DEPARTMENT OF CHEMISTRY

UNIVERSITY OF MICHIGAN

ANN ARBOR, MICHIGAN

• ACTIVATION ANALYSIS
• NUCLEAR CHEMICAL RESEARCH
• RADIOCHEMICAL SEPARATIONS

PROGRESS REPORT 10

November 1, 1961

Supported by

DEPARTMENT OF CHEMISTRY

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

DEPARTMENT OF CHEMISTRY

U N I V E R S I T Y O F M I C H I G A N

Ann Arbor, Michigan

PROGRESS REPORT 10

November 1960 - October 1961

ACTIVATION ANALYSIS
NUCLEAR CHEMICAL RESEARCH
RADIOCHEMICAL SEPARATIONS

Edited by

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November 1, 1961

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Department of Chemistry

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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, 1960 to October 31, 1961.

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
Progress Report 9 (TID-11009)	November 1960

FOREWORD

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 enought 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 the literature are often covered in a more abbreviated form.

(W. Wayne Meinke)

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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 center of core) for the past year on an average of two to three 8-hour days a week, and several times for a 16-hour day. The reactor has been shut down several times during the year with continuing control rod problems and other miscellaneous repairs.

The radiochemistry group has used ~ 90 hours of megawatt power making 553 irradiations. Of these, 20 irradiations were "in pool" while 533 were penumatic-tube runs. There were a total of 67 hours used for the "in pool", and 23 hours for the pneumatic-tube runs. The "in pool" irradiations included several samples for activation analysis plus production of some 13.6-hour Pd^{109} tracer. In addition many irradiations were made this year using the Cockroft-Walton accelerator. These are summarized in a later section. The pneumatic tube system has worked routinely during the past year with only a few breakdowns, mostly in the relay control boxes.

The rabbits as described in last year's Progress Report (1) have continued to work smoothly with no breaking or coming apart in the tubes. We have used the same rabbits for the past year with no indication of deterioration. The speed of the system has remained at 2.5-second transit time, allowing the group to work with the short half-life isotopes.

The pneumatic tube irradiations were handled in a routine manner [as described in previous progress reports and elsewhere

(1-3)] with a few modifications occasionally used to speed up transfer time in the hoods. It is possible to have a sample counting in the analyzer room 10 seconds after it has left the reactor core. The fingertab film readings for the group have not shown any unusually high readings during the past year.

(H. Nass)

1. Flux and Cadmium Ratios for the Ford Nuclear Reactor

In the past year, the flux at the pneumatic tube positions has varied only slightly due to an occasional shifting of a reflector element in the core. For about one month early in the year the flux was 2.2×10^{12} n cm^{-2} sec^{-1} and then stabilized at about 1.98×10^{12} n cm^{-2} sec^{-1} (these are for PL No. 2). The Cd ratio is 14.2 for PL No. 2 and 13.5 for PL No. 3 with a thermal neutron flux of 1.9×10^{12} for PL NO. 2 and 1.3×10^{12} for PL No. 3. The flux measurements are 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. A chart of the flux values for PL No. 2 at different times during the past year is shown in Fig. 1.

The foils were counted in a 1-3/4" x 1-1/2" NaI(Tl) well crystal which was calibrated against a 4π beta proportional counter. It shows an absolute efficiency for Au^{198} (based

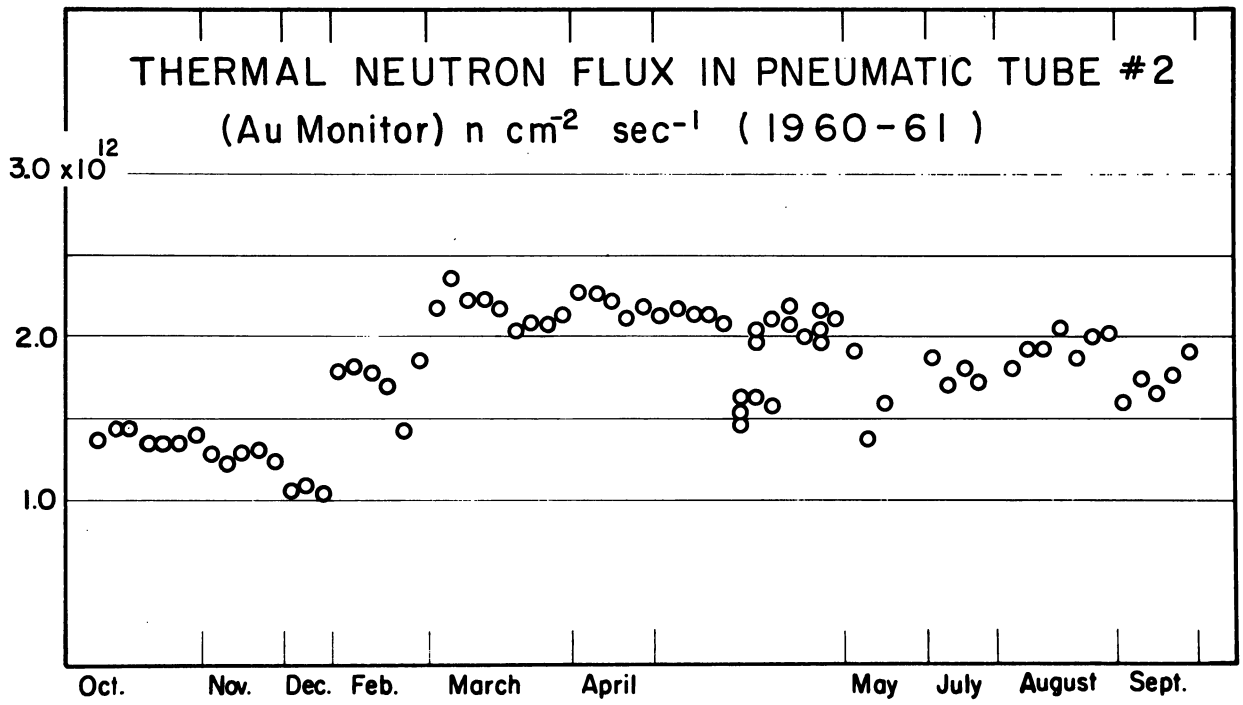

Figure 1. Thermal neutron flux in pneumatic tube No. 2 of Ford Nuclear Reactor operating at a power level of 1000 kw ± 10%. The precision of measurement of individual points should be better than 3%.

on the proportional counter) of 41.4%. In the near future it is expected that the flux will increase to ~ 4 x 10^{12} n cm^{-2} sec^{-1} with the removal of one row of reflectors, and that somewhat later the flux will increase to ~ 8 x 10^{12} when the reactor goes to 2 megawatts of power. (H. Nass)

B. Automatic Sample Transport -- "Bunny Rabbit" System

The bunny rabbit system as described in Progress Report 9 (1) has given good continuous service over the past year. Installation of tubes and control circuits has been completed to service both generator and reactor samples. The final bunny tube layout is shown in Fig. 2. Samples can be introduced into the

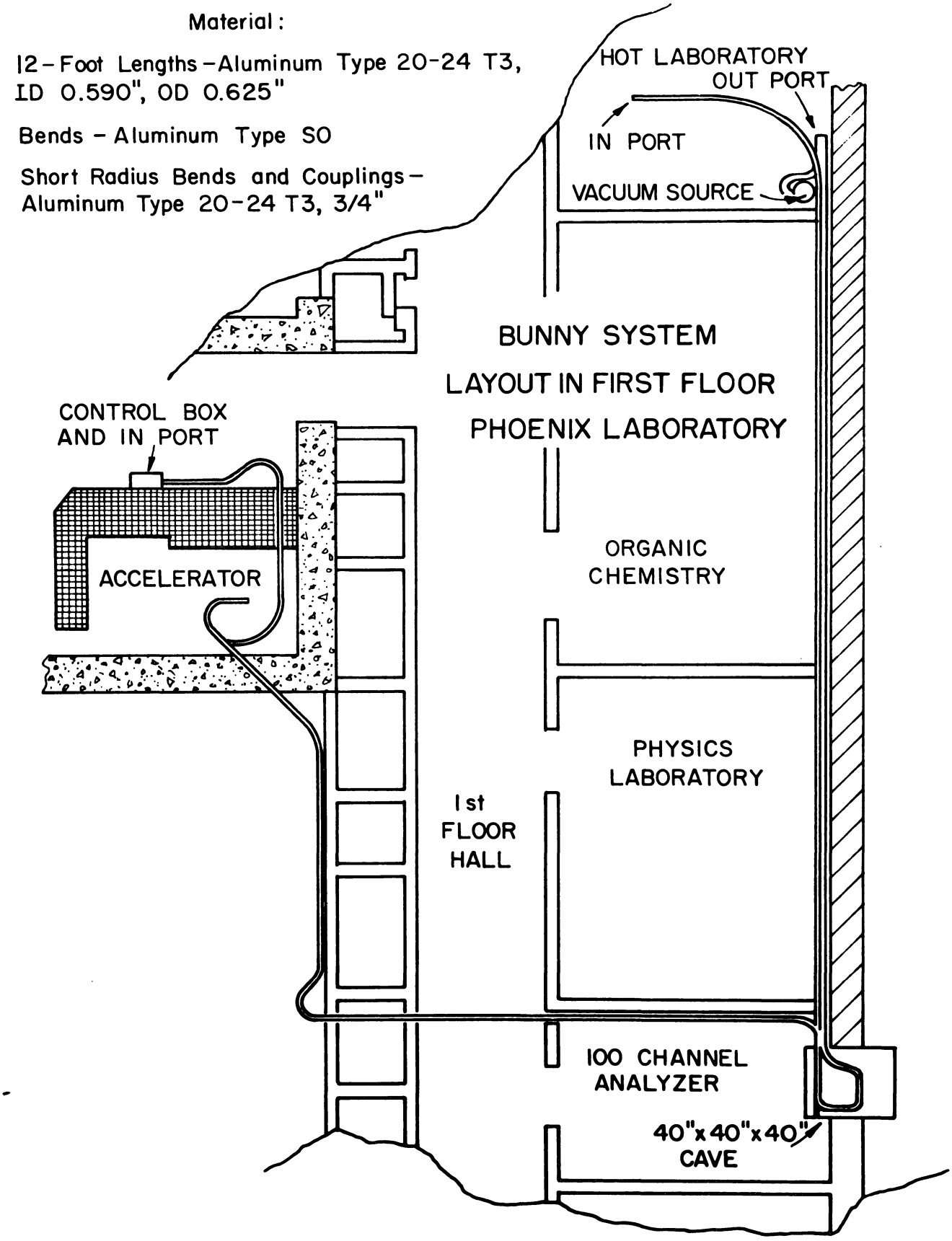

Figure 2. Bunny system layout in first floor of Phoenix Laboratory.

system at either the generator or the hot lab hood -- but all samples are returned to the hot lab. The system can be controlled from the hot lab, the accelerator room and/or the analyzer room.

The present arrangement of the bunny tube in the detector cave is shown schematically in Fig. 3 and is pictured in Fig. 4. As before (1), the tube can be moved from an operating position next to the crystal to a non-operating position when manual measurements are to be made with the detectors.

(R. Shideler, H. Nass)

1. Modifications

There have been several modifications and improvements in the "bunny" system in the past year. The mercury vacuum switch used originally had several drawbacks. Compressed air could not be used to help dislodge a stuck capsule; the arrival of a sample at the counting position preceded the turning on of the counting equipment by several tenths of a second; the vacuum differential was insufficient to trip the switch unless the sample was of a very specific size.

These and other problems led us to seek another solution. Accordingly a photoelectric switch was constructed. The original switch was comprised of a high vacuum photo cell (for fast response) and a two tube circuit (1 trigger amplifier, 1 flip flop). This circuit worked well over short periods of time but was unstable and subject to line fluctuations and noise to the extent that it was necessary to adjust






it before every run to assure reliable operation. The circuit was replaced with a much more carefully executed design with regulated power supply (Fig. 5) which has provided completely reliable operation for the last six months. The only failure of this system so far has been the pilot lamp supplying light to the photo cell.

With the new arrangement pictured in Fig. 4, samples are stopped in front of the crystal by a pair of spring loaded fingers operated by a solenoid. When the sample nears the counting position the light beam is broken triggering the photo-electric relay which shuts off the vacuum and starts the measurement.

The accelerator bunny system has been completed and is now automatic and tied into the main system. The control box is located behind the accelerator (see Figs. 7 and 8 in a later section) and the capsule (~ 1-1/4" x 1/2" is introduced at this point. The capsule is placed in the tube and sent into the irradiation position by turning the control knob to the left for a time long enough to assure entry (2 or 3 seconds). After the irradiation, the knob is turned to the right engaging the automatic system which, when the sample is in counting position, is shut off by the photo electric relay described above.

When the sample is inserted, the knob opens a gate valve in the control box and starts the vacuum, and the sample is drawn into the irradiation position. To send the sample out, the air flow is reversed by a solenoid actuated air valve

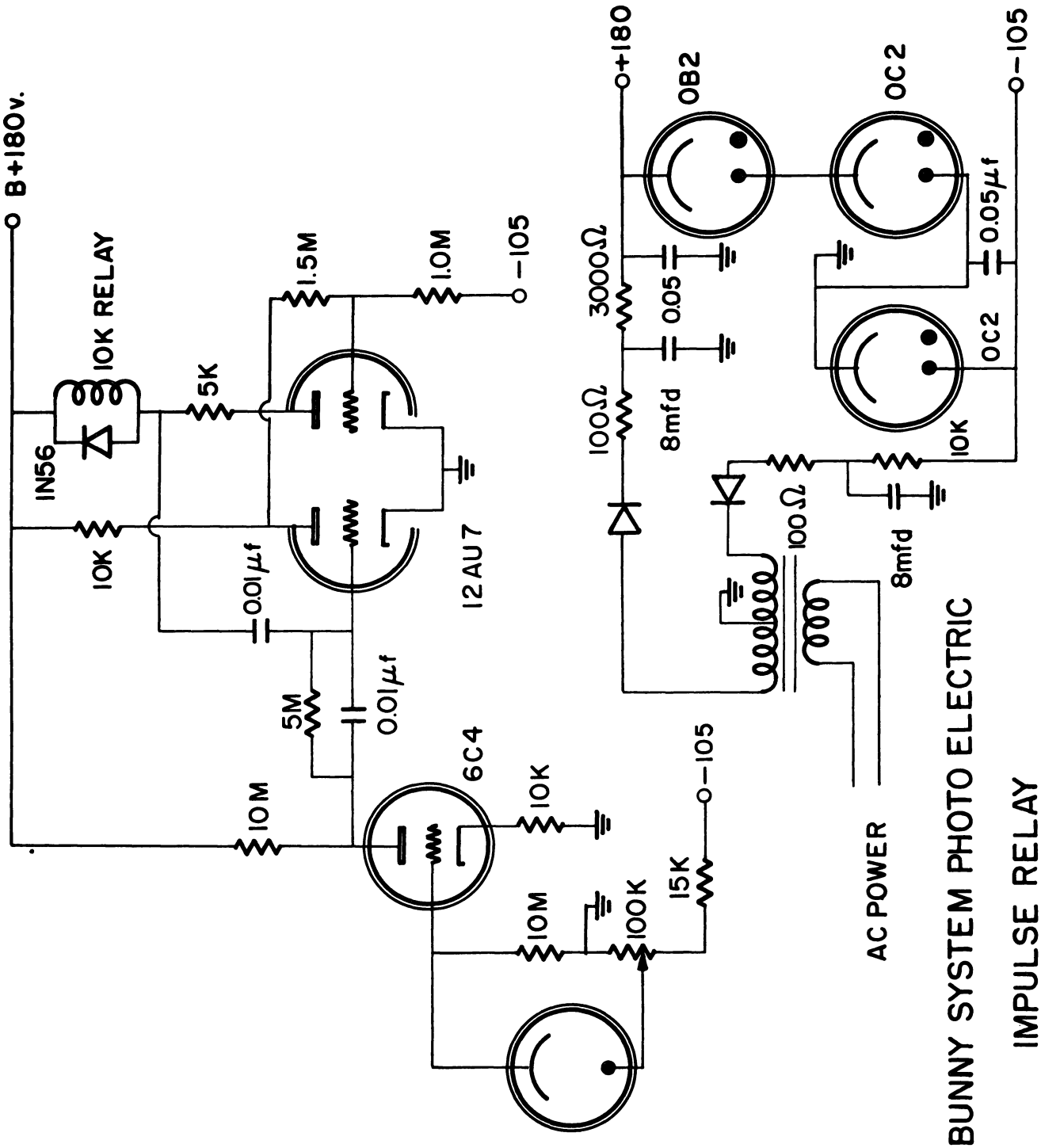

Figure 5. Diagram of power supply for modified bunny system control.

which allows air to enter behind the rabbit, thus drawing it to the analyzer room (see Fig. 2 above). A clock timer on the console measures the transit time to the analyzer so that accurate corrections can be applied. Modifications were made to the system inside the accelerator cave at the time the room layout was changed. A solenoid operated air valve was included and the sample tube leading to the target position was provided with a sliding joint to permit ease of positioning between the thermal irradiation position and the fast flux position (Fig. 6). (R. Shideler)

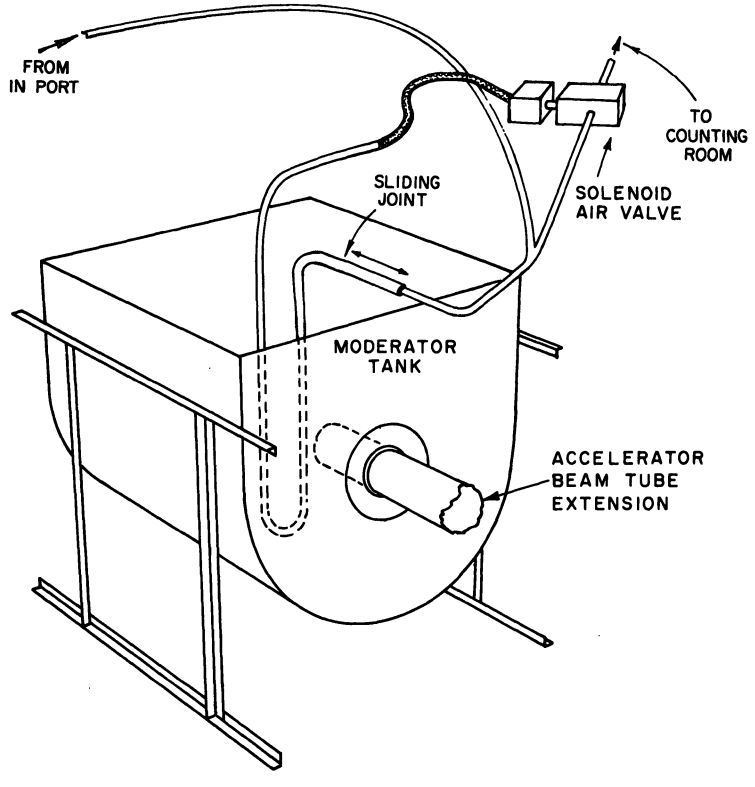

Figure 6. Water moderator tank (30"x30"x30") showing modification of bunny system inside accelerator cave.

C. Phoenix Laboratory Counting Room

The 100-channel analyzer room has not been changed much from

its description in Progress Report 9 (1). Some new equipment has been added and replacements made. The room still serves as the primary center of measurements for the group at the Phoenix Laboratory. In addition two detectors, a 4π beta proportional counter and a low-level beta Geiger counter, have been set up in the room next to the analyzer room. This equipment is discussed in a later section. (H. Nass)

D. Neutron Generator

1. Introduction

During the last year operations of the Texas Nuclear neutron generator have for the most part been routine. Irradiations have been made for several experimenters, both within and outside of our group. The bulk of these irradiations has been for activation analysis utilizing both fast and thermal neutrons (Steele, Kusaka, Wahlgren), but other non-activation experiments have also been made. These experiments are discussed laterin this report. Some further experiments have also been done on the machine to better understand its operation and to improve its usefulness.

Early in the year the machine was modified to be equivalent to the Texas Nuclear 150 Kv-IH unit which utilizes a 150 kv power supply (a standard Research and Development model supplied by Sorensen Electric Company, Norwalk, Conn.) rather than the original 100 kv. Raising the accelerating potential increases the neutron flux output of the machine without appreciably affecting target life. Other modifications have also been made to both the accelerator and auxiliary systems. A

sketch of the accelerator console as it now appears with its auxiliary equipment is given in Fig. 7. A photograph of the same equipment is shown in Fig. 8.

2. Experimental: Apparatus and Procedures

The operation of the Texas Nuclear generator which was outlined in detail last year (1) has remained substantially unchanged during the present year. The machine is now simply run at 150 kv instead of 100 kv and produces an increased neutron output. However, as we have obtained more experience with the machine we have made some changes and improvements.

One such change has been in our operating philosophy. At first the machine was run at beam currents of 1000 μa in an effort to standardize data and results. The machine was capable of these currents but could be kept operating at this current routinely only by great diligence on the part of the maintenance technician. (Beam currents as high as 1.7 ma have been measured.) More recently, standard operation has been set at 500 μa. Relieving the necessity of peak performance at all times has greatly increased the ease of operation and has reduced to a minimum the need for "tuning" and adjustment. The resultant sacrifice in beam current has not seriously affected most experiments. (The flux level is reduced by a factor somewhat less than 2 apparently due to higher ion source efficiencies at the lower output.)

In actual operation for short-term irradiations the machine is brought up to power prior to admission of the sample. After a short wait while beam current is adjusted


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and allowed to stabilize, the beam control switch is cut off and the sample sent into the bunny system as described in an earlier section. When the sample is in place, the beam is turned on. The beam stabilizes quickly to its preset value and "switch on" is considered the "beginning of the irradiation".

The irradiation is ended by actuating the bunny system "send switch". The capsule leaves the high radiation area almost instantly and this is considered the "end of irradiation". The transfer to detector is completed within 2 to 3 seconds. The photo circuit signals the arrival of the bunny in the counting cave and automatically starts the counting equipment. The accelerator is then shut down or else readied for the next irradiation.

Long term irradiations of a sample too bulky to fit the bunny system are carried out by first placing the sample by hand in the irradiation position and then bringing the machine up to power. Time errors during start up are not critical for irradiations of 5 minutes or more.

a) Shield modification and survey for 150 kv operation

With the aquisition of the 150 kv power supply, the neutron flux could be increased by a factor of about 4, and it was felt that the shielding arrangement used at the lower flux level might no longer provide the margin of safety desired within our plans for maximum versatility. At the same time the larger physical size of the new power supply required extra room inside the

shielding.

Since the easiest way of increasing total shielding was to add more shielding around the tank, the inner maze wall was moved outside the enclosure in order to increase the inner dimensions of the cave by ≈ 5 feet. The tank was then moved forward 27" to provide space for paraffin to be stacked behind and around it. A total of 125 boxes (measuring 10" x 12" x 18") of paraffin was stacked inside the cave.

The final shielding arrangement for operation at 150 kv is shown in Fig. 9. Monitoring information obtained with this shielding arrangement when operating at a fast flux (n,2n on copper; >10 Mev) of ≈ 2×10^9 n cm^{-2} sec^{-1} is shown in Table I. Two instruments were used in this survey, the Eberline model 725 fast neutron monitor and the Nuclear Chicago "Nemo".

It should be pointed out that the Eberline instrument is of the proton-recoil type and responds to energies of greater than 0.1 Mev, whereas the Nuclear Chicago "Nemo" detects all neutrons above the cadmium cutoff of 0.14 ev. Since as shown in Table II the tolerance for fast neutrons up to 0.1 Mev is much greater than for neutrons of higher energies, the Eberline meter provides numbers of greatest significance in this case.

Thus the portable shielding shown in Fig. 9 is more than sufficient for safe operation of this type of generator operating intermittently at full power. It should be

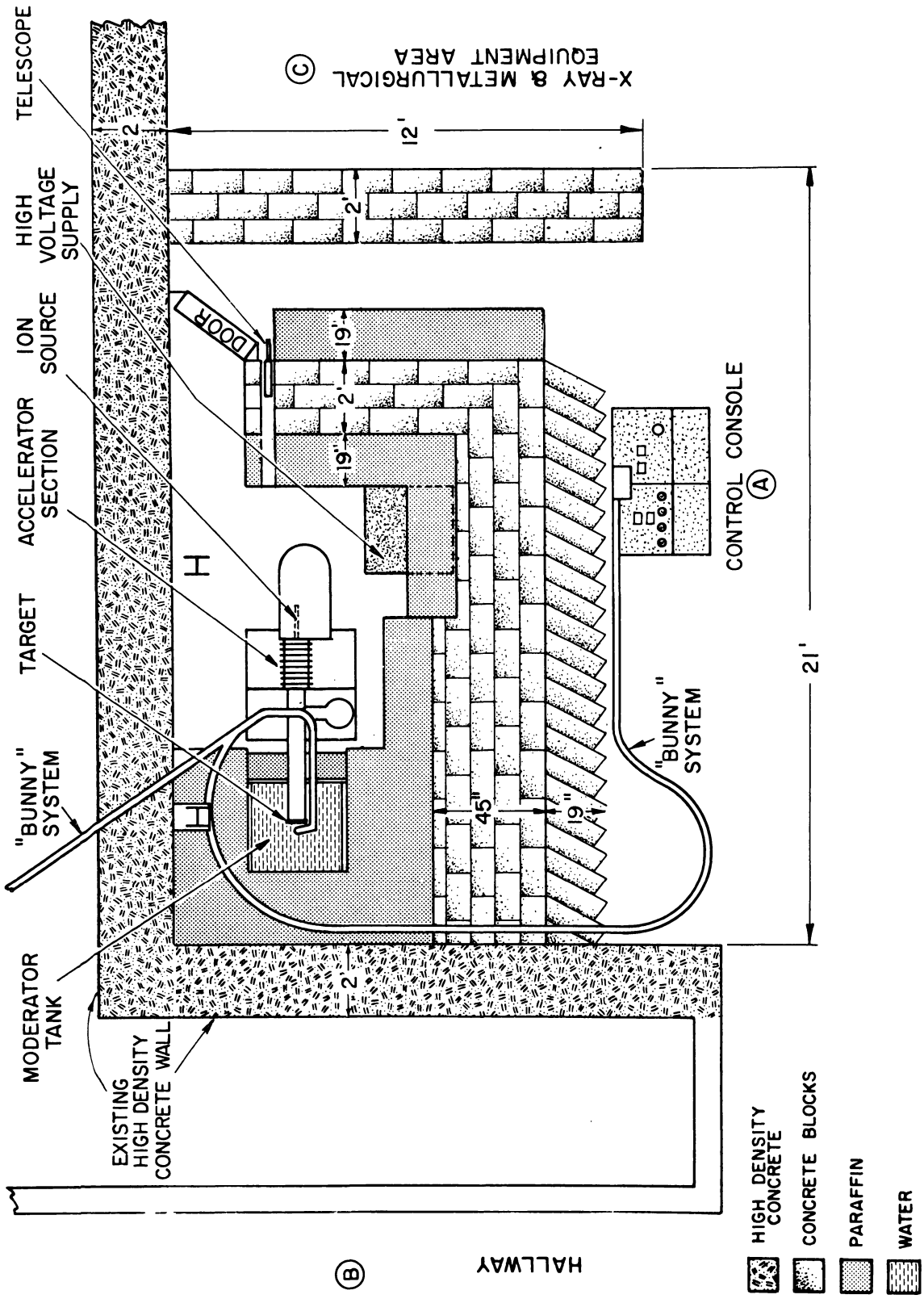


Figure 9. Shielding arrangement for neutron generator operating at 150 kv.

Table I. Neutron Monitoring (n $cm^{-2}sec^{-1}$) of Area Around Generator, Operating at 150 kv with a Fast Flux of $\approx 1x10^{9}$ n $cm^{-2}sec^{-1}$ at the Target Holder.

"Fast" values taken with Eberline 725 monitor (> 0.1 Mev).
"Epi-thermal" values taken with Nuclear Chicago "Nemo" (> 0.14 ev).
"Thermal" values taken with Nuclear Chicago "Nemo".

	With Water in Tank			Without Water in Tank		
Position	Fast	Epi-Thermal	Thermal	Fast	Epi-Thermal	Thermal
A Console	0	25	30	9	100	90
B Hallway	0	5	5	3	10	10
C X-Ray Room	0	10	10	5	100	100

Voltage: 150 kv Current: 500 ua Target age: ~ 30 ma min.
Note: Data taken after remodeling of shielding, February, 1961.

mentioned that for 14 Mev neutrons, concrete and paraffin have roughly the same slowing down power. Thus the large amount of paraffin inside the cave is not essential and could be replaced by an equivalent amount of less expensive concrete blocks.

b) Periscope

One difficulty encountered in optimizing the neutron

Table II. Maximum Permissible Exposure for Neutrons (4)

Neutron Energy	Flux to give 0.1 rem/40 hr
Thermal	670
100 ev	500
5×10^3 ev	570
2×10^4 ev	280
0.1 Mev	80
0.5 Mev	30
1.0 Mev	18
2.5 Mev	20
5.0 Mev	18
7.5 Mev	17
10 Mev	17
10-30 Mev	10

flux of the generator was that of knowing "in situ" where and over what area the deuteron beam was hitting the target. To meet the problem a periscope was constructed to permit direct observation of the target (Fig. 10).

The periscope is comprised essentially of two simple telescopes back to back with a small 90° prism situated between the objective in the beam tube and the second lens of the backward telescope. A mirror outside the system makes a second 90° bend of the light path to the viewing scope which is mounted in a 4" x 4" hole through the shield wall (Fig. 9). Although the shield is open through this port the fast neutron flux is sufficiently low (50-100

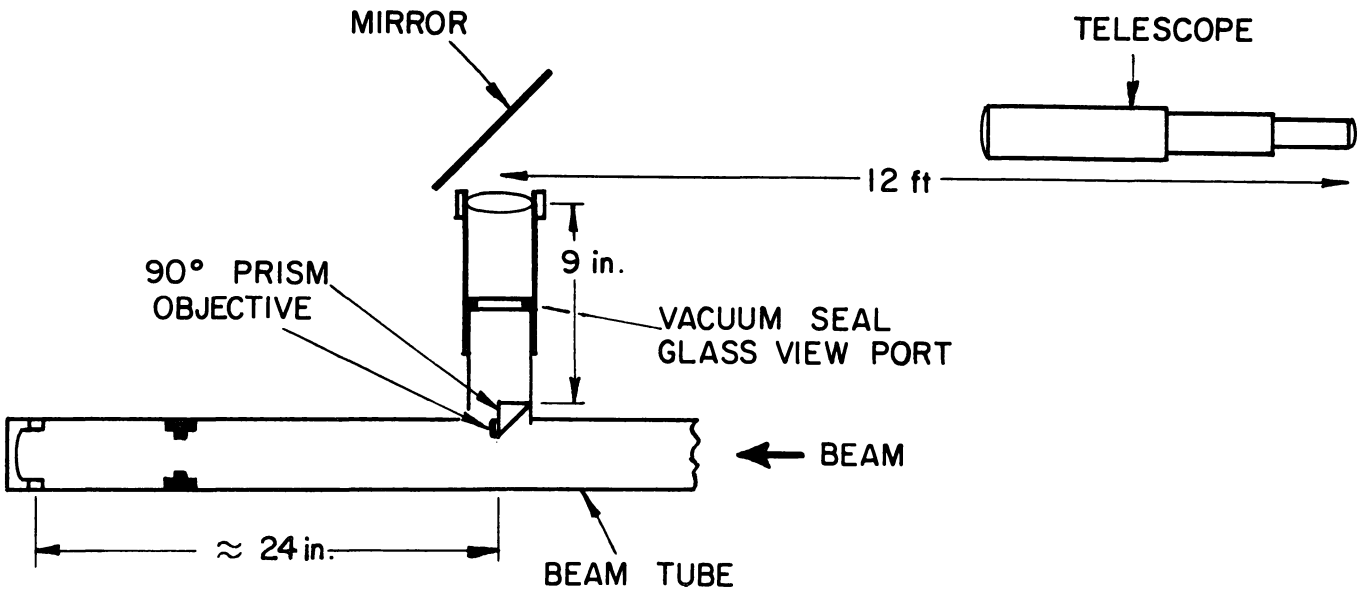


Figure 10. Periscope for target observation.

n cm^{-2} sec^{-1}) to permit short term observations at relatively high beam currents.

The objective lens of the periscope is a 6.5 mm diameter 50 mm focal length plane convex lens cemented to one surface of the 90° prism. A fixture was constructed to hold the prism so that the small objective lens protruded into the drift tube, still allowing plenty of clearance for the beam. The second lens is a plane convex lens 45 mm diameter 110 mm focal length located 9 inches from the prism in a lens tube clamped to the viewport ring on the drift tube. The viewing scope is an inexpensive 12 power telescope purchased locally. When the image inverting lens complex has been removed from this telescope, the image of the target is restored to its

proper orientation.

