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NBS TECHNICAL NOTE 508

Activation Analysis Section:

Summary of Activities
July 1968 to June 1969

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NATIONAL BUREAU OF STANDARDS

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> Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information[3]—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

[2] Located at Boulder, Colorado 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

UNITED STATES DEPARTMENT OF COMMERCE
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NBS TECHNICAL NOTE 508

ISSUED JULY 1970

Nat. Bur. Stand. (U.S.), Tech. Note 508, 147 pages (July 1970)
CODEN: NBTNA

Activation Analysis Section:

Summary of Activities July 1968 to June 1969

Edited by Philip D. LaFleur

Activation Analysis Section
Analytical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402
(Order by SD Catalog No. C13.46:508), Price $1.25.

FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine sections and about 100 technical personnel encompassing some 57 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is a highly important output of our laboratories. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information about our programs. A word is perhaps in order about the philosophy of these yearly progress reports. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication--yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment, etc., which often require months to perfect and yet all too often must be covered in only a line or two of a journal article.

Thus our progress reports endeavor 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 journal literature are covered in a much more abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. We plan to issue these summaries for all of our sections. The following is the third annual report on progress of the Activation Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

The Activation Analysis Section has the responsibility to develop and apply measurement techniques for the quantitative and qualitative analysis of materials through the use of nuclear reactions.

The basic activities of the Section may be divided into two general areas, the research and development area and the sample area. The Section has a very real responsibility for the development of new techniques, and the refinement of existing techniques, to increase the applicability of activation analysis and to reduce the cost of analysis to become more competitive with non-nuclear methods of analysis.

A very important part of the Section's activities is involved in the certification of Standard Reference Materials in cooperation with the other Sections in the Analytical Chemistry Division. The Office of Standard Reference Materials of the National Bureau of Standards is currently developing, or has issued, Standard Reference Materials of very high purity which are well characterized for their trace element content. The Activation Analysis Section has made a significant contribution in the certification of these standard materials.

Activation analysis is particularly suited for the analysis of trace and ultra-trace components of materials because of the very high sensitivity for many elements, the lack of a reagent "blank" in most analyses, and the opportunity for excellent accuracy when carefully done.

The Activation Analysis Section is composed of six groups three of which are oriented to a specific source of nuclear radiation: the reactor, LINAC, and Cockcroft-Walton generator groups, a group for the development of radiochemical separations, and, in recognition of the increasing emphasis on the analysis of biological materials in the Section, we are activating a project oriented to this important sample area. The sixth project, Instrumentation Techniques and Automation has, at present, no personnel assigned. Considerable interaction among the groups is encouraged so that activities of common interest are worked upon jointly in the several groups. In addition, the Radiochemical Analysis Section retains groups in nuclear instrumentation and nuclear chemistry which consult both Sections.

A roster of the groups in the Section is listed in Part 7. In the past the Section has enjoyed the presence of scientists from abroad, and from within the United States, who have worked for one to two years in the Section, and have contributed to a very stimulating environment. It is hoped that we may continue to utilize this program in the future.

In order to specify adequately procedures, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Philip D. LaFleur, Chief
Activation Analysis Section
Analytical Chemistry Division

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ACTIVATION ANALYSIS: SUMMARY OF ACTIVITIES
July 1968 to June 1969

Edited by Philip D. LaFleur

The design and installation of irradiation facilities for the NBS Reactor are described, and studies of the operating characteristics of the pneumatic tube facilities have begun.

Procedures have been developed for determining molybdenum in the presence of large amounts of tungsten and for the determination of uranium. Methods for determining a contamination free blank for application to liquid samples, a study of the application of neutron activation to the analysis of stained glass were begun.

The application of thermal and fast neutron activation analysis and photonuclear activation analysis to the NBS Standard Reference Material program is discussed.

Studies of the application of 3-MeV neutrons from a Cockcroft-Walton neutron generator to activation analysis and of the 3-MeV neutron buildup in 14-MeV neutron activation has been studied.

The determination of carbon by photonuclear activation has been extended to various metals other than sodium, thallium has been determined in glass samples by photon bombardment and the photofission of thallium, bismuth and lead has been studied.

Hydrated antimony pentoxide has been used to separate sodium from glass samples for subsequent instrumental activation analysis, and the antibiotic, tetracycline, has been applied to radiochemical separations.

KEY WORDS: Activation analysis; ancient stained glass; carbon; Cockcroft-Walton neutron generator; coincidence spectrometer; group separations; homogeneity testing; hydrated antimony pentoxide; NBS LINAC; NBS Reactor; neutron flux measurements; photofission; Standard Reference Materials; tetracycline.

1. INTRODUCTION

In October, 1968, the Third International Conference on Modern Trends in Activation Analysis was held at the National Bureau of Standards. The Conference was chaired by Dr. James R. DeVoe of the Radiochemical Analysis section with Dr. P. D. LaFleur as assistant chairman. Over 400 scientists attended the Conference, including 100 from outside the United States, making it truly an international conference. Over 160 technical papers were presented, covering all aspects of activation analysis. At the Conference, the report Activation Analysis: a Bibliography was distributed to attendees. The report, which was authored by G. J. Lutz, R. S. Maddock, R. J. Boreni and W. W. Meinke, has been received enthusiastically by workers in the field. This report, which will be updated periodically, represents the culmination of many years of effort in cataloging reports and papers in activation analysis. The Proceedings of the Conference will be published in June, 1969.

During the past year the application of activation analysis in the NBS Standard Reference Material program has expanded in the number of elements for which we analyze and in terms of the sophistication of the analyses.

Through the use of high-resolution gamma ray spectroscopy and group and/or individual element separations, we are beginning to approach the capability of performing rapid, economical multi-element analyses. The most serious problem facing our Section during the next year is the attainment of a much higher degree of automation in the processing of samples Attaining proficiency in automation will require much of our effort in the coming year.

The NBS Reactor has now operated at power levels from 2 to 10 MW since January, 1969. During this time we have been gaining experience with the reactor. Unsuspected leaks in the pneumatic tube systems, have kept us from using all of the tubes originally installed in the reactor, since ^{41}Ar activities were above the maximum permissible levels. The leaks in two of the tubes have been temporarily sealed and we have been using those tubes. The Reactor Radiation Division will replace all of the flight lines and air lines in the existing system with polyethylene tubing similar to that in the systems installed in the warm laboratories. This is scheduled for completion during July, 1969.

We have now completed the necessary temperature experiments, as described in the section on facilities, and will be installing terminals for the warm laboratory pneumatic tube system during July and August, 1969.

Studies of the solution of blank problems in oxygen analysis with the neutron generator have been completed. A comprehensive study of the application of 3 MeV neutrons in activation analysis is nearing completion, and a study of 3 MeV neutron interference in 14-MeV neutron activation has been studied.

The photonuclear analysis program has continued to operate whenever time was available. During the year the LINAC began operating on a 24-hour day, 4 days a week. The activation project has been operating on 12 hour shifts about three times a month. Efforts have been channeled in the analysis of carbon in steels and other metals, the analysis of oxygen in sodium metal, the determination of thallium in glass, and the determination of Bi by photofission.

2. LIAISON AND GENERAL FACILITIES IN THE NBSR

A. Introduction

The methods, techniques, and materials employed over the years in the construction and use of pneumatic transfer systems in research and test reactors have become generally accepted without much question and with a minimum of improvement in the state of the art. Except for a limited number of special application items, such as rabbit materials, flight tube materials, installation techniques, irradiation terminals, and instrumentation requirements have remained practically unchanged. However, in the case of a research reactor, such as the NBSR, with a power level of 10 MW, a neutron flux of 10^{14} $n.cm^{-2}.s^{-1}$ or higher, and gamma heating rates which could exceed 1.5 watts/gm in the sample, these standard systems are no longer adequate. Specifically, a more sophisticated safety system which will automatically return samples when the temperature exceeds a pre-determined level, or when there is a system malfunction or a loss of power, must be incorporated.

In addition to our new pneumatic transfer irradiation terminals, plans are completed for the installation of two vertical manual facilities and one terminal has been installed. We feel that the overall system design for use with the NBSR has advanced the state of the art considerably in the areas of rabbit system materials, design, safety features and instrumentation. Considerable progress in our flux and temperature measurement program has been made. Recent data, using temperature sensors, given in this report are being used to predict safe limits for sample irradiations.

B. Liaison

With the advent of full power operation of the NBSR, it is anticipated that the liaison activities of the section with outside users of the facilities will increase dramatically during the next several months. As has been pointed out in previous reports, the NBSR is designed to be a very useful facility for activation analysis as well as for experiments in physics and engineering. Our initial liaison activity has been with Mrs. Jacqueline Olin of the Smithsonian Institution in Washington, D. C. Since Mrs. Olin did not have at her immediate disposal the necessary laboratory space or radiation detection equipment, she has become a guest worker with the group and uses our equipment. The type of cooperation between the Activation Analysis Section at the National Bureau of Standards and outside users can vary from intimate involvement with the problem, as has been the case with Mrs. Olin, to such purely mechanical matters such as assistance in packaging samples for irradiations, assisting in irradiations, explaining operating philosophies of the Activation Analysis Section and the Reactor Radiations Division and all points in between. As is pointed out in succeeding sections of this report, we are obtaining a great deal of useful operating data about the NBSR which allows us to be of considerable assistance to outside users of the NBSR. We have recently registered our facilities with the Division of Nuclear Chemistry and Technology of the American Chemical Society in their Major Nuclear Centers program and welcome inquiries for the use of the NBS facilities, either on a cooperative basis where the scientists at the National Bureau of Standards become deeply involved scientifically, or for assistance in using the facilities without this level of involvement.

C. Pneumatic Tube System

A new pneumatic tube system has been installed by Reactor Experiments, Inc. of San Carlos, California* for use in the NBSR. The specifications for this system were tailored specifically to meet the operating and safety requirements of the NBSR. In the new system, samples can be sent pneumatically to three separate irradiation terminals. One of these terminals,

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*See disclaimer in Preface.

located in the thermal column, will be composed entirely of graphite in order to minimize flux perturbations in the thermal column itself. This terminal will accept a standard 1 5/16 in. diameter rabbit in a thermal flux of about $3\text{x}10^{11}\text{n.cm}^{-2}\text{s.}^{-1}$. This terminal has three separate send/receive locations, one in Room C002 in the Reactor sub-basement, and the other two in Rooms B121 and B144 of the warm and semi-warm laboratory area.

The remaining two terminals have vertical access to the reactor core and will accept a 3/4 in. diameter rabbit. Each tube has five separate send/receive locations. Although the design of these terminals has essentially been completed, tests are being conducted at this time in order to gain a better evaluation of the cooling requirements at their specific locations in the core. The location of the three new tubes, plus the relative locations of the four horizontal tubes already in operation and also the two manual access tubes discussed below. are shown in figure 1.

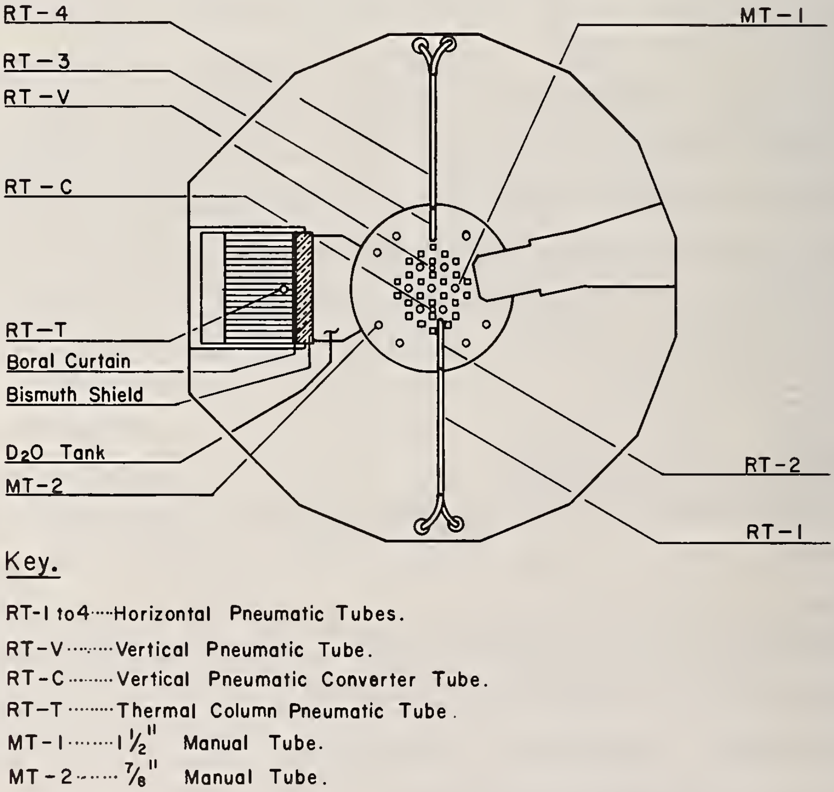

Figure 1. Location of irradiation facilities in the NBSR

1. Instrumentation and Operation

It was felt that with the possible simultaneous use of seven pneumatically operated irradiation locations which could be accessed from 21 separate send/receive stations, a completely automated and interlocked system was desirable. Since each irradiation location has a time limitation on a sample irradiation due to the heat build up, and since a positive seal is required where the tubes exit from the Reactor Building, several safety systems have been incorporated. In addition, to give the reactor operating personnel in the control room the final decision on a given irradiation, an IRQ, or irradiation request panel, was installed. This panel (fig. 2) will provide information on the status of any tube at any given time. The tubes are connected to turret type send/receive units pictured in figure 3.

Figure 2. Irradiation request panel

Figure 3. Send-Receive Terminal - 7/8" system

A typical control unit of the three-station 1 1/2 in. diameter tube system is shown in figure 4. From here the operator, by turning on the power to the unit, locks out all other stations in the system, (two, in this case). At the same time he receives a report on the status of the CO_2 propelling system, and the high pressure air system which operates the valves and switches in the pneumatic circuit. If the pressure in either of these two systems is insufficient to provide reliable operation, an indication is given and the system will not operate. Next, the operator must decide whether or not the CO_2 propelling gas is to be maintained at a reduced pressure, for cooling, after the sample reaches the terminal position. The sample return location is next selected by pressing the appropriate button and then a decision must be made whether to time the irradiation manually or to use the timer in the control unit. (As a safety precaution, the maximum length of time for which a sample can be irradiated in each location is predetermined and programmed into each system.

Figure 4. Control unit at send-receive station location

Therefore, regardless of which type of timing is selected, the sample will automatically return if this maximum irradiation time is reached.) This procedure completes the programming, and the system is ready to send the sample. To do this the permission Granted/Requested button is pressed. The indicator light comes on and blinks on the control panel and on the IRQ panel in the control room. If the reactor operator is ready for the sample to be sent, he presses the corresponding button on his IRQ panel, granting permission for the irradiation to take place. The sample may now be dispatched by activating the Send Sample button on the station control panel. As the sample approaches the core, a photocell system is triggered and indicates on the IRQ and station control panels the arrival of the sample in the reactor core. Although the sample travels at a speed of around 50 feet/second, the impact is reduced by the use of an air-cushion braking system.

While the sample is in transit, entering or leaving the core, all other stations and systems are locked out and will not operate until the routing sequence has been completed. The return of the sample at the end of an irradiation is accomplished by the automatic timer or by pressing the Manual Return button.

2. Safety Systems

As mentioned above, both the air pressure for operating the valves and switches in the system, and the CO_2 propelling gas pressure must be above a certain level before the system can operate. The system also has a Stuck Capsule alarm. This is accomplished by a delay timer which has been pre-set for some time greater than that required to return a heavy capsule. As the capsule return cycle is actuated, the timer starts and is reset as the capsule arrives at the receiver station. If, however, the pre-set time is exceeded, the system assumes a "stuck" or "lost" capsule situation and initiates the Stuck Capsule alarm. This alarm turns on lights at the station control and IRQ panel, and activates three rotating beacon lamps at various places in the building where personnel could be near the tubing and thus be exposed to radiation from the stuck capsule.

Another safety feature is the Automatic Emergency Return System (AERS). This system is actuated automatically in the event of a major scram, electrical failure, or inadvertant loss of CO_2 pressure. It can also be activated manually by pressing the Emergency Return button on the station control panel. The AERS sequence operates as follows. When initiated, all previously programmed logic is isolated, the system is switched to emergency power, and an external CO_2 bottle fires out any and all rabbits, in sequence, to a separate, shielded location. In the event of a major scram, this sequence is preceded by the closing of the three ball valves on either side of the containment wall (fig. 5) thus preserving the integrity of the reactor containment.

Figure 5. Penetration of containment building showing ball valves

The compressor and ballast tank which supply the recirculating supply of CO_2 for propelling the samples, and the central relay panel for the system are shown in figure 6.

The flight tubes (fig. 7) consist of a 1/8 in. thick polyethylene inner sleeve, through which the rabbit travels; a steel armour covering for structural reinforcement, and a polyvinyl chloride covering over the armour which provides a corrosion-resistant finish.

D. Manual Irradiation Facility

The manual irradiation tubes allow irradiations for a longer period of time than would be possible in a rabbit tube. The two types of manual irradiation tubes for installation in the NBSR are shown in figure 8. One type, holding a single sample container at a time, utilizes 1-1/2 in. diameter graphite buckets in a flux of $\sim 10^{14} n.cm^{-2}.s^{-1}$. These buckets will be suspended at the end of a thin aluminum wire. The second

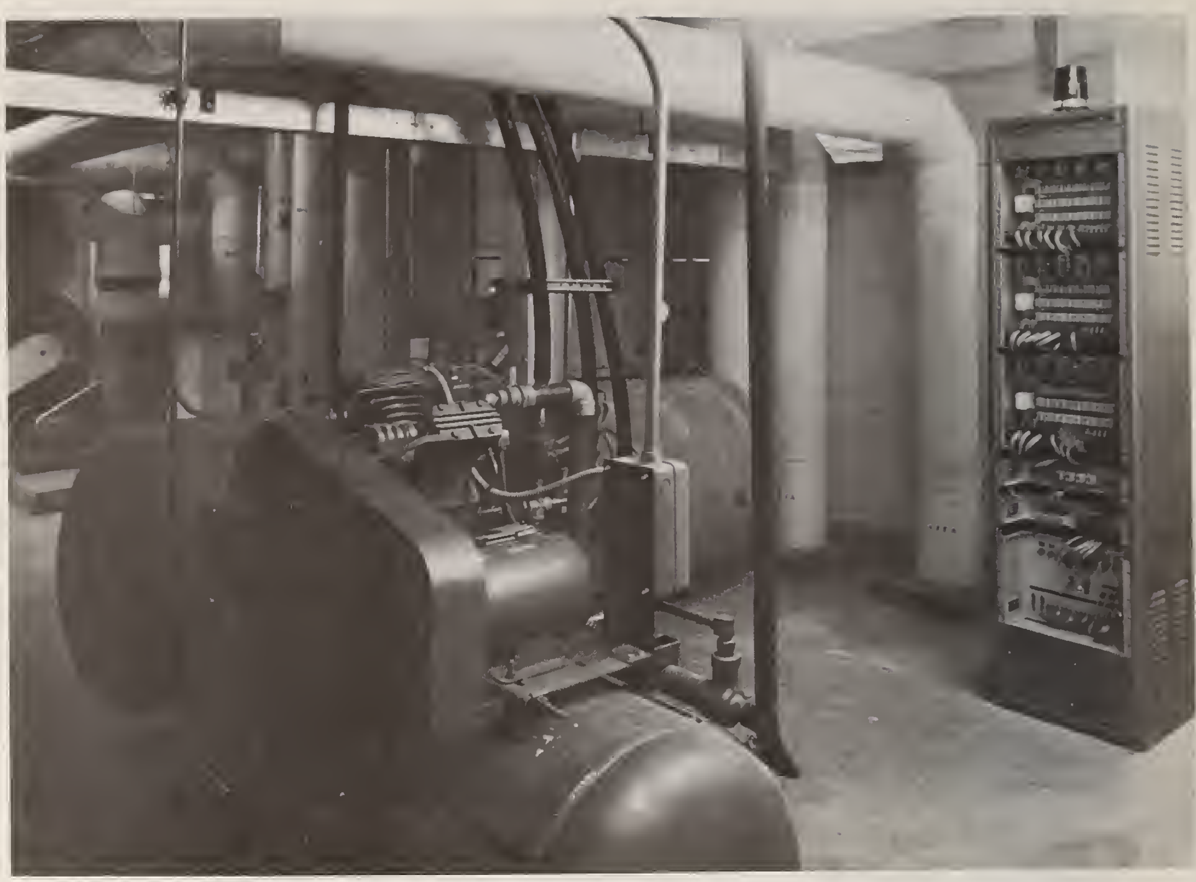

Figure 6. Compressor, ballast tank and central controller for rabbit system

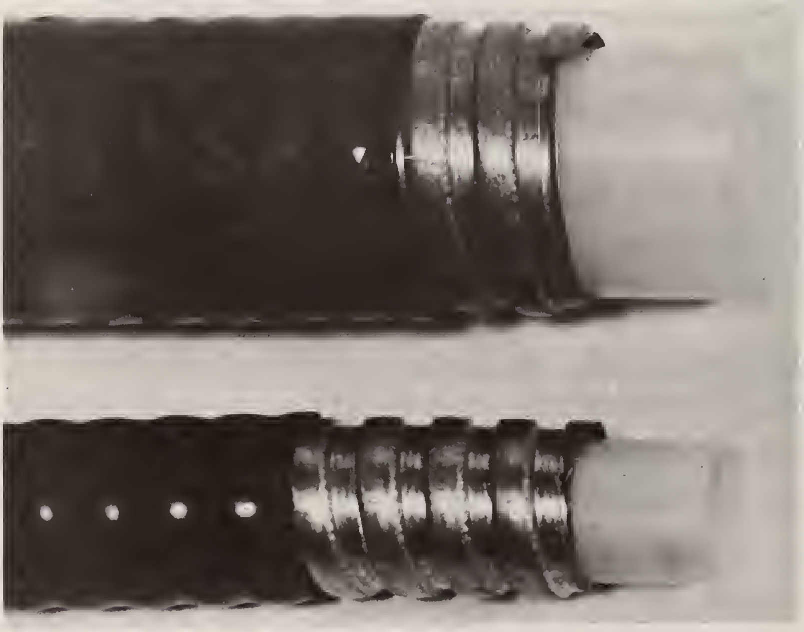

Figure 7. Flight lines of armoured polyethylene tubing for 1 1/2" and 7/8" systems

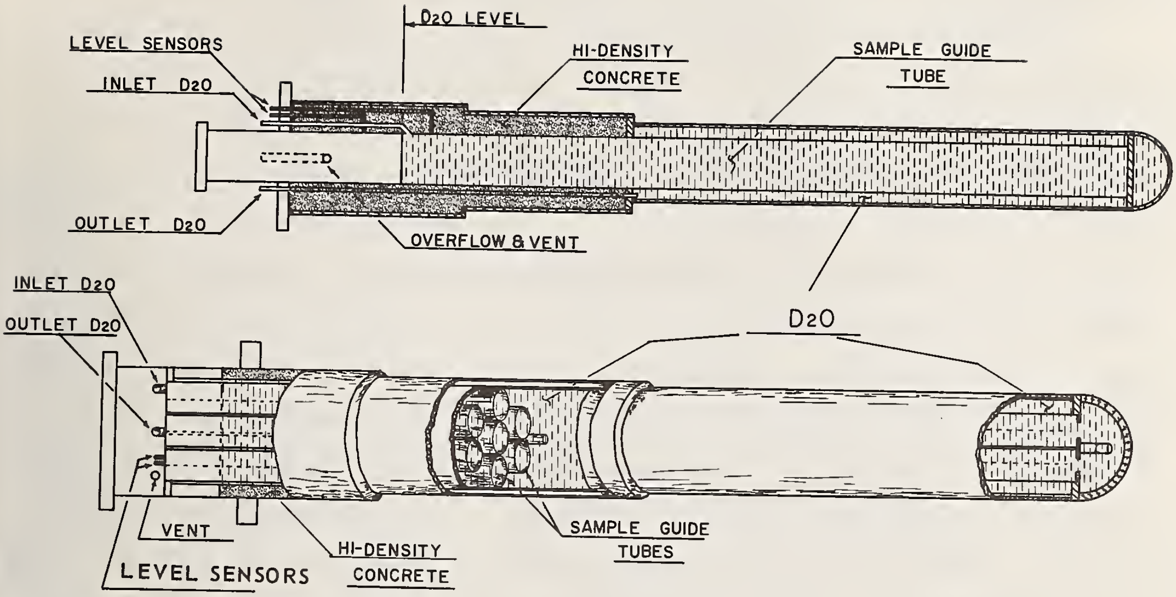

Figure 8. Long term irradiation facilities for NBSR

type will permit irradiation of up to seven 3/4 in. diameter samples simultaneously. This system will be located in the reflector area where a flux of about $5 \times 10^{13} n.cm^{-2}.s^{-1}$ will be available.

