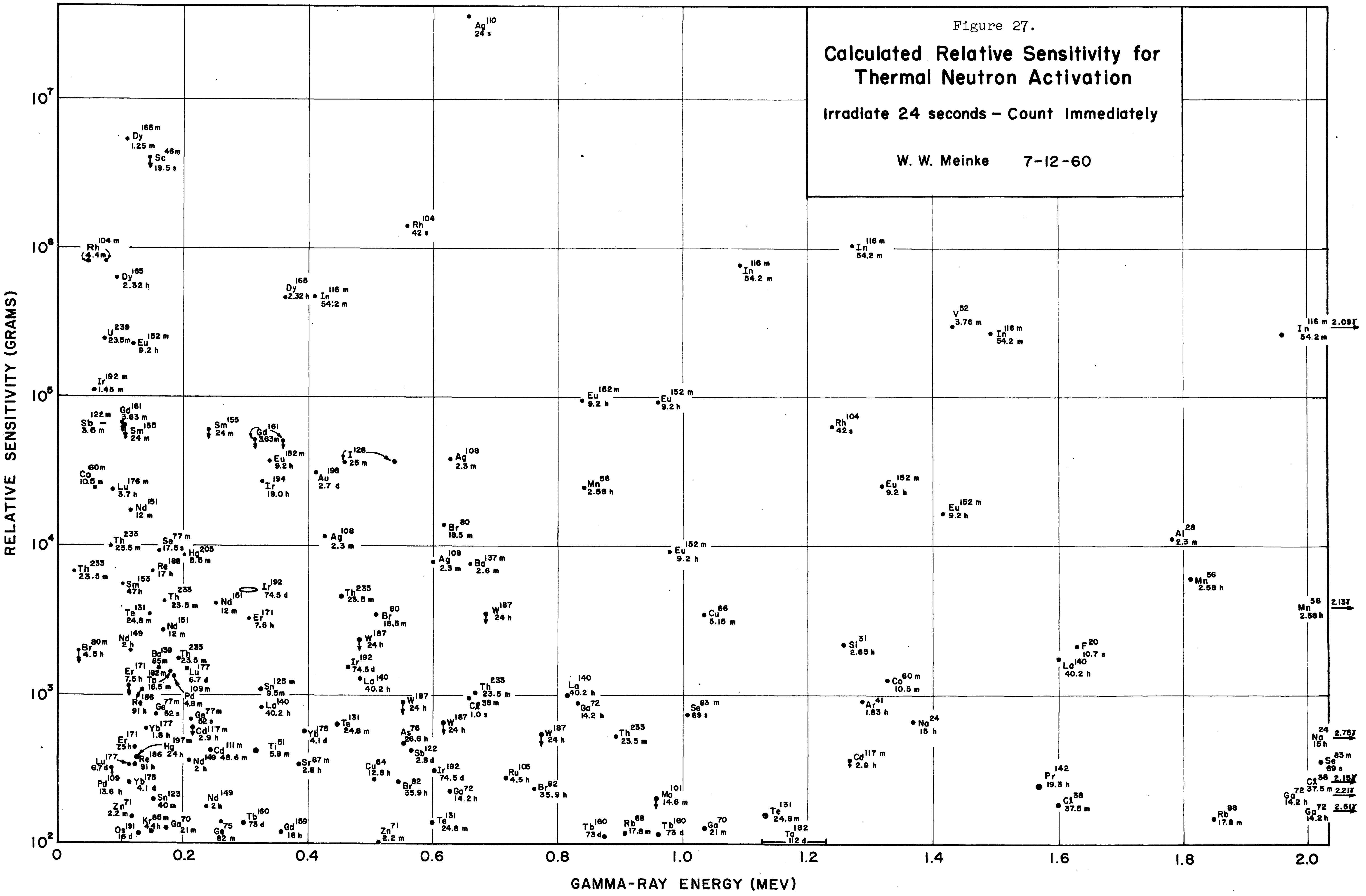


Figure 27.

**Calculated Relative Sensitivity for Thermal Neutron Activation**

Irradiate 24 seconds – Count Immediately

W. W. Meinke 7-12-60