The optical quality of the system is fair, providing an image of the target as it would be seen from 25 cm. Alignment of the mirror for the system proved to be quite troublesome, requiring occasional adjustment since the accelerator is movable and the shield is not. Since the periscope was used chiefly to establish operating conditions and procedures and not as an operational instrument, further refinement was not attempted.

c) Remote centering control

Observations with the periscope convinced us of the need for being able to center the target in the beam by remote means. It became clear that even minor changes of target or beam position could cause large variations in neutron output. A simple remote centering device was constructed from two high torque reversible timing motors (6 in-oz x 6 RPM), one for horizontal and one for vertical position. Each motor drives a 1/4" - 20 screw jack fitted to the flexible drift tube joint. Control switches are located both inside at the accelerator and outside at the console.

When a new target is installed it is aligned by eye first, then the operator brings the accelerator up to a low current beam and reads ring current versus target current [see page 41 of Progress Report 9 (1)]. The target is positioned by trial and error until the ring current is minimum or zero and then finally until maximum

neutron output is obtained as determined by the continuous monitor described in the next section. By scanning the surface of the target in this manner, unsuspected "hot spots" useful for one or two more runs could be found even on old "used" targets.

d) Continuous flux monitor for fast neutrons

For most experiments using neutrons it is important to have information about the neutron flux. This is particularly important with a generator where electronic changes can cause changes in beam and a short target lifetime causes a continual decrease in neutron flux. Foils of copper for 14 Mev neutrons, or indium or gold for thermal neutrons, can be irradiated with samples to obtain an integrated total neutron dose and can be used to calibrate secondary systems.

A continuous monitor is essential, however, to assure proper operation of the machine and to indicate flux levels while experiments are in progress. Different schemes have been used elsewhere utilizing sophisticated high energy α counters or moderated boron counters at a known geometry.

We have found it convenient, however, simply to measure the activation of the oxygen in the cooling water line to the target as a continuous indication of the fast neutron flux. We thus utilize the $O^{16}(n,p)N^{16}$ reaction and measure the high energy radiations from the 7.4-second N^{16} activity.

The electronic counting equipment is simple and inexpensive. A Nuclear Chicago Labitron monitor drives a Varian G-10 strip chart recorder (Figs. 7 and 8). The GM tube is located in a coil of 1/4" copper tubing through which the target cooling water circulates. In order to maintain a constant flow rate, a differential by-pass type pressure regulator supplies water to the target cooling system. In time, we expect that an accumulation of scale, etc. in the lines may change the flow rate and hence the calibration, but we have observed no substantial change after one-half year of operation.

Calibration of the monitor recorder is made by comparison to copper foil irradiations made in the bunny system (Fig. 11). Accuracy of the system as it now stands is limited, on the lower ranges at least, by the counting statistics of the recorder system. The dynamic range of flux output is greater than 10^4 extending from $>10^9$ n cm^{-2} sec^{-1} for a good new target down to $<10^5$ n cm^{-2} sec^{-1} for an old target or a low current run. The "Labitron" monitor is not really suited for this operation and is to be replaced with a new instrument of extended range. The present upper limit of the "Labitron" is 20,000 c/m full scale. By adjusting the position of the GM probe with respect to the source (cooling water coil) the full scale monitor reading was made to correspond to a flux of 10^9 n cm^{-2} sec^{-1}. Accuracy at this level is quite good ($< \pm 5\%$) but at a flux of 10^7 n cm^{-2} sec^{-1} where the count-

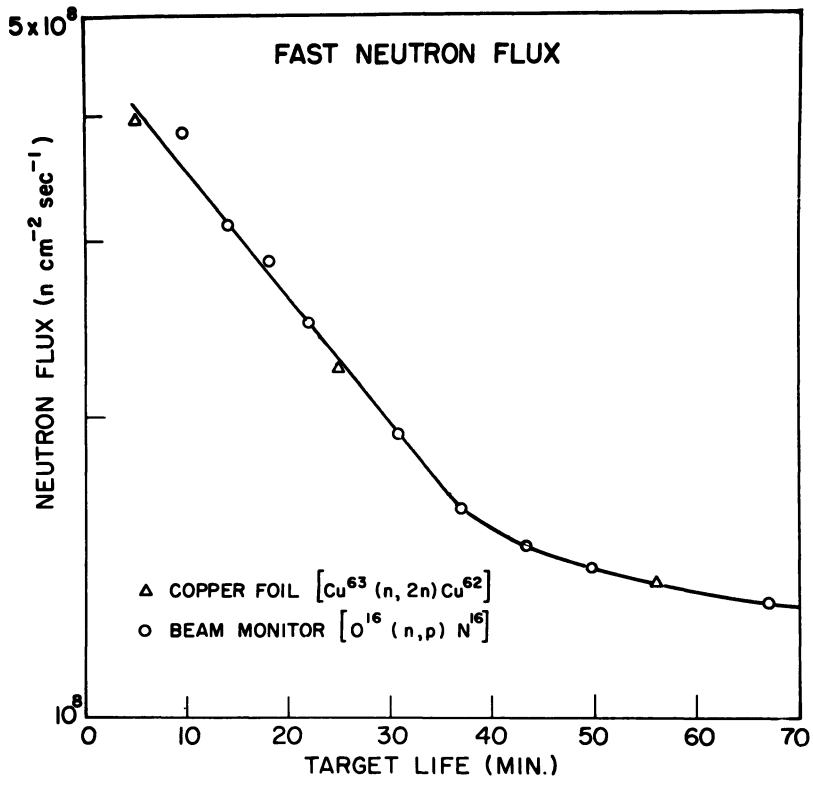


Figure 11. Standardization of fast neutron beam monitor with copper foils (5).

ing rate is approximately 200 c/m the statistical variation is $\approx \pm$ 18%. Further inaccuracies at low range result from normal background radiation. A wide-range rate meter would increase accuracies to better than $\pm$ 10% even at low ranges.

The inaccuracies mentioned above are not as limiting as they may seem, since they reflect short term variations of the count rate. All operations of the machine are done in a steady state condition and as such permit integration of the recorded curve over much longer time periods. Such interpretations, done either by visual inspection or actual summations, result in overall accuracies

much better than stated.

e) Long-lived target

To meet the problem of limited target life and decreasing flux we designed a target assembly (Fig. 12)

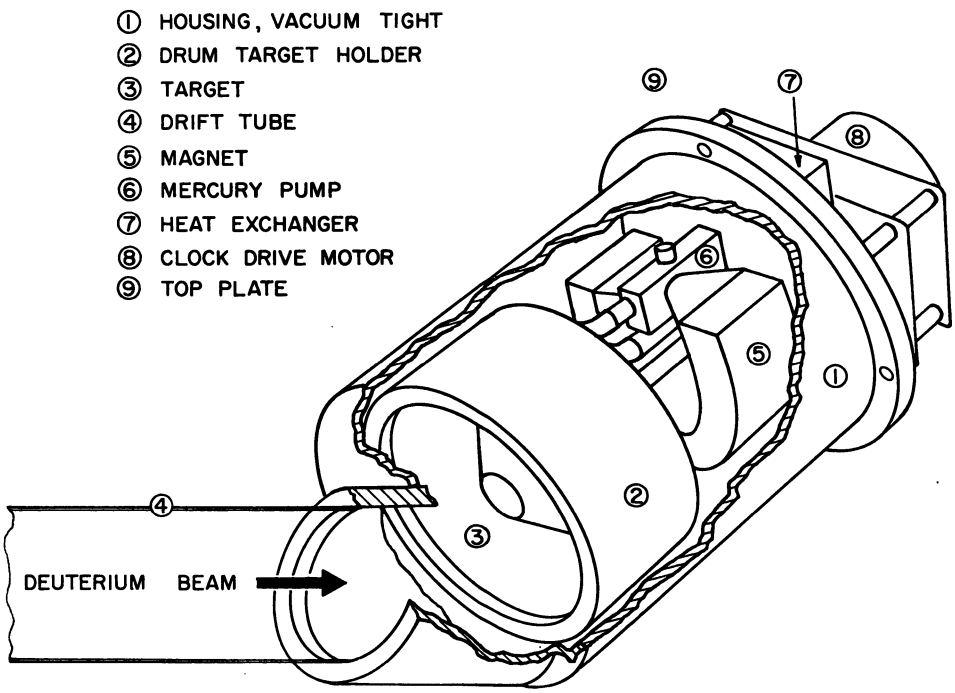


Figure 12. Long-lived target assembly.

which gradually rotates a long (10-1/2" x 2") Ti-H^3 target in front of the beam and should give an even flux for a period of approximately 22 hours.

The strip of target material is clamped to the inside of a stainless steel drum (Fig. 12 -2), the active side of the target forming the inner surface of a cylinder

3.5 inches in diameter (Fig. 12 - 3). Two groved rims support the sides of the target around the inside of the drum.

Expanded into place by wedge action on its ends a double ring applies sufficient pressure to form the target material into the groves of the drum. Goodyear "Pliobond" adhesive is used as a gasket seal between the drum and the target strip. A channel 1/8" deep behind the entire back side of the target provides a space through which mercury is circulated. In intimate contact with the target, the mercury cools with high efficiency and supplies a high thermal inertia to the system. The mercury is circulated through a water-cooled brass heat exchanger (Fig. 12 - 7) situated on the top plate. Circulation of the mercury is effected by a small magnetic pump (Fig. 12-5, 12-6) located inside the system and connected to the drum by a pair of small flexible "tygon" tubes.

The mercury pump, which we built, is comprised of a high strength permanent magnet (Fig. 12 - 5) with its field concentrated into a small region. The pump body (Fig. 12 - 6) is a "lucite" block with a passage channeling the mercury through the field region. A pair of electrodes is introduced into the mercury passage at right angles to the field and to the direction of flow. When a strong current (20 amp) is applied across the mercury in the magnetic field it is forced along the tube. This

system produces >1 mm Hg static pressure which is sufficient for flow in a closed loop system. The mercury side of the heat exchanger is vented to the vacuum system to prevent the possible build up of pressures behind the target.

An "O" ring seal on a rotary shaft transmits motion from a 24-hour clock drive (Fig. 12 - 8) situated outside the housing to rotate the drum at a rate of 0.00725" per minute corresponding to ≈ 200 minutes for ≈ 95% target utilization in a beam 1.5" wide at 1 ma. The drum target is so situated with its axis inclined to 45° of the beam axis that the beam strikes the target through the open end of the drum. This angle also increases the area of the target exposed to the beam, thereby lowering the beam current densities on the target.

The use of this equipment will increase the life of one (long) target to approximately 22 hours at an essentially constant fast neutron flux (hopefully $>10^{9}$ n cm^{-2} sec^{-1}). It will thus permit work with somewhat longer-lived activities than at present. If on the other hand operation were limited to short irradiations the overall target life might be several months. Thus in the future we anticipate the added flexibility of longer runs with little variation in flux and with considerably less time lost in changing targets.

Target economy is another factor involved. The long target gives increased neutron value since due to mounting

~ 72% of the purchased target area is useful versus only ~ 43% in the standard round targets. Quantity purchase also reduces the overall cost of targets. Further refinement of this system could probably achieve even greater economy and convenience.

This system has been built and will be tested within the next month or two. (R. Shideler)

3. Results

a) Initial operation with the 150 kv power supply

The conversion from a 100 kv power supply to a 150 kv supply presented difficulties beyond those of shielding already discussed. Arcing occurred at voltages greater than 125 kv. In order to determine the exact location of the arc, a camera with open shutter was rigged up in the darkened room. Several photographs of arcing between the ends of the resistors in the high voltage divider string were obtained (Fig. 13). The arrangement of these resistors has since been redesigned in the later Texas Nuclear models but had been overlooked in our conversion. The situation was remedied by attaching a small anti-corona ball to the end of each offending resistor, completely eliminating arcing, even at 10% over-voltage.

b) Beam studies

During the first few months of operation experiments were carried out under the assumption that the neutron flux would vary proportionally to the beam current, dropping off as the target age increased if high voltage and

At higher beam currents (≈ 500 μa), a ring of high intensity formed, leaving a less intense center. Beam currents near maximum output resulted in a beam generally diffuse over the entire target. Effects similar to the above were noted when varying the focus control while maintaining other settings constant, except that a fine 1/8" focus could be obtained at very low settings of the control. As the control setting increased, the beam current increased by as much as 10-15%.

Operation at 150 kv appeared to be substantially the same except that the position of the beam shifted as much as 0.5 inches between the two voltage settings. Unfortunately this dependence of beam position on high voltage made intercomparisons between the two settings difficult. Other shifts in beam position were also noted and could not be accounted for.

1) Nonuniformity of targets.

Normally at 150 kv an increase of 4 or 5 in neutron output over 100 kv operation could be expected for equal beam currents. However we discovered that sometimes the accelerator produced a higher neutron output (by a factor of 2 or 3) at 100 kv than at 150 kv. At first it seemed that either the atomic to molecular ion ratio somehow varied with high voltage or else that it was simply a centering phenomenon. Later, however, part of the trouble proved to be caused by a difference between targets, where the target that

showed an increase in output with reduced beam energy simply acted as a very thin target. In the thin target case the incoming deuterium ions traverse the entire tritium loaded layer before being degraded in energy to the point of highest cross-section (110 kev), thus lessening the chance for interaction to occur. The energy dependence of this reaction cross section is shown in Fig. 14. Several of the targets showed this behavior and were poor performers even as new targets, producing fast fluxes as low as 5×10^7 n cm^{-2} sec^{-1} when first installed. The measurable activity of these targets with a Juno ionization chamber was also low as compared to most other new targets. This would indicate that these targets were considerably below specification, but we have not as yet been able to establish any reasonable nondestructive method of measurement to check this. The periscope was invaluable in these studies in eliminating any mystery concerning the beam's whereabouts or mode.

2) Ion source behavior

Another interesting effect that became evident at this time concerned the extraction voltage of the ion source. As this voltage is increased the target current goes through a peak. It was discovered, however, that the neutron flux peak did not necessarily correspond to the peak in the current. In fact, as the current was increased beyond the peak position

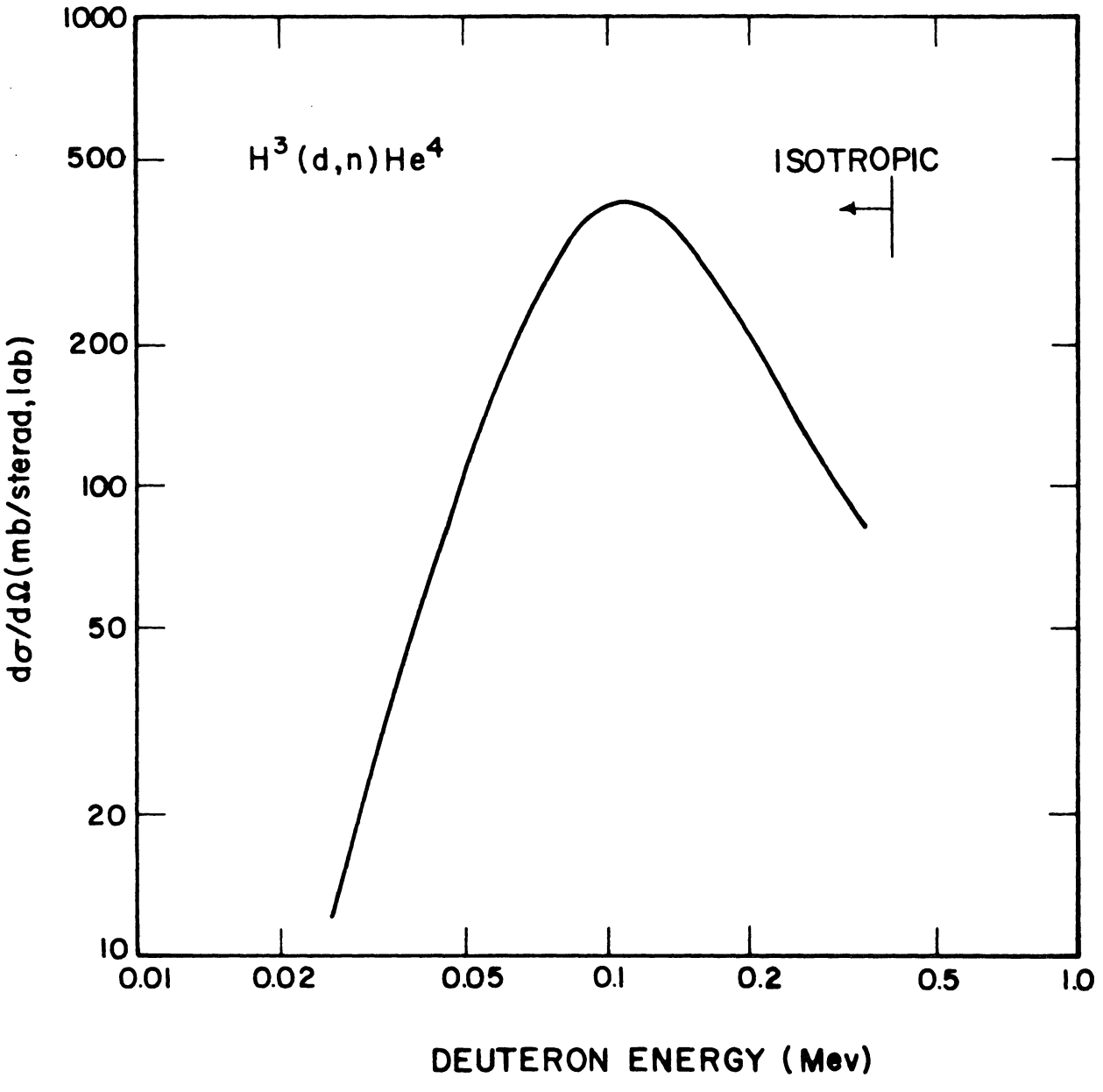


Figure 14. Depencence of cross-section for the $H^3(d,n)He^4$ reaction upon energy of the deuterons (6).

the neutron flux continued to increase until the target current had dropped off to a minimum of ≈ 80%.

Higher extraction settings increased the beam current but the neutron flux dropped off slowly forming a broad peak. Several such runs were made using varying deuterium pressures and each run showed a

similar pattern (Fig. 15). The run made at the lowest

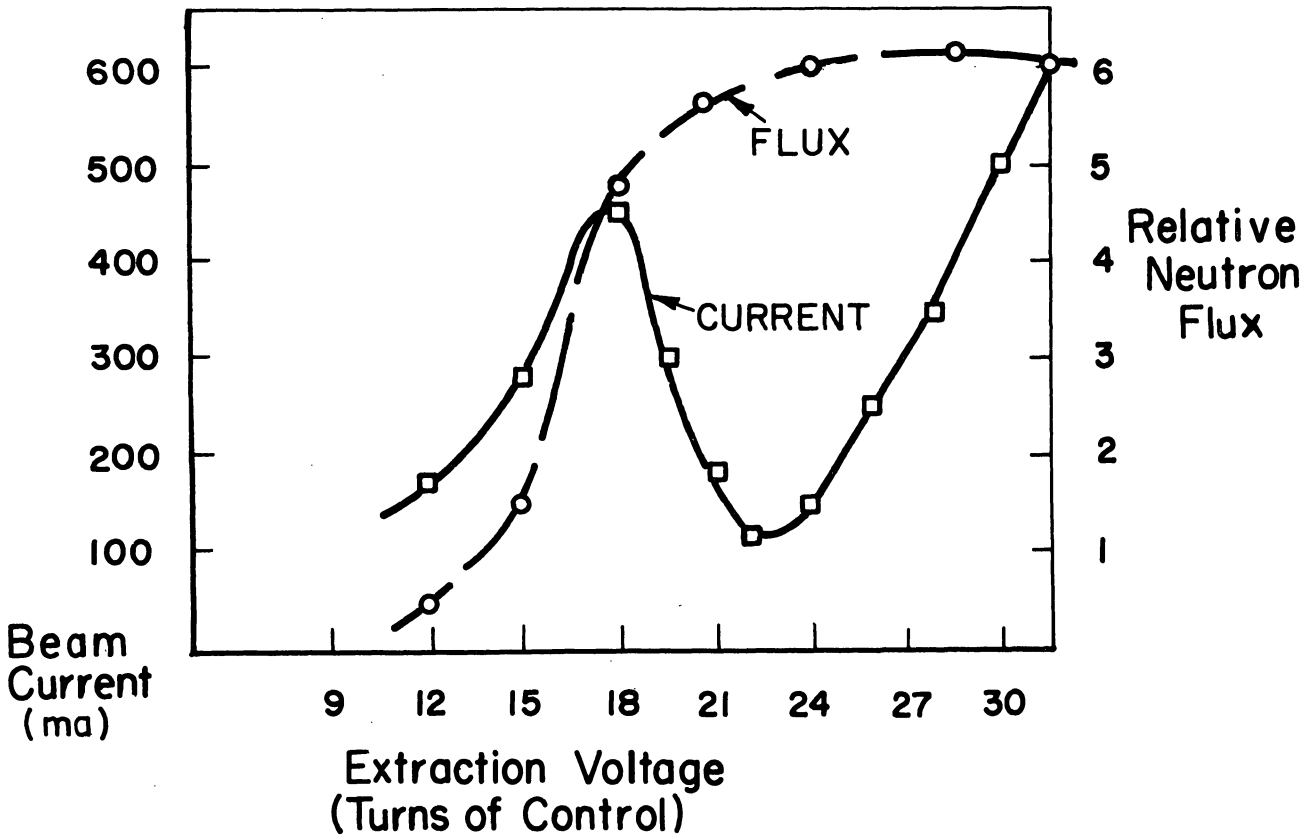


Figure 15. Dependence of beam current and neutron flux on extraction voltage.

deuterium pressure setting produced a slightly higher neutron output than the other runs. (These data point toward a much lower atomic to molecular ion ratic than would be expected from this type source).

The generator was operated at maximum extraction voltage for only a few minutes when severe outgassing caused the vacuum to fail along with arcing in the ion source. Upon removal, the ion source bottle showed severe overheating damage in the region near the canal opening, caused by ionic bombardment of the

plasma. Loss of the ion bottle discouraged further experiments along these lines, but maximum neutron output as recorded by the continuous monitor rather than maximum current output now determines operation for maximum flux. (R. Shideler)

c) Cooperative work with other groups

Work done in cooperation with other experimenters not within the Radiochemistry Group has been for purposes other than activation. The first of these experiments was made to determine the efficiency and response of a special scintillation neutron detector for high (14 Mev) neutron fluxes. This work was done in conjunction with the Nuclear Spectroscopy program of the Phoenix Memorial Laboratory directed by Professor J. King. A second experiment involved irradiation of an array of semiconductors with a total neutron dose of 10^{11} neutrons/cm^2, as part of a program to study effects of radiation on the solid state. This work was done in cooperation with an advanced student under the direction of Professor C. Kikuchi also at the Phoenix Memorial Laboratory.

One other experiment of a long term nature was done outside the group. This experiment was carried out by W. F. Wegst under the direction of Dr. C. Jordan and is summarized as follows.

"Several irradiations were made on mammalian tissue cells using 14.3-Mev neutrons from the Cockroft-Walton generator. These irradiations were part of a preliminary

study for a doctoral thesis program in the department of Environmental Health at the University of Michigan.

The cells used were mouse fibroblast cells, commonly designated "L" cells. They were irradiated in polyethylene bottles containing about 20 ml of nutrient medium with approximately 10^5 cells per ml. The centerline of the bottle was placed at 4 cm from the target and the irradiations were preformed with the shield tank empty. The data from these irradiations is shown in Fig. 16. The results of these experiments are inconclusive at this time since all but two of the irradiations

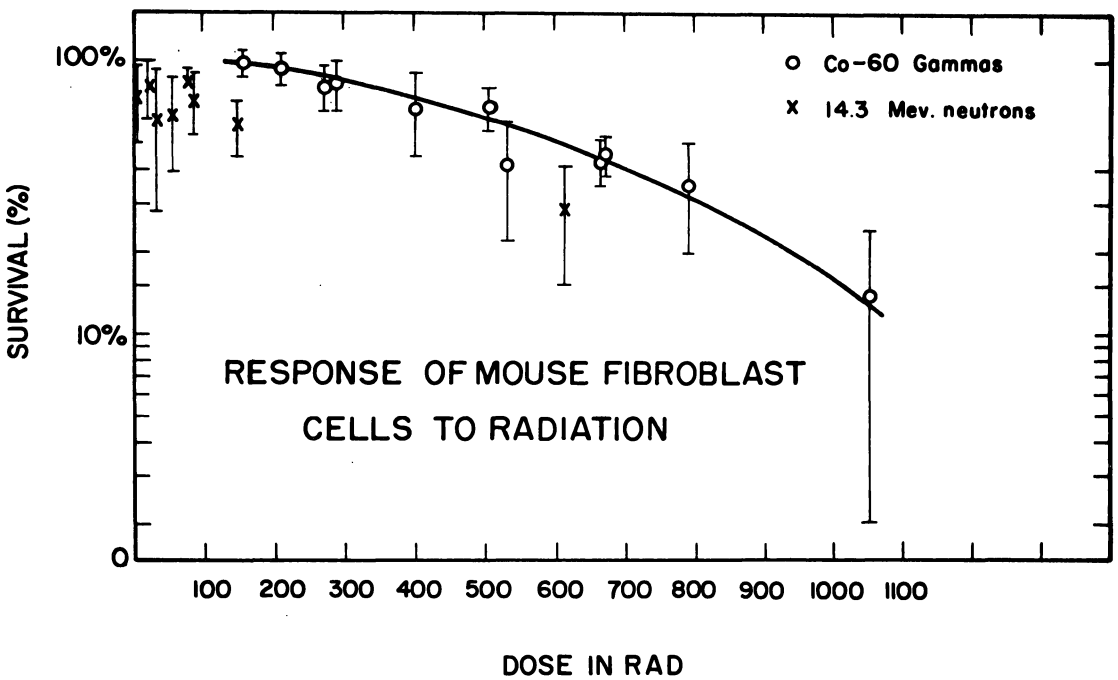


Figure 16. Response of mouse fibroblast cells to radiation.

are below 100 RAD. Data obtained from Co-60 gamma irradiations of these cells is also shown in Fig. 16 for comparison to the neutron data.

The relationship between neutron flux and dose (7.18×10^{-9} RAD/neutron/cm^2) was obtained from reference (7) and is based on the "first collision dose" for 14.1 Mev neutrons in water. This relationship is probably representative of the dose delivered to the system for two reasons: 1) the neutron flux is only slightly perturbed by the small bottle of nutrient (see Fig. 17) and 2) most of the energy is transferred to the system by

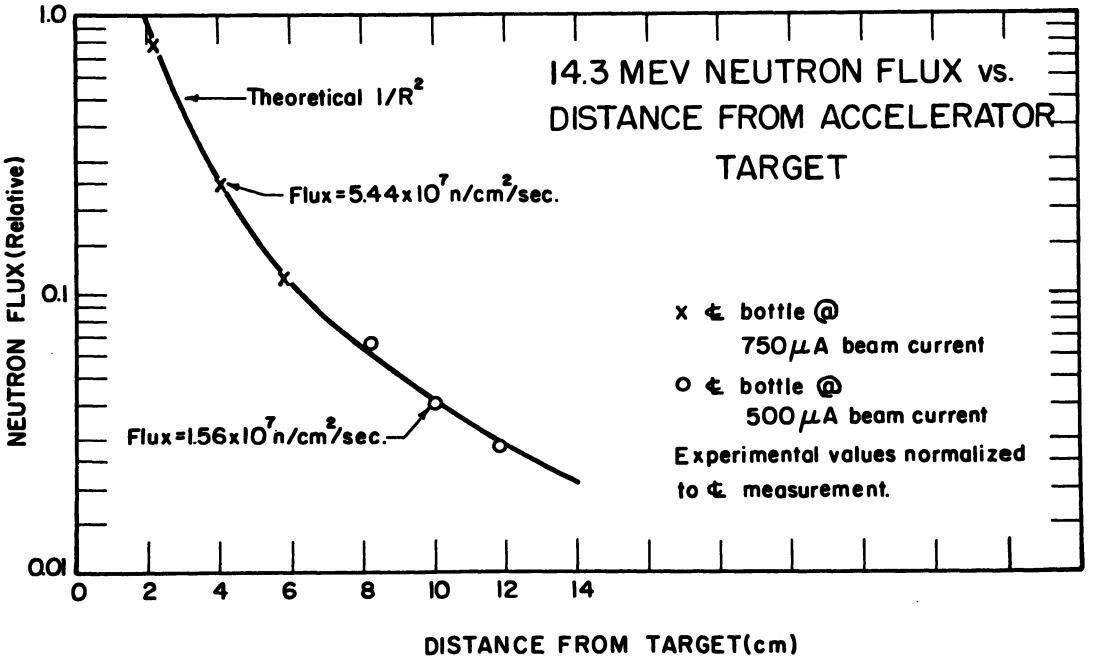


Figure 17. Flux vs distance curve--with serum bottles present.

(n,p) reactions and the bottle is large enough (2 cm diameter) to stop most of the protons. (The range of a 5 Mev proton in water is approximately 0.03 cm.)"

(W. F. Wegst)

II INSTRUMENTATION

A. 100-Channel Pulse Height Analyzer

The 100-channel analyzer has been used all year with only a few major problems causing lengthy shutdowns.

The analyzer has been operated on spectra for about 1500 hours and is always operating in a test mode except when shut down for failures. It has been operated frequently on a 30-minute recycle period for 10-12 hours with no shift in the spectra. Such stability requires, however, that the dead time for the sample be small and that there be no unusual shift in line voltage during the run.

The printer units on the analyzer (1) have been shifted only once during the last year showing the value of careful adjustments on the commutator assemblies.