The first system has been installed and temperature studies indicate that with no circulation of the D_2O in the tube, the 10 MW equilibrium temperature of 180°F can be expected. However, when the D_2O is circulating, the temperature is only slightly above ambient. Irradiation times equivalent to one reactor cycle (∿18 days) will be possible.

E. Status of Existing 1 1/2 in. Diameter Horizontal Pneumatic Tube Systems

The existing four 1 1/2 in. horizontal rabbit tubes have been discussed in detail in a previous report [1]. During the coming year the tubing in this system will be changed from aluminum to the armoured polyethylene type used in the new system since it was found that the many joints in the aluminum tubing resulted in excessive leakage of the CO_2.

F. Progress of Irradiation Facilities in NBSR

Insofar as the pneumatic tubes are concerned, all construction and installation of flight tubes, send/receive stations, main IRQ panel and safety systems have been completed. The irradiation terminals are in the design stage. These designs will be strongly influenced by experimental results of temperature and irradiation dose studies presently being conducted using the manual vertical facility and the existing horizontal tubes. The graphite terminal to be installed in the graphite thermal column has been completed. This terminal will be installed as soon as the shield plug to be located above the terminal has been suitably modified. Considerable progress has been made on the long term vertical manual facility. The final design was recently approved and the terminal has now been located in the reactor core and is undergoing tests. A temporary flow system has been set up to circulate D_2O in the terminal for 10 MW reactor operation. Experience with the temporary flow system will be used for a permanent installation incorporating all necessary safety features. A lead cask has been constructed to facilitate safe removal of samples from this terminal.

A complete modification of the existing horizontal pneumatic tube facility is being made by the Reactor Operations Group. It is hoped that all four tubes will be in service in the near future for operation at 10 MW reactor power.

(F. A. Lundgren, S. S. Nargolwalla, P. D. LaFleur)

G. Measurement of Temperature and Neutron Flux Characteristics of the NBSR Pneumatic Tube Irradiation Facilities RT-2 and RT-3

As discussed earlier in this report, the NBSR went critical and became available for use for the first time this past year. In order to fully utilize the capabilities of this reactor for neutron activation analysis, information must be known about each of the irradiation facilities available. The information required pertains to the thermal and fast neutron flux distributions and the temperature characteristics of different materials irradiated within each facility. These measurements are in progress. This segment reports on the information obtained to date on the pneumatic tube irradiation positions RT-2 and RT-3.

1. Design Information on Pnemuatic Tubes RT-2 and RT-3.

Specific information on these irradiation positions has been previously discussed [1,2]. Briefly, RT-2 and RT-3 are both located horizontally in the reactor core area. Pneumatic tube RT-2 terminates inside the core area itself while RT-3 terminates in the D_2O moderator just outside the fuel gap at midplane. At the outset of these measurements, very little was known about the temperature characteristics of various types of materials within these irradiation positions, or even whether polyethylene rabbits could be used for more than a few minutes.

2. Experimental

a. Neutron Flux Measurements. The neutron flux measurements were of two types. First, the homogeneity of flux distribution within the rabbits was measured for both RT-3 and RT-3. These measurements were made using 5 mil copper foil distributed both circumferentially and axially throughout the rabbit. In most cases the copper foils were gross gamma counted shortly after irradiation, and the flux distribution calculated. Second, the neutron energy distribution throughout the rabbits was measured. These measurements were of two kinds - cadmium ratio determinations and threshold foil determinations. The cadmium ratio determinations (with both gold and copper) have been completed and the threshold foil measurements are in progress.

b. Temperature Measurements. The temperature measurements were made using small temperature indicating stickers attached to each sample. These stickers were obtained in various temperature ranges, each indicator stating the temperature at which it irreversibly changes from white to black. These stickers were attached to various types of materials (polyethylene, quartz and lead) as shown in figure 9. A series of irradiations were made starting with small quantities of samples at low power levels and slowly increasing the irradiation times, the sample size, and the power level with each irradiation. To date, information has been obtained through the 5 MW level for both irradiation positions RT-2 and RT-3 using the three materials mentioned in various configurations.

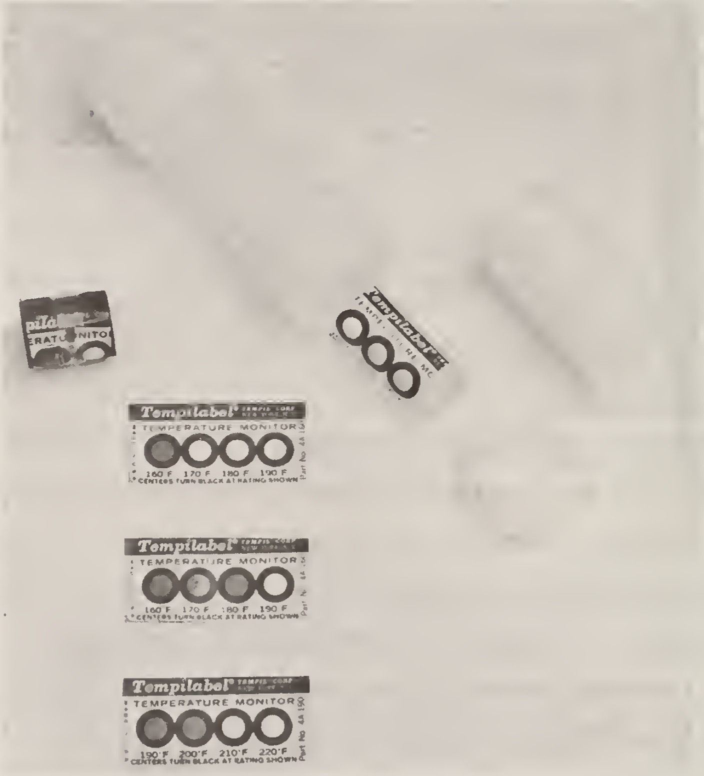

Figure 9. Temperature sensing labels, NBSR "rabbit" and quartz blocks used for temperature measurement

3. Results

a. Neutron Flux Measurements. The results of these measurements are found in tables 1-3 and figure 10. Table 1 shows the absolute thermal neutron flux as determined by both gold (0.0005 in. thick) and copper. These values are compared to the design estimates as given in NBSR-10 [2]. There

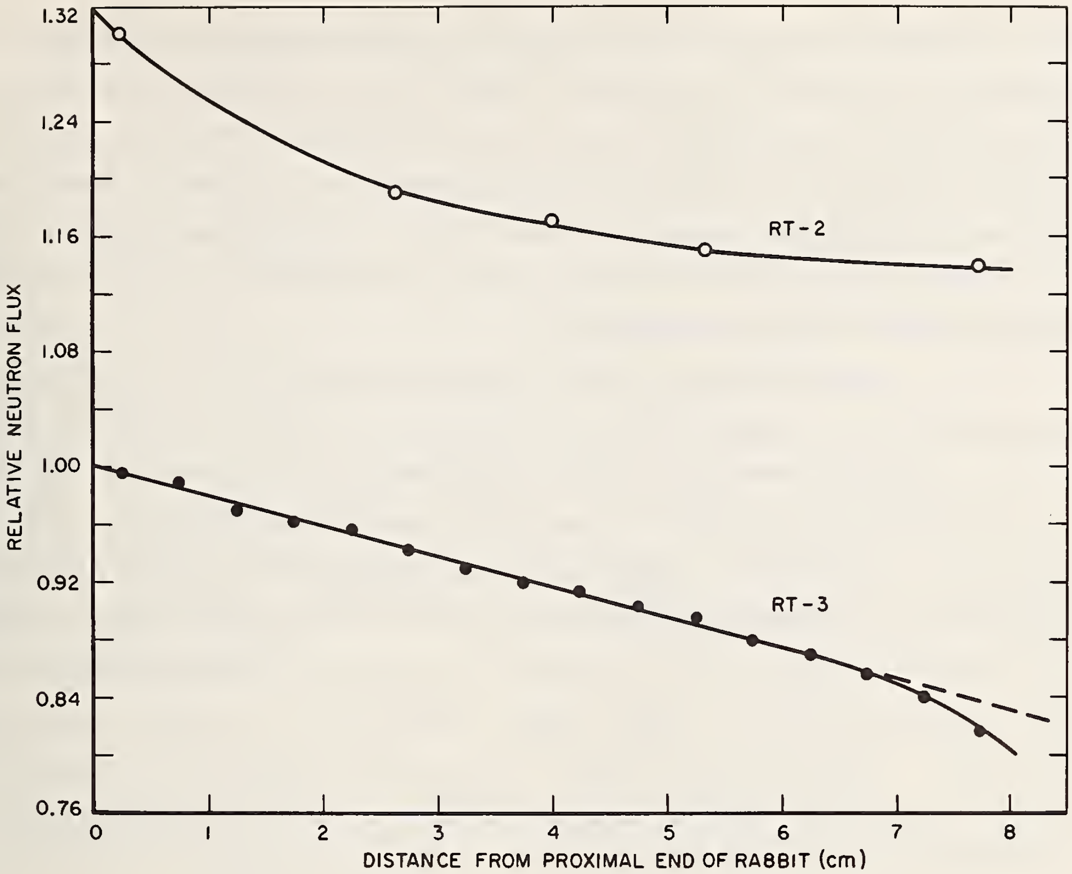

Figure 10. Axial flux distribution in RT-2 and RT-3

Table 1. Absolute Thermal Neutron Flux Determinations

Measurement	Element	Thermal Neutron Flux ($n.cm^{-2}.s^{-1}$) RT-2	Thermal Neutron Flux ($n.cm^{-2}.s^{-1}$) RT-3
Calculated[a]	-	$7.3x10^{13}$	$9.4x10^{13}$
Experimental[b]	Gold	$6.9x10^{13}$	$5.9x10^{13}$
Experimental[b]	Copper	$5.3x10^{13}$	$4.8x10^{13}$

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[a] Obtained from NBS Report 9081 (NBSR-10)

[b] Contribution to foil activity; measured at proximal end.

is a significant difference in the experimental flux as determined by gold and by copper. This discrepancy most likely results from the much greater variation of the gold cross section versus neutron energy compared to copper. Results for both elements show that RT-2 has a slightly higher thermal (subcadmium; <0.14eV) neutron flux than RT-3, a fact not expected from design estimates.

The circumferential flux distribution in the rabbits as determined by copper foils is given in table 2. Since the incore rabbit terminals are horizontal, the location of the foils within the rabbit itself was measured from the end closest to the core. The results indicate no significant flux variation circumferentially in either pneumatic tube. However, as shown in figure 10, the axial neutron flux distribution does vary significantly. This axial variation is quite irregular for RT-2. However, for RT-3 the axial variation is almost linear over the entire length of the rabbit, falling off slightly at the distal end.

Table 2. Circumferential Flux Distribution in NBSR Pneumatic Tube Facilities

Pneumatic Tube Facility	Location in Rabbit	Relative Neutron Flux	No. of Monitors
RT-3	Proximal	1.000±0.004[a]	7
RT-3	Middle	0.928±0.003	6
RT-3	Distal	0.829±0.003	7
RT-2	Proximal	1.300±0.007	7
RT-2	Middle	1.172±0.002	6
RT-2	Distal	1.136±0.003	7

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[a] Uncertainties are $ts/\sqrt{n}$ at 95% confidence level.

The results of cadmium ratio determinations made at both ends of the rabbit for RT-2 and RT-3 using copper and gold foils with 20 mil cadmium covers [3] are shown in table 3. The cadmium ratios for RT-2 were approximately 4 for gold and 16 for copper, and were the same at both ends of the rabbit. This large fast neutron component is to be expected due to the position of RT-2 between the fuel elements. Tube RT-3 has much larger cadmium ratios for both gold and copper, and shows a significant difference in cadmium ratio between the proximal and distal ends of the rabbit. This is also expected since the RT-3 position extends further into the D_2O moderator. It is obvious that when a sample irradiation position is chosen, consideration must be made for the fast neutron component in the neutron flux.

Table 3. Cadmium Ratios for the NBS Pneumatic Tube Facilities

		Gold-Cadmium Ratio		Copper-Cadmium Ratio	
Pneumatic Facility	Location in Rabbit	Au(Cd)	Average	Cu(Cd)	Average
RT-3	Proximal	9.6 11.6	10.6	65.0 65.5	65.3
RT-3	Distal	15.7 17.2	16.5	80.5	-
RT-2	Proximal	3.92	-	16.0 15.9	16.0
RT-2	Distal	4.03	-	15.8	-

b. Temperature Measurements. The compiled results of temperature measurements made to date are shown in tables 4 and 5. They are self-explanatory. The results listed are for maximum values only. A large number of preliminary irradiations were made to obtain these values. Much additional work will be performed at the 10 MW power level to precisely determine the safe limits for sample irradiations.

Table 4. Compilation of Temperature Measurements to Date in RT-2

Material	Configuration	Wt g	Power Level MW	Length of Irrad.	Results
Polyethylene	Sheet, 2 mm thick	1	2	20 m	120±5 °F
Polyethylene	Sheet, 2 mm thick	1	3	20 m	130±5 °F
Polyethylene	Empty rabbit	-	2	10 h	105±5 °F, no significant radiation damage
Polyethylene	Empty rabbit	-	2	20 h	Small amount radiation damage; still usable for irradiations.
Quartz	7 mm dia tubing open ends	1	2	60 m	120±5 °F
Quartz	Solid block	14	2	60 m	155±5 °F
Quartz	7 mm dia tubing open ends	1	3	80 m	125±5 °F
Quartz	7 mm dia tubing open ends	1	5	60 m	125±5 °F
Quartz	Solid block	4.6	5	20 m	210±10 °F
Quartz	7 mm dia tubing open ends	3.5	5	20 m	145±15 °F
Quartz	7 mm dia tubing open ends	3.5	5	20 m	200±10 °F
Lead	Sheet, 1 mm thick	1	2	5 m	200±20 °F

Table 5. Compilation of Temperature Measurements to Date in RT-3

Material	Configuration	Wt g	Power Level MW	Length of Irradiation Minutes	Results
Polyethylene	Sheet, 2 mm thick	1	3	12	<100 °F
Quartz	Solid block	15	2	120	105± °F
Quartz	7 mm dia tubing open ends	1	3	20	<100 °F
Quartz	Solid block	7	5	20	130±10 °F
Quartz	Solid block	14	5	20	155±5 °F
Lead	Sheet, 1 mm thick	1	3	30	120±10 °F
Lead	Sheet, 1 mm thick	1	5	20	160±10 °F
Lead	Sheet, 1 mm thick	2.1	5	20	180±10 °F
Lead-Quartz	Solid strip of lead Sheet in sealed quartz ampoule	1.13 (Pd) 3.63 (SiO_2)	5	50	155±5 °F

(D. A. Becker)

3. ACTIVATION ANALYSIS WITH A NUCLEAR REACTOR

A. Introduction

During this year we have continued our efforts to attain a high degree of versatility in terms of numbers of elements analyzed and matrices, while maintaining the highest possible standards of accuracy and precision. We intend to continue these efforts during the coming year, as well as begin investigations into areas in which we have not been active, such as epithermal neutron activation analysis and automated activation analysis. Now that irradiation facilities are available at the National Bureau of Standards, we shall also increase our efforts in activation analysis using short-lived isotopes.

Operation of the NBSR has been a great advantage to the Reactor Activation Analysis group as we are now able to perform all of our work at the Bureau of Standards. We have, of course, spent a considerable amount of time becoming acquainted with the operating characteristics of the reactor, and with the safety criteria for performing irradiations.

As usual, much of our research has been involved with the analysis of NBS Standard Reference Materials, but as our expertise improves, our research effort is becoming less applied to specific samples.

B. Facilities

1. Modifications to a Beta-Gamma-Gamma Sum Coincidence Spectrometer

This $\beta\gamma\gamma$ sum coincidence spectrometer has been described previously [3]. As originally designed, the sample to be counted was sealed between two thin plastic scintillator discs and optically coupled to two 3/4 in. photomultiplier tubes. (fig. 11a). A pulse from both photomultiplier tubes was required to indicate an event in the plastic scintillator, thus effectively eliminating noise pulses from the photomultiplier tubes. This feature did lower the background ∿10-20% (almost entirely in the low energy region [3]), however, we recently

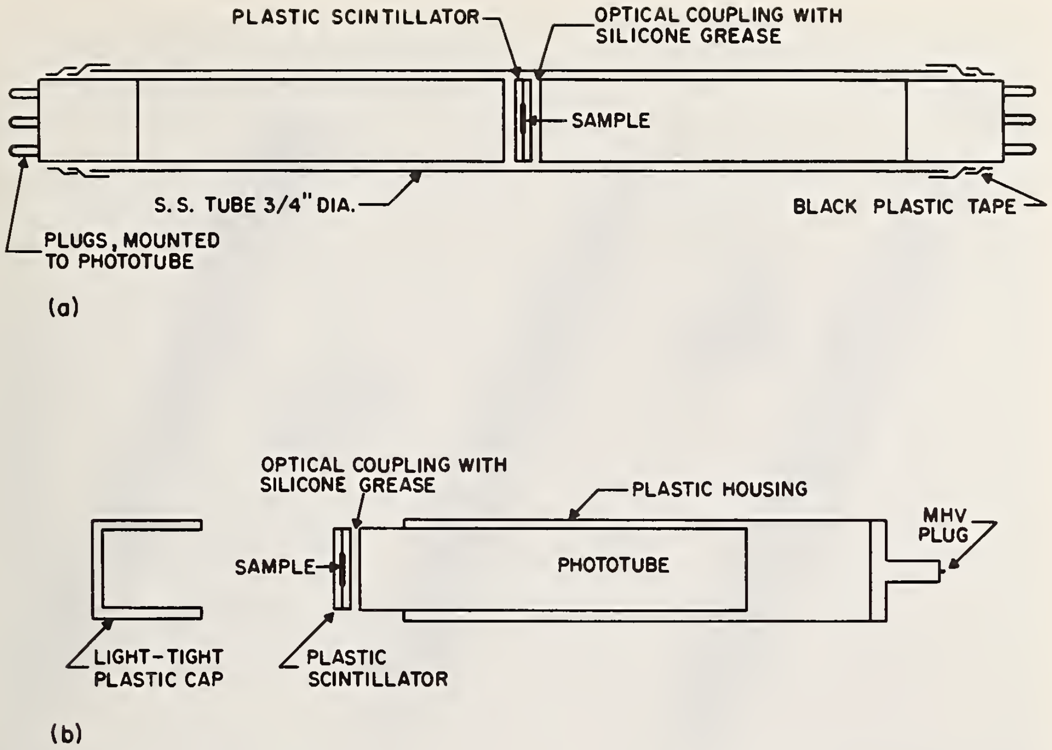

Figure 11. Mounting techniques for βγγ coincidence system
(a) Two phototube technique
(b) One phototube technique

discovered inconsistencies in counting efficiency. Repetative counting of the same ^{60}Co standard after remounting gave results differing by as much as 50%. After extensive testing and elimination of most of the possible electronic malfunctions, the remaining possibility was the optical coupling of the scintillator disks to the phototubes. Since the phototubes had ∿1 mm play from side to side in the stainless steel tubes, the possibility existed that one of the phototubes might drop away from the scintillator disks during counting resulting in loss of optical coupling. This would account for the variable results in the ^{60}Co standard counts..

To eliminate this problem, a revised detector system was devised using only one phototube (figs. 11b & 12). In this new system a 3/4-in. photomultiplier tube with associated electronics (fig. 13) was potted in a 1 in. OD bakelite tube with black RTV silicon compound. The junction plug which was

Figure 12. Sample mounting for one phototube technique

outside the phototube housing before, is now inside the bakelite housing. The HV and signal leads are brought through the rear of the housing using an MHV connector. A tight fitting cap of bakelite was made to enclose the source. Black electrical tape is used to keep the cap in place and prevent any light leaks.