The analyzer was inoperative for ~ 12 hours in late October due to a multidiode failure in the address scaler buffer and arithmetic circuits. In March a series of troubles with the printout circuits in both A and B units shut the analyzer down for about 8-9 hours, and in April the print control unit failed and was inoperative for about 5 hours. We have also had a series of miscellaneous troubles shutting down the analyzer for one to two hours. We have probably experienced an "up time" of ~ 90% this year, slightly lower than previous years due to an increasing number of small failures of 1-2 hours duration. These were for tube, diode, resistor and tube socket replacement. This type of failure is not unreasonable since the analyzer was three years old

in March of 1961 and during this time has had a heavy work load.
(H. Nass)

B. 3" x 3" NaI(Tl) Cylindrical Crystals

As reported in the last progress report (1) we had one crystal on hand which gave us (after repotting) 7.2% resolution. The second 3" crystal which had been ordered arrived in November. It was assembled in a preamp assembly and when operated at 980 volts showed a resolution of 7.4% for the Cs^{137} gamma ray at 662 Kev. Both crystals through the year have maintained their 7.2-7.4% resolution. With two excellent 3" crystals available we have been able to make measurements in arrangements such as $\sim 4\pi$, automatic alternate counting and Hoogenboom summing. The two crystals used in approximate 4π geometry were of great help in the oxygen analysis work described later. There is some problem, however, of the two crystals drifting apart electronically. This we hope to correct with the acquisition of a second linear amplifier and high voltage supply so that each crystal has its own high voltage and may be fed into a separate amplifier and then into the analyzer. Fig. 18 shows spectra taken using one crystal, and two crystals in $\sim 4\pi$. Actually the two crystals are ~ 3.8 cm apart. A sketch and a photograph of the mounting of these two crystals was given in Figs. 3 and 4. (H. Nass)

C. Dead Time Recording

In previous years before the installation of the "bunny tube" system with the resultant increased use of the analyzer, the dead time for a sample measurement was recorded by hand from the indication of the dead time meter associated with the analyzer. In

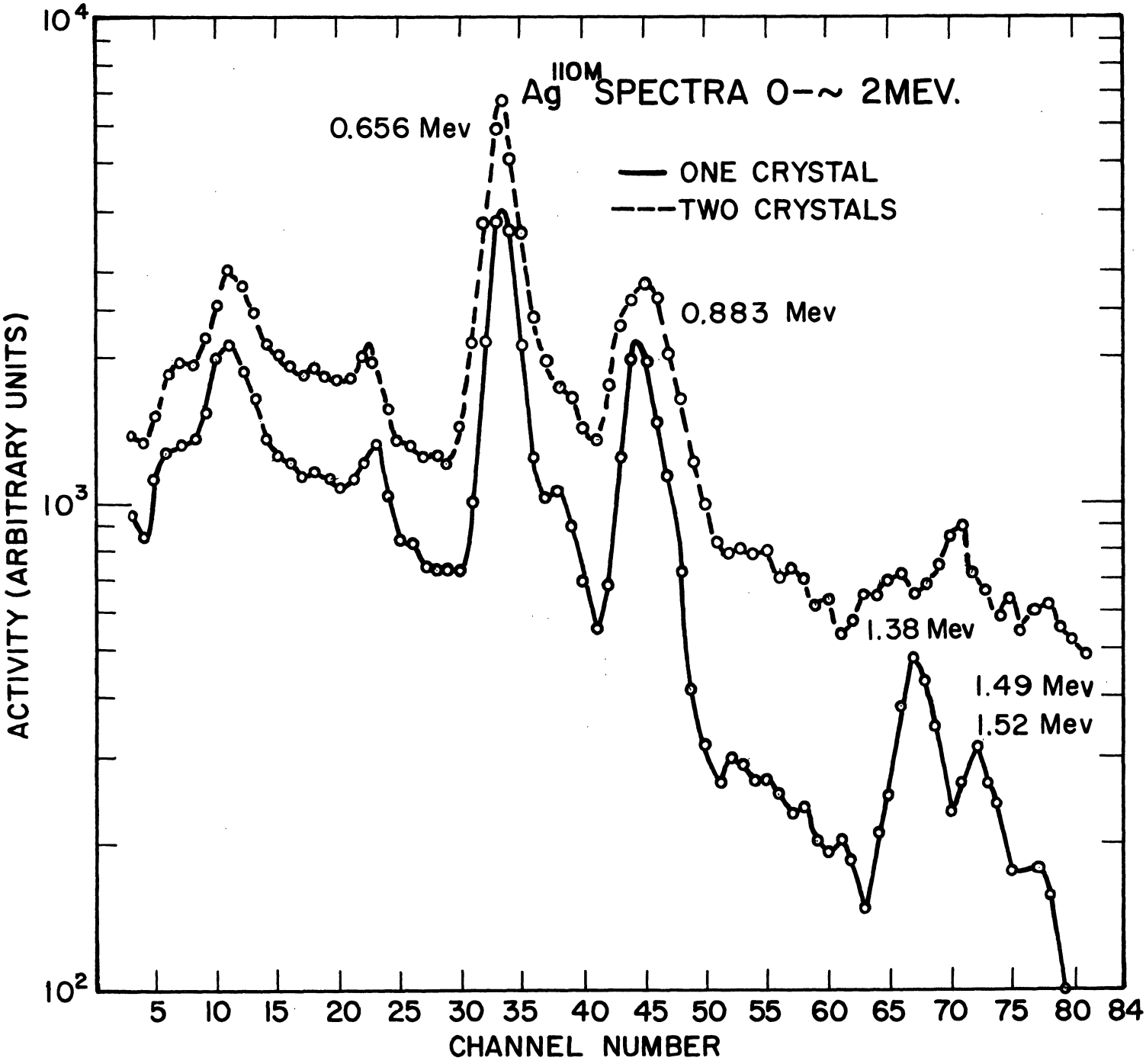


Figure 18. Silver^{110m} spectra showing comparison of one crystal vs two crystals in ~ 4π geometry.

the past year, however, the bunny system was speeded up a little, an extension run to the accelerator, and more work done on shorter half-life materials. Accurate recording of dead time by hand for

thus be obtained from the chart for any point during a recycle operation. (H. Nass)

D. Standard Counting Equipment

Some scaling equipment which has been used continuously for many years had to be replaced since repairs were becoming too expensive in time and effort. Thus a new RIDL scaler with a 1 μsec resolving time and 2 mv sensitivity was obtained for use with the well crystal in the Phoenix Laboratory. This is the unit used to measure gold monitoring foils for flux measurements. This unit has been modified to handle count rates as high as $\sim 2 \times 10^6$ c/m.

Three other scalers which had seen hard usage since 1949 in our Radiochemical Techniques laboratory course were also finally replaced by inexpensive student decade units from Nuclear Chicago. These units have given good service during one semester with only a few problems. (H. Nass)

E. Personal Monitors

There has always been a need to have an immediate indication of the radiation level while working with radioisotopes without having to interrupt the work or have a second person monitor. Such equipment has not been available. The closest approach has been a bench monitor sitting in one corner of the laboratory or a pocket dosimeter, neither of which was very satisfactory.

Recently, however, several small personal monitors with audible indications have become available from commercial firms. We have obtained one type which gives a good audible signal and may be clipped onto a pocket or belt. This allows the experimenter

to have an awareness of the radiation level (by the increase or decrease of signal rate) without stopping the process with which he is involved.

The units are sold under the name of "Sparrow" by the Gelman Instrument Company of Chelsea, Michigan, but are built by Wallac Oy of Finland. The two units, one of 1 mr sensitivity and the other of 10 mr sensitivity, have given satisfactory service. The units are, however, sensitive to shock which usually breaks the small Geiger tubes and new tubes apparently must be brought in from overseas; also the clip which is used to attach the unit to the belt is not sufficient and a stronger clamp should be used.

(H. Nass)

F. Low-Level Beta Counting System

For a number of years experimenters have used low-background systems for environmental surveys, carbon-14 dating, and low level tracer experiments. With intermediate and low-level neutron accelerators and sources becoming more common in activation analysis the user must be satisfied with lower sensitivities than with a reactor. One way of increasing this sensitivity, however, is by lowering the background of the detector. Thus we have initiated a study of the use of a low background counter in activation analysis.

We are using an LLB-40 low background counter from Technical Associates, Burbank, California. The system, pictured in Fig. 20, includes a scaler with anticoincidence circuitry built in, a preset timer and variable high voltage supply for both the guard and counter tube. The shield for the counter (Fig. 21) consists of


Frequency (Hz)
Amplitude (dB)

Frequency (Hz)
Amplitude (dB)

Frequency (Hz)
Amplitude (dB)

steel, lead and mercury enclosing the two tubes. The guard tube, an Amperex 18518, acts as an umbrella over the Amperex 18516 counting tube. The complete system is compact and easy to use but some problems with the electronics have arisen.

After only two weeks of operation, several tubes burned out and four of the silicon rectifiers in the low voltage supply failed. These were repaired and then several weeks later a resistor in the high voltage meter circuit failed producing false voltage readings. After the repairs, the scaler unit has functioned quite well for the last several months. The shield and sample carriage appear to have been designed very well and no problems have been encountered. The sample holder is easily decontaminated when necessary.

Fig. 22 shows several months of background counts which range from ~ 0.73 c/m to a high of 0.98 c/m. Each of these points was for a minimum count of 120 minutes and some for 900 minutes. The standard deviation for each point (based on the total number of counts taken) is also indicated in the figure.

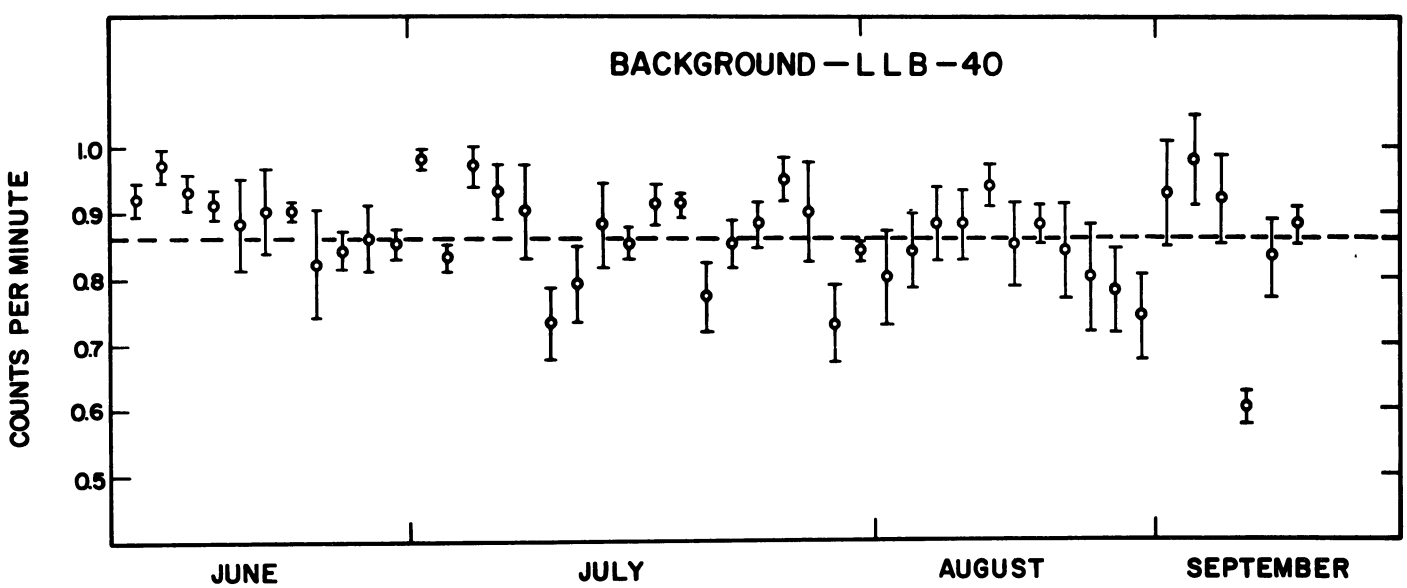


Figure 22. Chart of background counts on LLB-40. Brackets are standard deviations.

Several weeks were spent in becoming familiar with the counter and performing various calibration and standardization experiments. In determining counting efficiency for the detector several beta emitters were used and counted both on a 4π gas flow counter and in the LLB-40. Fig. 23 shows a plot of energy versus efficiency in this counter for small samples of relatively high specific activity placed in the center of a counting planchet.

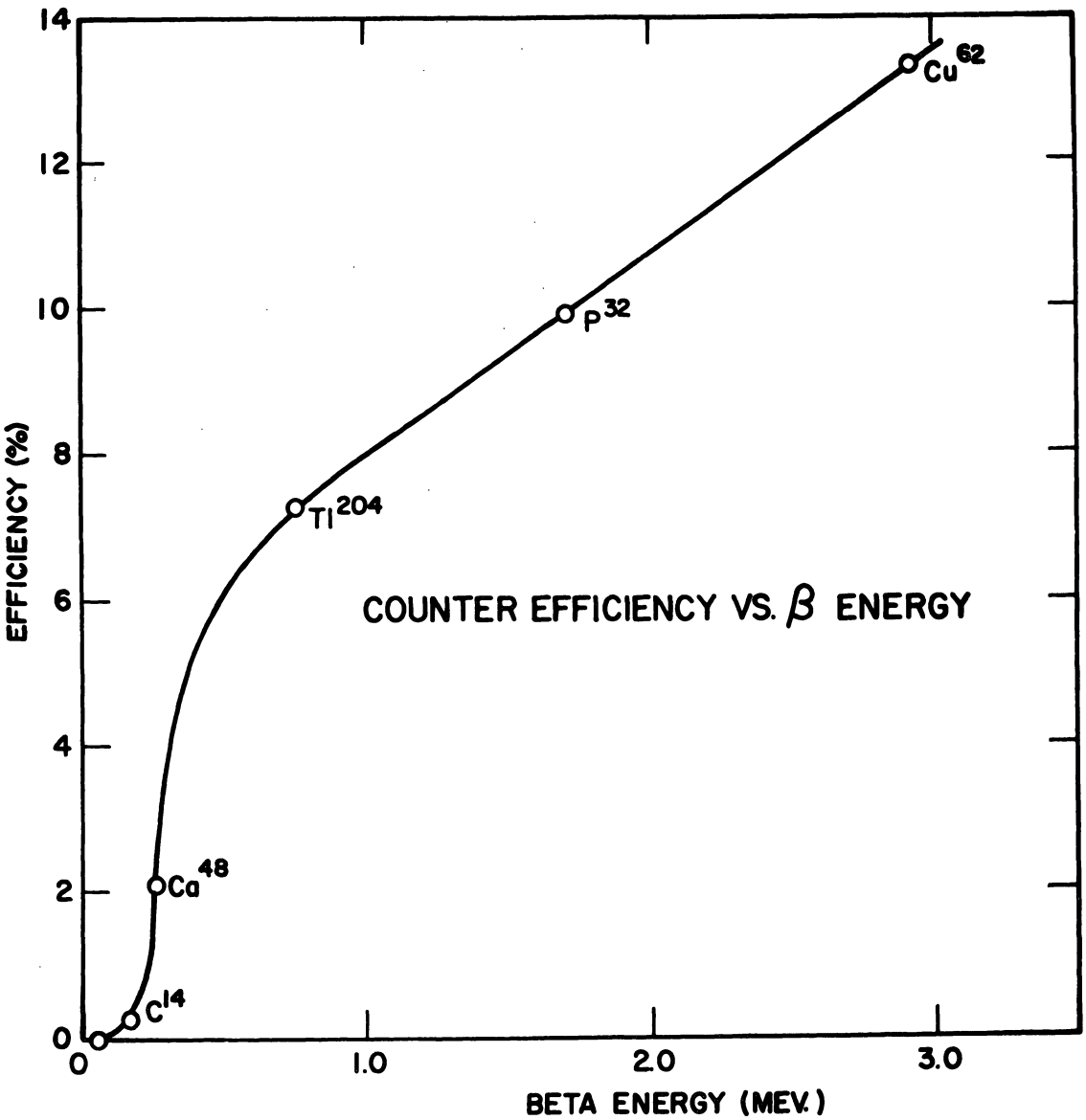


Figure 23. Plot of efficiency vs energy for LLB-40.

Several further experiments showed that there was a change in efficiency as the samples were spread out on a counting planchet. Ca^{45} with a 0.254 Mev β^- was used in 10 λ amounts and placed at different positions on a planchet and counted. Fig. 24 shows

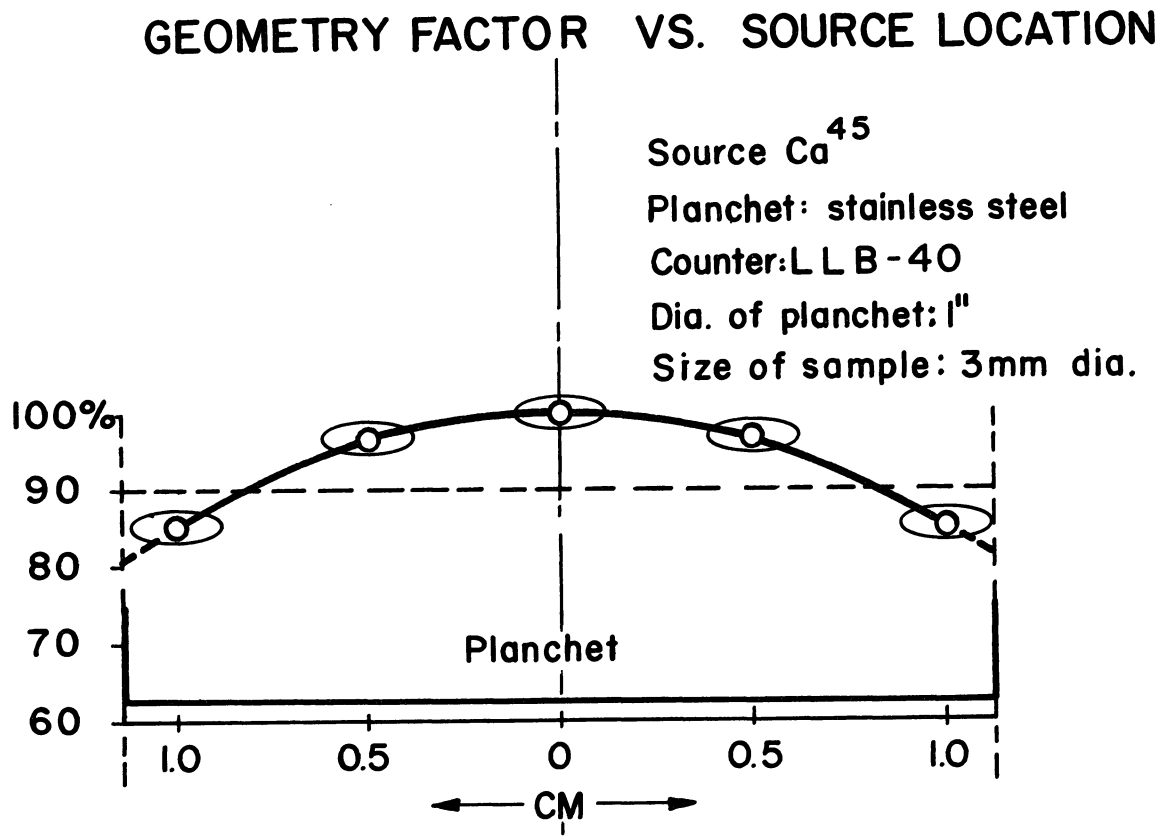


Figure 24. Plot of efficiency vs sample position for LLB-40.

a plot of geometry factor versus source location. The 10 λ of Ca^{45} solution spread to a circle of ~ 3 mm diameter when placed on the planchet. This plot indicates that sample size and location are critical for best results. (H. Nass, A. Tani)

III ACTIVATION ANALYSIS

The neutron generator has dominated our program in activation analysis this year although some work has also been done with the reactor. Emphasis has continued on utilization of the short-lived radioisotopes both with and without radiochemical separations.

A. Data Correlations

1. Cross-section chart for 14 Mev neutrons

Small, portable neutron generators of the Cockroft-Walton or Van de Graaff type produce 14 Mev neutrons by the $H^3(d,n)He^4$ reaction when used with a tritium target. Thus these high energy neutrons are now available to many laboratories for use on many problems including activation analysis.

For the activation analysis using thermal neutrons, charts of the activation cross-section values of the various nuclides versus the half-life values of the daughter product have been helpful for evaluating the relative analytical sensitivities of the various elements (8-10).

A similar chart which should be useful for 14 Mev neutrons has recently been prepared (Fig. 25). In the chart values of

$$\frac{\text{Activation Cross-Section} \times \text{Abundance Ratio}}{\text{Atomic Weight}}$$

are plotted against the half-life of the reaction product, since from this value it is more convenient to evaluate the relative sensitivity of the analysis than to use the simple cross-section value (10). Three kinds of reactions produced by 14 Mev neutrons are distinguished in this chart by the shape

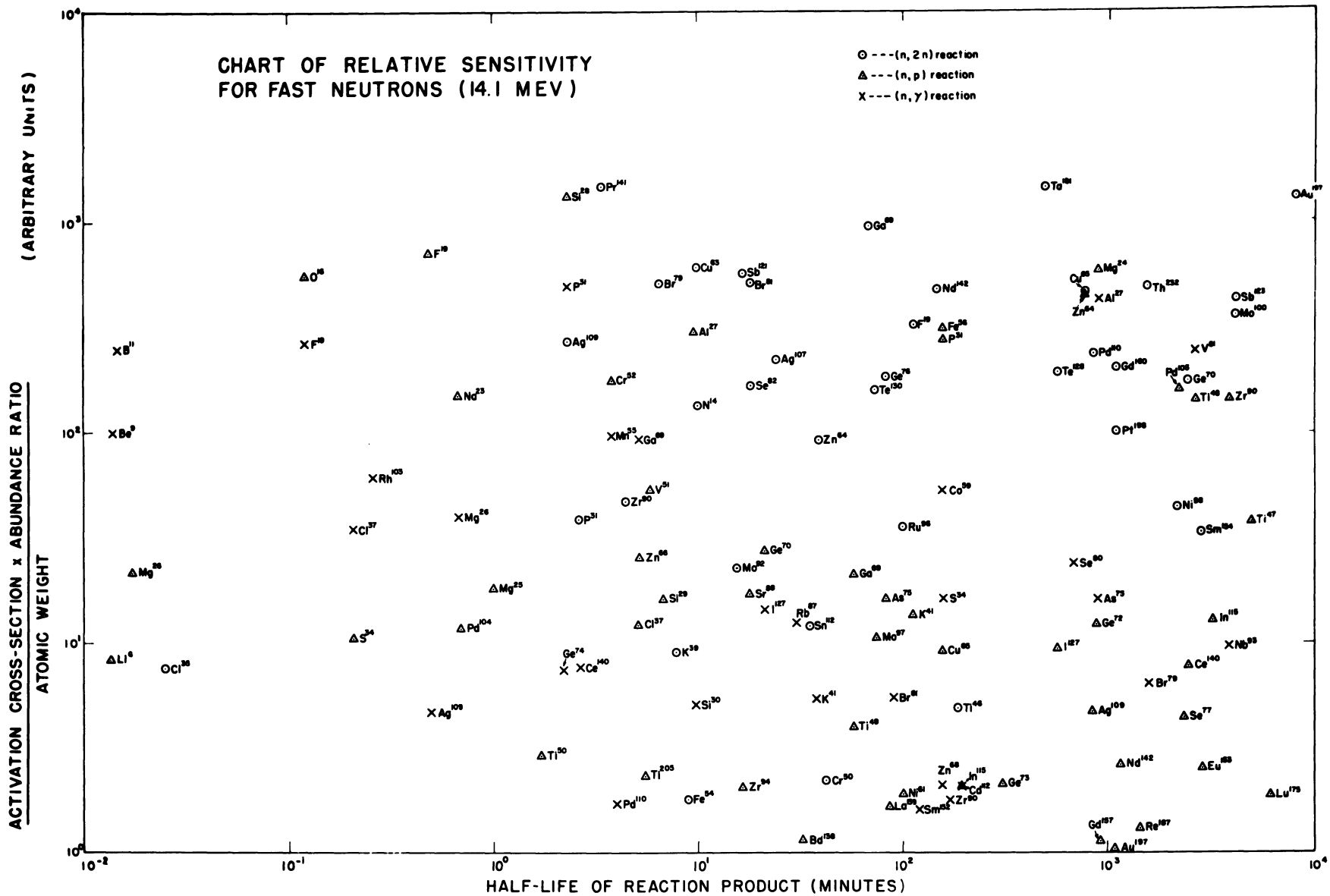


Figure 25. Chart of relative sensitivity for fast neutrons (14.1 Mev).

of the points. The nuclides described in the chart mean the target nuclide in the reaction.

Cross section values have been taken from Howerton (11). In the chart, values for 14.1 Mev neutrons were used where possible; where not the nearest value to 14.1 Mev was adopted. It is felt this chart should be very useful in presenting a survey of current values. (Y. Kusaka)

B. Activation Analysis of Oxygen Using the Neutron Generator

A study has been completed of oxygen analysis by neutron activation and a paper written entitled "Determination of Oxygen by Fast Neutron Activation Analysis Using a Low Cost Portable Neutron Generator". An abstract of this paper follows.

"Fast neutron activation analysis, using a low cost Cockroft-Walton design accelerator as a source of 14-Mev (deuterium-tritium) neutrons, has been found satisfactory for trace oxygen analysis. This method is rapid, sensitive and selective, and is free from most matrix interferences. Yet it uses equipment costing no more than good infrared or spectrographic instruments. Fast neutrons ($>$ 10 Mev) convert oxygen-16 by an (n,p) reaction to 7.4-second nitrogen-16. This in turn emits 6-7 Mev gamma rays which are measured by scintillation spectrometry. Samples containing 10 mg or more of oxygen have been analyzed to within $\pm$ 10% with a fast flux of $\sim 10^8$ n cm^{-2} sec^{-1}. Larger samples give smaller errors. By using all the sample area available with an average flux for irradiation of 10^8 n cm^{-2} sec^{-1} and using a proper transfer system, it should be possible by this non-destructive method to analyze to within $\sim \pm$ 10-15% for as low as 10 ppm of oxygen. The average time

for an analysis, including weighing, is approximately 7 minutes. The only interference encountered is from fluorine and this can be compensated for at F/O ratios below 10."

For this study oxygen samples, varying from 0.005 to 0.1 g, were sealed in medical grade polyethylene tubing and placed in a screw-cap, machined polyethylene capsule one inch long and one-half inch in diameter. With the accelerator beam switch in the off position, the samples were pulled into the irradiating position by means of a vacuum "bunny" system. The "bunny" system consists of 1/2" i.d. aluminum tubing and a vacuum cleaner along with the necessary solenoids, switches, and photoelectric circuits to start and stop the timers, cleaner motor, and multi-channel analyzer. Irradiations were started by turning on the accelerator beam switch and were timed with a stop watch. At the end of 30 seconds, the transfer system was turned on and the sample sent to the detectors. Two feet in front of the detectors, the sample capsule passed through a photoelectric beam which turns on the multichannel analyzer. The response time of the electrical circuit is approximately the same as the travel time of the remaining two feet, therefore, the analyzer was started at the same time as metal stops positioned the sample capsule between the two NaI detectors.

The radiations from the sample were detected, analyzed, and stored for one minute. This information was simultaneously recorded both graphically on an X-Y recorder and typed out in digital form by a Hewlett-Packard printer. A record of the multi-channel pulse analyzer dead time was taken continuously during the counting operation.

The number of scintillation counts in the 6-7 Mev photopeaks of nitrogen-16 is proportional to the weight of oxygen present. All counts were normalized for decay (to the end of irradiation), for analyzer dead time (to 0%), and for fast neutron flux (to 10^8 n cm^{-2} sec^{-1}). Background radiations from other activities in the sample were eliminated by an extrapolation of the base line under the photopeaks as illustrated in Fig. 26. The small oxygen con-

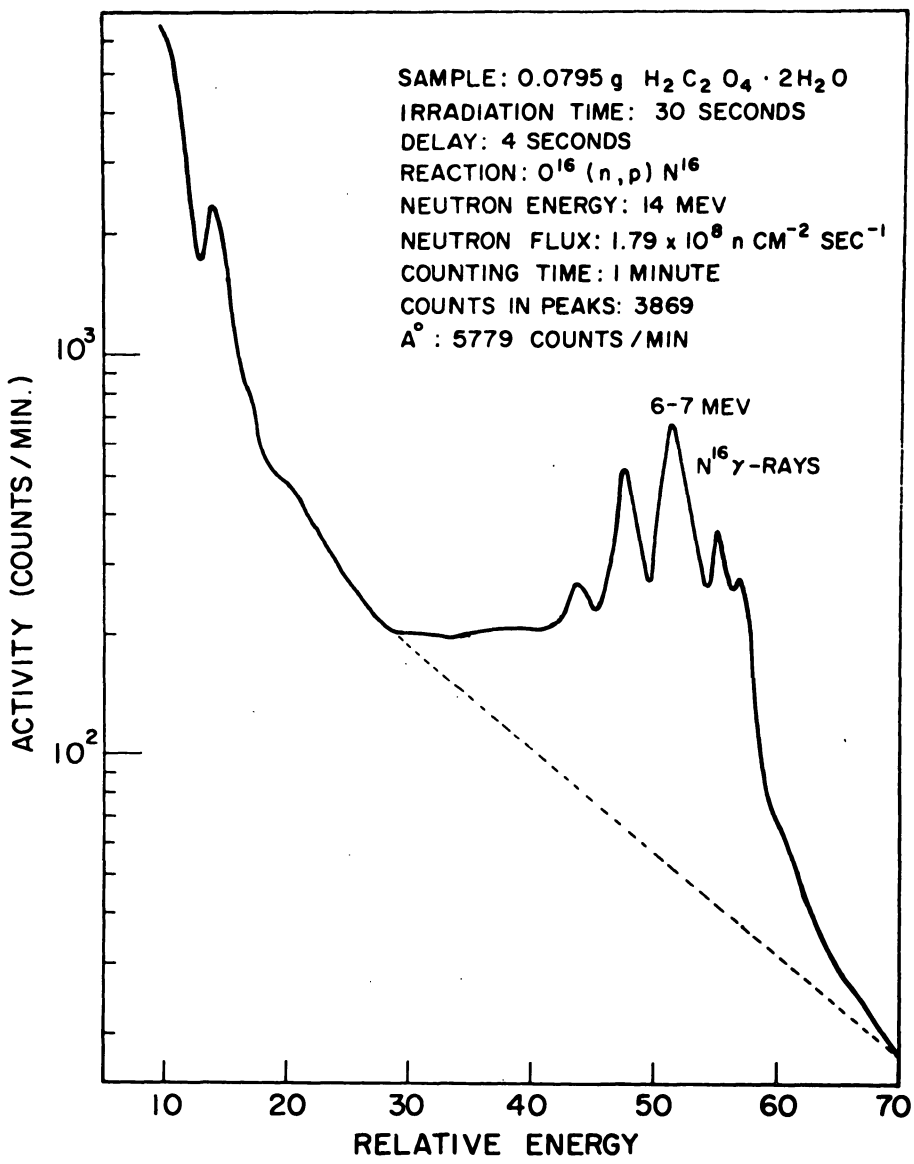


Figure 26. High energy gamma-ray spectrum of N^{16} showing extrapolation of base line under the 6-7 Mev photopeaks to eliminate contribution of other activities.

tamination from the packaging materials was determined by irradiations of identical polyethylene tubing and capsules. Samples containing less than 15 mg of oxygen were sealed and packaged in an atmosphere of nitrogen for the best results.

For a given sample the activity in the photopeaks was measured, normalized and compared with a calibration curve to determine the weight of oxygen.

The calibration curve was prepared by irradiating known weights of oxalic acid for 30 seconds, transferring these samples to the NaI(Tl) detectors and measuring the radioactivity for one minute with a 100-channel analyzer. Table III lists the results of this calibration and the curve is given in Fig. 27. A number

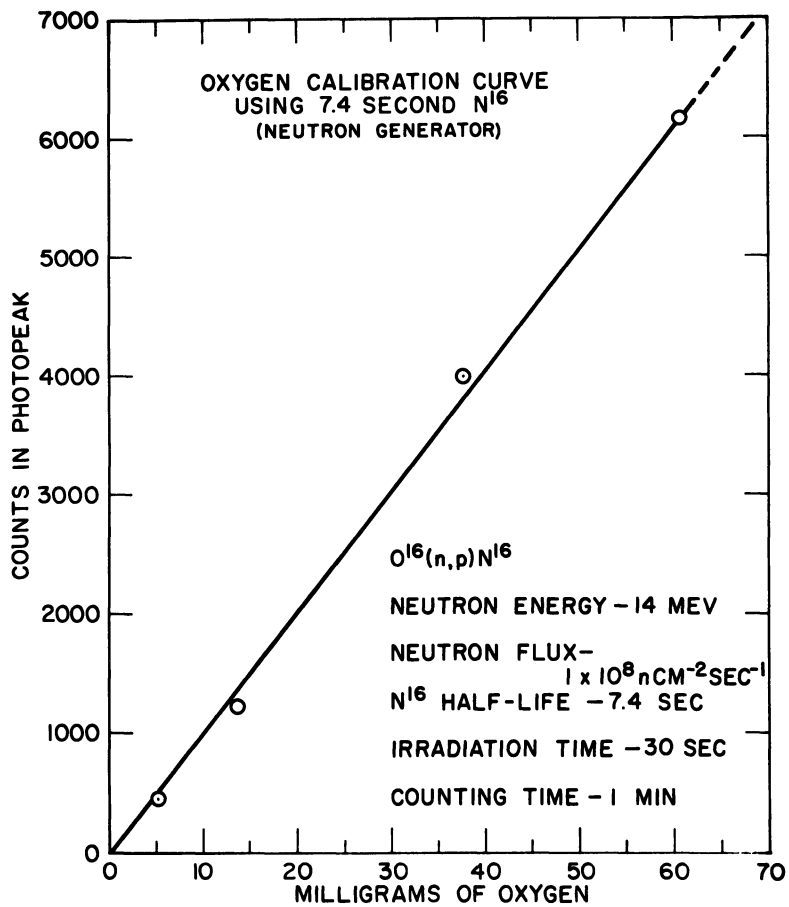


Figure 27. Calibration curve for oxygen.

Table III. Calibration Data for Oxygen Analysis Normalized to a Fast Neutron Flux of 10^8 n cm^{-2} sec^{-1}.

Sample	Oxygen (gram)	Irrad. Time (sec)	Transfer Time (sec)	Flux (n cm^{-2} sec^{-1})	A_o Photopeak* Counts min^{-1} at end of Irrad.	Specific Activity Counts min^{-1} g^{-1}
$H_2C_2O_4 \cdot 2H_2O$	0.0052	30	4	1.4×10^8	726**	96,919
	0.0135	30	4	1.8×10^8	2254	95,402
	0.0370	30	4	2.5×10^8	9303	100,984
	0.0606	30	4	1.8×10^8	10896	100,435
					Average	98,435 ± 2.4%***

* Corrected for analyzer dead time and neutron flux variation.

** Values are for a single sample determination.

*** Error is "standard deviation" of the four values. Statistically the higher counting values of A_o are more significant and hence some weighting factor should probably be used in determining the error. Such a procedure would tend to reduce the value of this error.

of standard samples of oxalic acid, sodium carbonate, p-aminophenol, and ammonium nitrate were then analyzed routinely to check this method and the results are given in Table IV. The relatively large errors for certain runs are probably due to the instability of the neutron beam monitoring system. It is expected that larger counting rates, which could be made available with modification of this experimental arrangement, would reduce the relative error in the 5-100 milligram range to $\pm$ 5%.