The new system has completely eliminated the counting inconsistencies. Repetative counting of both cobalt-60 and sodium-24 standards gave the following relative efficiencies: Tube A=91.4±2.1%; Tube B≡100%; tube C=94.3±2.2%. The averages quoted are for three separate determinations, for each detector, with 10,000-50,000 counts per determination. This system was used for the analysis of picogram quantities of sodium in microstandard particles, as described in part 3.

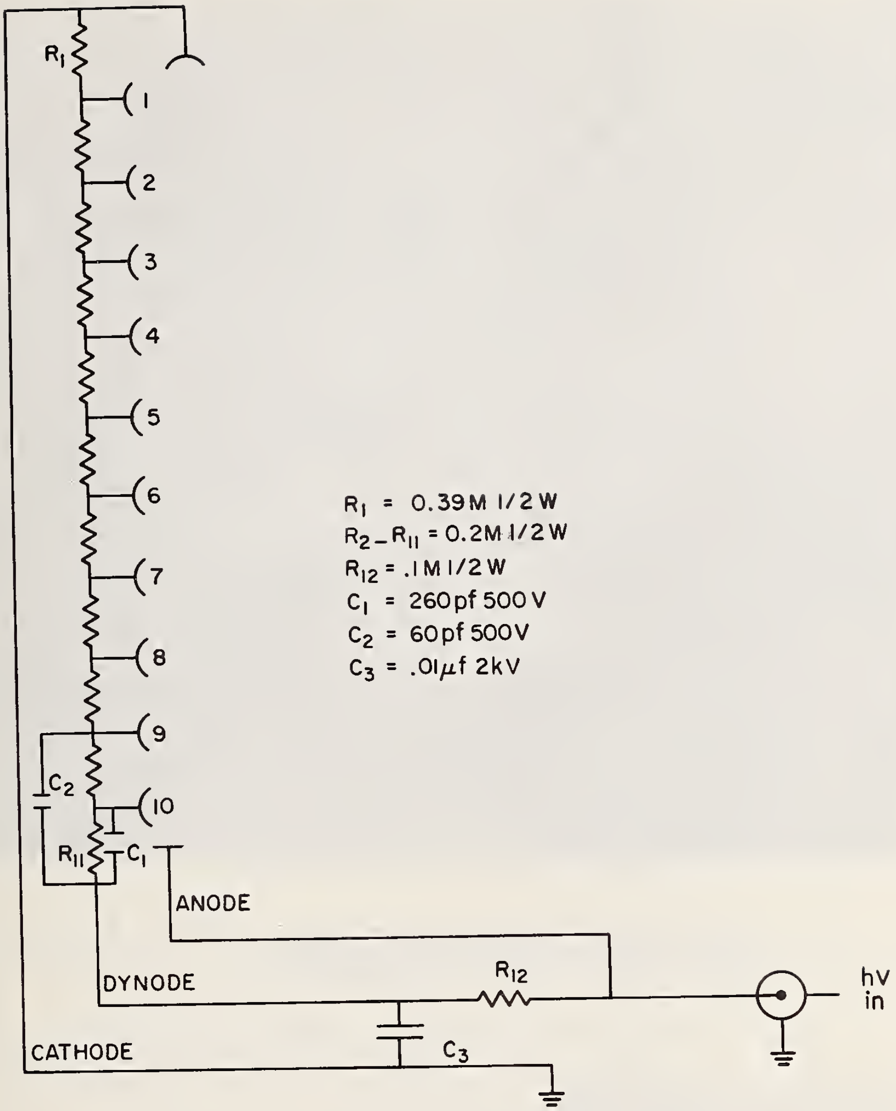

Figure 13. Electronics for one phototube technique
(D. A. Becker)

2. Counting Room

During the year we acquired a new 47-xx Ge(Li) detector with a system resolution of 4 keV. A view of the counting room configuration to include the shield for the new detector is shown in figure 14. Also shown in the picture is the new high-speed point plotter that was acquired during the year for plotting gamma-ray spectra. A view into the Ge(Li) detector shield is shown in figure 15.

Figure 14. Counting room showing shield for Ge(Li) detector and 4096-channel analyzer

C. Research Activities

1. Activation Analysis for Molybdenum in the Presence of Large Amounts of Tungsten

As part of the certification of SRM 480, a W-Mo alloy designed to be used as an electron microprobe standard, the Section was asked to determine Mo in some samples of the alloy. The samples weighed about 5 mg each and contained nominally 80% W - 20% Mo. Tungsten could easily be determined in the samples nondestructively, but a chemical separation was required for the Mo determination because of interference with the 0.142 MeV γ-ray of ^{99m}Tc used as a measure of the ^{99}Mo activity by the much more intense 0.134 MeV γ-ray of ^{187}W.

Figure 15. 47-cc Ge(Li) detector in shield

In steels, where the W-Mo ratio is of ten much lower than in these samples, it is frequently possible to allow the ^{187}W to decay until this interference is negligible [1,4] However, in these samples the W-Mo ratio is much too high to permit this approach and so a chemical separation was developed.

The method chosen was based on the results of research carried out in this group on the extraction behavior of a number of metal ions with bis(2-ethylhexyl) orthophosphoric acid (HDEHP) [5,6]. Using 11 $\underline{M}$ HNO_3 as the aqueous phase Mo can be quantitatively extracted into HDEHP while Tc is not extracted. The analytical procedure used incorporates these facts by first extracting the Mo into HDEHP from 11 $\underline{M}$

HNO_3. Tungsten is also extracted. Then, after allowing time for ^{99m}Tc to equilibrate with its ^{99}Mo parent, the organic phase is washed with 11 M HNO_3. The ^{99m}TTc is quantitatively removed from the organic phase and thereby separated from both W and Mo. This wash solution is counted directly using a 3 in. x 3 in. NaI(Tl) detector in conjunction with a 400 channel pulse height analyzer and the ^{99m}Tc peak used as a measure of the Mo present in the sample. The method is simple and rapid. Excellent decontamination from virtually all interfering activities is obtained. Corrections are made for decay of ^{99m}Tc after separation and for decay of ^{99}Mo up to the time of separation. No determinations of chemical yield are required since the yield in each step is quantitative. Four of the small samples of the W-Mo alloy were analyzed and the following results were obtained.

Table 6. Results of Mo Analysis of W-Mo Alloy

Sample	% Mo
#1	23.82±0.54[a]
#2	24.24±0.87
#3	24.36±0.51
#4	23.41±0.42

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[a] Limits quoted are $ts/\sqrt{n}$ for the 95% confidence level; $n = 6$.

Analysis of similar samples by differential spectrophotometry [7] gave results of 23.90±0.06% and 23.75±0.15% which is in good agreement with the activation analysis results.

The procedure has also been applied to the determination of Mo in NBS Standard Reference Material steels with the following results

Table 7. Results of Mo Analysis of SRM Steels

SRM No.	% Mo Found in this Work	NBS Certified Value
101e	0.428 ±0.005	0.426
20g	0.00260±0.00009	0.002, 0.003
36b	1.08 ±0.02	1.00

A paper describing this work was presented at the 156th National Meeting of the American Chemical Society held at Atlantic City, New Jersey, September, 1968. This paper has now been submitted for publication.

2. Ultrapure Reagents: Use of the Freezing Technique in the Quest for the Absolute Blank

In any analysis procedure, it is imperative to know the "blank" value, that is, the contribution to the analysis by the technique itself. Ideally, the blank will be zero, as when in activation analysis a solid is irradiated and then etched to remove any surface contamination. The sample can then be weighed and the analysis continued without consideration of a blank value. However, when sub-ppm levels of trace elements are to be determined in liquids, the possibility of leaching of impurities from the container is a serious problem. Brune [8] has shown that significant amounts of impurities are picked up from either polyethylene or quartz by both leaching and nuclear recoil processes. In the analysis of ultrapure reagents at NBS this blank problem is especially critical, since these reagents will be used by many other analytical competences for trace element analysis, and the "true" impurity content must be known.

The ultrapure reagent program and the special problems associated with it has been discussed previously [9]. This preliminary work demonstrated the need to develop a method of determining the blank values for the analysis of liquid reagents. An alternative would be the development of a procedure for analysis of these reagents which would eliminate contamination by the container, thus producing an "absolute blank."

The technique of freezing liquid samples prior to irradiation has been used previously both for the retention of volatile elements and for the prevention of contamination from container materials [10,11]. The procedure used consisted of irradiating the frozen samples allowing the surface to melt slightly to remove surface contamination, and processing for radiochemical separation or counting. After consideration of the possible methods of blank determination and reduction, this freezing technique was chosen as the most promising. This report describes experiments performed in an attempt to use the freezing technique to determine the trace metals content of high purity water without any contamination from the container materials. (This could then be considered an absolute "blank" for any reagents prepared with this water.)

a. <u>Experimental</u>

There has been a great deal of thought on which method is best for the taking of the sample. The high purity water used in the procedure development was filtered, deionized, 18MΩ water from a recirculating still. Ideally the sample should be frozen without contacting any container after removal from the still. This was accomplished by letting the water drip slowly from the top directly into a clean dewar of filtered liquid nitrogen (fig. 16a). The ice is caught in a clean platinum gauze basket before touching the sides or bottom of the dewar [technique 1]. There was, however a possibility that the droplets might pick up microscopic bits of frozen water from the liquid nitrogen so a second technique was developed to cross-check the results. This consisted of allowing the water droplets to fall directly into a frozen section of rigorously precleaned medical grade polyethylene

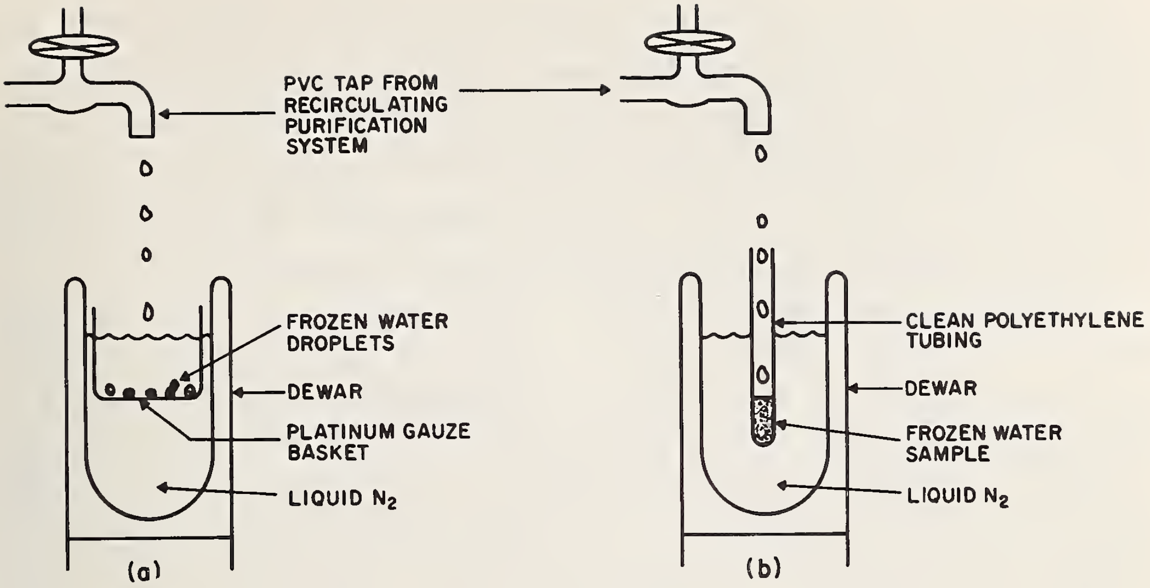

Figure 16. Technique for rapid freezing of ultra pure reagents
(a) Direct freezing method
(b) Polyethylene encapsulation freezing method

tubing. The bottom end of the tubing was heat sealed and immersed in liquid nitrogen leaving ∿1 inch protruding (fig. 16b). The water drops then only contact the polyethylene at -196°C, at which temperatures they freeze immediately [technique 2]. Using this technique the samples are larger and more easily "etched" after irradiation.

The samples are sealed before irradiation to prevent contaminants from contacting the samples, and to prevent atmospheric water from freezing on the surface of the samples and contaminating them. Using technique 1, the individual frozen droplets must be selected and transferred to cooled polyethylene tubing similar to the one described for technique 2. Forceps with polyethylene tubing covering the tips were used. For both techniques the tubing was clamped shut with a hemostat and the end heat sealed. This can be done with the other end either in liquid nitrogen, or quickly lifted out during sealing and then reimmersed. The samples are then ready for irradiation.

To date all irradiations were in the NRL Reactor, and were accomplished using a polyethylene bucket filled with dry ice. Refilling the bucket was necessary at about 15 minute intervals. After irradiation for 30-60 minutes the samples are removed and stored in dry ice for subsequent "etching" and counting (with or without radiochemical separations).

With the new NBSR facility, the irradiation procedure should be a great deal simpler. By packing a rabbit full of dry ice (with vent holes to let the gaseous carbon dioxide produced escape) an irradiation of at least 5-10 minutes at $4x10^{13}n.cm^{-2}.s^{-1}$ should be possible without refilling, which would be roughly equivalent to the 30-60 minutes at NRL. Longer irradiations, or use of a higher flux pneumatic tube, could be used to increase the sensitivities, although replenishing the dry ice might be required.

After irradiation, the samples are removed from the polyethylene container, allowed to warm to ~0°C, and "etched" to remove surface contamination. With the frozen individual droplets (technique 1) the samples are placed into a clean platinum gauze basket, and immersed into several different water baths, sequentially. The water baths are cooled to approximately 5-10°C, so the samples do not melt too quickly and the samples are rolled about in the basket to equalize surface contact and "etching." After about 20% of the mass has been removed, a blast of high pressure nitrogen gas is used to remove excess water, and the samples transferred to a clean container and allowed to melt. For samples prepared with technique 2, the solid sample is removed from the polyethylene tubing by cutting off one end, inserting halfway in a beaker of room temperature water for ~5 seconds, then squeezing the bottom of the tubing. The "etching" procedure is identical.

The element(s) of interest determined whether or not radiochemical separations were used. Sodium-24 activity is usually present in amounts that may mask other activities so radiochemical separations were usually employed. Also ^{41}Ar and ^{18}F produced from dissolved air and the water matrix may also mask other activities. The samples have been counted using gamma-ray spectroscopy, almost entirely with (NaI(Tl) detectors to increase the sensitivity, although some work has been done with a Ge(Li) detector.

In the future, βγ and βγγ coincidence counting will be used to lower the background.

b. Results and Discussion

Activity to date has been directed primarily to developing the techniques necessary to give meaningful results. Tests of the etching technique with ^{137}Cs indicated decontamination of at least a factor of 10 from contamination on the surface of the frozen droplets. Later refinements in the technique should increase this factor.

A test of the technique itself was made using copper which was found to be present in the high purity water irradiated as a liquid. The results in table 8 indicate that some contamination was picked up from the container when the samples were not frozen.

Table 8. Preliminary Results Using the Freezing Technique

No.	Sample	Procedure	Copper Conc. (ppb)	Sample Size (g)
1	Liquid Water	Poly Tubing	0.74	5
2	Liquid Water	Synthetic Quartz	0.74	5
3	Frozen Water	Technique 1	0.4	0.9
4	Frozen Water	Technique 2	0.45	5

(D. A. Becker)

3. Analysis of Ancient Stained Glasses by Neutron Activation Analysis

In cooperation with the Smithsonian Institution and Mrs. Jacqueline Olin, a guest worker at NBS from the Smithsonian, a program is in progress to study the characterization of medieval stained glasses using neutron activation analysis. Procedures have been developed using stained glass from the Washington National Cathedral and simulated medieval stained glasses prepared by Corning Glass, which incorporate both nondestructive analysis and radiochemical separations. Sodium removal with hydrogen antimony pentoxide (HAP) as described by Girardi and Sabbioni [12] and solvent extraction procedures have been used. To date four blue glasses and one green glass have been examined and all have different compositions of both major and minor constituents. Two spectra of one of these glasses taken 8 min. apart are shown in figure 17. The decay of 2.3 min. ^{28}Al, 3.75 min, ^{52}V, and 5.10 min. ^{69}Cu can be readily observed. It is expected that these procedures will be applied to the analysis of medieval stained glass samples in the near future.

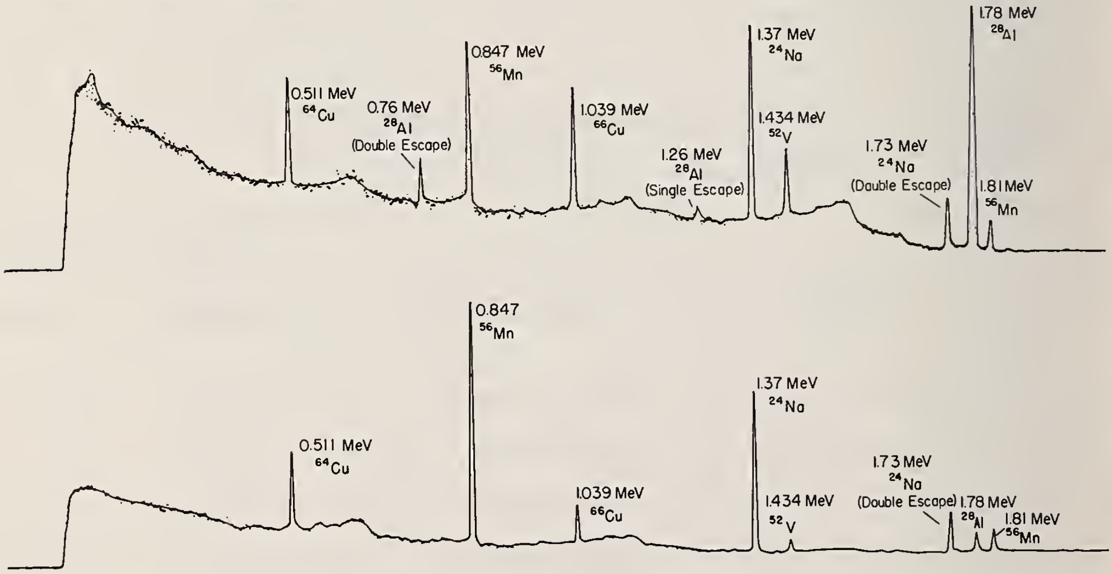

Figure 17. Gamma-ray spectra of an ancient stained glass sample at different decay times

(B. A. Thompson and J. Olin)

4. Rapid Radiochemical Separation of Uranium

The Activation Analysis Section is planning the compilation of a set of standard radiochemical separation procedures for use in the activation analysis of many of the elements. Many times when an analysis is needed quickly but cannot be done nondestructively, much time and effort is expended in searching out and evaluating the many radiochemical separations in the literature. It would be advantageous to have a set of standard procedures, including methods of separation from various matrices, for a given element. These would have been proven by repeated use, and would take advantage of the advanced instrumentation now available. As an example, for most situations, a quantitative separation of 2 to 5 elements in a group is much to be preferred to the isolation of a single element in high purity with a 60% yield, since solid state detectors usually may be used to resolve the gamma rays of a group of this size with little or no uncertainty.

An example of how handy this type of compilation would be occurred recently when the need for an analysis for trace amounts of uranium was requested. The inorganic chlorides to be analyzed contained many radioactive isotopes upon neutron irradiation, and the low energy, 75 keV, gamma-ray of uranium-239 was completely lost in the Compton continuum. The possibility of using the decay product neptunium-239 was considered also, but the matrix did not decay rapidly, and thus both techniques would require a radiochemical separation. For analysis using ^{239}U, which has a 23.5 m half-life, the uranium separation would have to be rapid.

Solvent extraction characteristics using the reagent bis(2-ethylhexyl) orthophosphoric acid (HDEHP) have been studied in great detail in this laboratory, and it was inevitable that this reagent should be suggested for the analysis.

a. Experimental

The samples and standards were irradiated for 30 seconds in the NBSR RT-3 pneumatic tube facility, at a thermal neutron flux of approximately 1×10^{13}n.cm^{-2} s^{-1}. After irradiation, they were allowed to cool for 1-2 minutes, and then transferred to a radiochemical hood for processing.

Previous experience with this reagent suggested that uranium would extract into HDEHP quantitatively in about 10 seconds from solutions of 1-10$\underline{M}$ nitric or perchloric acids.

The procedure is as follows. The irradiated sample was dissolved in 10 ml of 8$\underline{M}$ HNO_3 containing ∿50 μg of U carrier in a separatory funnel. Ten milliters of a solution of 0.75$\underline{M}$ HDEHP in petroleum ether was added and the mixture vigorously shaken for ∿1 minute. The two phases were allowed to separate and the aqueous phase was drawn off and discarded. The organic phase was washed twice with 10 ml of 8$\underline{M}$ HNO_3 for 30 seconds each time. After drawing off the last wash, a transfer pipet was used to very carefully remove the organic layer. This procedure prevents possible contamination by small amounts of the aqueous phase still clinging to the sides of the funnel stem. Total time for analysis is approximately 15 minutes.

b. Results and Discussion

Tracer studies using synthetic samples showed consistent yields of >99.9%. While some fission products are known to extract using these conditions, their activity was much less than that of ^{239}U.

Analysis of the samples submitted revealed no detectable amount of uranium. Sensitivity calculations indicate that the upper limit of uranium concentration in these samples is 0.016 ppm.

Increased sensitivity could be obtained for the analysis by irradiating in a higher neutron flux or for a longer period of time or both. Analysis of sub-ppb levels should be possible for a 20 minute irradiation at 10 MW, although the extraction of several of the fission products (e.g. ^{101}Mo and ^{97}Zr) may require another decontamination step (e.g. washing with HF may be possible).

(D. A. Becker and P. D. LaFleur)

D. Analysis of Standard Reference Materials (SRM)

1. Activation Analysis of SRM Steels Using Group Radiochemical Separations

The group radiochemical separation procedure described in NBS Technical Note 458 [1] and in the literature [4] has been applied to the analysis of a number of SRM steels. The procedure consists of two solvent extraction steps, thus dividing the sample into three groups. In the first step W and Mo are extracted into CHCl$_3$ from 3 N HCl as the α-benzoinoxime complexes. In the second step Fe and Sb are extracted into isopropyl ether from 7.5 N HCl. The W-Mo fraction is counted with a NaI(Tl) detector for W and, after ^{187}W has decayed, for Mo. The two fractions from the ether extraction are counted with a Ge(Li) detector for Cu, Cr, As, Co, Sb, Ga, and La. Where appreciable amounts of Ta are present, this element can be determined in the W-Mo fraction. The results reported on the various steels analyzed are given in the following tables.

Table 9. Results of Analysis of SRMs 101e, 101f, and 101g

Element %	101e[a]	101f	101g
Cu	0.355 ±0.016[b]	0.0289 ±0.00099	0.0292 ±0.0011
Co	0.017 ±0.013	0.0864 ±0.0028	0.0901 ±0.0023
W	0.0458 ±0.083	0.000261±0.000026	0.000282±0.000023
Mo	0.445 ±0.043	0.00862 ±0.00077	0.00286 ±0.00042
As	0.00769±0.00022	0.00283 ±0.00016	0.00277 ±0.00017
Ga	0.00444±0.00046	0.00398 ±0.00028	0.00325 ±0.00009
Sb	0.00504±0.00054	0.00092 ±0.00013	0.00130 ±0.00015

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[a] Limits quoted are $ts/\sqrt{n}$ for the 95% confidence level; n = 6.

[b] n = 5.

Table 10. Results of Analysis of SRMs 20g and 36b

Element %	20g	36b
Cu	0.003396±0.00079[a]	0.1882 ±0.0018
Co	0.00276 ±0.00024	0.01144±0.00016
Cr	0.0177 ±0.0013	2.286 ±0.030
Mo	0.00260 ±0.00009	1.08 ±0.02

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[a] Limits quoted are $ts/\sqrt{n}$ for the 95% confidence level; n = 6.

Table 11. Results of Analysis of SRMs 1261, 1262, 1265

Element %	1261	1262	1265
Cu	0.0418 ±0.0014[a]	-	0.00530 ±0.00015
As	0.0174 ±0.0007	-	0.000307±0.000020
Co	0.0253 ±0.0008	-	0.00607 ±0.00029
W	0.0152 ±0.0009[b]	-	0.000068±0.000020
Cr	0.605 ±0.020	-	0.00600 ±0.00045
Zn	-	-	<0.02
Sb	0.00145±0.00011[b]	0.0104 ±0.0004	<0.001
Ta	0.0277 ±0.0031[b]	-	-
La	0.00077±0.00004	0.00055±0.0004	-

---

[a] Limits quoted are $ts/\sqrt{n}$ for the 95% confidence level; n = 6

[b] n = 5.

Table 12. Results of Analysis of SRMs 1155 and 160b

Element %	1155	160b
Cu	0.194 ±0.006[a]	0.199 ±0.006
As	0.0097±0.0006	0.0107±0.0004
Co	0.101 ±0.005	0.101 ±0.0003

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[a] Limits quoted are $ts/\sqrt{n}$ for the 95% confidence level; n = 6.

Not all the above elements were determined in each steel and in fact for some, information was only required about a few elements. Typical spectra of the two fractions obtained from the ether extraction are shown in figures 18 and 19.

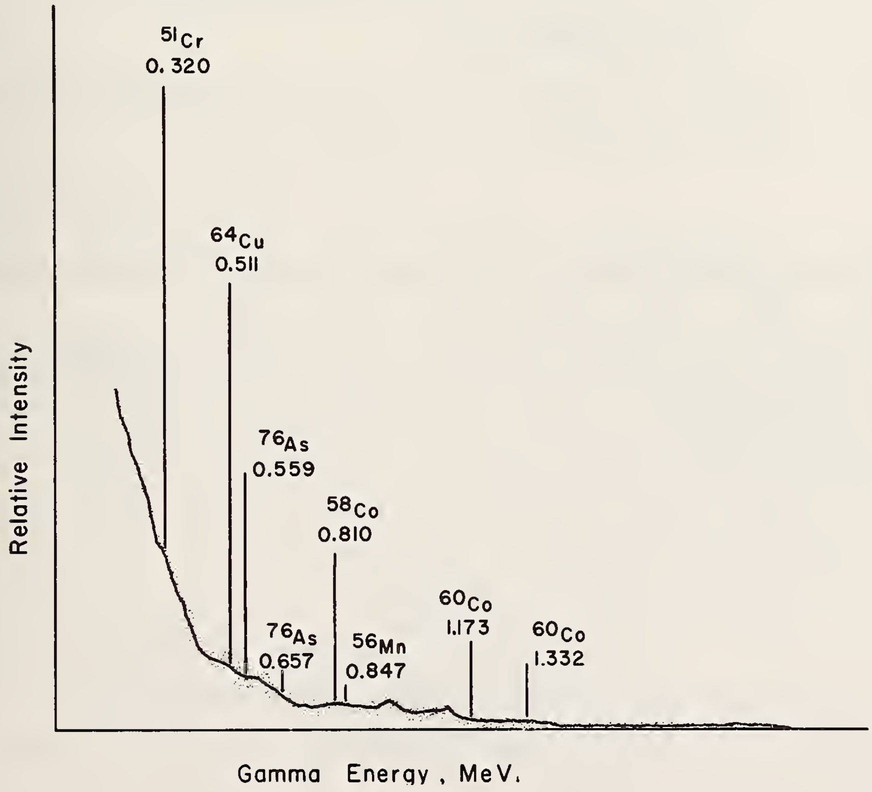

Figure 18. Ether fraction from group separations method

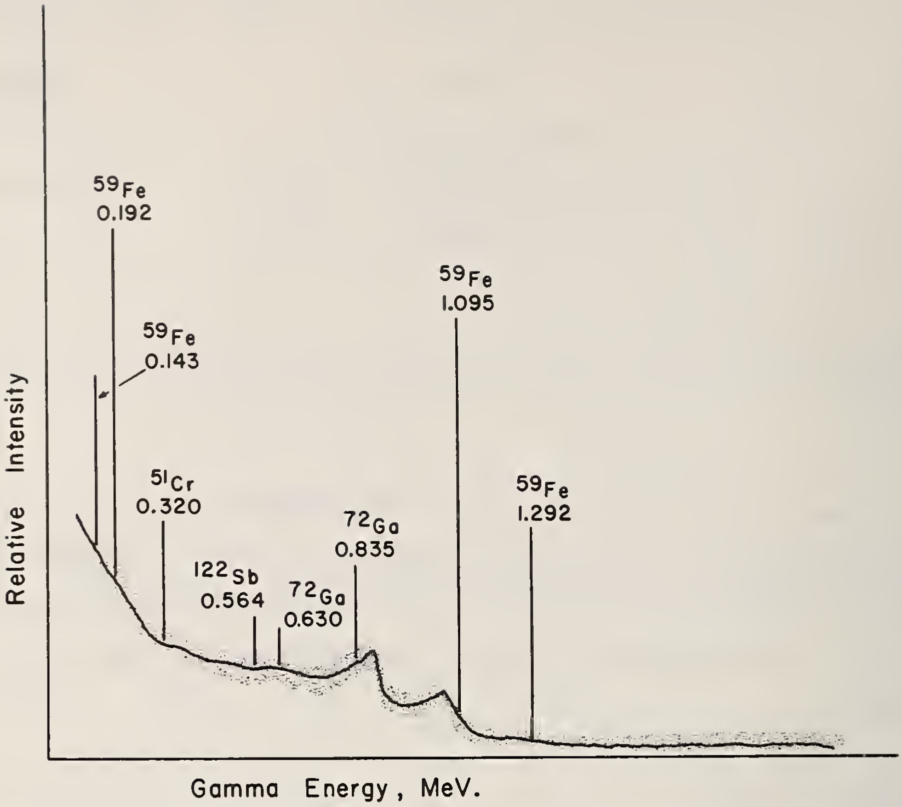

Figure 19. Aqueous fraction from group separation method for SRM steels

(B. A. Thompson)

2. <u>The Determination of Manganese and Vanadium in SRM Nos. 16b, 115, 1265, 1261, 36b, 20g.</u>

As a part of the NBS Standard Reference Material program, manganese and vanadium were determined in samples of six different steels using nondestructive neutron activation analysis. Similar analyses were reported in previous progress reports [1,9]. Possible interfering contributions to the gamma rays used in the analysis were evaluated by their half-life determinations and high resolution Ge(Li) gamma ray spectroscopy. No such contributions were discovered. For counting, a 3 in. x 3 in. NaI(Tl) scintillation detector and a 400-channel pulse height analyzer were used.

Due to the high manganese and low vanadium content in five of the samples, interference was expected in the vanadium analysis from the Compton continuum from the 0.845 MeV and 1.81 MeV gamma rays of manganese-56. Therefore, several preliminary experiments were performed which showed that better accuracy could be obtained when a complement subtraction technique was used. The following data shows the same sample analyzed with and without subtraction.

Table 13. Comparison of Vanadium Results in SRM 1261 With and Without Complement Subtraction of the Manganese Activity

	Vanadium Concentration (%)	
Sample No.	Without Subtraction	With Subtraction
1	0.0127	0.0113
2	0.0125	0.0108
3	0.0123	0.0107
4	0.0130	0.0113
5	0.0132	0.0106
6	0.0127	-
Average % V	0.0127±.0003[a]	0.0109±.0004[a]

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[a] ± values are $ts/\sqrt{n}$ @ 95% C. L.

The results obtained using the subtraction technique agree with those from other analytical methods.

a. Experimental

Samples were analyzed as received. Approximately 100 mg each of steel was sealed in a polyethylene snap-cap vial. Solution standards of vanadium (99.9+%) were pipetted onto filter paper (free of vanadium) inside the vials and evaporated. The vials were then heat sealed. Copper foils were attached to both the samples and standards.

The procedure used was as follows:

(1) The sample or standard was irradiated 1.0 minute.

(2) The sample was allowed to decay for 2.0 minutes. During this time the flux monitor was removed and the sample positioned on the detector.

(3) At the end of the decay time, the sample was counted for 4.0 minutes clock time in the add mode. The live time data is read out in channel zero.

(4) The vanadium is allowed to decay and manganese is subtracted by accumulating for approximately 4.4 minutes in the subtract mode.

Manganese-56 (2.56 hours half-life) was counted after the V and other short-lived activities had decayed. The peak areas of both manganese and vanadium were integrated using Covell's method [13]. The concentration of Mn for each sample was then calculated using the standard-comparator method. Flux variations from sample to sample were normalized using the flux monitors. Self-shielding and gamma-ray attenuation was calculated and found to be negligible for these conditions.

b. Results and Discussion

The analysis results for the six SRM's can be found in table 16. Replicate samples agree very well with each other and there appears to be no evidence of inhomogeneity within the limits of the precision of the analysis.

Table 14. Results of Manganese and Vanadium Analysis of SRMs 1261, 1265, 1155, 160b, 20g, 36b

SRM Sample	No. of Samples	Average % Mn Found	No. of Samples	Average % V Found
1261	6	0.6372±.0027	5	0.0109 ±.0009[a]
1265	8	0.0074±.0002	9	0.00054±.00002
1155	6	1.620 ±.034	6	0.0482 ±.0023
160b	6	1.634 ±.030	6	0.04864±.0017
20G	4	0.825 ±.051	4	0.0013 ±.0004
36b	3	0.402 ±.014	3	0.0031 ±.0003

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[a] Errors are reported as $ts/\sqrt{n}$ at the 95% confidence level.

(T. E. Gills and D. A. Becker)

3. The Analysis for Lanthanum, Tantalum and Selenium in SRM Special Iron No. 1265

The Office of Standard Reference Materials requested analyses for La, Ta, and Se as part of acceptance testing of a new SRM Iron. This particular iron (#1265) was the starting material for a series of special irons (#1261-1265) and was expected to have low concentrations of most of the elements of interest.

a. Experimental

The samples, which consisted of iron turnings, were weighed and encapsulated in polyethylene snap-cap vials. Standards of the elements of interest were also prepared. Copper foil flux monitors were attached to both samples and standards for later normalization of the neutron flux values. The samples and standards were irradiated for 4 hours in the NRL Reactor at a thermal neutron flux of approximately 8×10^{12} $n.cm^{-2}.s^{-1}$. After irradiation, the samples were brought back to NBS and allowed to cool for about one day. A 1000 minute count was made using a large volume Ge(Li) detector and a 4096 channel pulse height analyzer. The resulting spectrum was used for the lanthanum and tantalum analysis. As no gamma-ray peaks for tantalum-182 were observed, an upper limit for the tantalum content was calculated.

Due to the relatively low energy gamma rays and low sensitivity for selenium-75, a chemical separation was necessary to determine selenium. The procedure used was the precipitation of selenium metal with hydroxylamine-hydrochloride. The samples were dissolved in a mixture of nitric and perchloric acids, with ∿30 mg of selenium carrier present. After complete dissolution, the solution was taken to fumes of perchloric acid, making certain that nitric acid was present until all carbon (or organic material) was oxidized off. The resulting solution was taken up in 3<u>M</u> hydrochloric acid, and ∿10 ml of a 25% solution of hydroxylamine-hydrochloride added.

Several hours heating at 90°C assured complete precipitation of the selenium. The solution was cooled, filtered onto a glass-fiber filter pad, and counted. Tracer studies on similar samples which were not irradiated showed the chemical yield to be greater than 99%.

b. Results and Discussion

The lanthanum concentration found was 0.008 ppm. Since lanthanum is one of the more abundant rare earths, this value could be used to estimate the content of the other rare earth elements.

No tantalum was detected in these samples. The amount which would have been seen under these conditions was calculated to be 0.2 ppm; therefore, the amount of tantalum present is <0.2 ppm.

No selenium-75 was detected. The calculated upper limit was found to be 0.3 ppm.

(D. A. Becker)

4. The Determination of Homogeneity of Picogram Quantities of Sodium by Neutron Activation Analysis

The NBS Standard Reference Material program has just recently made available its first microstandard particles. These microstandards are small (5-25μ diameter) calcium loaded ion exchange beads, and are certified for calcium content[14]. The production and coordination for this SRM was provided by the Separation and Purification Section of the Analytical Chemistry Division.

The Activation Analysis Section was asked to determine the homogeneity of sulfonation of these ion exchange beads, since it was the only analytical competence with the capability of analysis at the picogram level for a convenient ion with the requisite precision (2-5%). The ion exchange beads were loaded with sodium for this analysis, since sodium can be determined at the required levels while calcium cannot.

The homogeneity of the sodium (in units of picogram/μ^3) was used to establish the uniformity of sulfonation of the ion-exchange copolymer. Then saturation loading of the beads with calcium ions yields a known amount of calcium per unit volume of bead.

a. Experimental

The samples, 1-2 mg of bulk sodium loaded ion-exchange beads, were encapsulated in quartz and irradiated for 5-7 hours in the glory-tube facilities of NRL Nuclear Reactor at a thermal neutron flux of $\sim 8 \times 10^{12} n.cm^{-2}.s^{-1}$. The samples were immediately returned to NBS and H. Dixon, of the Separation and Purification Section, selected individual beads for analysis using micromanipulators. Each bead selected was photographed under a microscope at a known magnification and prepared according to the specified procedure [14]. Although some irregularities in bead shape were noted, most beads were spherical. The beads to be analyzed by activation analysis were selected to be as nearly spherical as possible, since the measured diameter was used to calculate the volume of the resin bead.

After selection the beads were prepared for counting by sealing the individual resin beads between two 10 mil thick plastic scintillator disks. These disks were than mounted on the 3/4" phototube assembly and counted using the $\beta\gamma\gamma$ sum coincidence spectrometer described elsewhere in this report (see section 3.B.1).

Three of the samples were positioned between two 4"x8" NaI(Tl) gamma-ray scintillation detectors. The system logic requires that a beta particle and two gamma-rays (one in each detector) be detected within the resolving time of the coincidence unit. When such an event occurs, the pulses from the two gamma-ray detectors are summed and presented to the input of a pulse height analyzer. The pulses from each of the three samples are stored in a separate quadrant of the analyzer.

Since the sum of the two gamma rays of sodium-24 is 4.12 MeV, the energy range of the pulse height analyzer was set at 0.1-4.5 MeV. Most samples were counted for 900 minutes, and at least two sets of three samples were counted from each irradiation. A total of 42 resin beads, from five different irradiations, were analyzed for their relative sodium content. The standards used were several small granules of sodium sulfate (53-132 μg Na), and were irradiated for 1 minute in the same irradiation facility. All samples and standards had a copper-lead alloy flux monitor attached to normalize irradiation conditions. After irradiation, individual granules of the sodium sulfate were sealed in the plastic scintillators and counted exactly the same as the samples. Considerable decay was allowed for the standards so that the count rate was comparable to the samples, since serious errors can result when a comparison is made between sources with large differences in counting rate.

For the analysis, the total counts from 0.1-4.5 MeV were used, with an average background subtracted. The total background from 0.1 MeV-4.5 MeV averaged 3 counts per hour. The decay of several of the samples was followed for several half-lives and the purity of the sodium-24 radioactivity verified. In addition, a gross sample of the irradiated resin beads were counted on a 45cc Ge(Li) semiconductor detector and 4096 pulse height analyzer. No radioactivity other than sodium-24 was observed.

b. Results and Discussion

The results of the analysis are shown in table 15. The sodium concentration found (the ratio of sodium to unit volume) was approximately constant, averaging 0.136 pg/μ^3 with an uncertainty of 2% ($ts/\sqrt{n}$ @ 95% confidence level). The size distribution of samples analyzed is found in figure 20. Considering the difficulty in locating and separating the individual beads, the size distribution seems to adequately

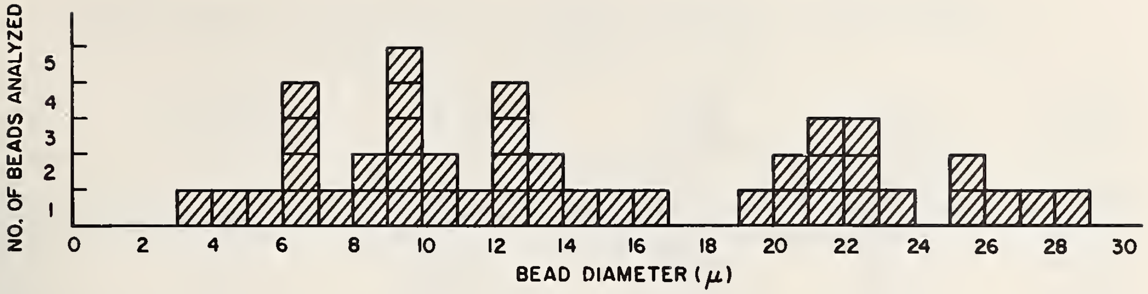

Figure 20. Size distribution of microstandard beads analyzed

represent the bead size range in the bulk sample. There is no immediately apparent systematic bias due to sample size. However, it can be seen from table 16 that the precision of the sodium concentration decreases significantly with bead diameter. This is to be expected, since the counting statistics are greater (fewer total counts) and the uncertainty in the measurement of the bead diameter is greater. It is not presently known whether some of the decrease in precision of the smaller beads is also due to an inhomogeneity in sulfonation in the resin bead itself.

The precision of the technqiue is estimated at ±2%, as determined by repetative counting of sodium-24 and cobalt-60 standards. The accuracy of the analysis is estimated to be ±10%, due primarily to the possibility of error introduced in the vastly different irradiation times for standard and samples. Additional work will be done on some larger beads and on an accurate determination of absolute sodium sensitivity.

One possible bias which has not yet been investigated is the effect of irradiation on the resin bead size. Since the size measurement for these analyses was made after the irradiation, the radiation effects on the bead, such as increased cross-linking of the polymer produced by the large neutron and gamma-ray fields in a nuclear reactor, could have a significant effect on the final bead size. This effect will be evaluated in the near future.

Table 15. Sodium Content of Microstandard Beads

Bead No.	Run No.	Net Counts	Diameter (μ)	Sodium per bead (pg.)	Sodium Conc. pg./$(\mu)^3$
1376	1-1A	41,260	16.776	320	0.129
1380	1-1B	9,315	9.793	66.3	0.135
1378	1-1C	7,099	9.327	53.6	0.126
1379	1-2B	9,367	12.659	148.1	0.140
1394	2-1A	10,128	10.877	86.9	0.129
1395	2-1B	5,085	8.247	39.9	0.136
1396	2-1C	12,432	11.549	103.6	0.128
1391	2-2A	7,806	12.950	152.3	0.134
1392	2-2B	9,703	13.770	173.0	0.127
1397	2-2C	6,231	12.132	118.1	0.126
1408	2-3A	25,996	26.315	1354	0.142
1409	2-3B	33,932	28.200	1617	0.138
1411	3-1A	2,271	6.470	20.2	0.143
1412	3-1B	501	4.012	04.08	0.121
1414	3-1C	7,348	9.553	63.6	0.139
1417	3-2A	1,185	6.691	22.9	0.146
1418	3-2B	1,370	6.510	24.2	0.167
1419	3-2C	2,516	8.646	47.2	0.139
1420	3-3A	1,461	9.701	61.6	0.129
1421	2-2B	5,000	13.786	192.9	0.141
1422	3-3C	5,273	14.318	216.4	0.141
1428	4-1A	1,375	5.896	14.7	0.137
1427	4-1B	325	3.755	03.19	0.115
1424	4-1C	3,541	7.925	36.9	0.142
1426	4-2A	860	6.356	20.2	0.150
1437	4-2B	3,285	10.201	70.5	0.127
1432	4-2C	2,364	9.229	53.9	0.131
1433	4-3A	4,207	15.253	251.7	0.136
1434	4-3B	13,847	22.088	757.8	0.134
1436	4-3C	2,197	12,555	127.9	0.124
1469	5-1A	61,653	22.730	861	0.140
1472	5-1B	61,771	22.107	789	0.139
1465	5-1C	93,374	25.896	1269	0.140
1475	5-2A	27,095	21.688	745	0.140
1474	5-2B	25,336	20.787	637	0.136
1471	5-2C	34,495	23.506	923	0.136
1477	5-3A	25,358	19.204	518	0.140
1473	5-3B	37,188	21,363	695	0.136
1481	5-3C	33,475	20.952	666	0.138
1480	5-4A	12,104	21.880	754	0.138
1479	5-4B	22,053	25.746	1256	0.141
1470	5-4C	25,697	27.749	1557	0.139

Table 16. Statistical Variation of Sodium Content With Microstandard Size

Microstandard Size Diameter	No. of Beads	Average Na Content (pg/μ^3)	Standard Deviation at 95% C.L.	$ts/\sqrt{n}$ at 95% C.L.
All Beads (3.7μ to 28.2μ)	42	0.136	13%	2.0%
Large Beads (20.0μ to 28.2μ	14	0.138	3.2%	0.9%
Medium beads (10.0μ to 19.9μ)	13	0.132_5	4.9%	3.5%
Small beads (3.7μ to 9.9μ)	15	0.137	18%	5.1%

(D. A. Becker)

5. The Determination of Impurities in Clinical Standards

The Office of Standard Reference Materials has begun a program of using a number of standards for clinical chemistry. The first of these standards, urea, createnine, uric acid, and calcium carbonate, have been issued. Because of the importance of trace metal content as possible enzyme poisons, the Activation Analysis Section was asked to survey these standards for trace metal and also for chlorine

a. Procedure

Samples of 1.0 gram of each material were irradiated for 1.0 hours at a flux of approximately $8x10^{12}n\ cm^{-2}s^{-1}$ in the in-core tube of the Naval Research Laboratory Reactor. Standards of the elements listed in tables 17 and 18 were irradiated simultaneously. Copper foils were attached to both samples and standards for flux normalization. For the determination of chlorine and aluminum, shorter irradiation and decay times were used.