Table IV. Analysis of Known Oxygen Samples by Fast Neutron Activation Analysis.

Sample	Milligrams of Oxygen		% Error
	mg added	mg found	
Oxalic Acid	5.2	5.0	-3.8
"	5.2	6.0	+15.4
"	5.2	5.5	+5.8
"	5.2	4.9	-5.8
"	5.2	5.4	+3.8
"	37.0	37.7	+1.9
Sodium Carbonate	31.2	33.0	+5.8
p-Aminophenol	23.8	22.1	-7.1
Ammonium Nitrate	10.4	11.3	+10.4
"	40.3	40.6	+0.7
"	54.0	55.1	+2.0
"	58.2	58.0	-0.3
"	58.2	59.1	+1.5

The calibration curve was established at the neutron flux level of 10^8 n cm^{-2} sec^{-1} from a consideration of target life and

sample area. Fig. 11 shows that fluxes of this order of magnitude are available for more than one hour at the irradiation position. Since the fast neutron flux varies approximately with $1/r^2$ in air, (where r is the distance from target to sample) a total sample area of 100 cm^3 is available for activation analysis for periods up to one hour per target with an average flux of 10^8 n cm^{-2} sec^{-1}. Neutron scattering in large samples ($\sim$ 100 cm^3) varies with the matrix; however, if the sample is homogeneous, this scattering can be determined readily by using thin copper foils. Self-absorption of the 6-7 Mev O^{16} gamma ray radiation in the sample is neglected. Work is progressing on the design of an irradiation facility to utilize such a volume.

The only other isotope that produces N^{16} under 14 Mev neutron bombardment is F^{19}. This is accomplished by the neutron-alpha reaction $F^{19}(n,\alpha)N^{16}$. Fortunately, F^{19} also undergoes a neutron-proton reaction $F^{19}(n,p)O^{19}$ to produce 29-second O^{19}. Be establishing calibration curves for both reactions, the interference of fluorine with oxygen analysis can be eliminated. We have found that fluorine-oxygen ratios as large as 10 can be tolerated before the signal-noise ratio becomes too small for accurate analytical determination. (E. Steele)

C. Fast Neutron Activation Analysis of Cr, Cu, F, Fe, N, Si and O

This program involved the application of 14 Mev neutron irradiations of chromium, copper, chlorine, iron, nitrogen, oxygen, and silicon using a low voltage (150 kv) Cockroft-Walton accelerator as a neutron source and gamma spectroscopy to measure the radionuclides produces. The neutrons were produced by the $H^3(d,n)He^4$

reaction. A sample transfer system was used which moved the sample from the irradiating position to the detectors in 2-4 seconds. Specific activities varied from 4×10^4 to 5×10^5 "photopeak" counts per gram per minute with a neutron flux of 10^8 neutrons cm^{-2} sec^{-1}. Irradiation times varied from 30 seconds for copper, fluorine, and oxygen to 25 minutes for iron. In each case, the time of irradiation was selected to conserve the tritium target. By using all of the area available with an average fast flux of 10^8 n cm^{-2} sec^{-1} for sample irradiation and a proper transfer system, it should be possible to analyze any of the seven elements in concentrations below 100 ppm.

Samples were irradiated in the bunny system of the generator as described in an earlier section. During operation, neutron fluxes at the center of the irradiation position, varied from 5×10^8 to 5×10^7 n cm^{-2} sec^{-1} depending upon the condition of the tritium target. At the end of the irradiation, samples were delivered to the detectors for measuring. Radioactive assays were made by gamma-ray spectroscopy using the two 3" scintillation crystals and the RIDL dual memory 100-channel analyzer. All samples were sealed in medical grade polyethylene and placed in a screw-cap polyethylene capsule one inch long and one-half inch in diameter for irradiation.

Radiations from the samples were detected, analyzed, and stored for one minute in the multi-channel analyzer which had been previously calibrated with cesium-137 and cobalt-60. This information was recorded photographically on an X-Y recorder and typed out by a Hewlett-Packard Printer. A record of the analyzer dead time was taken continuously during the counting operation.

1. Results

a) Chromium

Chromium irradiated with 14 Mev neutrons yields a 3.76 minute half-life vanadium-52 activity with a gamma decay energy of 1.44 Mev. Irradiation times of 3.75 minutes were used and the spectra obtained in the energy range of 0-2 Mev. The number of 1.44-Mev photopeak scintillation counts was corrected for analyzer dead time, transfer time, and normalized to 10^8 neutrons cm^{-2} sec^{-1}. Specific activity for chromium under these conditions was found to be 139,808 counts per minute per gram with an observed standard deviation of 9.3% in the 6.2 to 106 milligram range. Table V shows the results of runs on

Table V. Activation Analysis of Chromium Using Vanadium-52

Sample	Cr Weight (mg)	Photopeak cts min^{-1} (10^8 n cm^{-2} sec^{-1})	Specific Activity Cts min^{-1} gm^{-1} Cr
Chromic oxide	6.2	1002	166,613
Chromic oxide	20.0	2737	136,850
Chromic oxide	54.5	7254	133,038
Chromic oxide	106.0	13,541	127,732
		Ave.	139,808 ± 12,998 or 93% std. dev.

four chromium samples. Fig. 28 is a calibration curve for chromium. Manganese is the only serious interference encountered.

b) Copper

Copper irradiated with 14-Mev neutrons yields a 10-minute half-life copper-62 activity with a positron decay

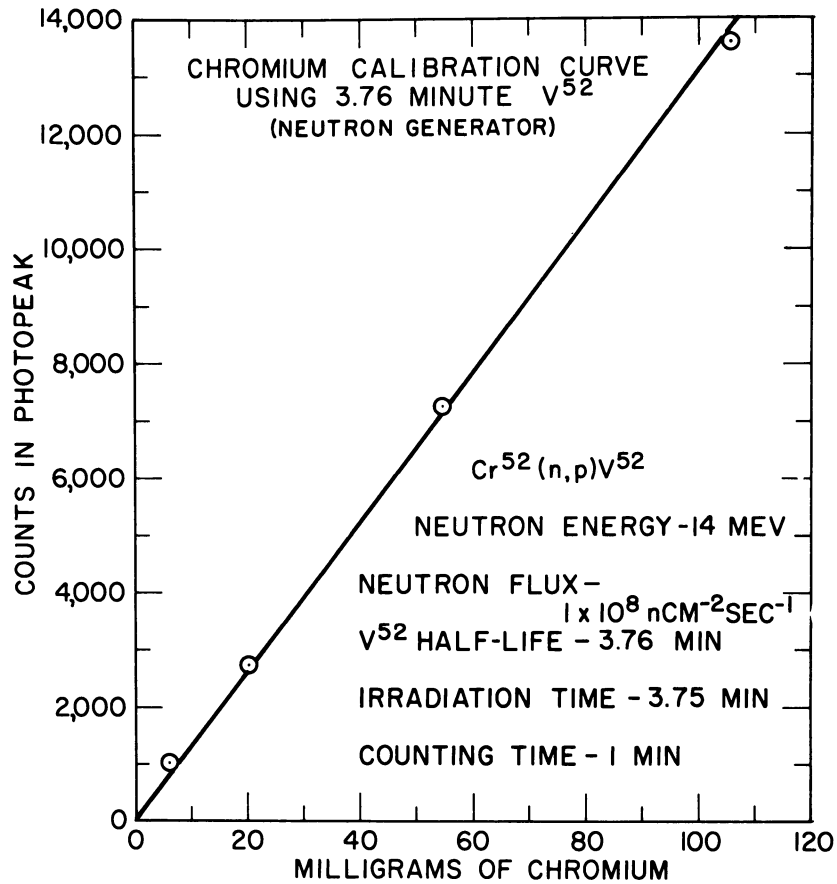


Figure 28. Calibration curve for chromium.

energy of 2.91 Mev. Irradiation times of 30 seconds were used and the spectra of the annihilation peak were obtained in the energy range of 0-1 Mev. Scintillation counts in the 0.551 Mev peak were corrected and normalized as described above. Specific activity for copper under these conditions was found to be 40,862 counts per minute per gram with an observed standard deviation of 0.9% in the 10.2 to 124.2 milligram range. Table VI shows the results of runs on four copper samples. Figure 29 is a calibration curve for copper. All positron emitters interfere with this reaction but nitrogen is particularly bad due to a similarity of half-life products.

Table VI. Activation Analysis of Copper Using Copper-62

Sample	Cu Weight (mg)	Photopeak cts min^{-1} (10^8 n cm^{-2} sec^{-1})	Specific Activity Cts min^{-1} gm^{-1} Cu
Copper	10.2	420	41,173
Copper	59.1	2,388	40,405
Copper	92.6	3,820	41,256
Copper	124.2	5,045	40,446
			Ave. 40,862 ± 362
			or 0.9% std. dev.

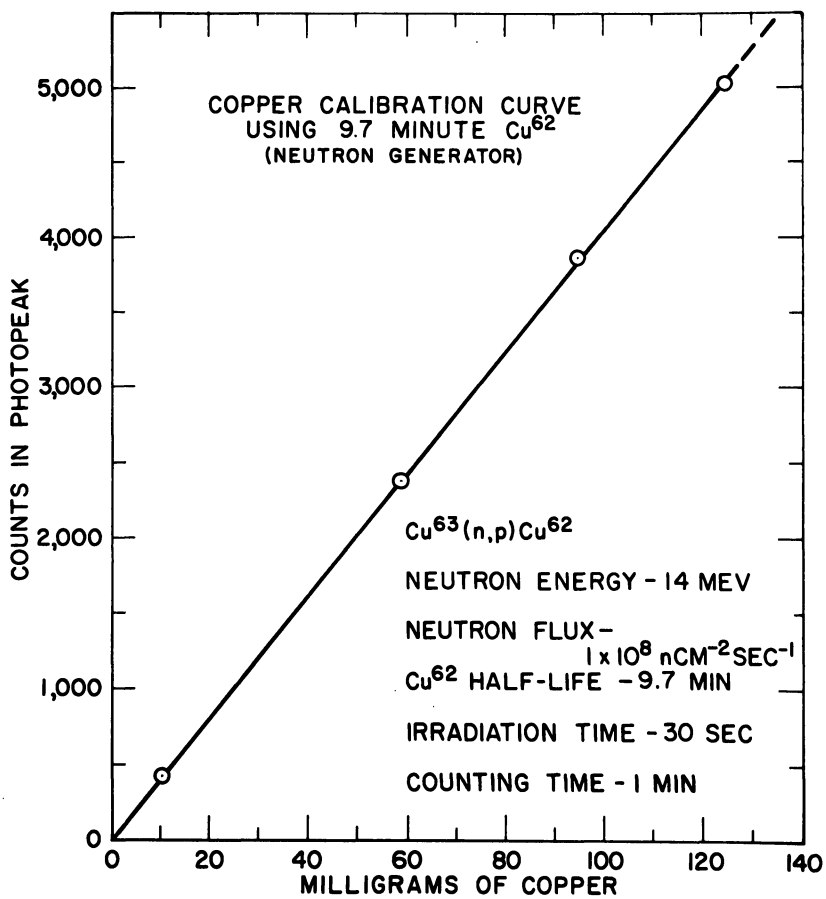


Figure 29. Calibration curve for copper.

c) Fluorine

Fluorine, irradiated with 14 Mev neutrons, yields a 118 minute half-life F^{18}, a 7.4-second half-life N^{16}, and a 29.4-second O^{19} activity. The $F^{19}(n,p)O^{19}$ was selected for analytical investigation because of the lack of interference from other radioactivated nuclei. The O^{19} has gamma decay energies of 0.197 and 1.37 Mev. Irradiation times of 30 seconds were used and the spectra obtained were in the energy range of 0-0.5 Mev. Scintillation counts in the 0.197 Mev photopeak were corrected as described above. Specific activities for fluorine under these conditions were found to be 269,684 photopeak counts per minute per gram, with an observed standard deviation of 9.7% in a 6.8 to 71.2 milligram range. Table VII shows the results of runs on four fluorine samples. Fig. 30 gives a calibration curve for fluorine.

Table VII. Activation Analysis of Fluorine Using Oxygen-19

Sample	Fluorine Weight (mg)	Photopeak cts min^{-1} (10^8 n cm^{-2} sec^{-1}	Specific Activity Cts min^{-1} gm^{-1} Fluorine
Lithium fluoride	6.8	1581	232,486
"	16.5	5063	306,817
"	33.1	8945	270,228
"	71.2	19174	269,734
		Ave.	269,283 ± 26,283 or 9.7% std. dev.

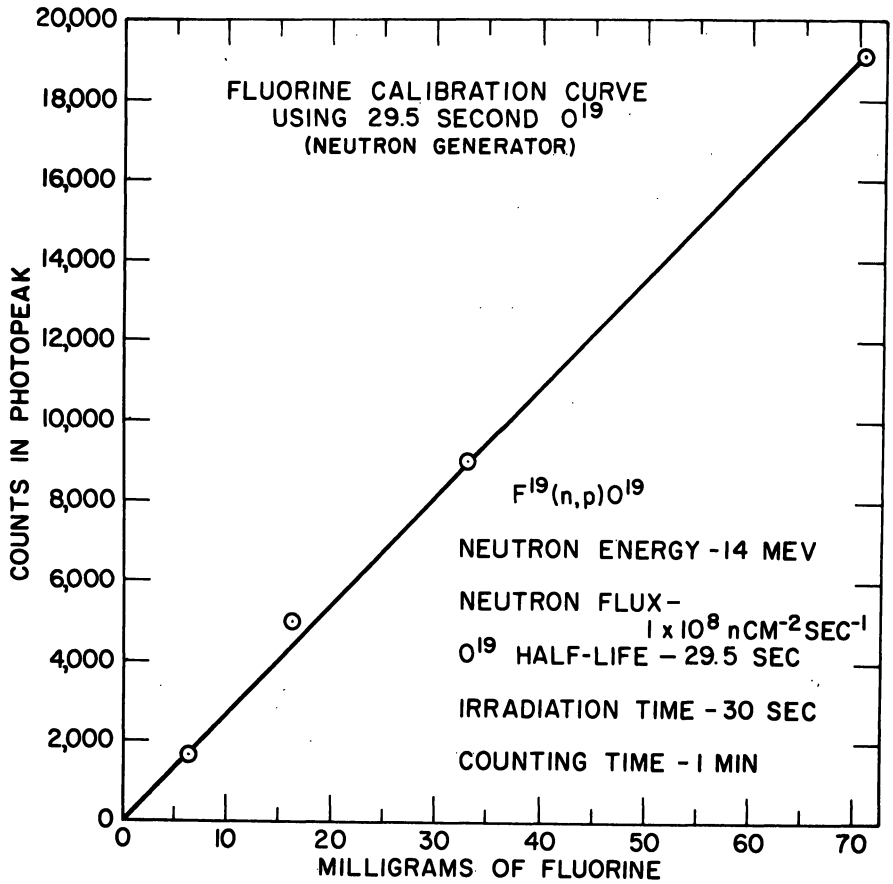


Figure 30. Calibration curve for fluorine.

d) Iron

Iron, irradiated with 14 Mev neutrons yields the 2.576-hour half-life Mn^{56} activity with gamma decay energies of 0.845, 1.81, and 2.13 Mev. Irradiation times of 25.8 minutes were used and the spectra obtained in the energy range of 0-1 Mev. Scintillation counts in the 0.845 Mev photopeak were corrected as described above. Specific activity for iron under these conditions was found to be 45,822 photopeak counts per minute per gram with an observed standard deviation of 6.4% in the 4.9 to 127.8 milligram range. Table VIII shows the results of five

Table VIII. Activation Analysis of Iron Using Manganese-56

Sample	Fe Weight (mg)	Photopeak cts min^{-1} (10^8 n cm^{-2} sec^{-1})	Specific Activity Cts min^{-1} gm^{-1} Fe
Iron	4.9	251	51,229
Iron	11.0	509	46,273
Iron	30.5	1307	42,834
Iron	85.0	3752	44,124
Iron	127.8	5710	44,652
			Ave. 45,822 ± 2919
			or 6.4% std. dev.

iron samples. Fig. 31 gives a calibration curve for iron. Cobalt interferes with this determination.

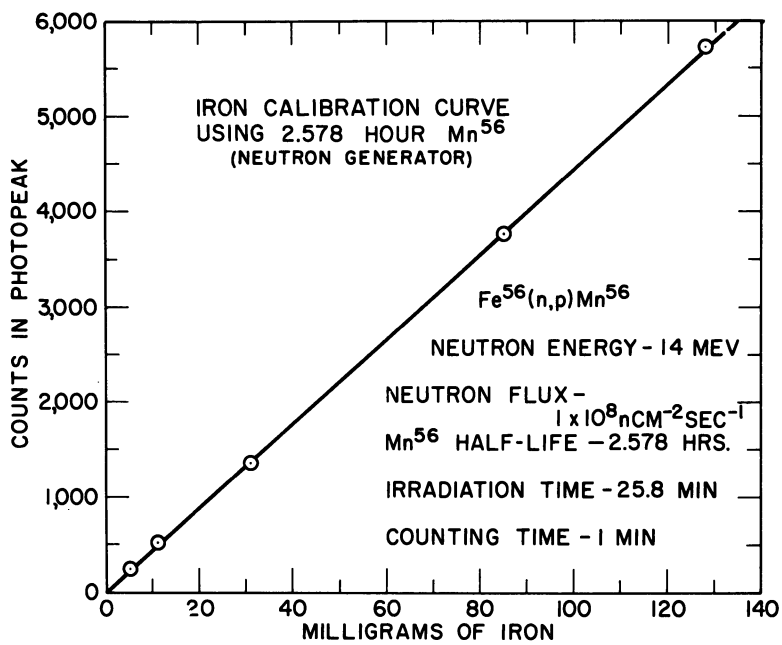


Figure 31. Calibration curve for iron.

e) Nitrogen

Nitrogen, irradiated with 14 Mev neutrons, yields the 10-minute half-life N^{13} activity with a positron decay energy of 1.24 Mev. Irradiation times of 5.0 minutes were used and the spectra of the annihilation peak were obtained in the energy range of 0-1 Mev. Scintillation counts in the 0.511 Mev peak were corrected as described above. Specific activity for nitrogen under these conditions was found to be 50,518 photopeak counts per minute per gram with an observed standard deviation of 9.2% in the 7.3 to 60.2 milligram range. Table IX shows the results of four nitrogen samples, while Fig. 32 gives a calibration curve for nitrogen. All positron emitters interfere with this procedure but copper is particularly bad due to a similarity of half-lived products.

Table IX. Activation Analysis of Nitrogen Using Nitrogen-13

Sample	N Weight (mg)	Photopeak cts min^{-1} (10^8 n cm^{-2} sec^{-1})	Specific Activity Cts min^{-1} gm^{-1} N
Ammonium nitrate	7.3	331	45,347
"	15.9	923	58,047
"	34.1	1683	49,346
"	60.2	2970	49,332
			Ave. 50,518 ± 4635
			or 9.2% std. dev.

f) Silicon

Silicon, irradiated with 14 Mev neutrons, yields the

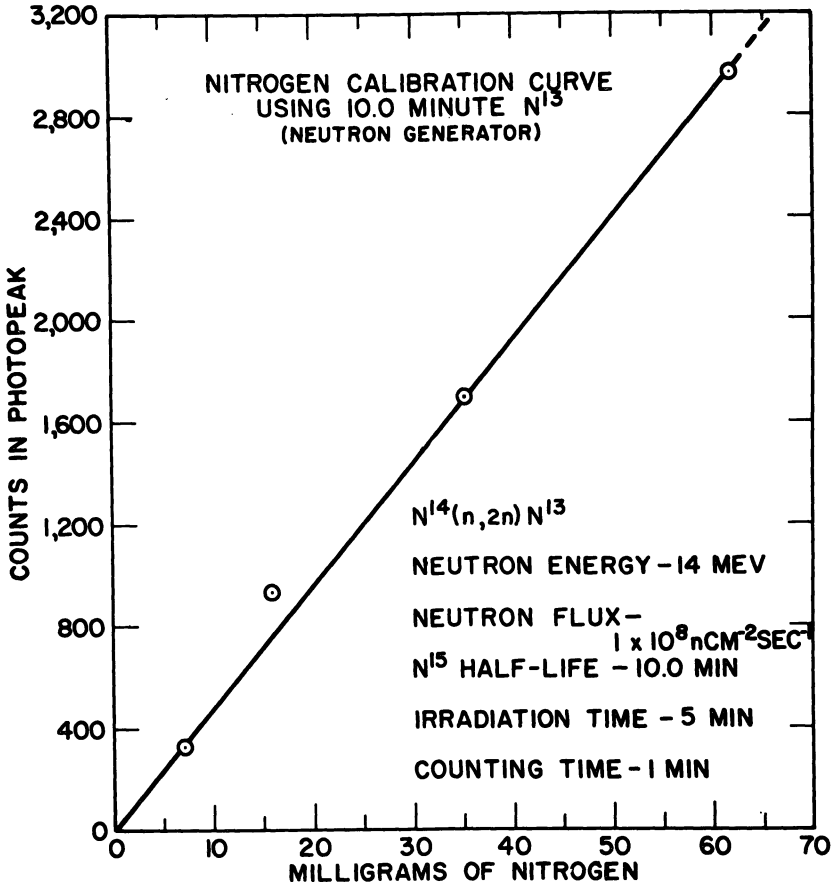


Figure 32. Calibration curve for nitrogen.

2.3-minute half-life Al^{28} activity with a gamma decay energy of 1.78 Mev. Irradiation times of 2.3 minutes were used and the spectra were obtained in the energy range of 0-2 Mev. Scintillation counts in the 1.78 Mev photopeak were corrected as described above. Specific activity for silicon under these conditions was found to be 532,629 counts per minute per gram with an observed standard deviation of 13.2% in the 9.5 to 63.3 milligram range. Table X shows the results of four silicon samples. Fig. 33 gives a calibration curve for silicon. Phosphorus is the only element which interferes with this procedure.

Table X. Activation Analysis of Silicon Using Aluminum-28

Sample	Si Weight (mg)	Photopeak cts min^{-1} (10^8 n cm^{-2} sec^{-1})	Specific Activity Cts min^{-1} gm^{-1} Si
Silicon	9.5	6210	653,665
Silicon	26.3	12865	489,127
Silicon	49.9	24172	484,407
Silicon	63.3	31875	503,505
		Ave.	532,626 ± 70,225
			or 13.2% std. dev.

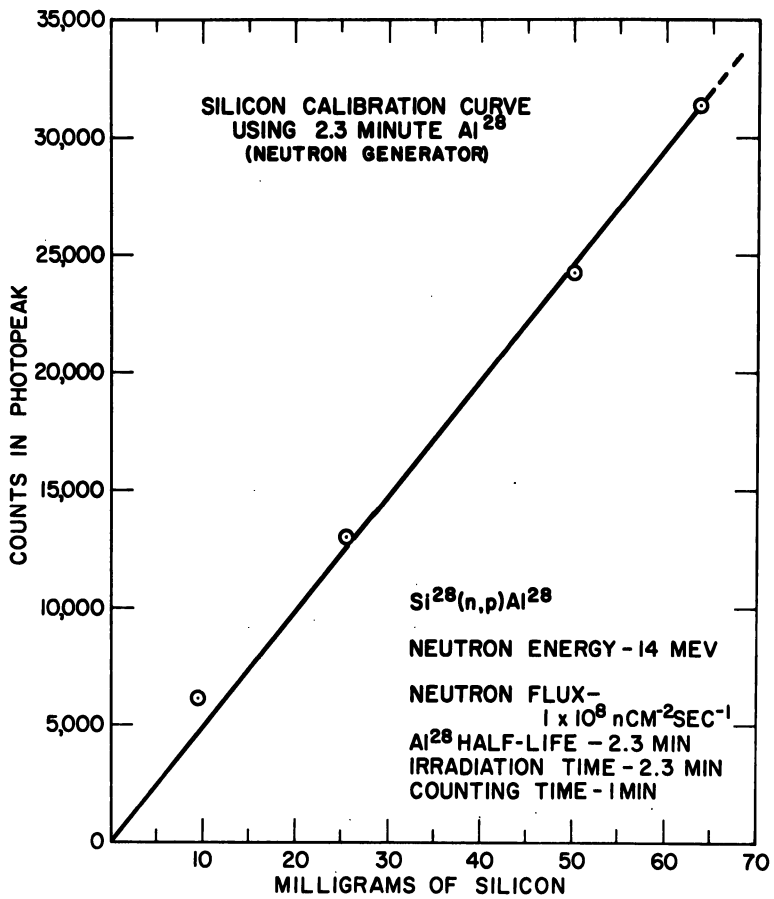


Figure 33. Calibration curve for silicon.

g) Oxygen

The determination of this element by fast neutron activation has been discussed in the previous section. Table III showed the results of four oxygen samples while Fig. 27 gave a calibration curve for oxygen. (E. Steele)

D. Non-Destructive Activation Analysis of Silver: Comparison of Reactor and Generator

The experimental work has been completed and a paper is being prepared for publication. A summary of the work is given below.

The Ford Nuclear Reactor (operating at 1 megawatt) and the Texas Nuclear Corporation Neutron Generator (deuteron current: about 500 μa, accelerating voltage: 150 kev) were used as sources of neutrons. The sample was irradiated by neutrons for 24 seconds and then, using the "bunny tube" facility, the sample was sent to the counting position in the counting room. Immediately, the 0.66 Mev gamma-ray peak of Ag-110 was measured for one minute by the two 3" x 3" NaI crystal assemblies with the 100-channel analyzer.

One of the important purposes of this work was to compare the above two neutron sources with each other from the viewpoint of activation analysis using short-lived radioisotopes, such as Ag-110. The results of the work are summarized in Table XI.

A second purpose was to apply the complement-subtraction method to the gamma spectrometry measurement. In general, especially in non-destructive analysis, the gamma-ray peak or the Compton scatter due to other coexistent radioactive impurities sometimes overlaps the desired peak and interferes with the measurement. If the half-life of the impurity is appreciably different from the desired

Table XI. Comparison Between Reactor and Generator in Non-Destructive Activation Analysis of Silver Using 24-second Ag^{110}

	Reactor	Generator
Thermal neutron flux	2×10^{12} *	$2.5 \times 10^{7} \rightarrow 0.5 \times 10^{7}$ **
Fast neutron flux	$\sim 1 \times 10^{10}$ * (> 5.3 Mev neutron)	$15 \times 10^{7} \rightarrow 3 \times 10^{7}$ ** (14 Mev neutron)
Ratio of fast neutron flux to thermal flux	0.0057 *	~ 6 **
Flux variation in one day	<5%	~ 10%
Time elapsed from the end of irradiation to the beginning of counting	12 sec	3.3 sec
Predominant nuclear reaction produced in sample	Thermal neutron reaction	Thermal neutron reaction plus 14 Mev neutron reaction
Sensitivity of silver analysis	0.006 μg Ag	0.6 mg Ag
Content range useful for silver analysis using 1 gm sample	0.05 ppm-1 ppm Ag	0.5-10% Ag

* PL-2 station

** At 2 cm distance from the target in water moderator

element, a "peeling off" technique is applicable for the "elimination" of the impurity peak, but it is somewhat time consuming.

Instead, a simple mechanical method for eliminating the long-

lived impurity component from the peak obtained should be applicable. This is the complement-subtraction method. The gamma spectrum of the activated sample is first stored in the memory of the multi-channel analyzer by the usual method. Then at a definite later time the long-lived radioactivity still remaining is subtracted in the analyzer memory from the first spectrum. Thus, the remaining spectrum in the memory shows only the short half-life component from the original spectrum.

From a simple theoretical consideration, it can be shown that $e^{-0.693\ t/T_{1/2}}$ of the peak height (or area) in the first counting period is subtracted from the first peak height (or area) by this method. The time interval, "t", means the time from the beginning of the first counting period to the beginning of the second "subtracting" counting period and $T_{1/2}$ is the half-life of the nuclide.

The value "$e^{-0.693\ t/T_{1/2}}$" can be called the "fraction subtracted" and, similarly, $1-e^{-0.693\ t/T_{1/2}}$ can be called the "fraction remaining". These values are shown as a function of $T_{1/2}/t$ in Fig. 34.

Thus if "t" is 1 minute, for example, the fractions subtracted are 0.18 for Ag^{110} (24 sec), 0.73 for Zn^{71} (2.2 min), 0.93 for Cu^{62} (9.8 min) and Sn^{125} (9.5 min), 0.97 for I^{128} (25 min) and 0.98 for Sn^{123} (39.5 min). These values were in good accordance with the values obtained experimentally.

This complement-subtraction method for silver analysis has been applied to various samples and the experimental results compared with those of the standard method. (Y. Kusaka)

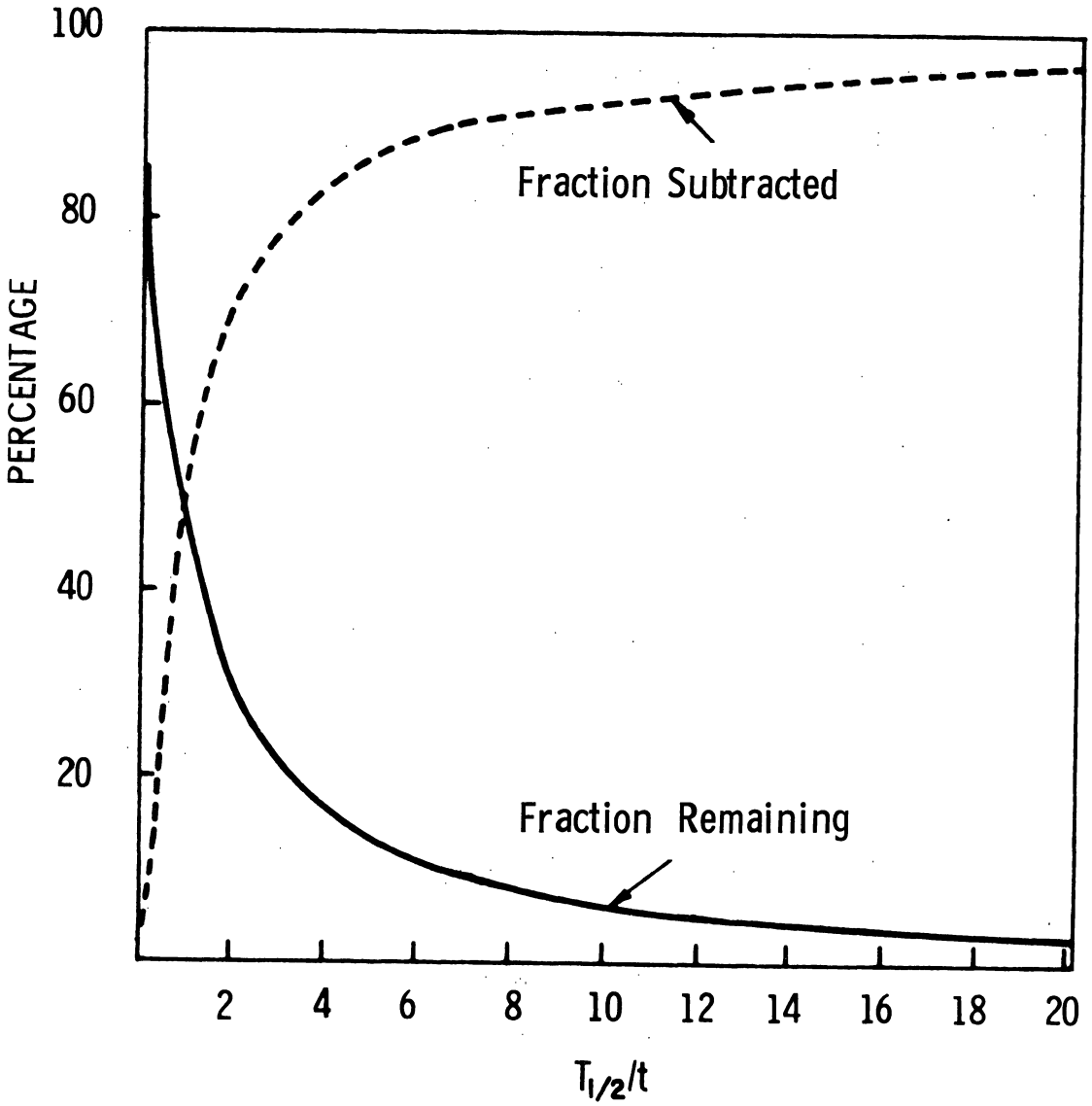


Figure 34. Graph for use in complement substraction method.