Table 17. Analytical Conditions for the Determination of Cl, Al, and Na in Clinical Standards

Element	Isotope	Irradiation Time	Decay Time	Counting Time	Peak Energy Used (MeV)	Counting System
Aluminum	^{28}Al	1.0 min.	1.0 min.	4.0 min. Clock	1.78	NaI(Tl)
Chlorine	^{38}Cl	10 min.	10 min.	4.0 min. Clock	1.6	NaI(Tl)
Sodium	^{24}Na	1.0 hr.	1.0 min.	100 min. Live	1.36	Li(Ge)

Table 18. Impurity Content of Clinical SRM's

	Concentration of Impurities (ppm)			
Element	Urea	Createnine	Uric Acid	Calcium Carbonate
Sodium	9	30	170	0.5
Copper	.27	0.20	2.4	0.9
Zinc	.24	< .5		< .2
Manganese	.008	.07	.28	0.6
Gold	.0001	-	-	-
Arsenic	< .01	< .01	< .01	-
Antimony	< .01	< .01	< .01	-
Chlorine	<1	330	-	< .01
Aluminum	.9		-	-
Potassium	-		-	11

(T. E. Gills, D. A. Becker)

b. Sample Dissolution and Standard Preparation

After irradiation, each of the materials was allowed to decay for 2.5 hours. The samples were then dissolved in a mixture of HNO_3 and $HClO_4$ to destroy any organic material. The samples were then evaporated to incipient dryness and made to 100 ml volume with deionized water. Ten milliliter aliquots were taken for analysis.

The standards were dissolved and made to 100 ml volume with deionized water. Chlorine and aluminum were determined nondestructively.

c. Separations

Gold, Copper: To three 10 milliliter aliquots of each of the samples 25 ml of a 2M solution of hydrochloric acid was added. Ten milligrams each of copper and gold carrier was added to each of the samples. Ten milliliters of 50% thioacetamide was then added to precipitate the sulfides. The samples were heated to coagulate the precipitate and allowed to cool. The samples were then filtered, using glass fiber filter pads, dried and counted.

Manganese: Another three 10 ml aliquots were made to 25 ml and 6N HNO_3. Ten mg of manganese carrier and approximately 25mg of potassium bromate were added. The samples were heated until the manganese dioxide coagulated and then filtered onto a glass fiber filter pad, dried and counted.

Zinc: The remaining solution was divided into 10 ml aliquots and zinc carrier (20 mg) was added. The solutions were then made to .01N in sulfuric acid. Ammonium phosphate was then added and the zinc precipitated as zinc ammonium phosphate. The precipitate was filtered onto glass fiber filter pads, dried and counted.

The elements and standards were counted using a 3 in. x 3 in. NaI(Tl) detector and a 400-channel pulse height analyzer. Half-life determinations were made for verification of spectral purity.

The determination of chlorine, aluminum and sodium was made by varying the irradiation and decay times. Table 19 shows the procedure used.

Table 19. Results of Gold Analysis in the SRM Cobalt-Aluminum Flux Wires

Sample	µg gold/gm wire (ppm)
3	4.12
8	4.29
11	4.26
Average	4.2±0.3[a]

---

[a] Average is $ts/\sqrt{n}$ at 95% confidence level.

Standards of each of the above elements were irradiated and counted at the same geometries and time sequences. Flux monitors were used to normalize flux conditions. Live time used for aluminum and chlorine analysis were those in channel zero of the analyzer.

d. Results

The concentration of each element was determined using the standard-comparator method. The results of the analysis are given in table 18. Upper limits were calculated for arsenic and antimony.

6. The Determination of Gold in the SRM Cobalt-Aluminum Flux Wires

During the cobalt analysis of these SRM neutron flux wires a significant gold impurity was discovered. The gold radioactivity produced with short irradiation and decay times was considerably greater than that due to cobalt-60. Since the gold was present in the wire, the homogeneity of the gold was investigated to see if it could be used as a second flux monitor element.

a. Experimental

Three samples of cobalt-aluminum flux wire (∿40 mg each) were cut, encapsulated and irradiated for 5 minutes in the NBSR pneumatic tube facility, along with a gold standard. After irradiation the ^{24}Na produced by the fast neutron reaction ^{27}Al(n,α)^{24}Na was allowed to decay for several days. At the end of this time, the samples and standards were counted. The 0.412 MeV gamma-ray of the samples was followed for several weeks and the decay curve of the integrated peak plotted to verify the identification of and gamma-ray purity of the ^{198}Au. The experimental half-life of 65.0 h agreed well with the literature value of 64.8 h [15].

Special mention may be made here about the danger of using gold metal (foil or wire) as a standard for neutron activation analysis. Our results show a significant (19%) neutron self-shielding effect for 1 mil thick gold foil. This agrees quite closely to the 23% self-shielding for 1 ml gold foil as found by Reynolds and Mullins [16]. Of course, the exact self-shielding effect depends upon the neutron energy spectrum in the irradiation facility used. In addition, Reynolds and Mullins found a significant (∿5%) thermal neutron enhancement effect for aqueous samples ca. 1.5 ml [16]. Thus, it has been our practice to prepare gold standards by pipetting a small aliquot (50λ) of a freshly prepared gold solution onto a "bed" of filter paper (∿2mm thick) inside a polyethylene vial, allowing the water to evaporate, and then covering with a fresh disk of filter paper before sealing the vial. This extra filter paper assures the gold will not leave the "bed" area, and thus maintains a sharply defined counting geometry. The wire samples were coiled to produce a similarly shaped counting source. Blank samples of the vial and filter paper showed no detectable gold radioactivity for the conditions used for this analysis.

The gold homogeneity data was obtained from the same data accumulated for the cobalt homogeneity analysis. Four different sets of data were used, and the results are shown below.

b. Results and Discussion

The results for the gold analysis are found in table 19. Three different cuts were analyzed, and averaged 4.2±0.3 ppm gold. This value agreed well with an analysis by spectrophotometry, which gave a value of 4.5 ppm gold.

The results of the homogeneity study are found in table 20. The values given are in terms of relative gold concentration, since no gold standard was irradiated with these samples. This second set of results show good homogeneity, especially for this level of impurity, giving an uncertainty of 1.3% for $ts/\sqrt{n}$ at the 95% confidence level.

Table 20. Homogeneity of Gold in Cobalt-Aluminum Flux Wires

Bag No.	Sample No.	Relative Gold Concentration	Average Relative Gold Concentration
11	11-1	1.012	0.993
11	11-2	0.961	
11	11-3	1.005	
12	12-1	1.032	1.013
12	12-2	1.007	
12	12-3	1.000	
13	13-1	0.993	1.007
13	13-2	1.036	
13	13-2	0.992	
14	14-1	0.991	0.998
14	14-2	0.976	
14	14-3	0.996	
Average of four different bags			1.0008±0.0133[a]

[a] Uncertainty values of $ts/\sqrt{n}$ at 95% confidence level.

7. Analysis of Simulated Lunar Glasses

a. Introduction

The Office of Standard Reference Materials has begun a program to make available samples of glass to which traces of 61 elements have been added. As part of this program, studies are being carried out to characterize the base glass before the addition of these trace elements. The base glass is 72% SiO_2, 14% Na_2O, 12% CaO, and 2% Al_2O_3. When this glass is irradiated for sufficiently long times to permit determination of impurities at the ppm or ppb level, 20 or more mCi of ^{24}Na are formed. Recently Girardi and Sabbioni [12] have described the use of hydrated antimony pentoxide (HAP) for selective removal of sodium from solutions containing many other elements. We have used this HAP for removal of ^{24}Na from the irradiated glass samples.

b. Experimental

The samples are dissolved in HF-$HClO_4$ after rinsing in alcohol and dilute HNO_3 to remove surface contamination. The dissolution is somewhat lengthy because of formation of insoluble CaF_2 which precipitates onto the glass surface and inhibits further attack of the SiO_2 by HF. By alternately adding small portions of HF and evaporating to fumes of $HClO_4$ to decompose CaF_2, dissolution of a 1 gm disk of glass ∿ 1 cm in diameter can be accomplished in 1-2 hours. The solution is then taken to fumes of $HClO_4$ and fuming continued for at least 30 minutes to remove SiF_4 and all traces of HF and to reduce the volume of $HClO_4$. The cooled residue is taken up in 15-20 ml of 12 N HCl. The solution is passed through a HAP column containing ∿ 5 gm HAP from which the fine particles have been removed by slurrying with 12 N HCl. The column is washed with a small amount of 12 N HCl and the effluent is collected in a polyethylene bottle and counted directly with a Ge(Li) detector. The decontamination observed is such that the HAP column may be reading as much as 1-2 r/hr while no ^{24}Na peak can be detected in the effluent after counting for 100 minutes. Occasionally, poorer decontamination (factors of only 10^2-10^3) from ^{29}Na is obtained and it may be necessary to pass the effluent through a second HAP column. The consistency of the results obtained for the various elements present (except for K) regardless of the number of HAP columns used confirms Girardi's results on the lack of retention of elements other than Na and Ta by HAP. A typical spectrum of the Na-free glass solution is shown in figure 21. Peaks corresponding to ^{72}Ga, ^{140}La, ^{42}K, ^{47}Ca (from the CaO in the matrix) ^{122}Sb - ^{124}Sb, ^{64}Cu, ^{198}Au, and ^{47}Sc (from decay of ^{47}Ca) can be readily observed. Table 21 summarizes the results obtained to date. These results were all obtained using our new 47-cc

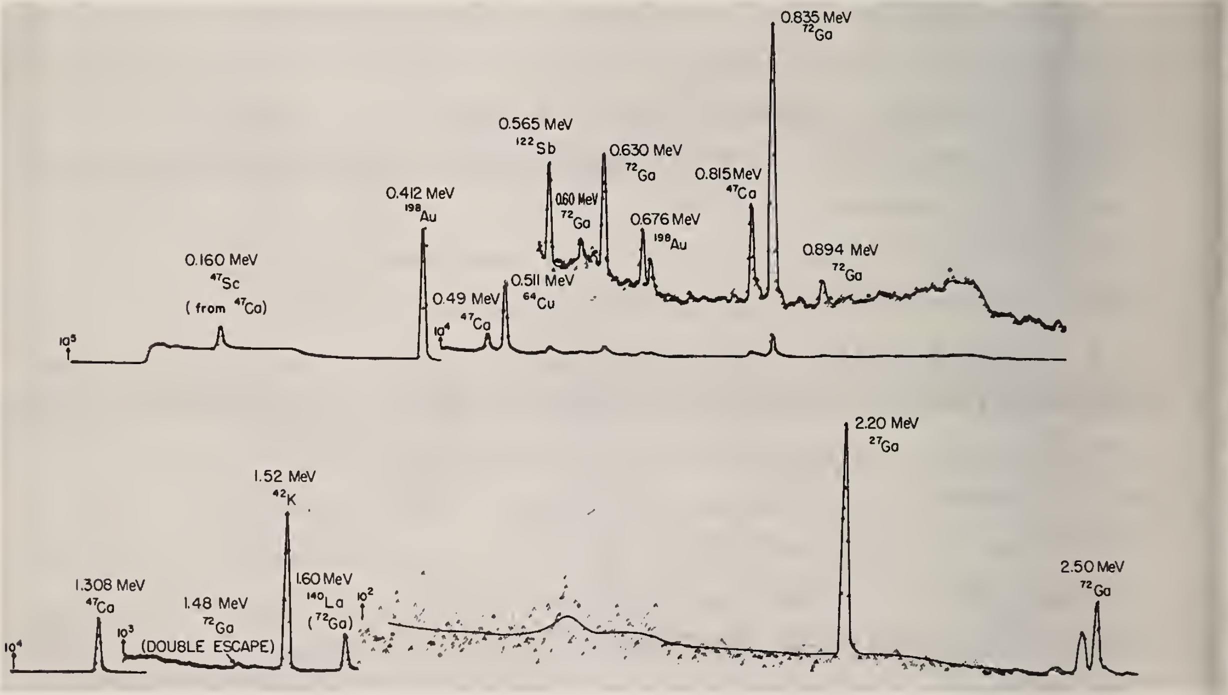

Figure 21. Gamma-ray spectrum of sodium-free glass solution

Table 21. Results of Analysis of Base Glass, ppm

Sample	Ca	Au	Sb	La	Ga	K
#61	0.91	0.22	0.064	0.032	0.34	25
#107	1.09	0.25	Not Determined			
#107A-1	0.95	0.26	0.076	0.033	0.33	8[a]
#107A-2	0.96	0 26	0.69	0.034	0.36	28
#61A	1.06	0.20	0.067	0.023	0.32	24[c]
#61A-2	1.29[b]	0.20	0.077	0.034	0.33	33
#87A-1	1.14	0.21	-	0.033	0.36	38
#87A-2	1.06	0.17	0.074	0.028	0.34	24
#31A-1	1.03	0.22	0.075	0.030	0.32	22
#31A-2	1.01	0.18	0.056	0.024	0.32	20[c]
#131A-1	1.05	0.18	0.064	0.030	0.34	29[c]
#131A-2	0.92	0.23	0.044	0.026	0.27	8[c]
#8A-1	1.04	0.18	0.064	0.026	0.32	8[c]
#8A-2	0.99	0.20	0.066	0.027	0.32	-
#41a-1	1.06	0.26	0.065	0.028	0.35	26
#41A-2	1.15	0.24	0.064	0.030	0.36	34
#117A-1	1.09	0.19	0.053	0.026	0.29	22
#117A-2	0.08	0.24	0.051	0.030	0.32	32

---

[a] 3 HAP Columns

[b] Some ^{24}Na present, possibly causing high results.

[c] 2 HAP Columns.

Ge(Li) detector, whose resolution is shown by figure 22 which is a plot of the 0.835 MeV peak of ^{72}Ga and the 0.847 MeV peak of ^{56}Mn as observed in this glass at an earlier time than represented by figure 21. A paper describing the results on the base glass has been submitted for presentation at the New York ACS meeting and for publication in the literature. The work will be continued incorporating the doped glasses.

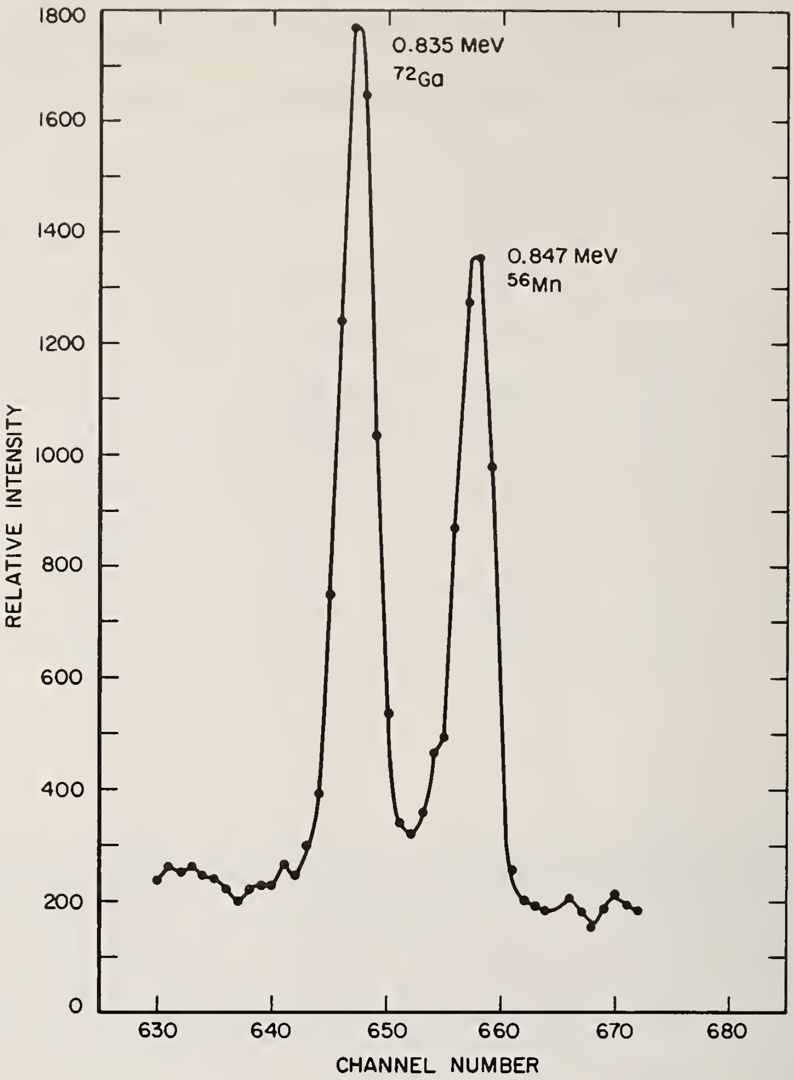

Figure 22. Resolution of gallium-72 and manganese 56 using a Ge(Li) detector

(B. A. Thompson)

8. Determination of Tungsten in SRM 480

Tungsten was determined by neutron activation analysis in the small samples of W-Mo alloy described above. The analysis was carried out twice. The first measurements were made on aliquots of the dissolved samples which had been irradiated in the glory tube facility of the NRL Reactor. The aliquots were counted using a 3 in. x 3 in. NaI(Tl) detector and a 256 channel pulse height analyzer and the area under the 0.480 MeV and 0.686 MeV peaks used as a measure of the W present.

The results obtained were:

Table 22. Results of W Analysis of W-Mo Alloy

	% of W
1	69.4 ±2.3[a]
2	73.1 ±1.8
3	68.4 ±0.9
4	67.75±1.2

---

[a] Limits quoted are $ts\sqrt{n}$ for the 95% confidence level; n = 6.

These results, added to the Mo results reported above, gave totals of less than 100%. It was noted during dissolution that small black flakes were present which were insoluble in HF-HNO_3 but which disappeared after fuming with $HClO_4$, indicating possibility of something other than W and Mo being present. However, it was decided to repeat the analysis as a check. Five additional samples were irradiated in the North rabbit of the NRL Reactor where the thermal-to-fast ratio is much higher and W was determined nondestructively. By using these two different irradiation facilities the magnitude of any resonance self-shielding could be observed.

The results obtained were:

68.92±1.26% W

confirming the previous values and showing that the resonance contribution is negligible. Results obtained by differential spectrophotometry also showed the sum of the W and Mo concentrations to be <100% in these samples.

(B. A. Thompson)

E. Service Analyses

1. Determination of Chlorine in Al_2O_3 and Ta_2O_5 by Activation Analysis

Several samples of single crystals of Al_2O_3 and of vapor-grown Ta_2O_5 were analyzed for chlorine by nondestructive neutron activation analysis. This determination was requested by the Inorganic Materials Division.

The samples, weighing about 200 mg each, were irradiated for 1 minute in the NRL rabbit. Two NH_4Cl standards were irradiated simultaneously with the samples. Both samples and standards were contained in polyethylene snap-cap vials with a Cu flux monitor taped to the outside of each vial. The samples were allowed to cool for 30 minutes, after which, they were transferred to new snap-cap vials and counted with a 3 in. x 3 in. NaI(Tl) detector and a 400 channel pulse height analyzer. The 1.60 and 2.17 MeV γ-rays of ^{38}Cl were used as a measure of the Cl present. The results showed less than 0.01% Cl in the Al_2O_3 and 0.02-0.03% Cl in the Ta_2O_5.

(B. A. Thompson)

2. Determination of Selenium in Electrodeposited Copper

The Activation Analysis Section was asked to determine selenium at the ppm level in a matrix of electrodeposited copper for the Electrolysis and Metal Deposition Section of the Metallurgy Division at NBS. There was a question as to whether the selenium present in the plating solution was finding its way into the copper deposit.

There are three distinctly different ways of performing this analysis, the choice being dictated by the sample characteristics. These are nondestructive analysis using selenium-77m ($t_{1/2}$=17s), nondestructive analysis using selenium-75 ($t_{1/2}$ =120d), and destructive analysis with chemical separation of selenium-75.

a. Experimental

The samples received were six pieces of copper metal, each several square inches in area and approximately .030 in. thick. The samples were cut in half to obtain duplicates for analysis. They had to be folded once to fit into the irradiation facility.

A test was made on one of the samples to see if selenium-77m could be used for the analysis. The large amount of copper radioactivity produced from even a very short irradiation (∿5 sec.) completely obscured any selenium present. Therefore, selenium-75 was used for the analysis.

The samples and a selenium standard were encapsulated in pre-cleaned polyethylene vials, and irradiated for two hours at a thermal neutron flux of $\sim 8x10^{12} n.cm^{-2}s^{-1}$. After irradiation, the samples were set aside for approximately one month to permit the copper radioactivities to decay. The selenium standard and copper samples were then counted using a large volume Ge(Li) γ-ray detector. The six selenium γ-rays at the proper energies and in the correct proportions (97keV, 3.3%; 121keV, 17%; 136keV, 57%; 265keV, 60%; 280keV, 25%; and 104 keV, 12%) served as positive verification of the selenium content. The 265keV peak was chosen for integration because of its higher abundance. Since the gamma-ray energies are quite low and the copper samples quite massive, it seemed likely that some gamma ray self-absorption was occurring in the sample. Calculations of estimated self-shielding showed that for a copper sample 1 mm thick the error would be ∿10%. Also, the counting geometry of the sample and standard were much different due to their different sizes, and this would be expected to create an additional bias. To determine a correction factor for these effects, two of the samples were carried through a chemical separation after the Ge(Li) counting.