E. Activation Analysis of Rhodium

The work on rhodium discussed in the last report (1) has been completed and will be published in Analytica Chimica Acta in the near future. The paper is entitled "Determination of Rhodium by Thermal Neutron Activation Analysis Using Gamma-Ray Spectrometry" and is co-authored by Edgar L. Steele and W. Wayne Meinke. A summary of the paper follows.

"Trace amounts of rhodium have been determined by thermal neutron-activation analysis using both destructive and non-destructive methods. With a neutron flux of 10^{12} n cm^{-2} sec^{-1} the lower limits of detection are ~ 0.1 µg and ~ 0.01 µg, respectively. A rapid sodium-peroxide fusion followed by a pyridine extraction was used in the destructive method to separate the 4.4-minute Rh^{104m} from its matrix. The 44-second Rh^{104} was used in the non-destructive method. Both radioactive isomers were measured by gamma-ray spectrometry with a multichannel pulse height analyzer. The average time required per non-destructive analysis was 7 minutes while the chemical method averaged 20 minutes."

(E. Steele)

F. Activation Analysis of Sodium Deposited on Gold Leaf

Several analyses have been made of very thin films of sodium which had been vaporized into gold leaf for use in cyclotron scattering experiments. Primary sodium standards were made up using $NaNO_3$ dissolved in double demineralized water and were irradiated with a known weight of gold at a flux of ~ 2.3 x 10^{12} n cm^{-2} sec^{-1}. The gold was dissolved in aqua regia and diluted to ~ 200 µg Au/100 λ of solution. The samples were than counted with a 3" x 3" NaI crystal with a plastic beta absorber shield using a multichannel analyzer.

The standard samples consisted of from 100 λ to 500 λ of standard sodium solution having 100.0 µg Na/100 λ plus 100 λ of Au solution containing ~ 200 µg Au/100 λ. The values obtained were plotted on log paper and extrapolated to form the calibration curve.

The samples of gold leaf having unknown amounts of sodium were packaged and irradiated in a manner similar to the standards. These were counted several times and the activity corrected to time zero for comparison. All samples were corrected by using a gold monitor foil to a specific activity of 2×10^6 c min^{-1} mg^{-1} of gold thus eliminating variations of reactor flux levels.

All samples were irradiated for 1.00 minutes using the pneumatic tube system.

The results showed that sample No. 1 had 35.5 μg ± 5.1% Na; sample No. 2, 11.3 μg ± 3.2% Na; and sample No. 3, 11.8 μg ± 3.2% Na. The errors are standard deviations for four runs.

The standard curve showed that for a one-minute irradiation 2.5 μg of sodium would give ~ 100 c/m in the photopeak (in the presence of 200 μg of gold). A longer irradiation time would increase the sensitivity so that smaller amounts of sodium could be determined. (H. W. Nass)

G. Analysis of Copper Wire for Trace Impurities

Several analyses were made of some high purity copper wire which had been used in electron diffraction work in the department. Copper, when irradiated, will form two radioactive isotopes: 12.8-hour Cu^{64} from Cu^{63} with a 4.4 barn cross-section, and 5.1-minute Cu^{66} from Cu^{65} with a 2.2 barn cross-section. With this high sensitivity large amounts of radioactive copper will be produced in an irradiation of copper compared to activity from microgram level trace impurities.

Two methods are available for activation analysis of this type. One would use very short irradiations (5-24 seconds) during

which time the Cu will become active but the trace impurities, if their isotopes had short half-lives and large cross-sections, might also produce measurable activities. The other involves activation of a Cu sample for a long period of time (several hours) and waiting for the Cu isotopes to decay, before looking for trace impurities with half-lives much larger than the 12.8-hour Cu^{64}.

The latter method proved to be the best for this copper wire analysis.

A sample of copper wire, weighing 0.500 gm, was irradiated at a flux of 10^{13} n cm^{-2} sec^{-1} for five hours and allowed to decay for about three days at which time it was divided into two fractions. One was kept as the solid wire and the other dissolved and passed through an ion exchange column in an attempt to separate the Cu from the trace elements possibly present. The ion exchange separation was unsatisfactory because of the amounts of Cu present which filtered through in each elution.

The solid wire was counted once every day until the Cu^{64} disappeared, at which point several other gamma-ray peaks became evident and identification and determination was made. Silver was found in a concentration of about 6×10^{-6} gm/gm of Cu and cobalt in a concentration of about 0.2×10^{-6} gm/gm of Cu. These values are probably good to within 10%. There were also several other gamma rays present which were so low in abundance that we were unable to identify them. (H. W. Nass)

IV NUCLEAR CHEMISTRY

A. Short-Lived Fission Gases

The work in this area outlined previously (1,2) has been completed and written up as part of a thesis entitled "Nuclear Decay Scheme Studies on Short-Lived Nuclides from the (n,γ) and (n, fission) Reactions". An abstract of this thesis follows.

"The objective of this research was the study of nuclear decay schemes, primarily of short-lived nuclides, utilizing the irradiation facilities of the Ford Nuclear Reactor at the University of Michigan. Multi-channel pulse-height analysis was applied to the study of short-lived fission products and to a search for unreported isomeric transitions among the (n,γ) reaction products.

"Irradiation and handling techniques were developed and instrumental modifications made to facilitate the study of short-lived nuclides. The neutron flux and flux distribution at the irradiation position were measured.

"A simple and rapid separation of gaseous fission products into krypton and xenon fractions was developed. The primary gamma-ray energies of 3.2-minute Kr^{89}, 33-second Kr^{90}, 1.2-minute Rb^{91m}, 41-second Xe^{139}, 41-second Xe^{139}, and 66-second Cs^{140} were determined and relative gamma-ray intensities measured. Maximum beta-ray energy end-points were measured for Kr^{89}, Kr^{90}, Xe^{139}, Cs^{140}, and 9.5-minute Cs^{139}, and lower limits established for the decay energies of these nuclides. The gamma-rays of the daughter activities, 14.9-minute Rb^{89}, 2.7-minute Rb^{90}, and Cs^{139}, previously reported in the literature were verified.

"An upper limit of 2 minutes was established for the half-life

of the fission product, Rh^{109}, by devising a chemical separation, requiring 6 minutes, giving decontamination factors of $>10^5$ from other elements.

"An isomeric level of Pt^{199} was detected and characterized by the (n,γ) reaction on normal and enriched platinum samples. The isomer decays with a half-life of 14.1 ± 0.3 seconds by emission of gamma-rays of 32 ± 2 kev and 393 ± 2 kev energy. The thermal neutron cross-section for the formation of the isomer is 28 ± 3 mb.

"A long-lived isomer of Ag^{108} was detected in Ag^{110m} tracer sources sufficiently old that the masking 270-day Ag^{110m} had decayed out. The half-life of the isomer is >5 years. 90% of the disintegrations proceed by electron capture followed by a cascade of three gamma-rays of 434, 616, and 722 kev energy, and 10% go by isomeric transition to 2.4-minute Ag^{108}. New values were determined for the branching ratios in 2.4-minute Ag^{108}.

"No unreported isomeric transitions, with half-lives in the range of 1 second to 10 minutes, were detected in the (n,γ) reaction on ruthenium, palladium, mercury, rhenium, barium, lanthanum, cerium, praseodymium, samarium, europium, gadolinium, terbium, holmium, erbium, thulium, ytterbium, or lutetium." (M. Wahlgren)

B. Formation of Gamma-Ray Induced Short-Lived Nuclear Isomers

An investigation of the possible application of gamma-induced short-lived nuclear isomer formation in monitoring of gamma and mixed-gamma radiation fields is being conducted. Exploratory experiments utilizing the $Au^{197}(\gamma,\gamma')Au^{197m}$ reaction have been performed to evaluate possible application of the method to monitor-

ing of a reactor gamma flux.

Measurements of gamma flux by isomer formation in a mixed gamma neutron field is complicated by the fact that such formation may be brought about not only by inelastic gamma scattering but by inelastic neutron scattering as well. Whereas the cross-section for (γ,γ') reactions are at most the order of several millibarns, the cross-sections for (n,n') reactions are generally several orders of magnitude larger in the energy regions of interest here. Further thresholds for neutron-induced isomer formation are appreciably smaller than the thresholds for the associated inelastic gamma scattering reactions.

Thus application of the proposed technique to gamma monitoring in mixed gamma-neutron fields is limited to cases where (a) the gamma flux is extremely large compared to the associated neutron flux, and (b) the neutron flux has negligible components of energy equal to or greater than the energy of the metastable state in the target nuclide.

A number of exploratory experiments have been performed with the pneumatic tube facility of the Ford Nuclear Reactor. This work is being evaluated at present and will be prepared for publication in the near future. (S. Prussin)

V RADIOCHEMICAL SEPARATIONS

This year a major portion of the project has been directed towards this area -- particularly towards experimental evaluation of separations using the amalgam exchange principle. Detailed studies involving several elements are summarized below. In addition the early work on extraction of aniline (12) has been completed for publication. Once again considerable effort on the part of the director has been expended as Chairman of the Subcommittee on Radiochemistry, of the Committee on Nuclear Science of the National Research Council. This Subcommittee has had two meetings during the year and has sponsored two special reports as well as many monographs.

The Subcommittee continues to concern itself with a wide spectrum of topics in the field of radiochemistry including low level contamination in reagents and materials, teaching experiments in radiochemistry, monographs on radiochemistry of the elements and on radiochemical techniques, and a source booklet for radiochemistry. The status of these efforts is covered in detail in the minutes of the meetings of this Subcommittee.

A. Subcommittee on Radiochemistry Program

1. "Source Material for Radiochemistry" Pamphlet

The first revision of this pamphlet (Nuclear Science Series Report No. 27 - Rev. 1) has been available since November, 1960 free of charge from the Division of Physical Sciences, National Research Council, 2101 Constitution Avenue, Washington 25, D. C. More than 200 sources of informa-

tion, grouped according to areas, are included. A short description of each is given in addition to specific information regarding availability. (W. W. Meinke)

2. Radiochemistry Monographs

Editing of the series of monographs on the "Radiochemistry of the Elements" has continued throughout the past year. The number of monographs actually in print has increased from the 14 of a year ago to 38 at present. An additional 10 titles have been processed here and sent to the Office of Technical Information Extension for publication. Besides these 48 completed monographs another 14 have been promised within the next two months so that this entire series should be completed by the end of the year.

Some progress has also been made on a second monograph series on "Techniques of Radiochemistry". Three monographs have already been published in this series and several more will soon be processed. Monographs in both series are now available for sale from the Office of Technical Services, Washington 25, D. C. at a price approximating 1 cent per page. They have been given document numbers such as NAS-NS-3001, NAS-NS-3002, etc. Arrangements can be made to receive the complete set of monographs as they are issued through a standing order account. (W. W. Meinke)

3. Teaching Experiments in Radiochemistry

The interests of the Subcommittee in this field have resulted in publication of a 50-page booklet compiled by

Gregory Choppin, "A Cross-Referenced Index of Radiochemical Teaching Experiments Applicable to Chemistry". This booklet is available as Nuclear Science Series Report No. 36 for $1.00 from the Publications Office, National Research Council, 2101 Constitution Avenue, Washington 25, D. C. The first section of the booklet contains lists of experiments from some 15 books, along with brief comments on the types of radioisotopes or types of techniques required for particular experiments. In the second section the experiments are divided into categories such as analytical chemistry, organic chemistry, physical chemistry, etc., and are cross-referenced according to the type of experiment.

Continued efforts will be directed towards this program in the forthcoming year to pick out gaps in the coverage of currently available experiments and then to try to sponsor development of experiments to fill these gaps. (W. W. Meinke)

4. Low-Level Contamination in Materials

This project which had been based here at Michigan and was sponsored by the AEC through the National Research Council on another contract was successfully concluded in early summer. Dr. James DeVoe who had worked on the project for over a year summarized in a detailed report the information he had collected during visits to more than 50 laboratories throughout the country. This report was entitled "Radioactive Contamination of Materials Used in Scientific Research" and was issued in June as Nuclear Science Series Report No. 34. It is available for $2.00 from the Publications Office

of the National Research Council, 2101 Constitution Avenue, Washington 25, D. C.

Quoting from Addendum I of this report: "The data collected in this report show that one substance, krypton, has been grossly contaminated to an extent which has seriously curtailed many of its possible scientific uses. This contamination probably could not have been prevented, but if its seriousness had been foreseen vigorous steps could have been taken to stockpile an adequate supply of uncontaminated gas. It is now too late to take these steps.

"A few other substances show a rather general low-level contamination which, while not very serious, is important enough to call to the attention of scientists. The contamination of much ruthenium with fission product Ru^{106} is an example of this. There are a few cases of incipient contamination of materials which are not general or serious at the present time but which could develop into a problem if the technical uses of radioactive materials were to become more widespread. The contamination of some steel with radioactive Co^{60} eroded from Co^{60} sources imbedded in the firebrick of steel furnaces is an example of this.

"The data cited in the report also indicate a number of examples of unexpected contamination of materials or reagent chemicals. In several instances this contamination was sufficiently great that it could interfere seriously with scientific investigation dependent upon the measurement of low-levels of radioactivity. This would be particularly true

if the experimentalists were unaware of this contamination. It should be emphasized, however, that the data are much too scattered and incomplete to support any conclusions about the general extent of such contamination."

No conference was held on this topic (as was anticipated last year) because of this general inconclusiveness. However the 135-page report of DeVoe's covers the current status of the field in detail such that it can be used as a base line for future discussions and investigations.

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

B. Preparation of Radiochemistry Monographs

Present or former members of this project have contributed a number of monographs to the series. In addition to those on cadmium, barium-calcium-strontium, and indium which were written last year, monographs on the "Radiochemistry of Vanadium" by James L. Brownlee, Jr., the "Radiochemistry of Titanium" by Chong Kuk Kim, and the "Radiochemistry of Silver" co-authored by D. N. Sunderman have been written. A techniques monograph on "Rapid Radiochemical Separations" by Y. Kusaka and W. W. Meinke has been almost completed while others on the "Radiochemistry of Thallium" and the "Radiochemistry of Palladium" are in preparation.

C. Review Papers of Academician Victor I. Spitsyn

In the fall of 1960 V. I. Spitsyn, Professor of Inorganic Chemistry at Lomonosov University in Moscow and Director or the Institute of Physical Chemistry of the Academy of Sciences of the U.S.S.R. visited the United States for a one-month tour under the

sponsorship of the Division of Chemistry and Chemical Engineering of the U. S. Academy of Sciences. Professor Spitsyn's first talks were given at the University of Michigan. During the course of our discussions Professor Spitsyn mentioned his interest in having the six review lectures which he was prepared to give published together in some form in this country.

These papers totaled almost 300 pages and reviewed the work in areas of radiochemistry and radiation chemistry as well as several areas of inorganic chemistry. They included close to 500 references mostly to the Russian literature and together presented a very useful guide to Russian work in these areas. Professor Spitsyn left a carbon copy of the papers with us in Ann Arbor and we were to type them on photo-offset mats preparatory to printing. It was hoped that typing could be completed by the end of the month so that the papers could be proof read by Professor Spitsyn before his return to Russia. No official sponsorship was immediately available for this publication but because we were convinced of the value of these papers we added the typing to our regular project schedule and planned to recover our expenses later.

The typing and proof reading was very difficult, especially for the many pages of Russian references, and it was possible to have only about one third of the pages proof read by Professor Spitsyn before his return to Russia. Copies of the remainder were later sent by air mail for correction. These corrections and changes were made on the master sheets and they were forwarded to the National Research Council for publication.

Unfortunately, despite the heroic typing efforts by our people in carrying these papers along with our annual progress report, the printing of the papers was delayed. The NRC authorized publication at an early date but because of divided responsibilities and interests of the groups within the NRC there were problems in obtaining sponsorship for the printing. In early summer arrangements were finally completed whereby the Office of Isotopes Development of the AEC would sponsor this volume, and it should be available in October or Novermber of this year. All costs incurred by this project in typing and reproduction, etc., have been covered by the sponsor. (R. S. Maddock, W. W. Meinke)

D. Radiochemical Separations by Amalgam Exchange

1. Cadmium

A paper entitled "Radiochemical Separation of Cadmium by Amalgam Exchange" by J. R. DeVoe, H. W. Nass, and W. W. Meinke will appear in the November 1961 issue of Analytical Chemistry. Since this paper is pertinent to several other summaries that follow it is reproduced in its entirety below.

ABSTRACT

The radiochemical separation of cadmium by an amalgam exchange technique has been critically evaluated. In the procedure the cadmium amalgam exchange step is followed by a back extraction with thallous ion to selectively remove the cadmium from contaminants in the mercury. Cadmium yields of 80% were obtained with less than 0.1% contamination of most typical elements. Indium, thallium, and selenium con-

taminate the separation to a greater extent. The procedure can be carried out in 8 minutes with no special equipment. Mineral acids below 1 M do not affect the exchange but oxidizing agents such as U^{+6} and Ce^{+4} must be given special attention. This procedure may prove particularly useful in studies of the decay schemes of short-lived cadmium fission products.

* * * *

A previous communication from this laboratory (13) described preliminary results obtained for a number of elements using a novel radiochemical separation technique based on 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 many 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 incorporated in the amalgam. In this it is somewhat similar to the isotopic exchange separation developed by Sunderman and Meinke (14).

A recent report (15) describes the successful application of this technique to analysis for Zn^{65} in reactor effluent. In the present paper we extend the preliminary survey of the method by a critical study of its application to the radiochemical separation of cadmium. Since considerable work has already been done in this laboratory on the element cadmium (16) this study provided an excellent opportunity to compare

the amalgam exchange method with several other methods which had previously been considered optimum.

The separation technique uses the exchange of cadmium amalgam in the extraction step, followed by a back extraction or elution with thallous ion to selectively remove the cadmium from contaminants in the mercury. The extraction step can be represented by the following reaction:

$$Cd\ (Hg) + Cd^{*++} \rightleftharpoons Cd^{*}\ (Hg) + Cd^{++}$$

where the asterisk denotes a radioisotope of cadmium. The procedure consists merely of shaking the cadmium amalgam with an aqueous solution containing the radioisotopes of cadmium. The degree of separation and yield of cadmium which can be obtained with such a separation technique were measured with the use of radioactive tracers.

APPARATUS, REAGENTS, AND PROCEDURES

Apparatus

During the separation, the amalgam was agitated in a 50 ml. round bottom centrifuge tube by an electric stirrer manufactured by Eastern Industries of New Haven, Connecticut. The stirring rod was 7 mm. in diameter with a glass propeller on the end.

Gross gamma-ray measurements were made with a Nuclear-Chicago scintillation well counter as described previously (14,16,17) and gamma spectrum measurements with a special 100-channel gamma-ray scintillation spectrometer (3).

Reagents

Cadmium metal foil, 99.9% pure, Belmont Smelting and Refining, Brooklyn, New York.

Chromous sulfate solution. Reduce chromic sulfate solution [~ 100 mg. chromium sulfate (green powder), $Cr_2(SO_4)_3 \cdot nH_2O$, J. T. Baker Lot 2487, per ml.] in 0.1 N sulfuric acid by stirring with 5% by weight zinc amalgam.

Copper pellets, Mallinckrodt, analytical reagent grade.

Mercury, Baker and Adamson, analytical reagent.

Nitrogen gas, water pumped, 99.99% pure, Liquid Carbonic Company.

Thallous acetate, Fisher Chemical Co., purified. Solution 75 mg. Tl^+ per ml. in 0.1 N nitric acid.

All other chemicals used were analyzed reagent grade.

All radioisotopes used as tracers have been described previously [Table I (16), and Table II (14)].

Preparation of Cadmium Amalgam

Wash cadmium metal foil in 1 N nitric acid until surface is completely etched. Wash with distilled water, dry and weigh. Add enough cadmium foil to a weighed portion of mercury stored under several ml. of 0.1 N nitric acid to make a 2% amalgam. Agitate for short time to completely amalgamate the cadmium.

Amalgam-Exchange Procedure

Place 2 ml. of solution containing tracers of contaminating ions plus microgram amounts of inactive cadmium in a 50 ml. centrifuge tube. Radioactive cadmium and non-radioactive

interferences are used for yield determinations. Chemical concentration of solution prior to amalgam exchange is given in Table XII. Add 50 λ (~ 0.68 gm) of cadmium amalgam containing 2% cadmium by weight (~ 14 mg.). Stir vigorously for 5 minutes. Remove aqueous phase by suction and wash amalgam twice with 2 ml. portions of 0.1 N nitric acid and twice with 2 ml. portions of distilled water. Transfer amalgam to a stoppered bottle containing 2 ml. of thallous acetate solution. Shake for 1 minute. Remove 100 λ aliquot of aqueous layer containing separated cadmium isotopes and count. Total time for separation is 8 minutes.

Cadmium Separation from Fission Products

Reduce sample of irradiated uranium with chromous sulfate solution. [In these experiments 100 mg. of uranyl nitrate were irradiated for 10 minutes at a flux of 10^{12} n cm^{-2} sec^{-1} in the pneumatic tube facilities of the Ford Nuclear Reactor of the University of Michigan (3). The sample was dissolved in 1 ml. of water and transferred to a stoppered bottle. To this solution was added 1.5 ml. of chromous sulfate solution to reduce the U^{+6} to U^{+4}. This was about 50% more than the stoichiometric amount of reducing agent.] Then use amalgam-exchange procedure above. Total time for separation is 10 minutes.

DISCUSSION AND RESULTS

A number of trial separations were made in which the concentration of the amalgam, the time of stirring, and the

volume of the aqueous phase were varied in order to maximize the separation yield for cadmium. Various selective back extractants were also tried to remove the cadmium metal from the mercury. The resultant optimum separation procedure was given above.

The degree of separation of cadmium obtained with this procedure from a number of elements representative of the periodic table is shown in Table XII. The elements have been listed in the order of their reduction potentials. The data in Table XII have been subdivided to show the degree of separation for the amalgam-exchange step and for the elution step using thallous ion. It can be seen that those elements above cadmium do not contaminate the exchange separation within the sensitivity of the experiments (i.e. with the amount of tracer used, 10^6 - 10^8 counts per minute). On the other hand, elements below cadmium do contaminate the amalgam-exchange step probably due to reduction of the ions by the amalgam.

When an eluent such as thallous ion is used, considerable selectivity can be obtained through the preferential oxidation of cadmium without oxidizing the contaminating elements in the mercury. From Table XII it can be seen that those elements between thallium and cadmium (i.e. indium) continue to contaminate the separation while elements below thallium with the exception of selenium and iodine do not contaminate the elution step.

It is suspected that the very small amount of I^{131} that

TABLE XII Separation of Cadmium and Contaminants (Amalgam Exchange Procedure)[a]

Tracer[b]	Solution for Exchange (No Carrier Added)[c]	Reduction Potential[d]	Percent Separated: Exchange Step	Percent Separated: Elution Step	Total Separation
I^{131}	I^-, 0.2 N HNO_3 (C.F.)	e	0.005	100	0.005
Cs^{137}	0.1 N HCl (20 μg)	-2.92	<0.01	f	<0.01
Ba^{140}-La^{140}	0.5 N HCl (C.F.)	-2.90, -2.52	<0.002	f	<0.002
Sr^{90}-Y^{90}	H_2O (C.F.)	-2.89, -2.37	<0.0001	f	<0.001
Ce^{144}-Pr^{144}	1.5 N HNO_3 (C.F.)	-2.48, -2.47	<0.01	f	<0.01
Zr^{95}-Nb^{95}	0.5 N $H_2C_2O_4$ (C.F.)	-1.53, -1.1	<0.001	f	<0.001
Zn^{65}	1.0 N HCl (0.8 mg)	-0.76	<0.001	f	<0.001
Cr^{51}	0.2 N HCl (0.1 μg)	-0.74	<0.001	f	<0.001
Cd^{115m}	g (18 μg)	-0.40	78 ± 3	98 ± 2	76 ± 3.3
In^{114m}	0.5 N HNO_3 (50 μg)	-0.34	8.3	.20	1.6
Tl^{204}	0.5 N HNO_3 (0.83 mg)	-0.34	100	5	5
Co^{60}	0.5 N HNO_3 (7 μg)	-0.28	1	<0.01	<0.01
Sn^{113}	0.9 N HCl (1.1 mg)	-0.14	20	0.1	0.02
Sb^{124}	SbO^+, 0.5 N HNO_3 (10 μg)	+0.21	100	0.1	0.1
Ru^{106}	$RuCl_5^=$, 0.5 N HNO_3, 0.7 N HCl (6 μg)	+0.60	17	<0.001	<0.0005
Se^{75}	H_2SeO_3 0.1 N HCl (0.12 mg)	+0.74	50	33	17
Ir^{192}	$IrCl_6^{-3}$ 0.1 N HCl (0.2 μg)	+0.77	33	0.001	0.0003
Hg^{203}	0.5 N HNO_3 (0.2 mg)	+0.79	100	0.05	0.05
Ag^{110m}	0.8 N HNO_3 (20 μg)	+0.80	100	0.1	0.1

(a) Average of duplicate runs.

(b) Elements have been listed in order of their reduction potentials.

(c) Weight of inactive element prior to separation indicated in parenthesis. C.F. = carrier free.

(d) Standard reduction potential of the form $M^{n+} + ne^- \rightarrow M$ where M^{n+} is the lowest stable oxidation state of the element (unless otherwise stated in previous column). Data taken from Latimer.

(e) Iodine is in its lowest reduced form.

(f) Not detectable since no measurable radioactivity in the amalgam.

(g) Cadmium yields are an average of separate runs made with each of the listed contaminants (inactive this time) in the medium specified. Error is "standard deviation".

separates with the amalgam adsorbs on the surface of the amalgam as the iodide and then elutes as thallous iodide. Selenium is reduced to the metal by cadmium amalgam but instead of amalgamating, forms a thin film on the surface of the mercury at the concentration of selenium used in these experiments. The selenium is then removed from the surface of the amalgam during the mechanical agitation in the elution step.

Interferences

The mineral acids (nitric, hydrochloric, and perchloric) in concentrations up to 3 N, do not affect the cadmium yield when the separation is carried out at room temperature. Sulfates, sulfites, sulfides, or fluorides decrease the yield considerably.

Air oxidation of the 2% cadmium amalgam does not affect the yield in a five-minute stir. However with the same amalgam the yield of the cadmium exchange step does decrease slightly upon prolonged stirring, presumably from air oxidation, as shown in Table XIII.

Table XIII. Cd^{115m} Exchange with the Same Cadmium Amalgam in 0.5 M $NaNO_3$ Solution for Various Times of Stirring

Time (min.)	Exchange (%)
1	29.0
2	47.0
3	63.6
4	79.0
5	93
10	90
20	90

The interference effect of various oxidizing ions in solution is indicated by the contaminating effect of those elements below cadmium in Table XII. If equilibrium is obtained in the exchange reaction, the per cent of cadmium (S) which is separated in the exchange step is given by the equation $S = \frac{n}{n+N} 100$ where

N = No. of cadmium ions in the aqueous phase.

n = No. of cadmium atoms in the mercury phase.

As long as $n \gg N$ the per cent separation will be large. Therefore, as long as the amount of cadmium in the amalgam is sufficient to reduce all of the reducible aqueous ions and still result in $n \gg N$, the yield will be satisfactory. There is, however, an upper practical limit to the value of N usable since the rate of exchange is inversely proportional to the concentration of cadmium in the aqueous phase (18).

Fission Product Separation of Cadmium

An example of a technique that can be used with oxidizing agents is given above in the separation procedure for cadmium from uranium and its fission products. The use of a chromous ion solution for reducing U^{+6} to U^{+4} is advantageous because at the final concentration specified chromous ion does not oxidize the cadmium amalgam. When the separation described above is carried out, a gamma-ray spectrum is obtained which shows tellurium contamination in addition to the cadmium peaks. This was anticipated from the contamination data of selenium in Table XII. A convenient removal of much of the tellurium was made by agitating the fission product solu-

tion with copper pellets prior to the amalgam-exchange step. The tellurium is thus reduced onto the surface of the copper.

After one copper pellet reduction step, the tellurium peaks were eliminated leaving a number of peaks which correspond roughly to gamma rays from the longer-lived cadmium fission products. Because of the lack of good information on the decay schemes of the short-lived cadmium fission products, it was difficult to establish exactly the degree of purity of the separation. However, this procedure and modifications of it should prove useful to the nuclear chemist in further study of these short-lived fission products.

SUMMARY

For radiochemical separation of cadmium, the amalgam-exchange technique has proved to be rapid (8-10 minutes) and in addition, to give a high degree of separation from many elements. Figure 35 shows how the amalgam exchange technique compares with that of the dithizone extraction and anion exchange techniques, the two best techniques for cadmium which had been developed previously (16).

For most elements this separation technique is at least 10 times better than the best separation technique previously used for cadmium in our laboratory (16). Of the 21 elements tested, only selenium, indium, and thallium contaminate the separation of cadmium radioisotopes to any extent.

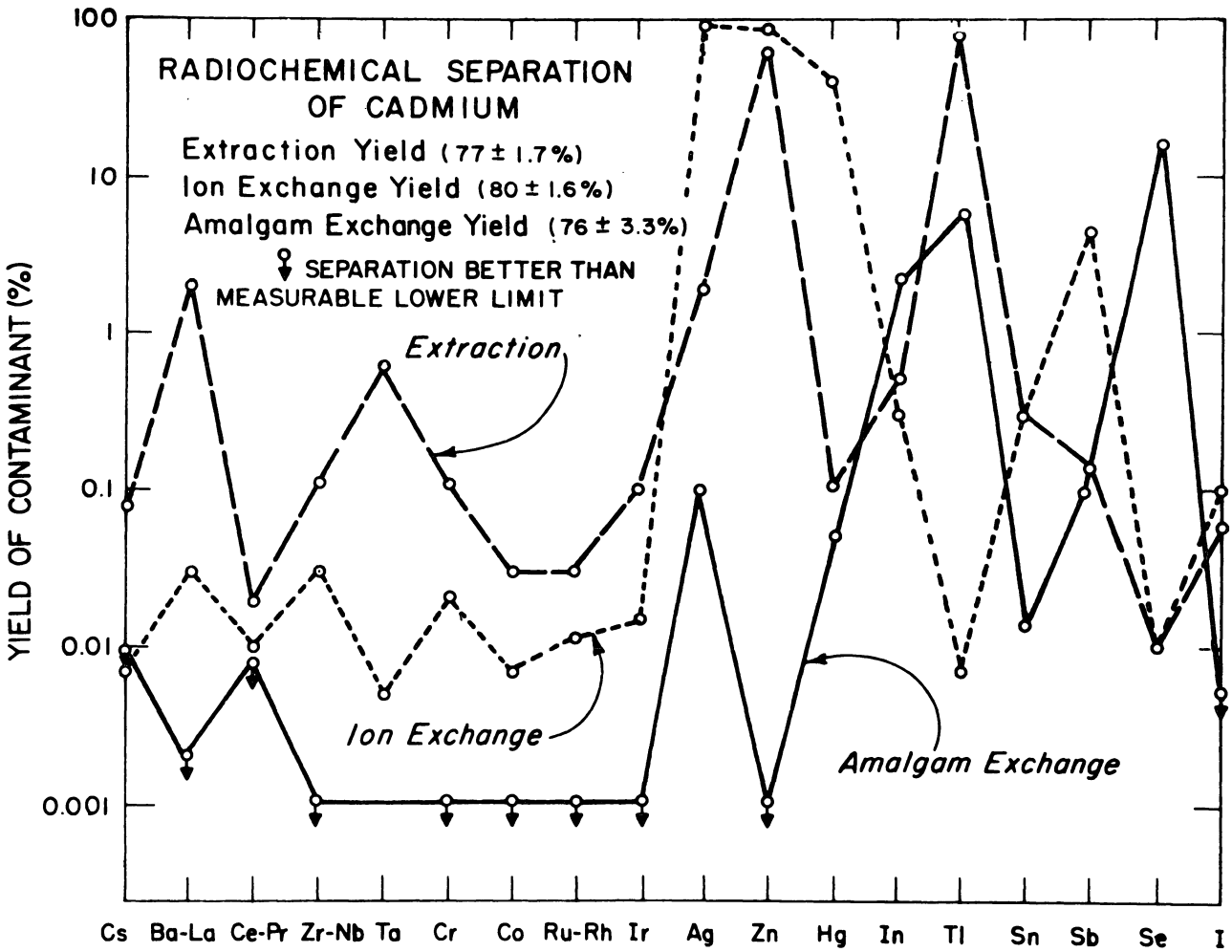


Figure 35. Experimental contamination for three types of cadmium separations.

2. Indium

A paper entitled "Radiochemical Separation of Indium by Amalgam Exchange" by R. R. Ruch, J. R. DeVoe, and W. W. Meinke has been accepted for publication in Talanta. The abstract of this paper is given below.

a) Abstract

"The radiochemical separation of indium by an amalgam exchange technique has been critically evaluated for the aqueous hydrogen-bromide system. The efficiency and contamination of the separation has been studied using tracers of 19 different representative elements.