The separation used was reduction of the selenium to the metal. After dissolution of the samples in dilute nitric acid with added selenium carrier present, several ml of perchloric acid was added and the samples evaporated to fumes of perchloric acid. The samples were taken up in ~10 ml of dilute HCl, and an excess of 25% hydroxylamine hydrochloride solution added. The solutions were heated at ~90°C for 1-2 hours, filtered through glass fiber filter pad, washed and mounted for counting. The selenium standard was treated identically. The separated samples and standards were counted on the Ge(Li) detector, this time with the same sample-detector geometry. Decay corrections were made in all cases.

b. Results

The results of this analysis are shown in table 23. These values include the correction factor determined by the chemical separations. The chemical separation has a yield of 99.9+% as determined by trials with synthetic samples. This agrees with the work of Gorsuch[17], who found that selenium does not volatize when heated in mixtures of nitric and perchloric acids. The estimated accuracy of the analysis is ±10%.

Table 23. Results of Analysis for Selenium

Sample No.	Weight (g)	Concentration Selenium (ppm)[a]
301-1 A	0.6319	10.3
303-1 B	0.6168	11.8
303-2 A	0.6234	11.0
303-2 B	0.6236	11.2
303-3 A	0.6771	11.8
303-3 B	0.6448	10.6
172-1 A	0.5883	0.8
172-1 B	0.5315	0.8
172-2 A	0.5790	0.4
172-2 B	0.5755	0.5
172-3 B	0.5986	0.7

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[a] Estimated accuracy of analysis is ±10%.

(D. A. Becker)

3. The Determination of Selenium by Neutron Activation Analysis

Selenium was determined in a number of organic and inorganic materials by nondestructive neutron activation analysis. These analyses were performed for the National Center for Urban and Industrial Health of the United States Public Health Service.

a. Experimental

The samples were analyzed as received. One hundred mg of each of the samples were encapsulated in a quartz ampoule. Selenium metal (99.9+%) was also encapsulated in quartz to be used as a standard. Copper foils were attached to both samples and standards for flux normlaization.

Both samples and standards were irradiated for five hours at a flux of approximately $8+10^{12}$n.cm^{-2}sec^{-1} in the glory tube of the Naval Research Laboratory Reactor. After irradiation the samples were removed from the quartz ampoules and placed in 2/5 dram poly vials for counting. The counting was done on a 30 cc Ge(Li) detector in conjunction with a 4096 pulse height analyzer. Verification of presence or absence of selenium was easily made using the four prominent selenium-75 gamma rays.

b. Results

The results of the analysis are given in the following table. For compounds where selenium was not detected upper limits are given. In most cases greater sensitivity could be obtained by radiochemical separations of the selenium before counting. The precision and accuracy of the results are estimated to be ±10 percent for the standard error.

Table 24. Selenium Content of USPHS Samples

Compound	Amount Found (ppm)
B-naphthylamine	< 2
1-amino-2-naphthol	< 1
Ethyl Carbomate	< 1
9, 10-dimethyl-1, 2-benzanthracene	< 1
3-methylchelanthrene	< 1
Beryl Ore	< 1
Low Fired Beryllium Oxide Lot #840	< 1
Benzo (α) pyrene	116
Betox 6	< 1
Beryllium Sulfate	< 1
Beryllium hydroxide	< 1
Nickel Sulfate	< 1

(Thomas E. Gills)

4. ACTIVATION ANALYSIS WITH THE COCKCROFT-WALTON NEUTRON GENERATOR

A. Introduction

In the time period covered by this report, research into possible application of the facility using 3 MeV neutrons from the $^{2}H(d,n)^{3}He$ reaction was emphasized. Information in literature pertaining to the use of 3 MeV (D-D) neutrons is virtually non-existent. Consequently, there was a need for quantitative analytical data which could provide a base for the evaluation of errors due to D-D neutron activation in 14-MeV neutron activation analysis, and to project possible new applications for 3 MeV neutrons for analysis purposes.

As was reported previously [1,18] the analysis of mixed halogens in photographic emulsions was made possible by the combined use of 14- and 3-MeV neutrons. This particular study provided sufficient incentive to initiate a systematic investigation for the measurement of D-D neutron activation response of most of the elements in the periodic table, with a view to establishing a catalogue of spectral and sensitivity data. Such catalogues for 14-MeV neutron activation analysis are quite common, however, one for D-D neutrons has not appeared in literature. Excluding the noble gases and the naturally radioactive elements, about seventy pure elements have been irradiated and gamma-ray spectra measured under normal experimental conditions, and sensitivities have been calculated. These data are presently being put into a form most useful to the analyst. Some typical information is given in this report.

Before information obtained from the above survey can be used in the assessment of systematic errors due to D-D activation in 14-MeV neutron activation analysis, the D-D flux build up with beam time on a tritium target must be determined precisely. Preliminary work has begun and special targets to be used in this study are presently being manufactured. These targets closely simulate a normal 0.8 Ci/cm^2

tritium target, the difference being the replacement of tritium by an equivalent concentration of hydrogen. By irradiating these hydrogen loaded targets, the build up of the 3 MeV flux as a function of integrated beam dose can be measured. These flux measurements can be used to predict D-D interferences in any analysis performed with 14-MeV (D-T) neutrons.

In addition, a research program has been initiated to evaluate thermalization of D-D neutrons using either D_2O or H_2O as moderators, with a view to the utilization of the thermal flux for the determination of key elements in geological samples. Although the incident D-D flux is about 200 times less than the D-T flux for our facility, thermalization of D-T neutrons is considered to be a very inefficient process due to significant contributions from the fast flux which can present serious interference problems. An analysis using thermalized D-D neutrons was very successful for the determination of sodium in a metallo-organic Standard Reference Material (SRM), and results from this study should yield many useful applications.

During the past year the neutron generator has been used for the analysis of four organometallic oil additives. Experimental details and final results are reported below. Comparisons with results obtained using chemical techniques on the same materials show good agreement. In addition to these analyses, service analyses have been provided to other sections of the Analytical Chemistry Division and some outside agencies. Notable among these are, the determination of oxygen in styrene-divinylbenzene copolymers used for the preparation of micro standard SRMs, and the analysis of oxygen in low-oxygen polyethylene vials manufactured by a special process.

Much of our total effort during the past year was concentrated upon the improvement and updating of the existing facility, which was prompted by breakdown of key ancillary components of the major facility, resulting in unavoidable downtime. Although repair in most cases represented only 10% of the total downtime, transportation of the defective device to and from the manufacturer accounted for the major portion of the delay. In order to avoid these delays in the future, we have gradually upgraded the facility itself as well as obtained sufficient knowledge to perform many of the repair functions in the laboratory. It is hoped that the entire facility will be self-sufficient in the near future. Some of the problems experienced and of interest to accelerator users have been described.

In the interest of maximum safety for all personnel in the vicinity of the neutron generator, additional 'fail-safe' devices have been installed and a rigid procedure for tritium contamination control established. In this respect the operational characteristics of the generator have been investigated from which optimum operating information can be obtained. Health physics survey information of the biological shield has also been given together with results of tritium monitoring of key accelerator components exposed to this environment over a long term period.

(S. S. Nargolwalla)

B. Research Activities

1. Experimental Spectra of the Elements and Calculated Sensitivities for 3-MeV Neutron Activation

In laboratories, both industrial and research, using neutron generators for activation analysis, effort has been primarily focused on the use of 14-MeV neutrons produced from the D-T reaction. The reason for this preferential use of the small accelerator is generally attributed to the high 14-MeV neutron output as compared with neutron outputs from the D-D reaction. Depending upon the acceleration voltage, target thickness and experimental configuration of the irradiation assembly, the 3-MeV neutron output from the D-D reaction is about 200-300 times lower. In certain applications, however, 3-MeV neutrons can be extremely useful. For example, undesirable radioisotopes induced only by 14-MeV neutrons due to the high threshold energies of the nuclear reactions, cannot be produced if D-D neutrons are used. The elimination of such interferences permits accurate analyses for major constituents which can be activated with 3 MeV neutrons. Further, certain elements have relatively large cross sections for (n,γ) or (n,n'γ) reactions at 3-MeV when compared to those for the matrix. If such samples were irradiated with thermal neutrons, matrix activation would prohibit the analysis. This "signal-to-noise" enhancement with 3-MeV neutrons can be exploited for certain applications. As described previously [1,18] the rapid and accurate determination of mixed halogens in a photographic emulsion matrix was possible only by the combined use of 14- and 3-MeV neutrons, because of the analytical constraints *viz*, rapid and nondestructive analysis. Although such applications may be limited in number, the importance of this aspect of accelerator usage was recognized and, we believe, justifies a detailed study. To provide solid groundwork for this study, a systematic investigation of D-D activation of the elements is necessary. This information can then be used to predict possible systematic errors in D-T activation from products induced by D-D neutrons from the D-D neutron flux build up as a function of deuteron beam time on a tritium target. This type of interference has been recognized for a long time, however, published data are confusing because of the lack of definitive information about target loading, beam characteristics and sample assemblies. All of these factors influence the flux build up from the interaction of a deuteron beam with embedded deuterons in a tritium target.

A knowledge of 3-MeV neutron activation spectra of the elements will be useful for evaluating this interference and may open up useful applications of 3-MeV neutrons. The calculation of experimental sensitivities under average laboratory conditions would be useful for the assessment of D-D interferences in D-T analyses. Much of this information has been published for thermal and 14-MeV neutron irradiations, but little or no information for 3-MeV neutrons has yet appeared. Since reaction cross sections for 3-MeV neutrons are virtually non-existent in the literature, we are systematically examining the gamma-ray spectra of each element under conditions normally found in most neutron generator facilities.

The investigation reported here involved the measurement of the gamma-ray spectra of seventy odd elements, excluding only those elements which are naturally radioactive and the noble gases. From the spectral data an experimental sensitivity was computed. The results from the entire study are presently being compiled for catalogue-type presentation. A typical gamma-ray spectrum is shown and useful analytical data are given below.

a. Experimental Facility

The neutron generator facility, which includes the neutron generator, pneumatic-tube transfer system, sample irradiation assembly, sequential programmer and associated counting and readout apparatus have been discussed in a previous report [1]. A fast point plotter was used to produce the spectra and deuterium targets (0.6 cc per cm^2) were utilized for the production of 3-MeV neutrons.

b. Procedure

The element or a pure compound of the element was irradiated in a D-D flux. The maximum limit placed on irradiation time was saturation or 20 minutes, whichever was shorter. In general, counting was started usually 0.5 min. after termination of irradiation and the counting time was the same as the irradiation time. Energy scale used for plotting varied from 2.5 keV per channel to 20 keV per channel. Printed teletype outputs were used to compute the experimental sensitivities. This method involved integration of pertinent

Table 25. 3-MeV Neutron Activation Data and Experimental Sensitivity

SAMPLE DATA

Element	Barium	$Z= 56$	
Sample	$BaCO_3$	Energy Scale:	5 keV per channel
Sample Weight	16.0904 g		
Element Weight	11.1976 g		
Sample Code	A		

ACTIVATION DATA

$T_{activation}$	T_{decay}	T_{count}	Neutron Flux ($n.cm^{-2}.s^{-1}$)
10 m	0.5 m	10 m	1.4×10^6

EXPERIMENTAL SENSITIVITY

Nuclear Reaction	Gamma Energy (MeV)	Half Life	Net Peak Counts	Experimental Sensitivity (Net peak counts/gram of element.$10^6 n.cm^{-2}.s^{-1}$)	
				Uncorrected for Sample Attenuation	Corrected for Sample Attenuation
$^{136}Ba(n,\gamma)^{137m}Ba$ $^{137}Ba(n,n'\gamma)^{137m}Ba$	0.662	2.554m	289260	1.8×10^4	2.3×10^4

peaks by a simple base line subtraction technique to obtain the net counts, and comparing the sensitivity per gram of pure element normalized to a D-D flux of $10^6 n.cm^{-2}.s^{-1}$. The observed sensitivity was corrected for sample attenuation using a method previously described[19]. Depending upon the amount of material available, three different types of samples were used Those listed under code A (see table 25) were packed in 8 cc capacity polyethylene vials. For code B type samples, 1.6 cc vials were used. Partially filled 1.6 cc vials are listed under code C. The absolute neutron flux was determined so that subsequent irradiations could be interrelated by using counts as registered by a neutron monitor. The stability of the neutron monitor was checked daily by irradiating a sample of ammonium iodide and monitoring the (n,γ) activity from the 25 minute ^{128}I activity under standard conditions. The ^{128}I activity was related to the neutron monitor count. Throughout these experiments the neutron monitor exhibited good stability.

c. Determination of Absolute D-D Neutron Flux

For this determination, a knowledge of the gamma-ray counting efficiency of the twin-detector system described previously [1] was necessary. This problem was quite complex because of the source-detector geometry shown in figure 23. A cylindrical standard source of ^{54}Mn closely approximating the sample in geometry was counted. The 0.84 MeV

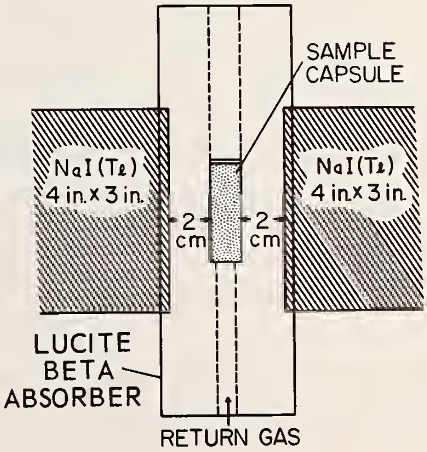

Figure 23. Source-detector counting geometry

gamma-ray peak was integrated and the detector efficiency calculated was 7.0%. Since the sample thickness can introduce systematic errors, this efficiency could only be related to a given sample by making appropriate corrections. A sample of Al_2O_3 was irradiated and the 0.84 MeV gamma-ray peak resulting from the 9.5 minute activity ^{27}Mg was counted. After peak integration, the counts were corrected for both incident neutron and counted gamma-ray attenuation using the appropriate attenuation correction factors [19]. Using the published cross section value of 1.5 mb for the $^{27}Al(n,p)^{27}Mg$ reaction, the absolute flux was calculated and related to the neutron monitor counts recorded during the same irradiation. The neutron flux was also determined using the $^{89}Y(n,n'\gamma)^{89m}Y$ reaction (σ=150 mb). The agreement between the flux values obtained by both methods was within 5% of the mean. The location of the neutron monitor with respect to the irradiation geometry is shown in figure 24. The ratio of the calculated flux to the counts per minute registered by the neutron monitor was 60. This factor was used for the computation of experimental sensitivities for all elements.

A typical example of the presentation of the data follows: In figure 25 the gamma spectrum of barium is shown. Useful nuclear analytical data related to this gamma spectrum is

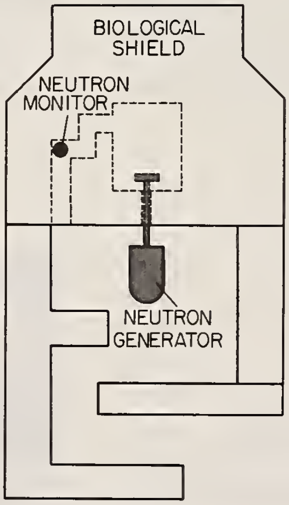

Figure 24. Irradiation geometry showing location of neutron monitor

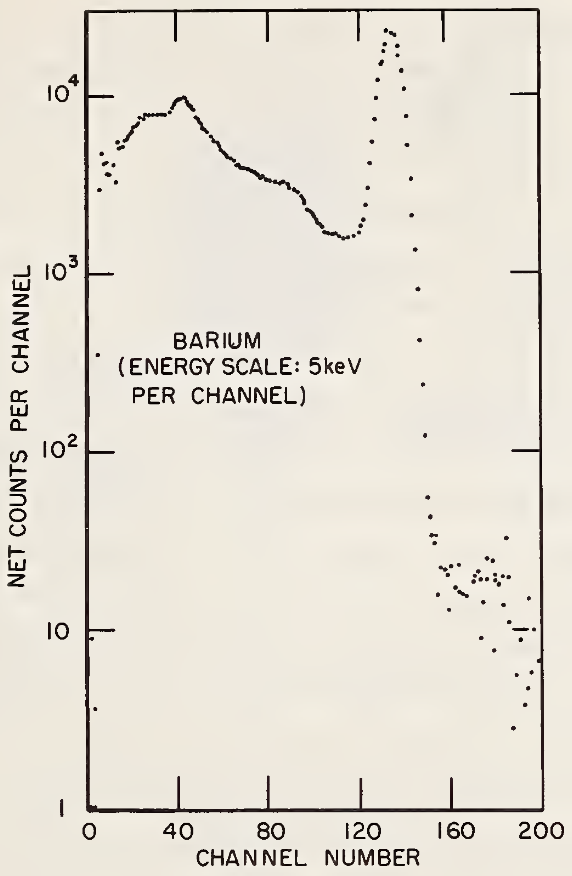

Figure 25. Gamma-ray spectrum from barium irradiated with 3-MeV neutrons

shown in table 25. For those elements which do not exhibit statistically good gamma-ray peaks for peak analysis in the spectrum, gross counts were taken over the full energy scale. From these counts the analyst may compute upper limits to evaluate the extent of interference in a particular situation.

At the present time spectra from over seventy elements have been recorded and their sensitivities computed. In view of the many approximations made in this study, an error of ±10% has been estimated and considered adequate for the purpose of this study.

(J. Niewodniczanski, J. E. Suddueth and S. S. Nargolwalla)

2. D-D Interference in D-T Analysis

As indicated earlier, D-D neutrons generated in a used tritium target can present interference problems. Having obtained the D-D spectra of the individual elements, it was necessary only to determine experimentally the D-D neutron build up in targets simulating the tritium loaded targets. The only difference here is replacement of tritium by hydrogen. Such targets are being fabricated. Some preliminary experiments with blank tantalum targets using the configuration shown in figure 24 are in progress. A deuterium beam accelerated to 200 keV is permitted to strike the "blank" target and the D-D output as a function of time measured by the neutron monitor. Using the flux normalization factor of 60 the D-D neutron build up is computed on an absolute basis. The parameters to be studied are: 1) Acceleration voltage effect 2) Beam intensity variations and 3) Beam characteristics such as spot size and distribution. From a knowledge of the D-D build up with time and using the computed sensitivities, it will be possible to predict, with reasonable accuracy, expected interferences due to D-D neutrons in any matrix during 14-MeV neutron activation analysis.

(J. Niewodniczanski, J. E. Suddueth and S. S. Nargolwalla)

3. Efficient Thermalization of 3-MeV Neutrons

Although the D-D neutron yield is about 200 times lower than the D-T output, the thermal flux obtained by the interpositioning of a suitable moderator such as paraffin, H_2O or D_2O between the target and the sample is relatively pure. An experiment has been designed to make these measurements and is shown in figure 26. The experimental arrangement has been designed and the thermal neutron output, using light and heavy water, will be measured. The neutron monitor location has been changed so that the primary D-D flux can be measured

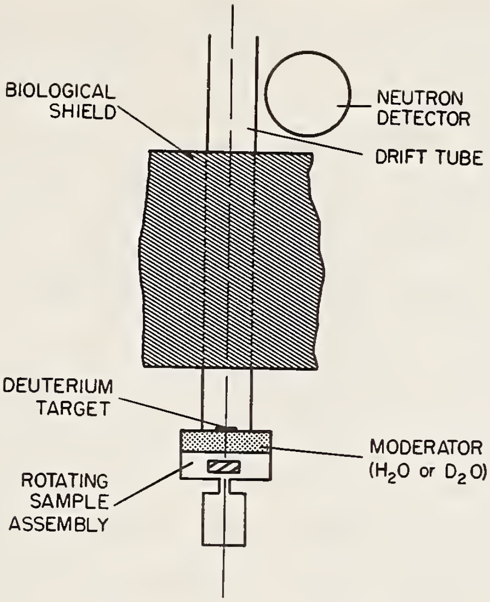

Figure 26. Plan view of experimental configuration used for D-D neutron thermalization study

without interference from the moderator. Cadmium ratio measurements will assist in assessing the purity of the flux bombarding foils or liquid samples located at various distances from the moderator. A number of moderator thicknesses will be examined so that the optimum irradiation position can be estimated. Information gained from these experiments will be used for the final design of the moderator and the pure thermal flux used for the determination of macro constituents in geological samples as well as organometallic SRMs.

Finally, we hope to use D-D neutrons as much as possible and reduce the analytical load on tritium targets. The advantages in this policy are immense. Tritium targets are generally good only for 6 or 7 mA-hours of beam time; deuterium targets, irradiated for over one hundred hours, still provide useful fluxes. In addition, neutrons from the D-D reaction can assist or complement the use of D-T neutrons in the solution of complex compositional problems.

(J. Niewodniczanski, J. E. Suddueth and S. S. Nargolwalla)

C. Analysis of Standard Reference Materials

As was indicated in an earlier report [1], the metallo-organic SRMs are ideally suited to activation analysis with the generator, and analytical results for four organometallic standards subsequently certified were obtained.

The quest for higher sensitivity for oxygen in steel has always been one of the main considerations in this project. As will be described below, a three fold increase in the D-T flux was realized by redesigning the target cooling cap. To further improve matters, it is now possible to obtain sample containers having an oxygen content about seven times less than the "low-oxygen" containers previously used. By simple extrapolation it appears that oxygen analyses below 10 ppm become a definite possibility and one of the first efforts to be made on receipt of the special containers will be to analyze the maraging steel (SRM 1094) for oxygen. This material has thus far been analyzed by vacuum fusion analysis and found to have 4 ppm of oxygen. Some of our early results obtained for oxygen in polyethylene vials are given in this report.

Our experience in oxygen analysis with 14-MeV neutrons enabled us to assist in the solution of a stoichiometric problem associated with the preparation of high purity styrene-divinylbenzene copolymers, for the microstandard bead SRM. Results of these analyses are given below.