Yields of contaminating elements are reduced in most cases to less than 0.1% while indium yields are usually above 95%. The procedure requires no special equipment and takes about 11 minutes overall. A number of factors affecting the separation have been studied and optimized."

Pertinent sections of this paper are given below in addition to the results of many individual runs which were not included in the published paper.

A procedure was developed for the aqueous hydrogen-bromide system, which gives high yields of indium with good decontamination. Many factors which affect the procedure such as concentrations of reagents, interferences, time of agitation, etc., were studied and evaluated.

The total separation procedure involves two isotopic exchange steps. In the first exchange, radioactive indium selectively exchanges with inactive indium in the mercury phase.

$$In\ (Hg) + In^{*+++} \rightleftharpoons In^{*}\ (Hg) + In^{+++}$$

The requirement here is that the concentration of indium in the amalgam be much greater than the concentration of indium in the aqueous phase. The mercury phase is then removed and the radioactive indium back exchanged into the aqueous phase by contact with higher concentrations of indium ion.

The amalgams were prepared by adding (under water purged with nitrogen) the appropriate weight of indium foil to 10 grams of reagent grade mercury which had been further purified by shaking with dilute nitric acid and

rinsing 3 to 4 times with distilled water. The indium foil had also been subjected to dilute nitric acid and distilled water rinses prior to weighing.

b) Amalgam-exchange procedure

Place 2 ml of 0.1 M hydrobromic-acid solution containing tracers of contaminating ions (10^5 to 10^6 counts per minute) plus microgram amounts of inactive indium in sample bottle. Chemical contamination added by the aliquots of contaminating tracers is negligible. Radioactive indium and non-radioactive interferences are used for yield determinations. Mix well. Add 1/2 ml of mercury as scavenger, cap bottle, and shake for one minute. Remove mercury layer. Purge the system (both liquid and air above it in bottle) with nitrogen gas for one minute. Add 75 λ (~ 1.0 gm) of indium amalgam containing 0.2% indium by weight (~ 2 mg). Quickly cap bottle and mechanically shake for four minutes.

Decant the aqueous layer, transfer amalgam to new bottle and wash twice with 2 ml portions of distilled water. Transfer amalgam to new bottle containing 2 ml of indium eluent solution. Add 1/2 ml mercury to dilute the amalgam, cap, and mechanically shake for five minutes. Take 100 λ aliquot of supernate for counting. Total time for separation is about 11 minutes.

c) Search for optimum conditions

A number of preliminary experiments were made to determine the optimum procedure to use for yield and contamination studies. Several solvent systems in addi-

tion to hydrobromic acid were investigated. For typical conditions 0.1 M systems of HF, HCl, HBr, and HI gave yields of about 3%, 91%, 98%, and 97% respectively. The last two appear to give similarly high readings but the presence of free iodine in the HI system, as evidenced by discoloration, could lead to complications because of its oxidizing character. Therefore hydrobromic acid was used.

Similar studies with different concentrations of HBr gave yields of 98%, 98% and 79% for procedures using 0.5 M, 0.1 M, and 0.01 M HBr respectively. Higher concentrations of acid generally tend to decrease the yield and thus 0.1 M HBr was used for the standard procedure. Results of these preliminary runs are given in Table XIV.

Initial agitation time. Time studies were made using the general procedure with 2% In(Hg) to find the time dependence of agitation upon the initial exchange. Results are graphed in Figure 36 and reveal a leveling effect after 3 to 4 minutes with high yield.

Nitrogen purging time. The time effect of purging the aqueous HBr system with nitrogen was investigated employing the general procedure with 0.2% In(Hg). The results are graphed on Figure 37.

Failure to purge the system with nitrogen leads to a noticeable decrease in yield. For a 0.2% indium amalgam, however, only a fraction of a minute is required to rid the system of this oxygen effect. If no purging with nitrogen is performed, there is sufficient oxygen trapped in the bottle above the solution to oxidize indium from

Table XIV Preliminary Data on Radiochemical Separation of Indium by Amalgam Exchange.
2% In(Hg), ~ 1 μg In (including In^{114})/2 ml.
No back exchange performed. All results are of single runs.

Solvent	Conc. (M)	N_2 Purge (min)	Agitation (min)	Indium Yield (%)
HCl	.1	0	5	78
	.1	1	3	82
	.1	1	10	91
HBr	.1	1	5	95
	.1	1	10	98
	.5	1	5	98
	.5	1	10	98
	.5	0	5	75
	.1	0	5	88
	.01	1	5	79
HBr + .1 g NaBr	.1	1	5	96
HBr + .3 g NaBr	.1	1	5	83
HBr + .5 g NaBr	.1	1	5	98
HI	.1	0	5	66
	.1	1	5	97
	.5	1	5	97
	2.7	1	5	90
	5.5	1	5	0
HI + .3 g KI	.1	1	5	92
HF	.1	1	5	3

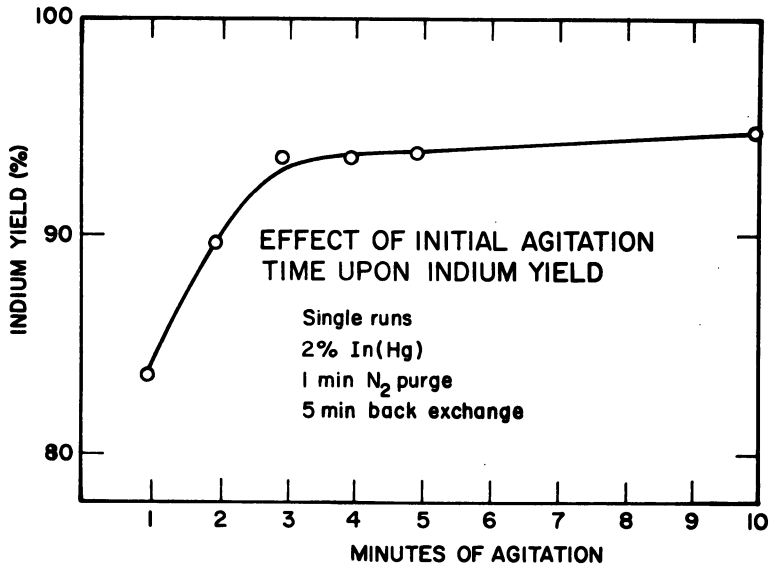


Figure 36. Effect of initial agitation time upon yield of indium.

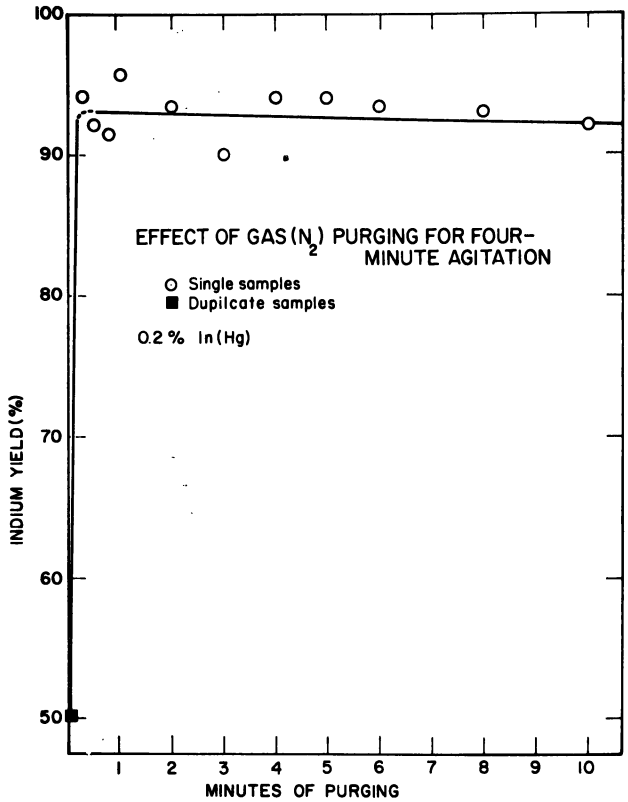


Figure 37. Effect of gas (N_2) purging for four-minute agitation.

the amalgam into the aqueous phase on vigorous agitation, and thus to decrease the capacity of the amalgam for overall isotopic exchange.

Agitation time for back exchange. The effect of the agitation time for back exchange was investigated employing the general procedure with 0.2% In(Hg). The results are graphed on Figure 38 and show that a time of

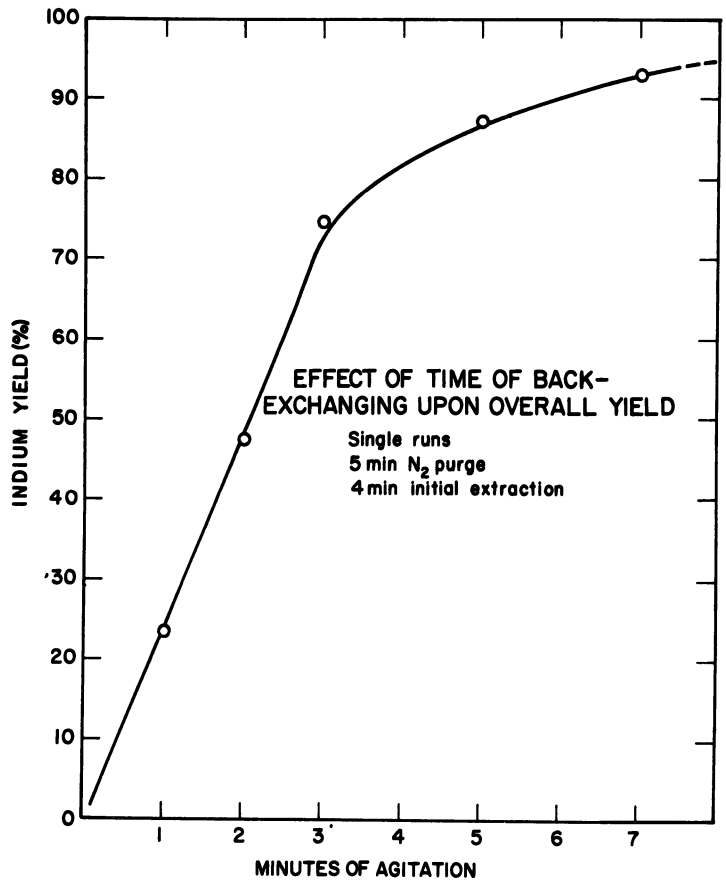


Figure 38. Effect of time of backexchanging upon overall indium yield.

5 to 6 minutes is required for high yield. Systematic errors in the runs may have shifted the entire curve to somewhat lower values but the relative shape of the curve would remain the same.

Indium concentration in aqueous phase. In the amalgam exchange procedure, 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 many 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 incorporated into the amalgam.

Since the conditions used for these separations are far from ideal, experiments using different amounts of indium in the amalgam and in the aqueous layer indicate the limiting practical conditions which should be applied to this separation. Procedures using a 2% amalgam gave yields of 94-96% for concentrations of 0.4 to 50 ug of indium per ml in the aqueous solution. A slight reduction in yield to 90% was observed when this aqueous concentration was increased to 500 μg/ml. These are summarized in Table XV.

Table XV. Dependence of Indium Yield on Concentration of Indium in Aqueous Phase.
Single Runs. 2% In(Hg).
1 Min. Purge; 5 Min. Agitation; 5 Min. Back Extraction.

Concentration μg In^{+++}/ml	% Yield of In
0.4	94
2	96
4	95
8	94
50	96
500	90

Indium concentration in amalgam. With an aqueous concentration of ~ 2 ug In per ml, yields of about 97, 96, 90, 44, and 1 were obtained for amalgams containing 2%, 0.2%, 0.02%, 0.002%, and 0.0002% indium respectively. Since the results with 2% and 0.2% amalgams are about equally good, both have been used in some of the experiments.

Problems of air oxidation of the amalgam and of oxidation by microgram concentrations of the contaminants combine to reduce the yields at lower amalgam concentrations, so that it was felt that no smaller than 0.2% amalgam should be used for a general procedure.

Yields also depend upon the duration and type of agitation employed for the initial extraction and for the back extraction. With the equipment mentioned above, yields increased regularly with time of shaking and leveled out after 3 to 4 minutes of agitation. In the back extraction process there was a sharp rise until about 3 minutes with a gradual continuation of the rise after this time. Thus, the conditions chosen as optimum were a 4-minute agitation for the initial extraction and a 5-minute agitation for the back extraction.

Methods other than shaking might be used to produce an intimate contact between the amalgam and the solution and thus to speed up this approach to equilibrium. Some preliminary studies have been made using an ultrasonic generator to disperse the drop of amalgam in

the aqueous phase, but this method was so violent that it left some of the amalgam in suspension, and subsequent centrifuging was required to clear the solution.

Decontamination. The resultant optimum procedure used a 4-minute agitation for the initial extraction and a 5-minute agitation for the back extraction. The degree of separation of indium obtained with this procedure from a number of elements representative of the periodic table is shown in Table XVI. For many of the elements the decontamination afforded was greater than could be measured with the levels of tracer used. It should be kept in mind, however, that these high decontamination values are meant to give only a general indication of results anyway, since at these levels, amounts of contaminants carried along are very dependent upon the techniques of manipulation.

These results are also plotted in Figure 39 along with comparative data for decontamination by other optimum methods such as bromide extraction, ion exchange, and sulfide precipitation (17). In general, the amalgam exchange procedure gives somewhat better decontamination than the bromide extraction and considerably better than the other two methods. In addition, it is more convenient and less messy than the bromide extraction.

The yield of the amalgam exchange procedure can be affected by macro quantities of different reagents. The yield is quite insensitive to mineral acids except for

√

Table XVI. Separation of Indium and Contaminants (Amalgam Exchange Procedure)[a].

Tracer[b]	Weight (ug)[c]	Reduction Potential (volts)[d]	Percent Separated
I^{131}	C.F.; I^-	e	< 0.01
Cs^{137}	·1	-2.92	< 0.01
Sr^{90}-Y^{90}	C.F.	-2.89, -2.37	< 0.01
Ce^{144}-Pr^{144}	C.F.	-2.48, -2.47	< 0.01
Zr^{95}-Nb^{95}	C.F.	-1.53, -1.1	< 0.01
Ta^{182}	970	-0.81	< 0.01
Zn^{65}	200	-0.76	< 0.01
Cr^{51}	2.5	-0.74	< 0.01
Cd^{115m}	10	-0.40	0.7
Tl^{204}	420	-0.34	30
In^{114m}	3	-0.34	96.6 ± 0.5
Co^{60}	2	-0.28	< 0.01
Sn^{113}	270	-0.14	28
Sb^{124}	3.5 (SbO^+)	+0.21	1
Ru^{106}-Rh^{106}	6 ($RuCl_5^=$)	+0.60, +0.25	0.1
Se^{75}	11.5 ($SeO_3^=$)	+0.74	< 0.01
Ir^{192}	1 ($IrCl_6^=$)	+0.77	< 0.01
Hg^{203}	140	+0.79	1
Ag^{110}	16	+0.80	0.04

(a) Average of duplicate runs except for indium, which is the average of five runs. Error is "standard deviation".

(b) Elements have been listed in order of their reduction potentials.

(c) Weight of inactive element present before separation. C.F. = carrier free.

(d) Standard reduction potential of lowest stable oxidation state to the elemental state. Data taken from Latimer.

(e) Iodine is in its lowest reduced state.

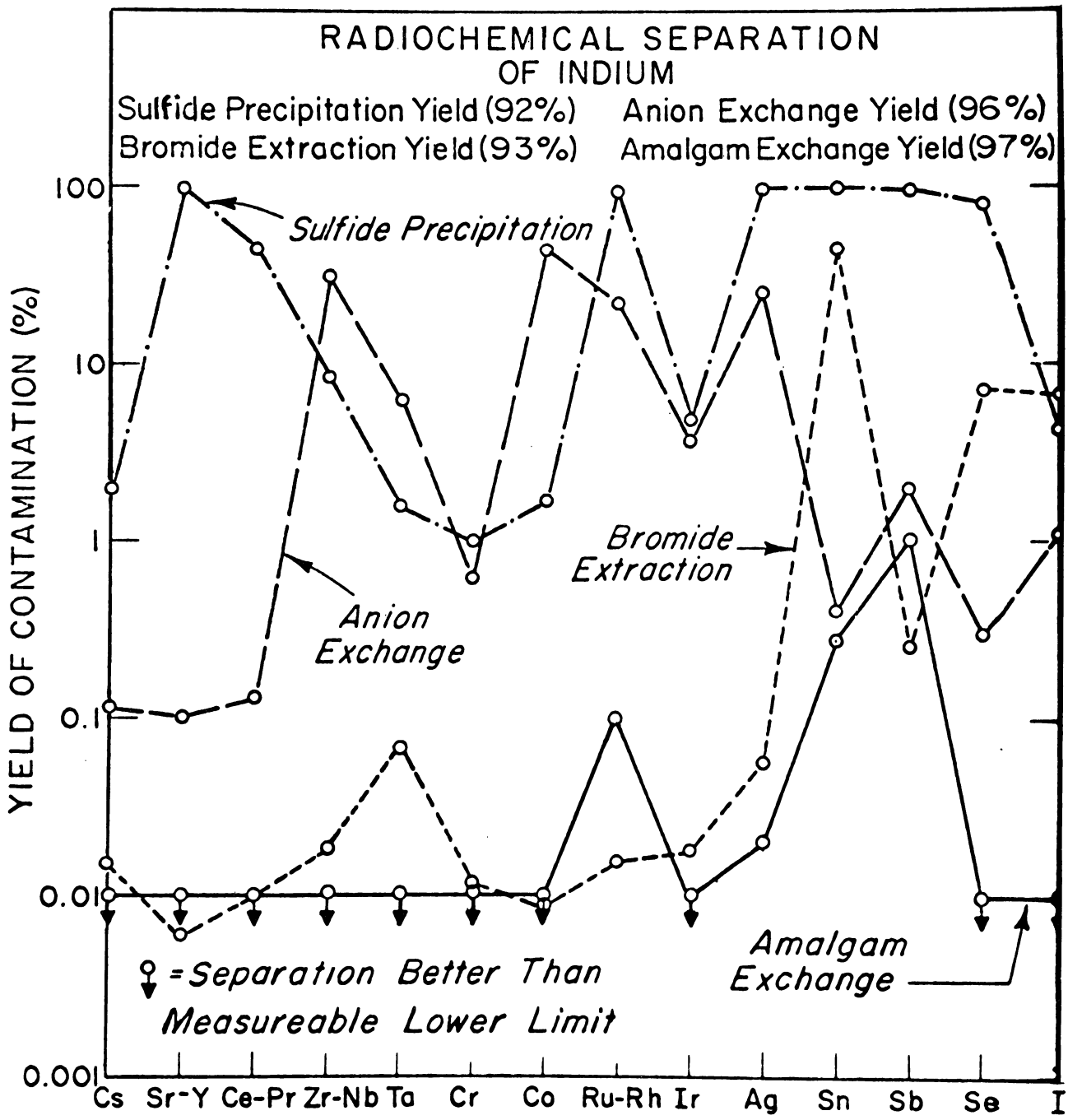


Figure 39. Experimental contamination for four types of indium separations.

oxidizing acids such as nitric acid in higher concentrations. Sulfates, phosphates, and alkaline materials

decrease the yield considerably as do oxidizing agents in general. The fact that HBr is present in 0.1 M amounts during the exchange procedure, appears to "buffer out" some of the possible difficulties with certain reagents. For example, when HF is used alone at 0.1 N concentration, a yield of only a few per cent is obtained whereas in the presence of 0.1 M HBr the yield is above 90%. These interference studies are summarized in Table XVII.

Interferences from foreign cations appear to be small except where their reduction potential is such that they might be reduced by the amalgam or form precipitates with the reagents (Table XVIII). When a cation is also an oxidizing agent, additional problems are encountered and reduction to its lowest state by something like chromous sulfate is necessary before the exchange step should be attempted (see work on cadmium).

The yield of selenium in Table XVI is surprisingly low in contrast to the 17% yields found in the study of the cadmium amalgam exchange procedure. This discrepancy is apparently caused by a difference in manipulation. In this indium work the amalgam drop was brought into contact with an absorbent tissue to remove excess water after washing and before the back extraction. At this point, the selenium, which upon reduction had formed a thin film on the surface of the mercury, mechanically rubs off on the tissue.

Table XVII. Effect of Interfering Substances on Yield of Indium in Presence of 0.1 M HBr. 0.2% In(Hg). All Are Single Determinations.

Species	Conc. M	% Yield In^{114}
HF	0.005	93
	0.05	94
	0.12	92
	0.25	92
	0.5	88
	2.5	89
	3.0	81
HCl	0.25	93
	1.0	94
	5.5	92
	10.0	86
HI	0.25	93
	1.0	93
	2.0	90
	5.5	43
$HClO_4$	0.25	92
	2.5	92
	4.0	90
	6.0	91
HNO_3	0.25	92
	1.0	85
	2.0	~ 0
H_3PO_4	0.25	92
	0.5	90
	1.0	65
	2.0	57
H_2SO_4	0.13	94
	0.5	83
Na_2SO_4	0.25	84
	1.0	32
NH_4NO_3	0.25	90
	1.0	86
$NaClO_4$	0.25	94
$NaHSO_3$	1.0	3
$(NH_4)_2HPO_4$	0.75	0
Citric Acid	0.5	90
Sodium Formate	1.0	37
Sodium Tartrate	0.05	92
	1.0	13
Sodium Acetate	1.0	85

Table XVIII. Interference of Foreign Cations. 0.1 M HBr; 0.2% In(Hg). All Are Single Determinations.

Interferring element	Concentration μg/2 ml	Yield $[In^{+++}]$ = 3 μg/2 ml
Zn	5	96
Cs	5	96
Sr	5	96
Ce-Pr	5	96
Co	5	96
Zr-Nb	5	96
Cd	5	96
Rh-Ru	6	87
Se	10	92
Sb	1	96
Sn	5 (500)	97 (74)
Tl	5 (500)	94 (76)
Ag	20	87
Ir	5	91
Hg	5	91
Ta	5	92
Cr	5	95
Ga	5	92

It may be noted yields are generally well above 90% in the low microgram concentrations. As concentrations rise, the yield tends to diminish.

The amalgam exchange procedure for the separation of radioisotopes of indium is rapid and selective. It yields high decontamination from most elements and is relatively insensitive to interferences except for oxidizing agents. It is somewhat better than the best previous radiochemical separation (bromide extraction) for this element and is more convenient to use since it avoids the necessity of working with inflammable ethers and the separation of phases is much more simple because of their high immiscibility. (R. R. Ruch, J. R. DeVoe, W. W. Meinke)

3. Strontium

A paper entitled "Radiochemical Separation of Strontium by Amalgam Exchange" by I. M. Qureshi and W. W. Meinke is being prepared for publication. Parts of this paper are given below.

Abstract

The radiochemical separation of strontium by an amalgam exchange technique has been critically evaluated using a saturated aqueous solution of potassium chloride as exchange medium. A number of factors affecting the separation were studied and optimized. Mineral acids and alkalies above 0.1 M considerably decrease the yield, due to the decomposition of the amalgam. The potentialities of the procedure were tested by making decontamination studies with tracers of 16 different elements, representative of the periodic table. In comparison with the fuming HNO_3 precipitation method, the yield of the amalgam exchange procedure is relatively low but the decontamination is better and corrosive reagents are avoided. The procedure takes about 8 minutes for overall separation with no special equipment.

Preparation of Amalgam

Strontium amalgam at first was prepared by reducing a saturated aqueous solution of $SrCl_2$ with sodium. The amalgam so prepared was not pure but contained a small amount of sodium, therefore an electrolytic method for the preparation of amalgam was tried.

The main difficulty encountered in the electrolytic method lies in the fact that the amalgam begins to react with the electrolytic solution ($SrCl_2$) and is readily decomposed by it. In order to avoid the decomposition of the amalgam by aqueous $SrCl_2$ solution, absolute alcohol was used as a solvent and various compounds of strontium [$Sr(NO_3)_2$, $SrBr_2$, $SrCl_2$, and $(CH_3COO)_2Sr$] were tried. However, the results obtained were not satisfactory. After a number of trials the following method was used.

Place 60 grams of pure mercury in an electrolytic vessel to serve as the cathode, and then add 10 ml of saturated aqueous solution of strontium chloride. Electrolyze the solution for 15 minutes at 7.5-8.0 volts and 2.5-3.0 amps, using a platinum electrode. Strontium will deposit on the mercury cathode forming the amalgam. It is essential, for the success of the preparation, to keep the surface of the mercury cathode constantly covered with a layer of $SrCl_2$ crystals, so as to prevent the decomposition of the amalgam by the electrolytic solution; otherwise, decomposition will greatly reduce the current efficiency.

The amalgam so prepared was washed, dried, and weighed to determine the composition. It contained one percent strontium by weight. The amalgam was kept in an air-tight bottle for three days and washed with benzene before use. It has a pasty consistency and sticks to the sides of the containing vessel.

Amalgam Exchange Procedure

Place 2 ml of saturated aqueous solution of potassium chloride containing tracers of contaminating ions plus a microgram amount of inactive strontium in sample bottle and agitate well to secure thorough mixing. Radioactive strontium and nonradioactive interferences are used for yield determination. Add 100 λ of strontium amalgam (~ 1.36 gm) and shake for three minutes. Remove the supernate by suction, dry the amalgam with Kleenex tissue (do not wash the amalgam, otherwise some of the activity will be lost due to decomposition of the amalgam by water). Then destroy the amalgam by transferring to a bottle containing 2 ml of 2 N HCl and shake for 3 minutes.

Search for Optimum Conditions

In order to determine an optimum separation procedure, a number of trail separations were made in which the shaking time, the concentration of the amalgam, the concentration of the exchange medium, and the exchange medium were varied. The results obtained are tabulated in Tables XIX and XX.

The main difficulty encountered in selecting a suitable exchange medium lies in the fact that strontium amalgam is very sensitive and is readily decomposed by aqueous solution and acids. Therefore, a medium should be used in which the decomposition is minimum. A saturated solution of potassium chloride was found to permit maximum exchange with minimum decomposition.

The exchange is dependent on the duration of agitation.

Table XIX. Preliminary Data on Amalgam Exchange Separation of Strontium. 1% Sr(Hg).

Exchange Medium	Shaking Time	% Yield Sr
HCl (0.1 M)	2 min.	17
HCl (0.1 M)	3 min.	15
HCl (0.5 M)	2 min.	9
HCl (0.5 M)	3 min.	8
$NaNO_3$ (0.5 M)	3 min.	46
$NaNO_3$ (0.5 M)	5 min.	47
$NaNO_3$ (0.5 M)	6 min.	46
KCl (0.5 M)	3 min.	47
KCl (0.5 M)	5 min.	46
KCl (0.5 M)	7 min.	46
KCl sat'd. soln. in absolute alcohol	5 min.	19
KCl sat'd. aqueous solution	2 min.	50
"	3 min.	57
"	5 min.	55
"	7 min.	53

Table XX. Dependence on Amount of Strontium in the Amalgam

Exchange Medium	Amount of Sr in the Amalgam	Shaking Time	% Exchange
$NaNO_3$ (0.5 M)	1.7%	5 min.	48
$NaNO_3$ (0.5 M)	1.0%	5 min.	47
$NaNO_3$ (0.5 M)	0.6%	5 min.	45
KCl sat'd soln.	1.7%	3 min.	58
KCl sat'd soln.	1.0%	3 min.	57
KCl sat'd soln.	0.6%	3 min.	53
KCl sat'd soln.	0.3%	3 min.	41

It increases with the shaking time and reaches a maximum at 3 minutes of agitation and then begins to decrease gradually. This may be due to the decomposition of amalgam upon prolonged agitation in this case. However, DeVoe and Kim have observed a similar unusual behavior of elements with two oxidation states such as thallium.

The exchange also increases with the increasing concentration of strontium in the amalgam and nearly levels out at one percent strontium concentration. Therefore, one percent strontium amalgam was used in the separation procedure.

A number of back extractants were used to try to strip off the strontium from the amalgam into an aqueous solution. A solution of 2 M HCl was found to be the best back extractant with a 3 minute agitation time (Table XXI).

The resultant optimum procedure has been described above, and gives a maximum yield of 34% for strontium. The whole

Table XXI. Summary of Back Extraction Experiments

Back Extractant	Shaking Time	% Yield of Sr
$Mg(NO_3)_2$ in 0.5 N		
HNO_3 10 mg/ml	5 min.	23
"	7 min.	24
$LaNO_3$ in 0.5 N		
HNO_3 10 mg/ml	5 min.	19
$Sr(NO_3)_2$ in 2 N		
HNO_3 10 mg/ml	5 min.	25
HCl (0.1 N)	2 min.	29
HCl (0.5 N)	1 min.	31
HCl (0.5 N)	2 min.	33
HCl (0.5 N)	3 min.	33
HCl (1.0 N)	3 min.	33
HCl (2.0 N)	3 min.	34
HCl (2.0 N)	4 min.	34

separation procedure takes about seven minutes. To reproduce the yield, it is necessary to follow exactly the same procedure as outlined above, otherwise low yield will be obtained because of the decomposition of the amalgam by the exchange medium.

Purging the system with nitrogen does not produce any appreciable increase in the yield, but it does precipitate some of the potassium chloride from the saturated aqueous solution.

Interferences

The yield of the amalgam exchange procedure is affected by the presence of mineral acids and alkalies. It was found that the acids (HCl, HF, NHO_3, H_3PO_4, and H_2SO_4) seriously interfere, even at as low a concentration as 0.1 N. The yield is also considerably decreased by alkalies (NaOH and NH_4OH), although the interference due to the alkali is less than that of the acids. The interference is so much, that a yield of only a few percent is obtained in the presence of acids and alkalies. The results are tabulated in Table XXII. The considerable decrease in the yield is due mainly to the decomposition of the amalgam by acids and alkalies. Thus, the best yield would be obtained with a neutral solution. This is a serious draw back of the method which narrows and limits its scope and general applicability.

In a radioactive sample, the spectrum of elements present may be broad; it is therefore worthwhile to know the behavior of other elements under the condition of separation. Thus the potentialities of the amalgam exchange procedure were tested by making decontamination studies with tracers of 16 different elements representative of the periodic table. The results are tabulated in Table XXIII. These results are compared in Figure 40 with the decontamination data for the 80% nitric acid precipitation method. The degree of separation of strontium obtained in this procedure from a number of other elements is better than that obtained with the 80% nitric acid precipitation method, although the yield is low. In the

Table XXII. Effect of Acids and Alkalies in Initial Exchange Step on Strontium Yield.

Substance	Concentration	% Yield
HCl	0.05 N	14
HCl	0.1 N	11
HCl	0.5 N	9
HF	0.1 N	10
HF	0.5 N	7
HNO_3	0.1 N	7
HNO_3	0.5 N	5
H_2SO_4	0.1 N	5
H_2SO_4	0.5 N	3
H_3PO_4	0.1 N	8
H_3PO_4	0.5 N	5
NaOH	0.1 N	16
NaOH	0.5 N	11
NH_4OH	0.1 N	18
NH_4OH	0.5 N	12

nitric acid and other precipitation methods, antimony is a prominent interference and gives a large contamination due to the formation of hydrous oxide and the precipitation of basic salts in weakly acid solution. In the amalgam exchange method, the decontamination of antimony is more than 10 times better than any of the precipitation methods.

In general the decontamination values obtained in this

Table XXIII. Separation of Strontium and Contaminants (Amalgam Exchange Procedure)[a]

Tracer[b]	Chemical form of tracer[c] (no carrier added)	Reduction potential (volts)[d]	Percent separated
I^{131}	I^- in 0.1 N NaOH	e	0.03
Cs^{137}	CsCl in 0.016 N HCl	-2.92	0.12
Ba^{140}-La^{140}	$BaCl_2$ in 0.97 N HCl	-2.9, -2.52	5.45
Sr^{90}	H_2O	-2.89	34 ± 2
Ca^{45}	$CaCl_2$ in 0.92 N HNO_3	-2.87	1.7
Ce^{144}-Pr^{144}	$CeCl_3$ in 1.46 N HCl (diluted with H_2O)	-2.48, -2.47	0.42
Y^{91}	YCl_3 in 0.75 N HCl	-2.37	0.32
Zr^{95}-Nb^{95}	0.5 N $H_2C_2O_4$	-1.53, -1.1	0.57
Ta^{182}	$K_8Ta_6O_{19}$ in 0.50 N KOH	-0.81	0.83
Cr^{51}	$CrCl_3$ in 0.2 N HCl	-0.14	0.16
Co^{60}	0.5 N HNO_3	-0.28	0.27
Sn^{113}	$SnCl_2$ in 0.19 N HCl	-0.14	3.7
Sb^{124}	SbO^+ in 0.5 N HNO_3	+0.21	1.9
Ru^{106}-Rh^{106}	$RuCl_5^=$ in 0.5 N HNO_3	+0.60, +0.25	0.5
Se^{75}	H_2SeO_3 in 0.1 N HCl	+0.74	0.06
Ir^{192}	$IrCl_6^{-3}$ in 0.096 N HCl	+0.79	0.25
Ag^{110}	$AgNO_3$ in 0.8 N HNO_3	+0.80	1.08

(a) Average of duplicate runs except for Sr, which is the average of five runs.