(S. S. Nargolwalla)

1. Analysis of Organometallic Compounds

Four different metallo-organic SRMs were analyzed for their metallic component. The results obtained are compared with those from standard chemical techniques and are shown in table 26. Attention is drawn to the excellent agreement between the two methods of analysis. The techniques employed for the individual SRMs are described below.

Table 26. Analysis of Organometallic Compounds

Organometallic Compound	Element Determined	Comparison of Analytical Techniques					
		14-MeV Neutron Activation Analysis				Chemical Method Certified Value	
		No. of Samples (k)	Number of Determination per Sample	Element Concentration %	Standard Deviation of a Single Determination[b]	Element Concentration ppm	Uncertainties[c]
Sodium Cyclohexanebutyrate [SRM 1069b]	Sodium	4	4	11.90±0.26[a]	0.52	12.12	0.15
Tris(1-phenyl-1,3-butanediono)iron (III)	Iron	2	4	10.45±0.04	0.08	10.45	0.03
Bis(1-phenyl-1,3-butanediono)copper (II) [SRM 1080a]	Magnesium	2	4	16.37±0.69	1.4	16.37	0.01
Octaphenylcyclotetrasiloxane [SRM 1066a]	Silicon	3	6	14.14±0.11	0.22	14.14	0.03

[a] Uncertainty of the mean of (k) sample means at the 95% confidence level computed from $t\,S_B/\sqrt{k}$ where S_B is the computed standard deviation of a single mean with (k-1) degrees of freedom.

[b] Approximate standard deviation of a single determination based on Poisson counting statistics.

[c] The uncertainty shown represents 95% confidence limit for the mean plus allowances for known sources of systematic errors. See certificate for more details.

a. Sodium in Sodiumcyclohexanebutyrate, SRM 1069b

In this analysis thermal neutrons obtained by the thermalization of 3-MeV neutrons were used. The neutrons were thermalized by interposing about 1.5 inches of paraffin between the tritium target and the irradiation sample assembly. Four samples from the same batch of this renewal SRM were analyzed in quadruplicate. SRM 1069a (Na=11.9%) was used as the standard. The 1.37 MeV gamma-ray peak from ^{24}Na decay was counted in the multiscaler mode.

b. Iron in Tris(1-phenyl-1, 3-butanediono) iron (III) SRM 1079b

Two samples of this material were analyzed by comparative 14-MeV neutron activation analysis using SRM 1079a (Fe=10.30%) as the standard. Four determinations were made on each sample (weighing approximately seven grams). A sample and a standard were simultaneously irradiated for 10 minutes and after a 10 minute decay, counted sequentially for ten minutes each. The 1.81 MeV photopeak from 2.576 hour ^{56}Mn produced by the ^{56}Fe(n,p)^{56}Mn reaction was counted in the multiscaler mode. This insured an interference-free analysis. After analysis, each sample and its associated standard were dried according to the procedure outlined in the Certificate of Analysis (SRM 1079a), and the results calculated for a dry weight basis.

c. Copper in Bis(1-phenyl-1, 3-butanediono) Copper (II), SRM 1080a

Quadruplicate determinations on each of the two samples received were made using 14-MeV neutrons. Weights of all samples were about seven grams each. SRM 1080 (Cu=16.5%) was used as the standard.

A sample and a standard were simultaneously irradiated for 10 minutes and, after a twelve hour decay period, counted sequentially for 10 minutes each with a 20 minute decay between counts. All samples were irradiated late in the evening and counted the next morning. The 0.51 MeV annihilation radiation from the decay of ^{64}Cu ($T_{1/2}$=12.8 hour) was counted in the multiscaler mode. The results are reported on a dry weight basis. Drying procedure followed was that recommended in the certificate for the standard (SRM 1080).

d. Silicon in Octaphenylcyclotetrasiloxane, SRM 1066a

Three samples of this standard were analyzed using 14-MeV neutrons and SRM 1066 (Si=14.1%) as the standard. Weights of all samples were about eight grams each. Determinations were made in quadruplicate. The three samples represented the top, middle and bottom fractions of the bulk material. Results indicated no detectable inhomogeneity (within the precision of the method) and are reported on a dry weight basis. Each sample and its standard were simultaneously irradiated for 2 minutes and after 2 minutes decay, counted sequentially for one minute each with a one minute delay between counts. The 1.78 MeV gamma ray from the decay of the 2.31 minute ^{28}Al produced by the ^{28}Si(n,p)^{28}Al reaction was counted in the multiscaler mode.

(S. S. Nargolwalla, J. E. Suddueth, J. Niewodniczanski,
E. P. Przybylowicz and Gilbert W. Smith)

2. Analysis of Oxygen in Styrene-divinylbenzene Copolymer

Four samples of this copolymer were analyzed for oxygen. The only difference between them, insofar as a physical examination was made, was the mesh size. Each sample was carefully prepared in a nitrogen atmosphere and analyzed in quadruplicate using a method previously described [19]. Each sample was compared with a benzoic acid standard. Systematic errors due to neutron and gamma attenuation were calculated and found to be negligible in this case, due to the close similarity of the sample and standard matrices. The results are given in table 27.

Table 27. Analysis of Oxygen in Styrene-divinylbenzene Copolymer

Sample Identification	Oxygen Concentration[a] %	Uncertainty[b]
W-121	3.46	0.07
D-103	0.134	0.006
I-11	0.37	0.01
I-22	0.44	0.01

---

[a] Results are weighted means of 4 determinations with the weights equal to the reciprocal of estimated variances; estimated variances based on Poisson counting statistics and propagation of error formulas.

[b] Errors are the standard errors of the weighted means.

(S. S. Nargolwalla, J. E. Suddueth and J. Niewodniczanski)

3. Analysis of Oxygen in Low-Oxygen Polyethylene Vials

Low-oxygen polyethylene vials have been on the market for about five years. These vials are made by taking appropriate precautions to avoid air oxidation of the hot plastic during the molding process. Several laboratories, including ours, have obtained such vials and subjected them to analysis. The wide inconsistency of data has made it impossible to fully evaluate the potential of polyethylene vials as carriers for metal samples containing trace amounts of oxygen. Recently however, we were able to obtain a few samples of a new batch The oxygen content of these vials was determined using the technique described earlier, and the results have been compared to those from our earlier studies in table 28. A small batch of the new vials have been ordered and one of the first tests will be to analyze maraging steel (SRM 1094) which

Table 28. Analysis of Oxygen in Low-Oxygen Polyethylene Irradiation Capsules

Capsule Identification	Capsule Number	Oxygen Concentration ppm[a]	Uncertainty ppm[b]
Normal Capsules	1	373	14
Low-oxygen Capsules [Old Stock]	1	440	15
	2	600	18
Low-oxygen Capsules [New Stock]	1	78	7
	2	87	7
Inner Liner Polytubing	1	75	7

---

[a] Results are weighted means of 4 determinations with the weights equal to the reciprocal of estimated variances; estimated variances based on Poisson counting statistics and propagation of error formulas.

[b] Errors are the standard errors of the weighted means.

reportedly contains only 4 ppm of oxygen. The new vials showed marked improvement in their low-oxygen content. With a three fold increase in flux and a better signal-to-noise ratio, we are now in a position to analyze metal samples weighing 10 grams and containing less than 10 ppm of oxygen.

(J. E. Suddueth and S. S. Nargolwalla)

D. Operational Characteristics of the Neutron Generator

The operational characteristics of our neutron generator were studied after about one year from date of installation. Normally, these experiments are performed at the time when the machine is operated for the first time. However, we deliberately delayed these studies so that all components of the accelerator had had an opportunity to age, and also to permit us to correct any deficiencies in the system in its early stages of beam operation. During this year about 30 mA-hour of beam was drawn using tritium targets and over 150 mA-hour using deuterium targets. Some important characteristics are described below.

a. Effect on Beam Current and Beam Diameter with Variations in Accelerating Voltage

In neutron generator systems it is well known that the accelerating voltage also acts as a focusing device. Briefly, the change in diameter of the beam spot (as visually observed) at five different beam currents was estimated as a function of accelerating voltage. At the start of each observation a particular beam current was obtained and the focus peaked. Then the high voltage was reduced in steps of 5 kV and the change in spot size and beam current observed. The results are shown in table 29.

b. Effect of Focus Control at 200 kV on Beam Diameter

The high voltage was fixed at 200 kV and measurements made at five different beam currents which were obtained by peaking the focus. The focus control was now reduced in small increments and the effect on the peaked beam current and spot size observed. These results are shown in table 30.

Table 29. Effect of Acceleration Voltage on Diameter of Beam Spot

Acceleration Voltage, kV	Peaked Beam Current, mA Approximate Diameter of Beam Spot, in.				
	0.5	1.0	1.5	2.0	2.5
200	0.5	0.625	0.75	1.25	1.5
195	0.5	0.75	1.0	1.5	
190	0.625	0.75	1.25		
185	0.75	1.0	1.5		
180	0.75	1.25			
175	0.75	1.5			
170	1.0				
160	1.5				

Table 30. Effect of Focus Control at 200 kV on Diameter of Beam Spot

Focus Control (Arbitrary Units)	Beam Current mA	Beam Diameter in.
54	0.5 (peaked)	0.5
49	0.49	0.75
44	0.46	1.25
39	0.34	1.5
55	1.0 (peaked)	0.625
50	0.95	0.625
45	0.95	0.75
40	0.80	1.0
35	0.55	1.5
56	1.5 (peaked)	0.75
50	1.5	0.75
45	1.4	1.00
40	1.0	1.25
57	2.0 (peaked)	1.0
45	1.5	1.5
58	2.5 (peaked)	1.5

(J. E. Suddueth and S. S. Nargolwalla)

E. Health Physics

1. Monitoring of Biological Shield

Soon after installation of the new neutron generator and modification of the biological shield [1], a thorough survey was carried out by the Reactor Building Health Physics staff. The hot cell area in which the facility is located is shown in figure 27. The total dose as measured at waist level at the locations designated by arabic letters gives the dose extrapolated for a 2.5 mA beam impinging on a new 0.5-0.8 Ci/cm^2 tritium target. At the console it is seen that the total dose from gammas, slow and fast neutrons is about 27 mrem per hour.

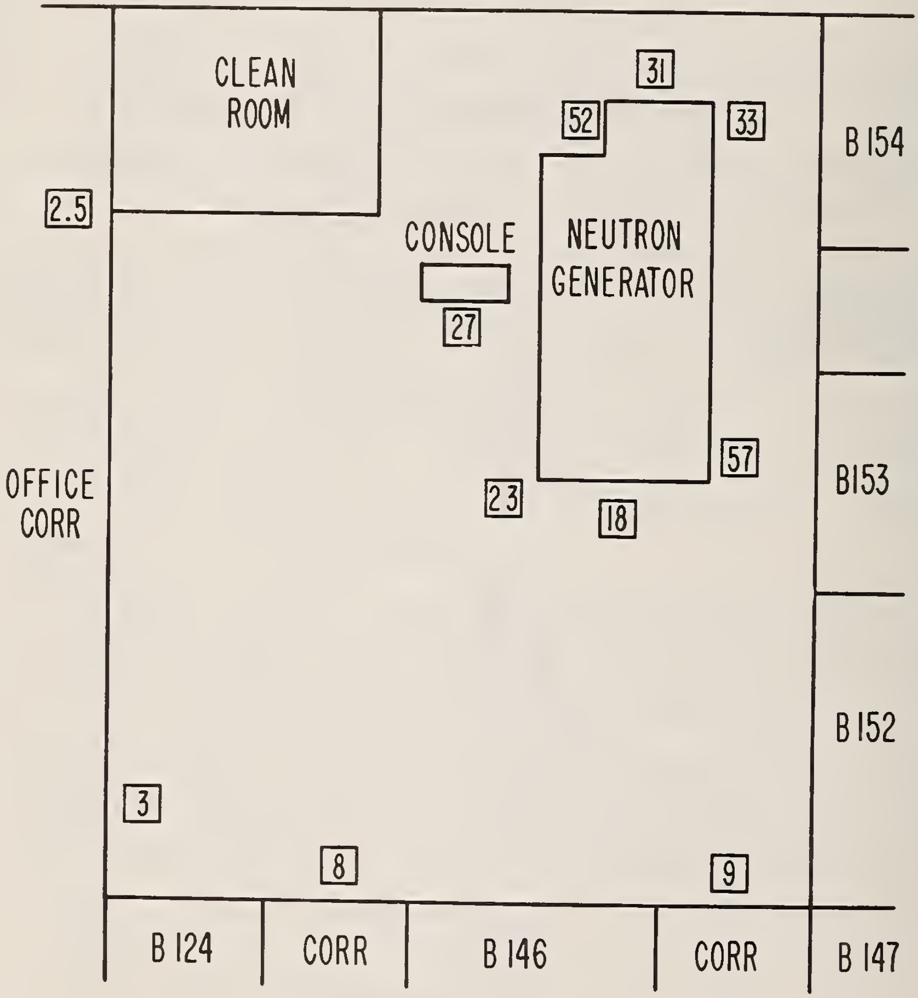

Figure 27. Location of radiation monitoring sites around the neutron generator facility

It is therefore possible to operate the accelerator for about 3 hours a week at full beam on a new target. Since the target depreciates by a factor of two every 2 mA-hours, permission has been granted by the Health Physics staff for operation times up to 10 hours per week. In the context of 14-MeV neutron activation analysis this is a very large amount of beam time using tritium targets. With deuterium targets, however, it is possible to operate over forty hours per week.

2. Tritium Contamination and Control

Tritium contamination problems associated with all D-T type accelerators were examined in great detail after 1 1/2 years operation of the accelerator. During this period of time about 30 mA-hours of beam was used on a total of four tritium targets. The accelerator was subjected to a thorough check for tritium levels inside various components integral to the accelerator and inside subsidiary systems.

A summary of this investigation is shown in table 31. The exact locations at which sampling was done are designated and shown in figure 28. Despite the extreme care we have taken in

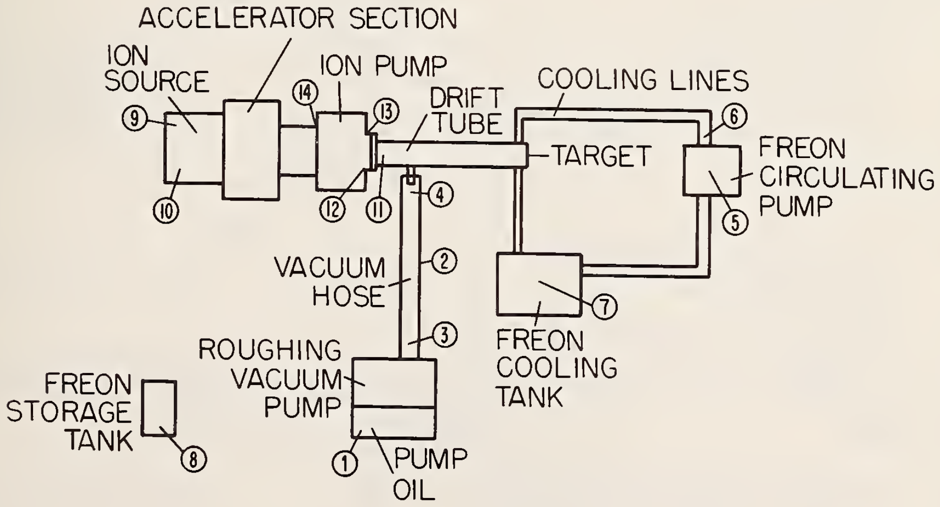

Figure 28. Location of tritium monitoring sites on the neutron generator

Table 31. Tritium Contamination of the Neutron Generator After 30 mA-hrs. of Beam Operation on four 0.8 Ci/cm^2 Tritium Targets (∿ 1 1/2 Years Operation)

Component Monitored	Monitoring Location (Fig. 6)	Tritium Contamination
1. Roughing Pump System		
(a) Pump Oil	1	0.1μCi/ml
(b) Roughing Pump Hose		
(i) External	2	$1x10^{-5}$μCi/swipe
(ii) Internal (pump end)	3	$1x10^{-2}$μCi/swipe
(iii) Internal (Generator End)	6	$6x10^{-3}$μCi/swipe
2. Circulating Cooling Pump		
(a) Inside Seal	5	$7x15^{-4}$μCi/swipe
(b) Inside Pipe Threads	6	$5x10^{-4}$μCi/swipe
3. Freon Cooling Tank	7	0.2 μCi/swipe
4. Plastic Container-Freon Storage	8	$3x10^{-2}$μCi/swipe
5. Ion Source		
(a) Inside	9	$2x10^{-3}$μCi/swipe
(b) Electrodes	10	$7x10^{-4}$μCi/swipe
6. Drift Tube		
(a) It Inside Ion Pump Connection	11	0.1 μCi/swipe
(b) Inside at Ion Pump Flange	12	$7x10^{-2}$μCi/swipe
7. Ion Pump		
(a) O-ring (Front of Pump)	13	$4x10^{-4}$μCi/swipe
(b) O-ring (Rear of Pump)	14	$1x10^{-3}$μCi/swipe

the installation of tritium targets some degree of contamination has always existed in our target assembly hood. The Health Physics staff are now monitoring this hood daily. At the accelerator site, however, tritium contamination of the outer surfaces of the accelerator is negligible.

3. Bremsstrahlung Dose Measurements

When positive ions are accelerated onto a target, the emitted electrons are accelerated in a reverse direction. In a generator these electrons are suppressed, however a great majority are accelerated back to the terminal end of the accelerator and generate bremsstrahlung. The maximum energy of the bremsstrahlung is 200 keV and present a hazard even when protons are accelerated on to a blank target. The extent of this hazard can be assessed from the results given in table 32 with the aid of figure 29 which shows the locations of dose measurements.

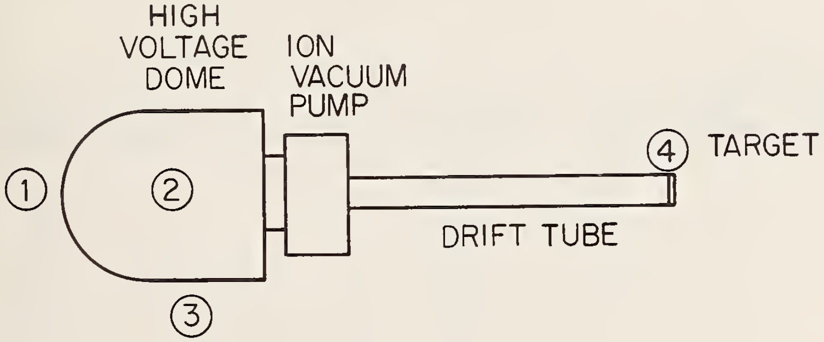

Figure 29. Bremsstrahlung dose measurement sites around the neutron generator

Table 32. Bremsstrahlung Dose Measurements as a Function of Beam Current (Hydrogen on Blank Cu Target) at 200 kV Acceleration Voltage

Location Monitored (Fig 7)	Beam Current mA	Dose mrem/hr at Contact
1. High Voltage Terminal Dome		
(a) Back (1)	0.5	15
(b) Side (2)	0.5	100
(c) Bottom (3)	0.5	20
(a) Back	1.0	40
(b) Side	1.0	310
(c) Bottom	1.0	50
(a) Back	1.5	80
(b) Side	1.5	1750
(c) Bottom	1.5	100
(a) Back	1.75	175
(b) Side	1.75	2500
(c) Bottom	1.75	200

2. Target End Between Suppressor and Cooling Cap (4)	Beam Current mA	Dose mrem per hour
	0.5	0.6
	1.0	1.4
	1.5	2.8
	1.7	3.0
	2.0	5.8
	2.35	9.5

(J. E. Suddueth and S. S. Nargolwalla)

F. Status of the Neutron Generator Facility

For the first year after its installation, the neutron generator performed flawlessly. After this, certain key components began to fail causing significant amounts of downtime for repair. Some of the more serious breakdowns and the measures taken to reduce downtimes are described. During this period of time inovations were also made to insure safety of operating personnel and the generator; and also to increase the available D-T flux by a factor of about three. At the present time we are in the process of becoming self-sufficient in terms of fabricating key components in our shops and obtaining knowledge necessary for reconditioning of other components in our laboratory. The major part of the delay has been in the transportation of the defective unit to and from the manufacturer. In the near future we hope that this self-sufficiency approach will prevent breakdown and also reduce downtimes to negligible proportions.

1. Vacuum Ion Pump Failure

A direct short in the pumping elements necessitated the removal of the pump for installation of new elements. Due to the large tritium load in the pump, difficulties were experienced in its transportation from the laboratory. The ion pump was returned after six weeks and found to be working at very low efficiency. Since then, however, the manufacturer has shipped a new pump. Experiments carried out showed that the pump, when pumping on itself, could not reduce the vacuum below 10^{-7} mm Hg. This was unacceptable to us, as the pump when installed was capable of pumping down to 10^{-9} mm Hg. It is suspected that there may be a leak in the pump housing itself.

2. Ion Source Burnout

After a very good performance for over a year, the ion source finally burned out. Insofar as this type of source is concerned, this performance is difficult to exceed. On dissassembly, it was discovered that the anode was extensively burned. The dissassembled source is shown in figure 30. From left to right are the mechanical gas leak attached to the source housing, burned anode, retaining sleeve, front cathode and assembly holder. In figures 31 and 32. the burned anode shown indicates the extent of the damage. Despite this damage, the source was still operating at about 40% of its rated capacity; a fact which speaks highly for the Penning type source. In figure 33 the location of the back cathode and the anode electrode is shown. The assembled source with magnets is shown in figure 34.