(b) Elements have been listed in order of their reduction potentials.

(c) Initial chemical form of the tracer.

(d) Standard reduction potential of lowest stable oxidation state to the elemental state. Data taken from Latimer.

(e) Iodine in its lowest reduced state.

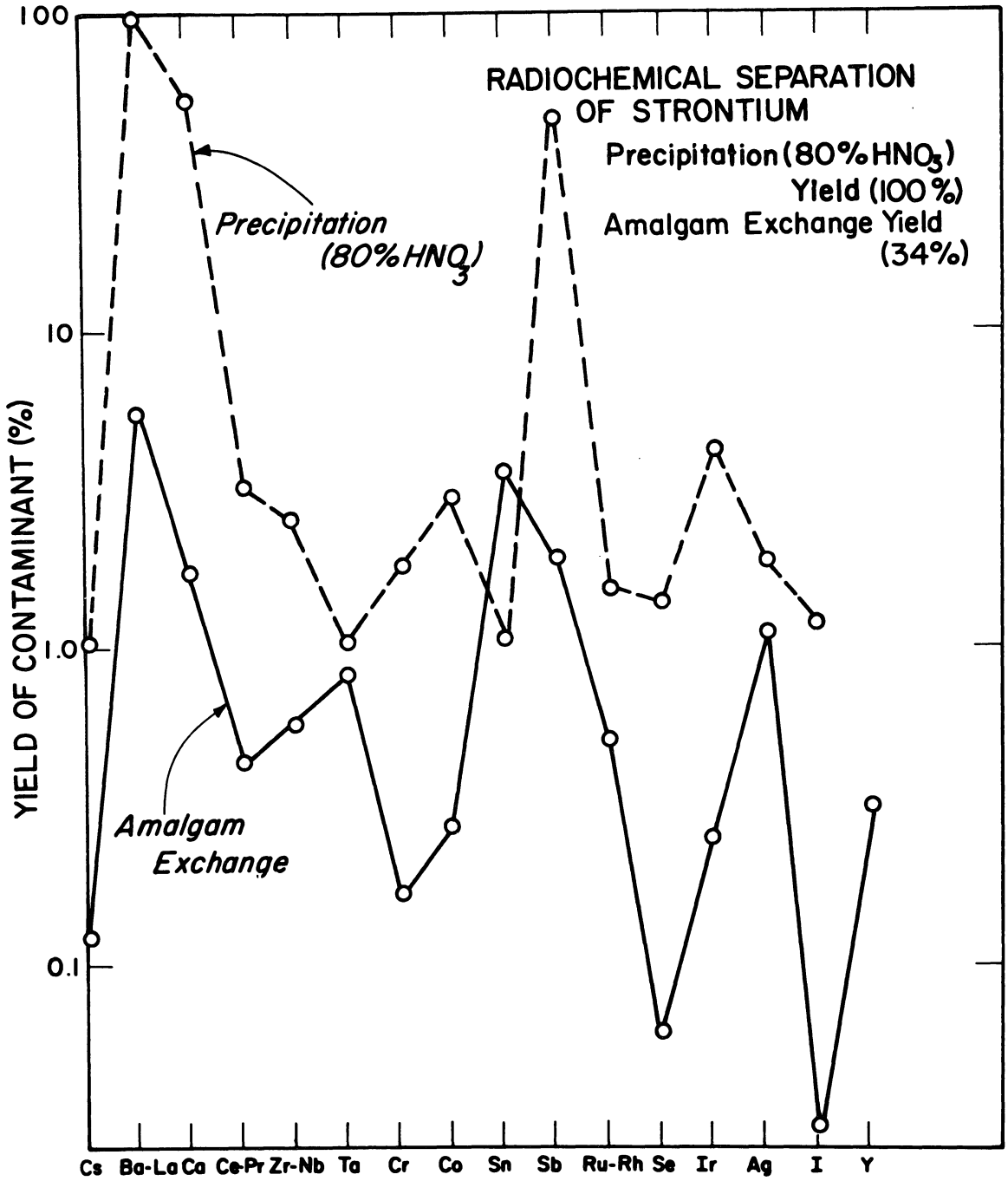


Figure 40. Experimental contamination for two types of strontium separations.

method are not as good as that obtained in the case of cadmium and indium amalgam exchange procedures described above. Probably the reason is that strontium is high up in the electromotive series and its amalgam has a high reducing

power and can reduce the ions of many elements which are below it. This may be regarded as the source of contamination.

A better decontamination may be obtained by scavenging these elements from the solution by agitating it with sodium amalgam. However, a detailed study on this aspect was not made except for a few preliminary experiments.

(I. Qureshi, W. W. Meinke)

4. Bismuth

A study has been made of the radiochemical separation of bismuth by amalgam exchange. The separation technique uses the exchange of bismuth amalgam in the extraction step, followed by a back-extraction or elution step with bismuth ion to selectively remove the bismuth from contaminants in the mercury.

The procedure consists merely of shaking the bismuth amalgam with an aqueous solution containing the radioisotopes of bismuth, and the elution step of shaking the bismuth amalgam with the incorporated radioisotope with an aqueous solution containing a higher content of bismuth ions. The concentration of bismuth in the amalgam is known and cannot be more than 1.4% at room temperature.

Preparation of Bismuth Amalgam

Add the appropriate weight of bismuth metal to the mercury under water purged with nitrogen. The mercury has to be previously washed with diluted HNO_3 and rinsed. Heat the system while shaking until the amalgam is formed. Mercury

oxide is also formed but it does not seem to affect the reagent.

Amalgam-Exchange Procedure

Place 2 ml of solution containing tracers of contaminating ions plus milligram amounts of inactive bismuth in a bottle. Chemical contamination added by the aliquots of contaminating tracers is negligible. Radioactive bismuth equal or less than 0.75 mg/ml was used for yield determinations. Mix well.

Add 200 λ , $\sim$ 2.7 g bismuth amalgam (1%), purge the system (both liquid and air above it in bottle) with nitrogen gas for one minute. Quickly cap the bottle and mechanically shake for three minutes.

Remove supernate by suction and wash amalgam with water. Transfer amalgam to a new bottle containing 2 ml of bismuth eluent solution (260 mg Bi/ml), cap, and mechanically shake for four minutes. Measurements of the yield were made by taking and counting aliquots at the beginning and at the end of every step.

Search for Optimum Conditions

A number of experiments were made to determine the optimum procedure to use for yield and contamination studies. The theoretical yield at the point of equilibrium was calculated for the described conditions using the low specific activity radioisotopes available to us (RaE). It was 95% for the first step and 95% for the second step, with a total yield of 90%. Experimentally we found yields of 84.2 $\pm$ 5.5

for the total determination where the error is the standard deviation.

The exchange medium was investigated for several solvent systems as shown in Table XXIV. In general acid media

Table XXIV. Dependence of Bismuth Yield on Exchange Medium[a]

Exchange Medium	Shaking Time	% Bi Yield[b]
Distilled water	7	74
$NaNO_3$ 0.5 M	7	no exchange
Tartaric acid	7	73
HBr 5 N	7	40
H_2SO_4 0.5 N	2	93
H_2SO_4 1 N	2	92
H_2SO_4 1 N	7	73
HF 2.5 N	2	64
HCl 5 N	2	92
HNO_3 2 N	2	92
Citric acid 2 M	3	89
HNO_3 4 N	2	89
$HClO_4$ 1 N	3	92

a) Yields are for concentration of Bi^{+3} in aqueous solution of 0.75 mg/ml.

b) This yield is for the extraction step.

are favorable to the exchange and can be used interchangeably. Halogen acids cannot be used in low concentration because there is a precipitation of BiOX.

Failure to purge the system with nitrogen leads to a noticeable decrease in yield. If no purging with nitrogen is performed, the surface of the droplets of the amalgam will become covered with mercury oxide so the exchange will have interference. This is true for any amalgam with a high tendency to form mercury oxides such as bismuth amalgam.

Yields also depend upon the duration and type of agitation employed for the initial extraction and for the back-extraction. Table XXV summarizes the dependence on initial shaking. Other methods of shaking were also attempted as shown in Table XXVI. There was little difference between the

Table XXV. Dependence of Bismuth Yield on Time of Shaking

Exchange Medium	Shaking Time	% Bi
H_2SO_4 0.5 N	7 min.	71
H_2SO_4 0.5 N	3 min.	93
H_2SO_4 0.5 N	2 min.	92
H_2SO_4 0.5 N	1 min.	80
H_2SO_4 0.5 N	15 sec.	74

This is for extraction step and 0.75 mg/ml of Bi^{+++}

Table XXVI. Dependence on Type of Shaking

Exchange Medium	Shaking Time	Type of Shaking	% Bi
H_2SO_4 0.5 N	3 min.	Shaker Burrell	93
H_2SO_4 0.5 N	2 min.	Vortex	88
H_2SO_4 0.5 N	3 min.	Ultrasonic	71

This is for extraction step and 0.75 mg/ml of Bi^{+3}

methods of shaking as long as an intimate contact between the amalgam and the solution was obtained. When an Ultrasonic generator was used to disperse the drop of amalgam in the solution, however, further centrifugation to clear the aqueous phase was necessary.

The same yield as obtained in the extraction step with 3 minute shaking at room temperature was obtained in 30 seconds by shaking at a temperature of ~ 90°C (Table XXVII)

Table XXVII. Dependency of Time of Shaking on Temperature

Exchange Medium	Shaking Time	Temperature	% Bi
H_2SO_4 0.5 N	3 min.	25°C	93
" "	15 sec.	45°C	82
" "	30 sec.	90°C	92

Extraction step and 0.75 mg/ml of Bi

When the back extraction step is done at high temperature, the time for reaching equilibrium is also diminished but there is partial decomposition of bismuth nitrate and a precipitate is formed.

The degree of separation of bismuth obtained with this procedure from a number of elements representative of the periodic table is shown in Table XXVIII. The elements have been listed in the order of their reduction potentials.

Good decontamination is obtained for a number of representative elements. Iodine and copper contaminate the separation to a great extent. (F. Orbe)

Table XXVIII. Separation of Bismuth and Contaminants (Amalgam Exchange Procedure)

Tracer	Chemical Forming Tracer (no carrier added)	Reduction Potential	Percent Separated
I^{131}	I^- in 0.1 N NaOH		51.3
Cs^{137}	CsCl in 0.016 N HCl	-2.92	0.16
Ba^{140}-La^{140}	$BaCl_2$ in 0.97 N HCl	-2.90,-2.59	0.7
Sr^{90}-Y^{90}		-2.89,-2.37	0.02
Ce^{144}-Pr^{144}	$CeCl_3$ in 1.46 N HCl (dil. H_2)	-2.48,-2.47	0.2
Zr^{95}-Nb^{95}		-1.53,-1.1	
Zn^{65}		-0.76	
Cr^{51}	$CrCl_3$ in 0.2 N HCl	-0.74	1.6
Cd^{115}		-0.400	1.5
In^{114}		-0.34	0.2
Tl^{204}		-0.34	0.2
Co^{60}		-0.28	0.05
Sn^{113}	$SnCl_2$ in 0.19 N HCl	-0.14	0.35
Sb^{124}	SbO^+ in 0.5 N HNO_3	+0.21	0.2
Cu^{64}		0.521	12
Ru^{106}-Rh^{106}	$RuCl_5^=$ in 0.5 N HNO_3	0.60,0.25	0.2
Se^{75}		0.74	
Ir^{192}	$IrCl_6^{-3}$ in 0.096 N HCl	+0.77	1.1
Ag^{110}	$AgNO_3$ in 0.8 N HNO_3	+0.80	0.1

E. Extractions with Aniline

The preliminary work on aniline extraction reported in Progress Report No. 7 (12) has been completed at CERN in Geneva and a paper on this work entitled "The Silver-Aniline System" by E. Bruninx will be published in the near future in The Journal of Inorganic and Nuclear Chemistry.

The procedure used in the study is as follows:

Twenty ml of a buffer solution of known pH, 5λ(5.10^{-3} ml) of the radioactive silver solution (by ultra micropipet), and twenty ml of aniline were put in a fifty ml screw-cap vial. The mixture was then shaken for 30 minutes and the phases allowed to separate for about 1 hour. From each phase an aliquot of about 5 ml was then taken, centrifuged, and 2 ml of the clear solution (organic or aqueous) was pipetted into a small 5 ml screw-cap vial, and the activity determined with a well-type NaI (Tl) crystal. Each phase was counted to get a total of at least 10,000 counts.

After completion of the counting, the pH of the aqueous phase was determined by means of a Beckman pH meter. No attempt was made to control the temperature, which varied between 22° and 25°C.

Studies of the distribution ratio as a function of pH are given in Table XXIX, and plotted with similar values for some substituted anilines in Figure 41. In the same way information regarding distribution coefficient as a function of ionic strength is given in Table XXX and Figure 42. The effect of aniline concentration is shown in Figure 43.

Table XXIX. Distribution Ratio of Silver as a Function of Initial pH. $\mu = 0.2$

pH Initial	pH Final	D	pH Initial	pH Final	D
3.64	5.26	26 ± 5	5.20	6.00	46 ± 3
3.81	5.31	27 ± 5	5.40	6.20	45 ± 3
4.02	5.30	23 ± 1	5.60	6.37	54 ± 5
4.22	5.38	30 ± 6	5.93	6.68	63 ± 3
4.40	5.47	36 ± 15	6.25	6.99	70 ± 2
4.62	5.57	32 ± 8	6.61	7.33	84 ± 4
4.80	5.69	38 ± 4	7.74	-	94 ± 24
5.00	5.83	39 ± 3			

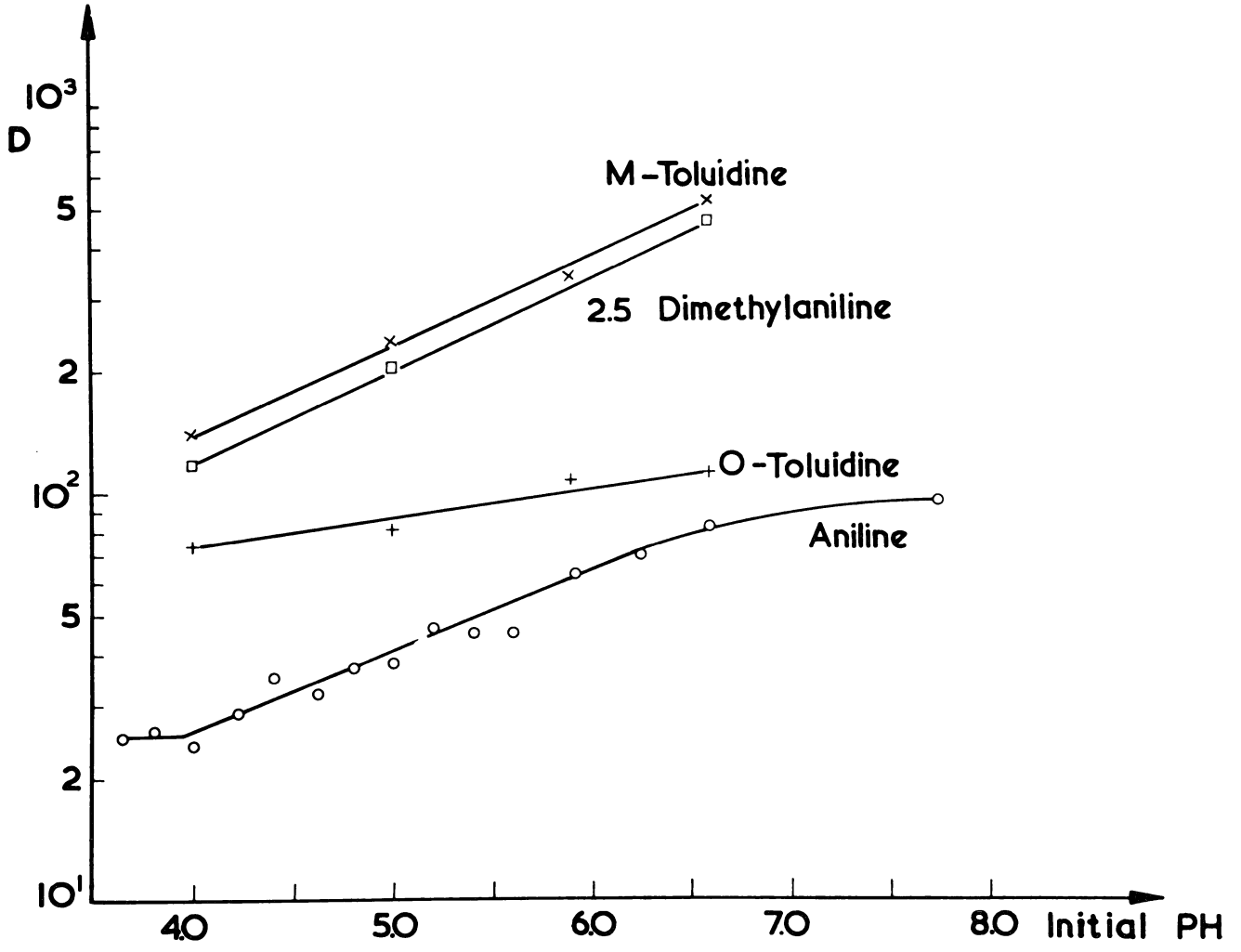


Figure 41. The distribution ratio of silver as a function of pH for different amines.

Table XXX. Distribution of Silver as a Function of Ionic Strength at Initial pH = 4.00

μ	D	μ	D
0.2	26 ± 2	1.6	95 ± 1
0.4	36 ± 1	2.0	106 ± 17
0.6	40 ± 2	2.5	132 ± 37
0.8	53 ± 1	3.0	164 ± 9
1.0	62 ± 2	4.0	208 ± 50
1.2	78 ± 6	5.0	221 ± 46
1.4	92 ± 22	6.0	213 ± 49

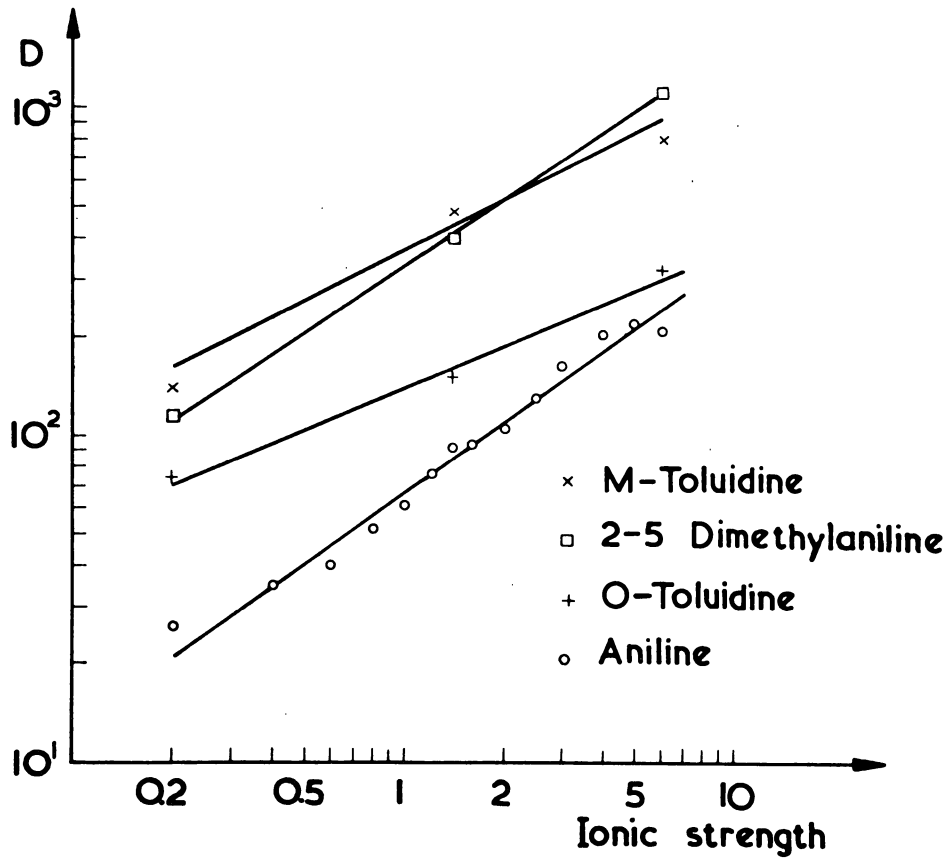


Figure 42. The distribution ratio of silver as a function of ionic strength for different amines.

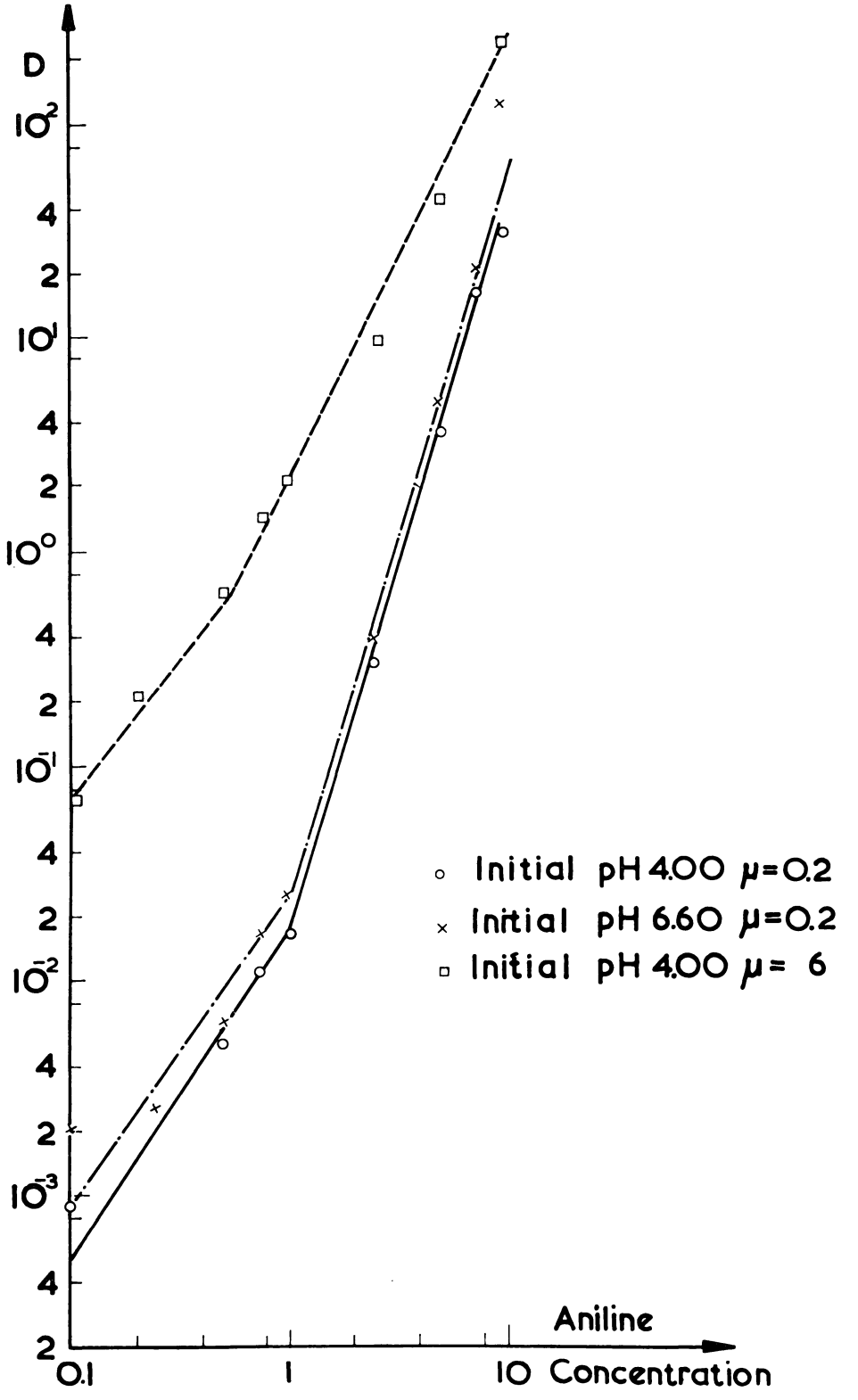


Figure 42. The distribution ratio of silver as a function of the aniline concentration for different amines.

Behavior of Other Elements

The extraction of other elements besides silver was examined having 20 ml of buffer mixture of initial pH = 5.40 (μ = 0.2) and 10 λ of tracer of the element equilibrated for 30 minutes with 20 ml of aniline. The results are given in Table XXXI.

(E. Bruninx)

Table XXXI. Extraction of Different Elements with Aniline

Element	Chemical Form	Tracer Used	Concentration*	D
Co	$CoCl_2$	Co^{60}	CF	$1.9\ 10^{-2}$
Ru	$RuCl_3$	Ru^{106}	10^{-5} M	77.2
Cr	Na_2CrO_4	Cr^{51}	10^{-5} M	0.2
Mn	$MnCl_2$	Mn^{54}	10^{-5} M	$1.31\ 10^{-3}$
Zn	$ZnCl_2$	Zn^{65}	10^{-5} M	$8.9\ 10^{-2}$
Sr	$Sr(NO_3)_2$	Sr^{90}**	10^{-5} M	$8.1\ 10^{-4}$
Fe	$FeCl_3$	Fe^{59}	10^{-5} M	0.2
Sb	$SbCl_3$	Sb^{125}	CF	2.10^{-3}
Pd	$PdCl_2$	Pd^{109}	10^{-4} M	8.8
Hg	$HgCl_2$	Hg^{203}	10^{-4} M	8.65
Se	Na_2SeO_3	Se^{75}	10^{-4} M	$7.7\ 10^{-4}$
In	$InCl_3$	In^{114m}		0.27
Be	$BeCl_2$	Be^{7}	10^{-4} M	$8.5\ 10^{-2}$
Na	NaCl	Na^{24}	10^{-4} M	$5.\ 10^{-2}$
Cs	$CsCl_2$	Cs^{137}	CF	$9.8\ 10^{-4}$
Cd	$CdSO_4$	Cd^{115m}	10^{-5} M	0.22
Te	Na_2TeO_3	Te^{124m}	10	$8.7\ 10^{-3}$
Yb	$Yb(NO_3)_3$	Yb^{169}	10^{-2} M	$3.6\ 10^{-3}$
Sn	in presence of oxalate	Sn^{113}	10^{-5} M	$2.2\ 10^{-2}$

* CF = carrier free

** In equilibrium with Y^{90}

VI INDIRECT NEUTRON ABSORPTIOMETRY

A. Indirect Neutron Absorptiometry - I

A preliminary investigation was undertaken in the late summer and fall of 1960 to ascertain the feasibility of applying indirect neutron absorption techniques to analytical processes. The fact that many elements possess high thermal neutron cross sections, lends support that this nuclear characteristic may be used as an analytical measurement of a substance indirectly through known stoichiometry. Thus as a continuation of the work reported last year (1) as attempt was made to determine the merits of gadolinium and boron as applied to the indirect determination of fluoride and potassium respectively. In conjunction with the specific analyses listed, a general investigation of optimizing instrumentation factors was also undertaken.

1. Instrumentation

In general four components are required for neutron absorption work: a neutron source, moderator, sample container, and a thermal neutron detector.

The neutron source should be safe from a handling and storage point of view. Preferably it should not also emit gamma rays. A 5-curie Pu-Be source was employed and found to be quite satisfactory. The moderator can either be water or paraffin. This laboratory used refined Standard Oil Paraffin.

The sample container may be of glass or polyethylene. Results show polyethylene is somewhat superior to Pyrex glass in that the boron content in Pyrex glass decreases the thermal neutron flux available to the sample by a factor of almost five.

Since polyethylene is easily adapted, it is highly recommended.

The neutron detectors employed were BF_3 types from Nuclear Chicago Corporation (NC 203, 5-3/8" x 9/16" dia. and NC 206, 9-3/4" x 1" dia.).

The first arrangement utilized consisted of a 55-gallon drum partially filled with paraffin. The 5-curie source was placed in the paraffin about 4-1/2 inches from a 2" dia. glass sample tube with a large BF_3 detector in an "in line" arrangement. The overall count rate was approximately 10,000 to 20,000 cpm. The main disadvantage was that it was possible for neutrons to interact with the detector without ever traversing the sample since they could easily be scattered toward the detector by the paraffin surrounding the sample. Such a situation gives a high count rate but only small differences in count rate are observed between a blank (no neutron absorbing material) and a sample. If all neutrons recorded by the detector interacted first with the sample, then the flux would be utilized more efficiently and greater differences between blank and sample would be observed.

Thus a different arrangement was designed for future experiments. A wooden box container, 2' x 2' x 2', was filled with paraffin. The 5-curie source was then positioned in a well approximately at the center. A small NC-203 BF_3 neutron detector is placed in a second well about 3-1/2" from the source and is covered with a Marinelli type sample container assembly with a volume capacity of 50 ml for a measurement. Holes were also drilled approximately 1-1/2 and 2-1/2 inches from the sample-detector well to permit further positioning of source for a different flux

pattern. With the Marinelli beaker arrangement at 3-1/2" from the source about 160,000 cpm were recorded.

It is noticed by experimentation that the BF_3 counter (NC-203) in our early arrangement was not able to maintain the sustained flux over any appreciable length of time, but gradually decreased after 10-15 minutes. The tube should have been able to record up to 200,000 cpm. Measurements of up to 60,000 cpm were observed to maintain constancy with time over 1 to 2 hours. It is possible to move the source farther away or employ a 1-curie source to reduce the counting levels to this value. However, the higher the flux, the better the results for a given counting time. Later modifications of the system in which the leads from the counter to the scaler were shortened and were replaced with better shielded wire seemed to improve this problem but it was felt that a simple preamplifier at the detector might prove to be the answer to the problem.

2. Use of Boron as the Tetraphenylborate for the Determination of Potassium

The determination of potassium as its tetraphenyl borate is well known. The equation is as follows:

$$K^+ + B\emptyset_4^- \rightarrow \underline{KB\emptyset_4}$$

Since a major portion of the time expended for such a procedure involves the drying of the final precipitate to constant weight, a procedure in which the final washed but wet precipitate could be rapidly measured might have some advantages. Using a procedure from the Oak Ridge Master Analytical manual, various amounts

of potassium (5-30 mg) were precipitated with excess tetraphenyl borate, washed, redissolved in acetone, diluted to 100 ml, and counted in the neutron flux. A blank solution was also counted. The difference in cpm between the blank and sample was a measure of the boron present in the sample, which in turn was stiochiometrically related to the potassium.

Data obtained using the first instrumentation arrangement show deviations of the order 30 to 50%. This was neither sensitive nor accurate enough to compete with existing methods known for potassium in this range. However, no determinations were attempted with the second instrument arrangement, so it is probable that deviations could be reduced with longer counts. Inherent in the low accuracy and reproducibility, however, is the fact that 1 mg of boron represents 3.61 mg of potassium. Thus, any error in boron estimation is amplified by this factor. If a polyethylene sample holder can be employed, if constant counts in the range of around 200,000 cpm can be obtained, and if a reliable standard curve can be obtained, the sensitivity and accuracy of the indirect neutron absorption method may become more competitive.

3. Use of Gadolinium for the Determination of Fluoride

Gadolinium, like other rare earths, forms a highly insoluble fluoride. The K_{sp} is 6.7×10^{-17}. It is feasible, therefore, that a modified gravimetric method could be used for the determination of fluoride by indirect neutron absorption. The method is inherently more accurate than using boron for potassium since 1 mg of gadolinium is equivalent to 0.36 mg of fluoride and thus the factor is to our advantage.

Various amounts of fluoride (NaF) were precipitated in pH 2 to 3 aqueous media with excess gadolinium. Two procedures were then attempted for the final measurements.

The first procedure consisted in slurrying the washed GdF_3 precipitate with excess NaOH and heating to metathesize the fluoride to the hydroxide. After sufficient washing, the hydroxide was dissolved in dilute HNO_3, diluted to 100 ml and counted in the neutron flux. In general this procedure yielded the better accuracy but poorer precision than the second procedure.

The second procedure involved adding a known excess amount of gadolinium to the fluoride sample, and quantitatively diluting the supernatant liquid for measurement. In general poor accuracy was obtained, but the precision was better.

Both the preceding two procedures gave low results from calculated amounts of fluoride present. It is possible that solubility effects and incomplete precipitation caused low results. Visual colloidal suspension could be completely eliminated by proper addition of citric acid and precipitation at a high temperature. In all instances the fluoride sample was added to the gadolinium solution.

Since low results persisted, a different approach was attempted whereby the gadolinium was added to the fluoride sample in a stoichiometric ratio of approximately 2 to 1. In all cases the results were higher than the theoretical amounts of fluoride present. When the stoichiometric ratio was lowered to approximately 1.1 to 1.0 the results were still high but closer to the theoretical. Also ease of precipitation and colloidal formation problems appeared to

be improved. The use of a non-complexing perchloric acid medium was tried and results were very low and erratic.

The problem persists in getting the fluoride to precipitate precisely and quantitatively. It is best precipitated at a pH of approximately 2 to 2.5. If the pH is less than 1.5, the results are low; if higher than 3.5, the results are high due to double salt formation and formation of $Gd(OH)_3$. A buffer solution probably should be employed if possible.

Another problem of complex formation exists. If citric acid is present in the gadolinium precipitation solution prior to its addition to the fluoride, no precipitation of GdF_3 occurs because of gadolinium citrate formation. The citrate must thus be added after the initial precipitation. If no citrate is added, a permanent colloidal suspension occurs which is not eliminated by heat or centrifugation.

If the precipitating medium is not heated sufficiently to above 70 to 80 degrees C, insufficient coagulation occurs and the solution must be centrifuged excessively. More controlled work is needed on this aspect.

An attempt was started to find a suitable medium for the dissolution of GdF_3 other than the process of metathesizing the fluoride to the hydroxide and then dissolving this in dilute HNO_3. The latter process may entail loss of gadolinium due to solubility because of the repeated washes necessary to wash the fluoride from the system.

Nitrilo-tri-acetic acid was tried in pH 4-5 media with no success. Higher concentrations of NTA at pH 3-8 also proved fruit-

less. EDTA over an extended pH range and in media to high concentrations (1M) did not successfully dissolve the gadolinium fluoride. It is known that excess aluminum in 6 N HCl dissolves calcium fluoride, thus this solution was tried and completely dissolves the GdF_3 immediately. This single step dissolution process eliminates approximately 3 steps and roughly 5 to 10 minutes working time for each sample. No quantitative results were obtained with the aluminum dissolution procedure because of preparation of the modified instrumentation.

A different approach to the determination of fluoride via the gadolinium fluoride precipitation was attempted directly near the end of this study. Replicate samples of fluoride were titrated with progressively larger amounts of standardized gadolinium, at pH 2.5, the supernate diluted and then counted. A neutron absorption titration curve resulted with a 70°-80° angle at the intersecting lines. However, the results were low on the 2 samples run. Much more work should be attempted to define the end point. It is possible that only 2 or 3 points are needed and that short counts would suffice. Solubility factors and precipitation problems might be corrected empirically by normalization.

4. Future Considerations

Since most of the quantitative estimations were determined using the first instrumental arrangement, employment of the new instrument should be attempted on the more promising aspects of the determinations involved. Once a high count rate can be maintained, sensitivities, accuracies, and reproducibilities should be ascertained.

As noted before, controlled studies concerning pH, solubility, aging, optimum concentration, best dissolution procedure, interfering elements, different forms of sample, optimum precipitating ratio, optimum sample size, and other factors should be made and elucidated. Instrumentation problems and initial exploration during the limited time allowed prevented the complete solution of those factors mentioned.

A word of appreciation is due the Nuclear Chicago Corporation for loan of the Pu-Be source and some other equipment during part of this study. (R. Ruch)

B. Indirect Neutron Absorptiometry - II

The study of the use of gadolinium for the determination of fluoride initiated by Ruch (as described above) has been continued. From the preliminary work it appeared that precipitation of fluoride by adding gadolinium in a nitric-acid medium should prove adequate for the determination. Precipitation in a controlled pH range of 2 to 2.5 and at temperatures of 60-70°C appeared to overcome the problem of colloidal suspension during precipitation.

Previous work had shown that gadolinium trifluoride could be dissolved easily in a mixture of aluminum nitrate in 6 N HCl. However, it was realized near the end of that program that the chloride of HCl does show some neutron absorption and thus affects the value obtained if the blank measurement is made on water solutions. Thus for this work the solvent medium was changed to 1 M aluminum nitrate in 1 M nitric acid which seemed satisfactory at 70-80°C for complete dissolution.

Thus it is possible to make a determination within about 20

minutes for samples larger than 5 mg of fluoride and in about 10 minutes for samples less than 2 mg.

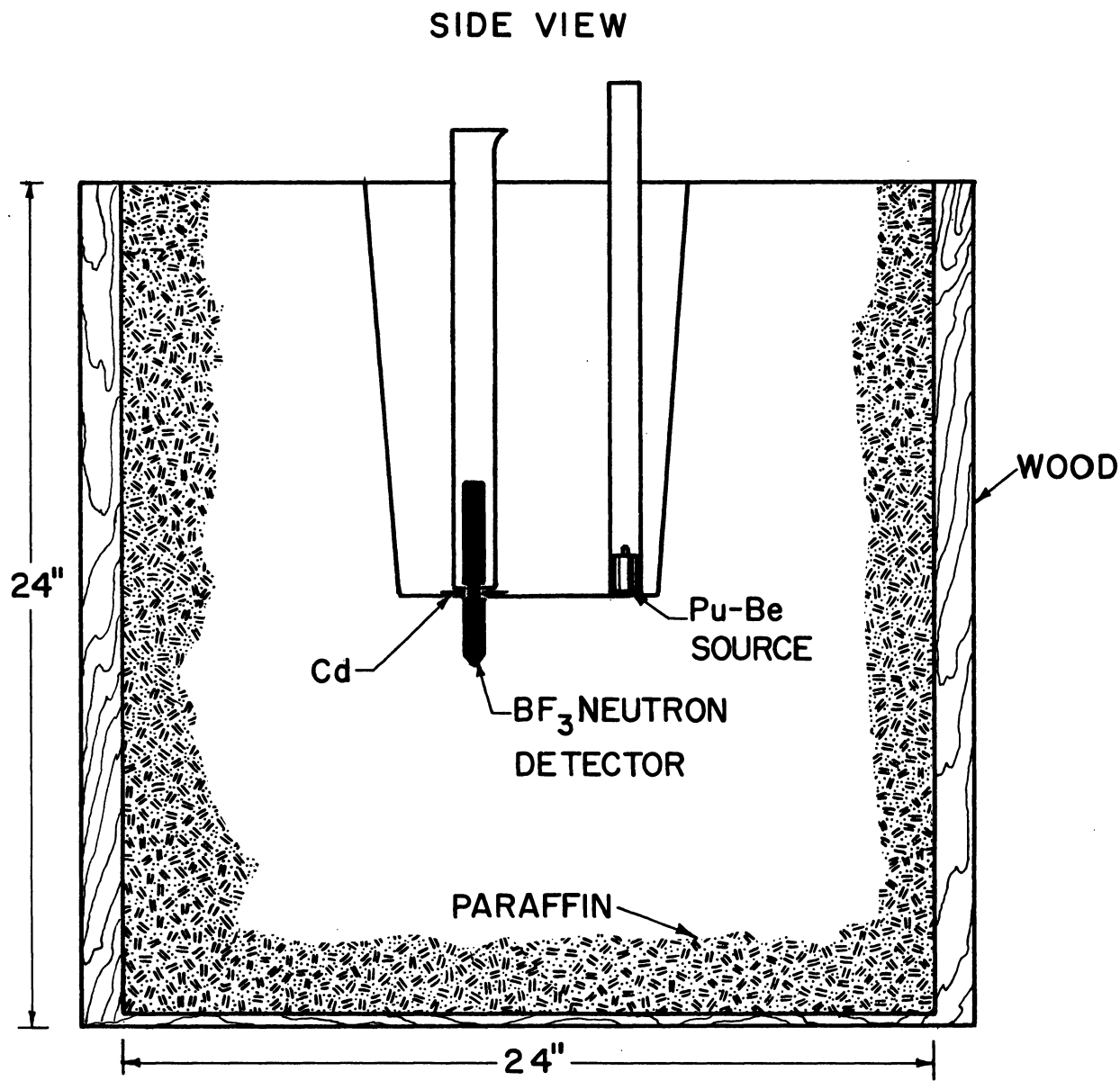
1. Instrumentation

Two different plutonium-beryllium neutron sources have been used, one a 1-curie source giving about 25,000 neutron counts per minute and the second a 5-curie source giving about 160,000 cpm in our experimental arrangement.

The sources were used in a cube of refined paraffin arranged as in Figs. 44 and 45. The neutron detector used was a BF_3 type NC 203 from Nuclear Chicago Corporation. Standard Nuclear Chicago scalers were used with this tube.

Two types of centrifuges have been used. One, a regular International clinical centrifuge, was used with the larger amounts of precipitate and larger volumes of solution. This centrifuge required considerable time to clear the solution. For more rapid procedures a Misco electric microcentrifuge manufactured by Microchemical Specialities Company, 1825 East Shore Highway, Berkeley 10, California was used. The speed of this centrifuge was regulated by means of a Powerstat. 1 ml capacity centrifuge tubes, cushioned with glass wool to prevent breakage, were used for the determinations. The high speed available with this unit is able to completely clear a sample in no longer than 1 minute on an intermediate setting of the Powerstat. At higher speeds than this there were problems of breakage of centrifuge tubes.

A Vortex Jr. mixer obtained from Scientific Industries Inc., 15 Park Street, Springfield 3, Massachusetts was used to



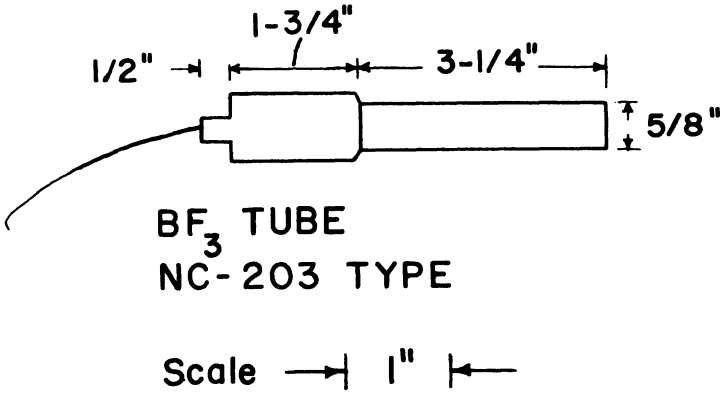


Figure 44. Side view of paraffin housing.

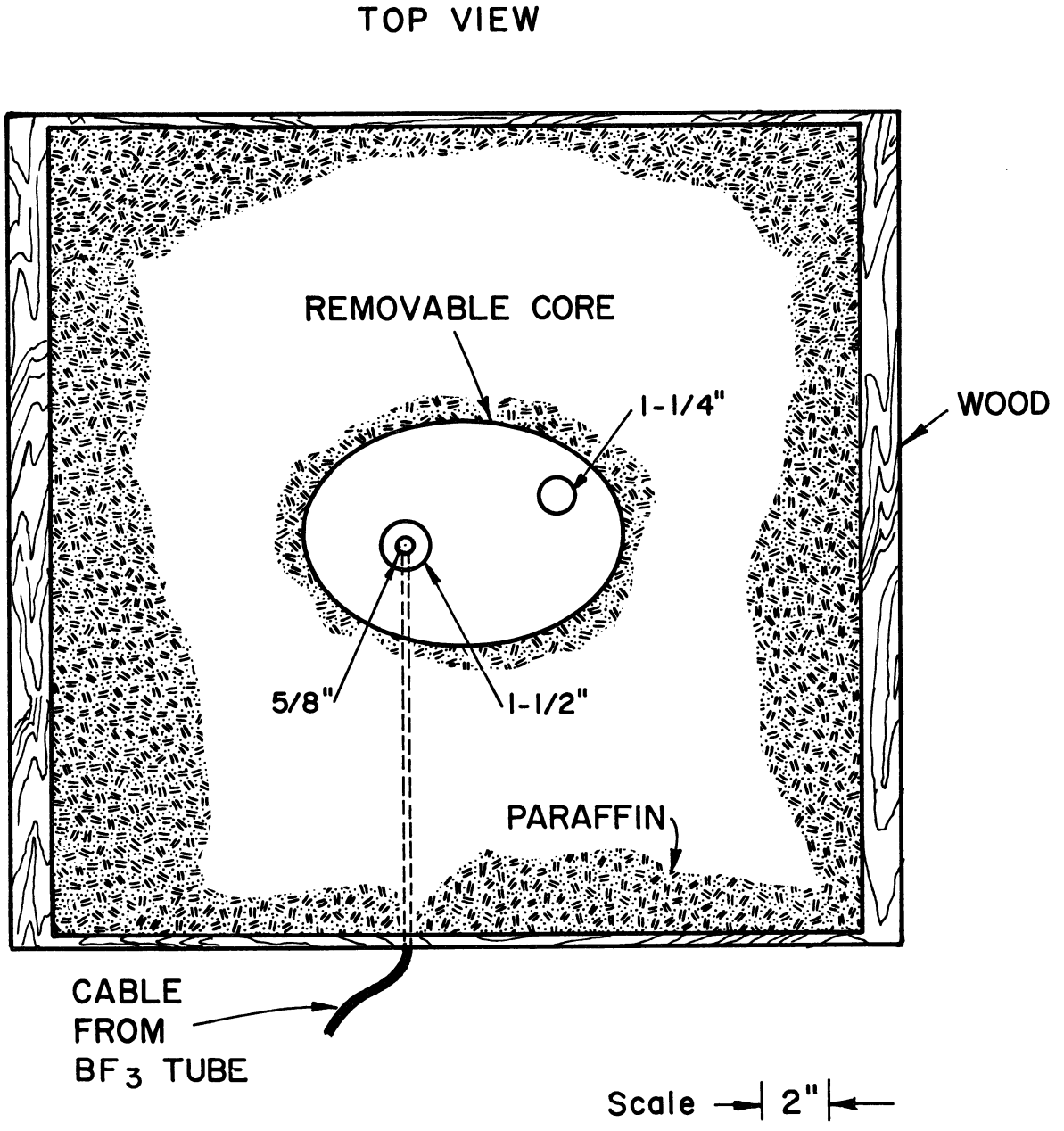


Figure 45. Top view of paraffin housing.

provide a homogeneous quick mixing of the samples during washing.

Chemicals used were all analytical reagent grade. The gadolinium oxide was 99.9% pure and obtained from Research Chemicals of Burbank, California.

2. Results

Many runs have been made to evaluate the effect of variables on the precipitation and the measurement, and to try to optimize some of these variables. A few general results of these experiments are listed below.

It was finally decided to try to avoid use of any neutron absorbing material in the processing of the precipitate so that blank measurements made on pure water would be true values.

Many difficulties were encountered with colloidal suspensions which required long periods of centrifugation to separate and many of the adjustments of the conditions of the precipitation were involved with this problem.

A second problem involved the uncertainty of the stoichiometric composition of GdF_3 under certain kinds of conditions. On the basis of analytical data on the rare earth fluorides Kury states that "one must consider the species MF_2 and in the case of GdF_3 approximately 10% of the total gadolinium (III) was present as GdF_2" (19). The precipitation in this case was carried out in a perchlorate-perchloric acid medium. Our experiments took the approach of trying to find conditions which would yield 100% measurements on the fluoride based on GdF_3.

Considerable difficulties were encountered as a result of instrumentation problems and failures. Some of the difficulties described by Ruch above regarding drift of counting rates with the neutron tubes were also encountered and there was difficulty in keeping a scaler in complete working operation for these

large numbers of counts. In addition to this general problem there does seem to be a gradual deterioration of the detector over periods of several months which has been mentioned by other authors such as Amiel in their analytical application work (20). Fortunately all of the work done on this problem was performed on a relative basis but nevertheless it is still disturbing to have the characteristics of detectors shift during the period of a set of experiments.

Some of these problems were improved when the entire counting arrangement was moved to a counting room that was air-conditioned with stable humidity of around 50%. At the same time the sensitivity of the scaler was adjusted so that operation was made at a point of good stability.

Finally a 5-curie plutonium-beryllium source was substituted for the 1-curie source used earlier on a temporary basis which permitted the accumulation of 1 million counts for each measurement and permitted much improved statistics in the measurements.

The procedure finally adopted as optimum is as follows. To a sample containing between 0.25 and 2.5 mg of fluoride is added a small amount of solution at pH 3 (10 M ammonium nitrate plus ammonia). The mixture is then placed in a hot water bath until it is at a temperature of 70-80°C. Then sufficient gadolinium to give about a 100% excess is added (the gadolinium solution is 1 M in ammonium acetate) and the solution mixed by the Vortex Jr. mixer. Finally the pH is adjusted to 2.5 and the mixture digested for 3 minutes in the hot water bath. The

mixture is then cooled for 3 minutes in ice water and centrifuged for 1 minute with the high speed centrifuge.

Samples were then washed with a few drops of 1 M ammonium nitrate solution and centrifuged again for 1 minute. The precipitate is then dissolved in 1 ml of a solution 1 M in ammonium nitrate and 1 M in nitric acid. It was found that if the samples had been previously dislodged from the tube with the Vortex mixer that this dissolution could be done within 30 seconds whereas other means required the order of 2 minutes or so. The dissolved sample is then diluted to 50 ml and the neutron absorption measured. A comparison with a blank run taken with no neutron absorber present gave a value which was proportional to the gadolinium, and thus the fluoride, present in the sample.

The sensitivity of neutron absorptiometry, unlike that of neutron activation, is not dependent only upon the flux of neutrons available. Thus a higher flux can give higher counting rates but the sensitivity of the method is dependent upon the difference in count rates between the blank and the sample. For higher sensitivities one is dealing with the difference between two large numbers which can introduce problems of statistical significance.

In the following table are given some absorption results in the determination of sodium fluoride in the range of 0.25 mg to 2 mg as compared with absorption of standard amounts of fluoride equivalent gadolinium. Near the end of this work a few runs were also taken using perchloric acid as indicated at the

Table XXXII. Indirect Neutron Absorption Results

Amount of F (mg)	% Absorption of Standard ± σ	% Absorption of Samples	
1	3.16 ± 0.14	3.4	
		3.32	
		3.32	
0.75	2.65 ± 0.14	2.86	
		2.86	
0.65	2.33 ± 0.14	2.47	
		2.39	
0.6	2.12 ± 0.14	2.39	
		2.24	
0.5	1.67 ± 0.14	2.08	
		2.08	
0.25	0.69 ± 0.15	1.05	
		1.1	
2	6.1 ± 0.14	6.56	
		6.06	
			$HClO_4$ Added
1	3.16 ± 0.14	3.12	0.1 M
		3.19	"
		3.12	"
		3.04	1 M

end of Table XXXII, and this material seemed to improve the determination. Additional runs including the perchloric acid are being planned for the other quantities of fluoride.

In conclusion it can be pointed out that by this procedure it does appear to be feasible to determine amounts of fluoride in the 0.25 to 2.5 mg region in a matter of 10-20 minutes with simple equipment except for the neutron absorption apparatus. This is accomplished by using about 0.25 M gadolinium as a precipitating agent at a final pH of 2.5 and using a small high speed centrifuge for the separation of the precipitate. Further studies are being carried out to better define the limits of this particular procedure. (G. Romero)

C. Experiences in Procurement of a 5-curie Pu-Be Source

One might expect that if one were interested in studying problems of neutron absorption such as described in the previous two sections that it might be quite easy to obtain a plutonium-beryllium source for this work. Certainly the news releases and publicity of the AEC and of some of the commercial companies would lead one to this conclusion. However, we found ourselves trapped on several occasions by interminable red tape and I think it worthwhile to summarize our experiences here.

National Laboratories of course have been using Pu-Be sources for a number of years and Leddicotte's group at Oak Ridge has also been making use of Am-Be sources. Similarly many nuclear engineering courses in universities throughout the country make use of Pu-Be sources in subcritical assemblies and the like. Thus I was unprepared for the problems which faced me when I tried to obtain a source for our own use.

The initial work on this idea was performed with a 5-curie

Pu-Be source which was kindly loaned by Nuclear Chicago for a few months until we got some general feeling for the experimental potentialities of the indirect neutron absorption method. In order for us even to use someone else's source we had to have a license for this "special nuclear material" -- a license which is completely different from our regular general radioisotope procurement license at the University of Michigan.

Instructions for preparation of an application to the AEC for such a license are quite complicated and require information set forth in paragraph 70.22 of the Code of Federal Regulations. Unlike most other AEC applications, no forms are provided. After several inquiries and discussions with people it was learned that a letter to the Division of Licensing and Regulation including the information mentioned in the Code of Federal Regulations was satisfactory, and this letter was composed and sent in. Once the application had been submitted we were very pleased by the assistance given us by the people in the Licensing Division in expediting our application to allow us to start experimental work at an early date.

After a few months, however, we had to return the original source to Nuclear Chicago and then began the long effort to obtain a source of our own. It appeared that it was possible to get a source on an "educational grant" from the AEC but this requires the same kind of detailed program description and support that are required by much larger grant requests and this was not the approach we desired. Instead we wanted to purchase this source with available funds. (Actually one does not "purchase" the source but instead one pays for the encapsulation plus a small fee of a few

dollars a year for lease of the plutonium.)

Finally we discussed our problems with Mound Laboratory and placed an order with them for delivery of a suitable source within a few weeks. Soon thereafter we found that politics had entered the field and that the AEC was no longer permitted to make up Pu-Be sources for purchase. Instead private enterprise in the form of NUMEC (Nuclear Materials and Equipment Corporation of Apollo, Pennsylvania) was to make available all types of sources.

NUMEC now has a booklet available describing the sources and prices for encapsulation, and also describing the procedures which must be gone through in order to obtain such a source. Since the Chemistry Department also had on hand a Nuclear Chicago neutron howitzer which we were interested in using in our course in radiochemical techniques and in the production of short-lived isotopes for use in the department, we also wanted the source to fit the howitzer. Unfortunately, the standard 5-curie Pu-Be source (price $1200) is too large for the howitzer, but NUMEC obliged by making a special source (for $1325) for us which is rather an odd size, 4.425 inches long and 1.020 inches in outside diameter, but at least is usable in both our pieces of equipment.

Even when one has a license to use the material and the money to pay for the encapsulation there is still another bit of red tape which was very confusing to us and which was not mentioned in NUMEC's booklet, namely the lease agreement.

This lease agreement has been designed for large users of special nuclear materials and consists of a many-page legal document setting forth the lease terms. Presumably other groups at the

University must have signed similar leases when they obtained similar type sources for Nuclear Engineering, but it was impossible to locate such leases on campus and it was necessary to have this lease signed in the name of the University superceding outstanding leases. The cost of leasing this particular source per year is only a few dollars and therefore is insignificant, but there surely has been a tremendous amount of paper work involved in this source procurement.

It is hoped that now that NUMEC is a full-fledged supplier for Pu-Be sources and that Nuclear Chicago is making more of an effort to sell their neutron howitzers which use these sources that there will be much less red tape involved in getting such a source, or at least that there will be more experienced help available to guide one through the red tape.

My suggestion now to anyone interested in procuring a Pu-Be source would be to first contact NUMEC and ask for their booklet and price list. This booklet even contains suggestions as to the procedures to be followed by foreign governments and customers.

(W. W. Meinke)

VII SEPARATION PROCEDURES

RADIOCHEMICAL SEPARATIONS

Element Separated: Strontium

Target Material:

Type of bbdt:

Yield: ~34%

Degree of purification: See remarks

Advantages: Simple and rapid

Procedure by: Qureshi

Time for sep'n: 8 min

Equipment required: Mechanical stirrer, Boston round bottle with polyethylene insert screw cap.

Procedure:

(1) To a 2 ml solution of "carrier-free" activities, add sufficient KCl to make a saturated solution. Add 100 (~1.36 g) of 1% (by weight) Sr(Hg). There are ~14 mg of Sr in the amalgam. The elements that are not reduced by Sr(Hg) can be present in micro quantities.

(2) Agitate the solution mechanically in a 1/2 oz. Boston round bottle for 3 minutes, remove the supernate by suction, dry the amalgam with Kleenex tissue papers (do not wash the amalgam, otherwise some of the activity will be lost due to the decomposition of amalgam).

(3) Transfer the amalgam to another Boston round bottle containing 2 ml of 2 N HCl. Agitate for 3 minutes.

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

Remarks:

(1) Decontamination factors for Cs, Ce-Pr, Zr-Nb, Y, Ta, Cr, Co, Ru-Rh and Ir are greater than 10^2; Ba-La, Ca, Sn, Sb and Ag are greater than 10; I and Se are greater than 10^3.

(2) Oxidizing agents which oxidize Sr from the mercury must be reduced before separation.

(3) Acids and alkalies above 0.1 M concentration seriously interfere.

(4) Preparation of strontium amalgam: Place 60 grams of pure Hg in the electrolytic vessel to serve as a cathode. Add 10 ml of sat'd aqueous sol'n of $SrCl_2$ and electrolyze for 15 min. at 7.5-8.0 volts and 2.5-3.0 amp using a Pt electrode. It is essential to keep the surface of the Hg cathode covered with a layer of $SrCl_2$ crystals during electrolysis. Amalgam contains 1% Sr by wt.

VIII PERSONNEL, PUBLICATIONS, TALKS, MEETINGS

A. Personnel Listing

Project Director Meinke, W. W.

Post Doctoral Høgdahl, O. (Exchange fellow from Norway)
Kusaka, Y.(') (Michigan Memorial Phoenix Project No. 191)
Steele, E.(')

Exchange Students Orbe, F. (Ecuador)
Rengan, K. (India)
Tani, A. (Japan)

Graduate Students Prussin, S.
Qureshi, I.
Singh, S.*
Ruch, R.(')
Wahlgren, M.*(')

Assistant in Research Maddock, R. S.
Nass, H. W.

Assistant in Research (Electronics) Shideler, R. W.

Typing Coleman, F.
Hoffman, B.(')

Hourly Student Help Atkins, T.(')
Brown, S.(')
Dowsett, S.
Fry, E.
Fuertch, T.(')
Romero, G.*
Weigant, N.

* Half time

(') Terminated

B. Papers and Reports Published

1. Absolute (d,α) - Reaction Cross Sections of Zirconium, Molybdenum, Titanium, and Sulphur. Oswald U. Anders and W. W. Meinke. Phys. Rev. 120, 2114-2119 (1960). 1 fig.

2. Indirect Neutron Absorptiometry. W. Wayne Meinke. Talanta 5, 264-266 (1960).

3. Activation Analysis; Radiometric Assay; Radioisotope (assay). W. Wayne Meinke. McGraw-Hill Encyclopedia of Science and Technology. McGraw-Hill Book Company, Inc., New York, 1960. 1 page.

4. The Radiochemistry of Vanadium. James L. Brownlee, Jr. Nuclear Science Series Report NAS-NS-3022, Subcommittee on Radiochemistry, National Research Council, Washington 25, D. C. 1-76 (December 1960). 13 figs.

5. The Radiochemistry of Titanium. Chong Kuk Kim. Nuclear Science Series Report NAS-NS-3034, Subcommittee on Radiochemistry, National Research Council, Washington 25, D. C. 1-23 (March 1961). 1 fig.

6. Nuclear Decay Scheme Studies on Short-Lived Nuclides from the (n,γ) and (n,fission) Reactions. Morris A. Wahlgren. U. S. Atomic Energy Commission Unclassified Rept. TID-11807, Ph.D. Thesis, 1-143 (February 1961). 49 figs.

7. Book Review Activation Analysis Handbook. R. C. Koch. Academic Press, Inc. (1960). Reviewed by W. Wayne Meinke in Anal. Chem. 33, No. 4, 78A-80A (1961).

8. Radiochemical Separation of Cadmium by Amalgam Exchange. J. R. DeVoe, H. W. Nass, and W. W. Meinke. Anal. Chem. (In press, November 1961).

9. Radiochemical Separation of Indium by Amalgam Exchange. R. R. Ruch, J. R. DeVoe, and W. W. Meinke. Talanta. (In press).

10. The Silver-Aniline System. E. Bruninx. Journal of Inorg. and Nuclear Chem. (In press).

11. Determination of Rhodium by Thermal Neutron Activation Analysis Using Gamma-Ray Spectrometry. Edgar L. Steele and W. Wayne Meinke. Anal. Chim. Acta. (In press).

12. Radiations from Short-Lived Gaseous Fission Products. Morris A. Wahlgren and W. Wayne Meinke. (Submitted).

13. Activation Analyses of Vanadium, Arsenic, Molybdenum, Tungsten, Rhenium, and Gold in Marine Organisms. Rinnosuke Fukai and W. Wayne Meinke. (Submitted).

14. Determination of Oxygen by Fast Neutron Activation Analysis Using a Low Cost Portable Neutron Generator. Edgar L. Steele and W. Wayne Meinke. (Submitted).

15. Two Years Experience in Applying a Low Cost Neutron Generator to Activation Analysis. W. Wayne Meinke and Ronald W. Shideler. (Submitted).

16. Rapid Radiochemical Separations. Yusuru Kusaka and W. Wayne Meinke. Nuclear Science Series Report NAS-NS-3104, Subcommittee on Radiochemistry, National Research Council, Washington 25, D. C. (Submitted).

C. Talks

1. W. Wayne Meinke, "Activation Analysis", 1960 Eastern Analytical Symposium, New York City, November 2, 1960.

2. W. Wayne Meinke, "Activation Analysis Utilizing Fast Radiochemical Separations and Portable Neutron Generators", Michigan Nucleonics Society, Ann Arbor, November 10, 1960.

3. Morris A. Wahlgren, "The Neutron Generator in Chemical Research", U. of M. Chemistry Department Seminar, Ann Arbor, November 16, 1960.

4. W. Wayne Meinke, "Use of Radioisotopes in Analysis", American Chemical Society Student Affiliate Meeting, Ann Arbor, November 22, 1960.

5. W. Wayne Meinke, "The Potentialities of Activation Analysis", Chemistry Department Seminar, Illinois Institute of Technology, Chicago, November 29, 1960.

6. W. Wayne Meinke, "Activation Analysis with a University Research Reactor", Chemistry Department Colloquium, The Pennsylvania State University, University Park, December 1, 1960.

7. W. Wayne Meinke, "The Potentialities of Activation Analysis", Battelle Memorial Institute Colloquium, Columbus, Ohio, December 7, 1960.

8. Morris A. Wahlgren, "Studies of Short-Lived Fission Products", U. of M. Chemistry Department Colloquium, Ann Arbor, December 8, 1960.

9. W. Wayne Meinke, "Applications of Radiations and Radio-Isotopes", Guest Lecture, National Polytechnic Institute, Quito, Ecuador, December 15, 1960.

10. W. Wayne Meinke, "Nucleonics in Analysis", Guest Lecture, National Polytechnic Institute, Quito, Ecuador, December 16, 1960.

11. W. Wayne Meinke, "Activation Analysis with the University Reactor", U. of M. Chemistry Department Colloquium, Ann Arbor, April 13, 1961.

12. W. Wayne Meinke, "New Applications for Nucleonics in Chemical Analysis", 7th National Symposium on Instrumental Methods of Analysis, Instrument Society of America, Houston, Texas, April 17, 1961.

13. W. Wayne Meinke, "Activation Analysis with a University Reactor", Symposium and Dedication of Reactor of The New York Nuclear Research Center, Buffalo, New York, April 19, 1961.

14. W. Wayne Meinke, "The Current Status of Activation Analysis", Arkansas Section, American Chemical Society, Fayetteville, Arkansas, April 26, 1961.

15. W. Wayne Meinke, "The Potentialities of Activation Analysis", Graduate Lecture, Texas A and M College, College Station, Texas, April 27, 1961.

16. W. Wayne Meinke, "Activation Analysis", Guest Lecture, AEC-NSF-Summer Institute of Radiobiology, University of Michigan, July 25, 1961.

D. Committee Meetings

1. W. Wayne Meinke, Committee on Nuclear Science, National Research Council, Washington, D. C., November 1, 1960.

2. W. Wayne Meinke, AEC Office of Isotopes Development Information Meeting, Washington, D. C., November 30, 1960.

3. W. Wayne Meinke, Advisory Committee to the Analytical Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., February 23-24, 1961.

4. W. Wayne Meinke, Subcommittee on Radiochemistry, Committee on Nuclear Science, National Research Council, Berkeley, California, March 3, 1961.

5. W. Wayne Meinke, Advisory Committee to the Analytical Division, National Bureau of Standards, Washington, D. C., June 22, 1961.

6. W. Wayne Meinke, Subcommittee on Radiochemistry, Committee on Nuclear Science, National Research Council, Argonne National Laboratory, Illinois, October 6, 1961.

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