Figure 30. Penning ion source: disassembled

Figure 31. Penning ion source: inside view of burned aluminum anode

Figure 32. Penning ion source: side view of burned aluminum anode

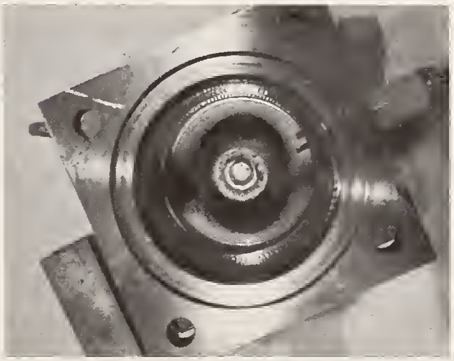

Figure 33. Penning ion source: inside view of back cathode and protruding anode head

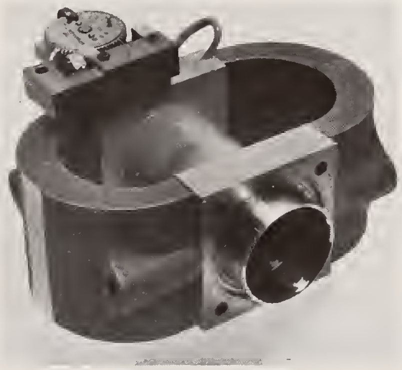

Figure 34. Penning ion source: assembled, showing mechanical gas lead, and U magnets

These sources are extremely rugged in construction and require little attention. The art apparently lies in the replacement of anodes and cathodes. The back cathode, however, requires a special tool and great care in its installation. Although a spare source was purchased, we are now in the process of reconditioning ion sources ourselves.

3. High Voltage Breakdown

Recently, arcing in the main high voltage tank was experienced. A careful examination which included a thorough cleaning of the oil and all components did not reveal the cause. However, a closer examination of the heavy polyethylene covered high voltage cable showed a pin hole in which carbon deposits could be seen. The cable was cut off at this point. The defective piece was carefully trimmed and showed multiple discharges via carbon tracks to the 1/4 in. diameter copper conductor. A photograph illustrating this discharge pattern is shown in figure 35.

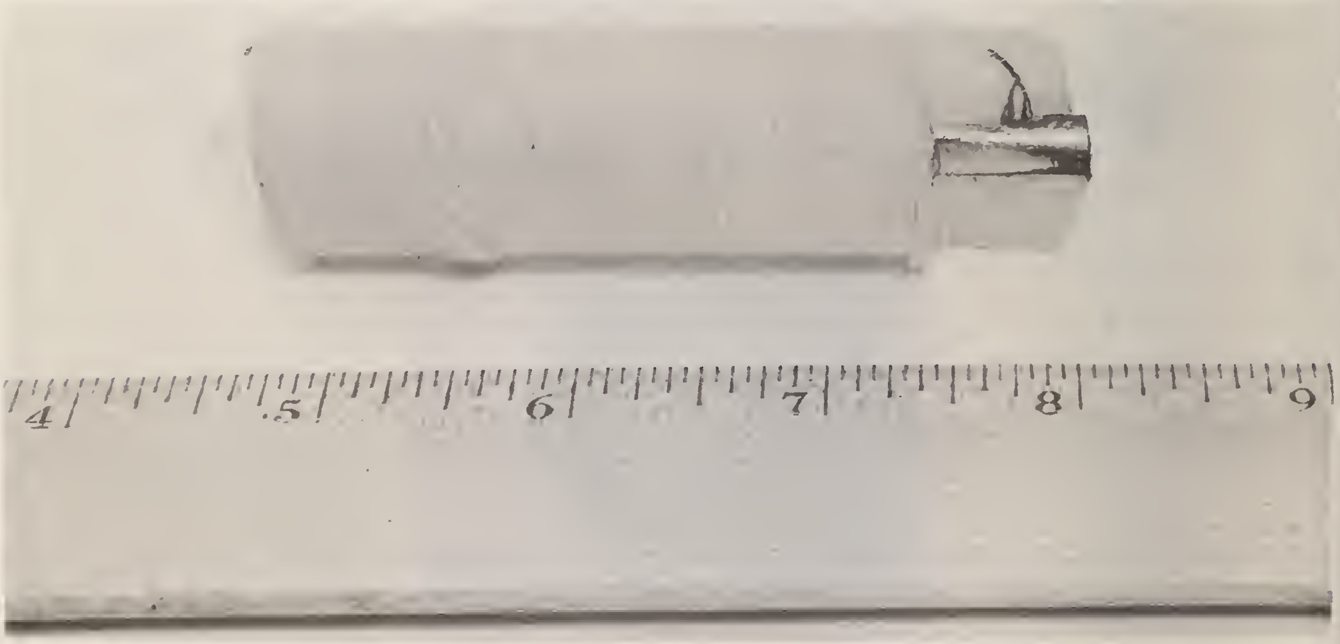

Figure 35. 200kV conductor showing electrical break-down of insulator

4. Cooling Problems

The use of Freon as a coolant required the use of a specially designed cooling cap shown in figure 36. Although cooling is extremely efficient, the design of this cap was such that the minimum distance a sample could be placed from the target was almost 1.5 cm. We have now changed over to water cooling and employed a thin stainless steel cooling cap and have realized a factor of three in flux. The minimum distance from target-to-sample is less than 1 cm. The exact distance is difficult to determine since the target itself bulges inward under vacuum and from the water pressure in the cooling cap. It was also discovered that with the Freon cooling cap, tantalum blank targets could not be used since they did not bulge inward being much stiffer than the copper backing plate of the tritium target. Due to this fact the cooling cap would make contact with the blank tantalum plate with loss of cooling surface. In figures 37 and 38, the beam side and cooling side of a typical tantalum plate in which a hole has been burned through by the deuterium beam are shown.

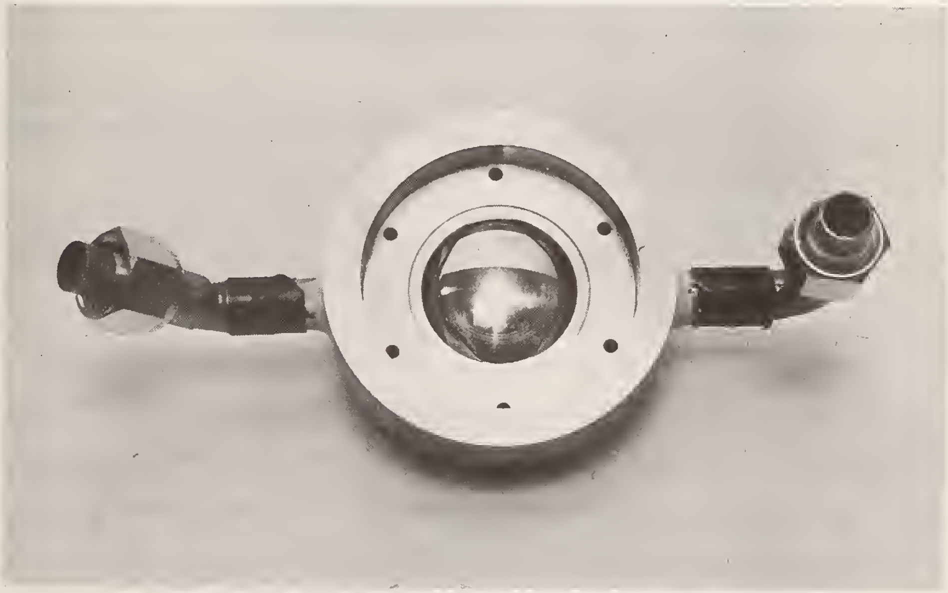

Figure 36. Target cooling jacket used with Freon

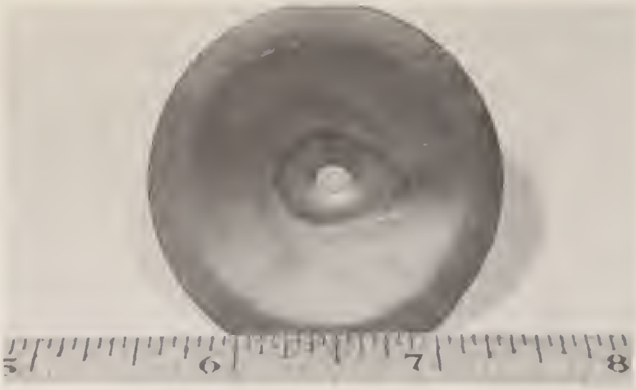

Figure 37. Beam-side of blank tantalum target showing burned hole

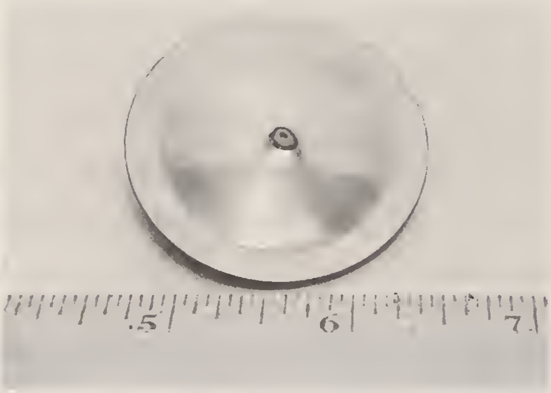

Figure 38. Coolant-side of blank tantalum target showing burned hole

5. Safety Devices

About one year ago a serious accident was reported in another accelerator facility. An investigation into this event indicated short comings in the interlock systems employed. Since then we have re-examined our system and added to it. Previously it was possible to turn on the beam and not know whether anybody was inside the irradiation area. Our double interlock system makes it mandatory to check inside once the interlock door has been opened for any reason whatsoever.

To protect the facility efficiently, we have installed thermocouples in the coolant input and output lines with external readouts. The heating effects can be monitored continuously during beam operation. At a flow rate of about 0.5 gallons per minute, the temperature rise from the ambient is about 20°F at 2.5 mA beam current. The refrigeration system controls the coolant input temperature to about 60°F over long periods of beam time. If the refrigerator is shut down, the tank water supply temperature increases at the rate of about 1°F per minute. On the basis of this it is still possible to run the accelerator up to thirty minutes should the refrigerator fail. In view of our efforts to upgrade the facility and improve its performance and reliability we expect insignificant downtimes in our future operations.

(J. E. Suddueth, S. S. Nargolwalla and J. Niewodniczanski)

5. ACTIVATION ANALYSIS WITH THE NBS LINAC

A. Introduction

The primary emphasis in the LINAC project for this report year has been the development of procedures for the trace determination of carbon in a variety of metal samples, more work on oxygen and carbon in sodium and the development of methods for the determination of thallium at trace levels in simulated lunar samples. In addition, some preliminary experiments have been performed for the determination of bismuth by photofission.

B. Facilities

The second rabbit terminal installed in the 45 degree irradiation facility behind the original terminal continues to function in a satisfactory manner. This rabbit terminal has been used for the production of isotopes for Mössbauer spectroscopy and radiochemical separations as well as for preliminary experiments in activation analysis. Figure 39 shows a portion of the control console. The control lights indicate a sample in both irradiation positions. A view of the LINAC activation analysis laboratory in Service Area 2 at the Radiation Physics Building is shown in figure 40.

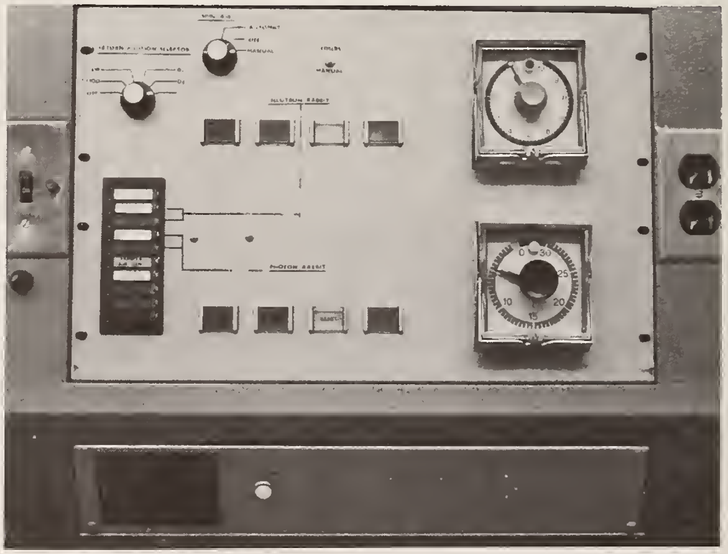

Figure 39. LINAC Control Console

Figure 40. LINAC Activation Analysis Laboratory in the Radiation Physics Building

The zinc sulfide phosphor previously described [1] continues to function well and is of assistance to the accelerator operators in beam positioning. Only very recently has the phosphor deteriorated and been replaced.

1. Carbon in High Purity Metals

A substantial effort to develop methods for determination of carbon in a variety of high purity metals has been initiated. Preliminary experimentation with perchloric acid oxidation was not successful as yields were low and not reproducible.

A resistance heated furnace was obtained and separations were made using "classical" procedures with modification when appropriate. The samples were irradiated in metal rabbits and etched or ultrasonically cleaned after irradiation.

Irradiations were monitored with a small piece of graphite in the lid of the metal rabbit. Standards were spectrographic grade graphite. Counting was done with the coincidence unit described in the sodium section. The resistance furnace and collecting train is shown in figure 41.

Figure 41. Resistance furnace and collecting train for carbon determination

As a check on the method, samples of SRM 131a (iron) which is certified at 44 ppm were analyzed. Values of 45, 48, 45, 43, 40 and 46 ppm were obtained.

Three Standard Reference Materials; 680 (platinum), 682 (zinc) and 685 (gold) were also analyzed for carbon content.

Gold. The gold samples, weighing about six grams each, were etched after irradiation in aqua regia to remove about 3% of the sample. Approximately four grams of lead flux was added and the extraction was carried out at 1200°C with an oxygen flow rate of 500 ml/min. Extraction times were approximately fifteen minutes. Values obtained were 0.44, 0.39 and 0.49 ppm. The decay curve associated with one of these samples, is shown in figure 42.

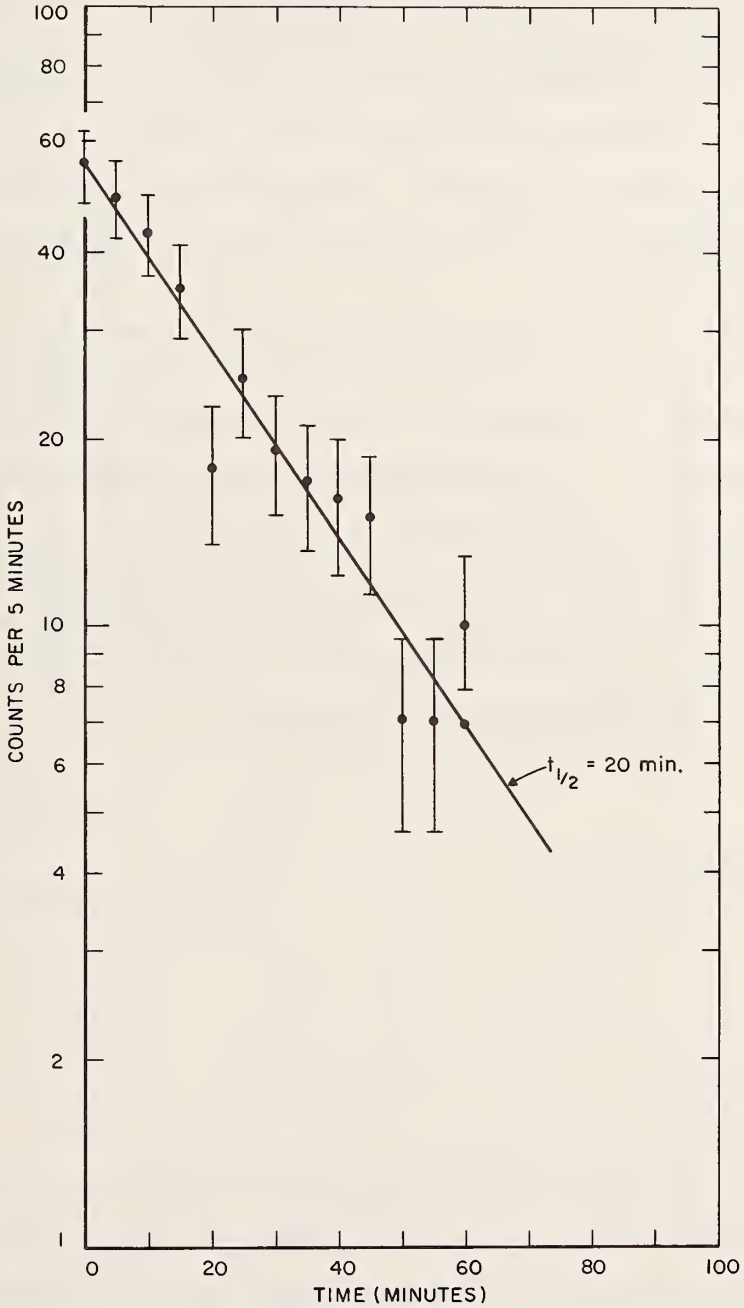

Figure 42. Decay curve for carbon-11

Zinc. The zinc samples, weighing about ten grams each, were etched after irradiation in dilute hydrochloric acid to remove about 20% of the samples. No flux was used. The combustion was carried out at 950-1000°C with an oxygen flow rate of 500 ml/min. The oxygen was moistened by passing it over 1M H_2SO_4 to control the combustion. The extractions were carried out in a transparent quartz tube so the course of the reaction could be observed. After the burning had subsided (typically 10-15 minutes), the system was allowed to flush a few minutes before counting. Inspection of samples after burning indicated complete combustion. Values obtained were 0.3, 0.2 and 0.2 ppm.

Platinum. The samples, weighing between 0.5 and 2 grams each, were etched after irradiation in aqua regia to remove varying amounts of sample, or were cleaned ultrasonically before extraction. Approximately four grams of lead flux were added and the extraction carried out at 1200°C with an oxygen flow of 500 ml/min. Extraction time was approximately 15 minutes. Table 33 shows values of apparent concentration of carbon as a function of amount of sample removed by etching from the surface before separation.

Table 33. Effect of Etching on Apparent Carbon Concentration

Amount of Sample Removed	Carbon Found (ppm)
0	17, 24
~1%	6.5
~5%	1
9%	0.5

A value of 27 ppm also obtained with 9% etching was rejected as obviously not in line with the rest of the results. The 0.5 ppm value has a large uncertainty associated with it and probably cannot be considered different from the 1 ppm value.

2. Thallium in SRM Glass

The Office of Standard Reference Materials has obtained a series of glass samples which have been doped with 61 trace elements at levels of 500 ppm, 50 ppm, 1 ppm and 20 ppb. We are investigating the determination of thallium in these glasses by photon activation analysis.

The nuclear reaction involved in these determinations is $^{203}Tl(\gamma,n)^{202}Tl$. The product nuclide decays with a half-life of 12 days by electron capture with the emission of the 70 keV mercury X-ray in coincidence with a 439 keV gamma ray. The cross section for (γ,n) reactions increases and the threshold decreases with increasing atomic number; thus the intrinsic sensitivity for thallium, with the 203 isotope having a 29.50% abundance, is good.

Since a substantial amount of activity from the other 60 elements, as well as the major constituents of the glass, are present after irradiation, a separation is required. From work on tetracycline extractions reported elsewhere in this report (Part D) it was determined that thallium (III) could be extracted in a wide pH range with benzyl alcohol.

A sample of the 50 ppm glass was obtained and about one gram irradiated in the 45 degree facility of the NBS LINAC for about 45 minutes.

The sample was dissolved after irradiation in a mixture of 10 ml of perchloric and a few ml of hydrofluoric acids with heating. To insure the presence of thallium (III), 10 ml of HCl was added to the perchloric acid with 10-12 drops of hydrogen peroxide. Excess peroxide was expelled by heating and the solution was siluted to 40 ml with distilled water. The purpose of the dilution was to prevent concentrated perchloric acid from destroying the benzyl alcohol. This solution was extracted twice with ten ml portions of benzyl alcohol for several minutes. After each extraction, the separatory funnel was centrifuged for a few minutes to facilitate phase separation. The organic layer was washed three times with a mixture of 10 ml $HClO_4$, 10 ml HCl and 20 ml H_2O. Centrifugation was also necessary after each wash. The organic phase was then drawn into a two oz. polyethylene bottle for counting. Tracer experiments showed that the separation was quantitative.

The organic phase was counted with a Ge(Li) detector and 2048 channels of analyzer memory. Gamma ray lines that could be ascribed definitely to gold activities and tentatively to antimony activities were observed in addition to the thallium activity.

3. Photofission of Tl, Bi and Pb

The nuclear track technique has been a method predominently used to study radiation induced trails in plastic solid state detectors by thermal neutron irradiations [20-24]. Currently, investigations are underway to study the determination of several heavy elements by counting tracks produced by photofission. Fission tracks have been produced in Lexan* polycarbonate from photofission of thallium, lead, bismuth, thorium, and uranium produced by 35 MeV photon irradiation. However, five minute irradiations for one microgram samples indicated that only the latter three elements should be considered for quantitative measurements.

Since trace determination of bismuth is difficult by neutron activation analysis and thorium and uranium are relatively easy, Bi appeared to be the most promising element for initial attention even though sensitivity for bismuth, 3.13×10^{-7} grams per track, was found to be less than those for thorium and uranium, 4.17×10^{-9} grams per track and 1.72×10^{-9} grams per track respectively. Since the uranium and thorium sensitivities were greater than that of bismuth, a pre-irradiation separation had to be performed on the material to be analyzed.

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*See disclaimer in Preface.

a. Experimental

The bismuth containing material was dissolved in dilute HNO_3 and the solution mixed with 10 ml of a mixture containing 50 grams of Na_2EDTA and 50 grams of NaCN dissolved in 1 liter of 1.5N NH_4OH. One milliliter of a 2% solution of sodium diethydithiocarbamate was added and the bismuth extracted into 10 ml of CCl_4 [25]. The CCl_4 layer was drawn off, 1 ml of dilute HNO_3 was added and the mixture heated until all of CCl_4 had evaporated. After diluting to 10 ml, 100 µl of the dilute HNO_3 solution was placed on Lexan slides 10 mm wide x 25 mm long x 0.25 mm thick. The solution was then evaporated, covered with collodion, and irradiated for a minimum of five minutes with bremsstrahlung produced by 35 MeV electrons. After irradiation the slides were etched in 6.5N NaOH at 50° ± 2°C for 45 minutes to develop the tracks. The tracks were then counted and values were compared with values obtained from standards irradiated simultaneously.

b. Conclusions

Analysis on both fractions of solvent extraction layers by the nuclear track technique showed that all the uranium remaining in the aqueous phase. Tracer experiments with ^{207}Bi and the track technique indicated that 95% of the bismuth was being extracted into the CCl_4. These results indicate that trace quantities of bismuth and uranium can be analyzed in the same matrix.

4. Yttrium in Rare Earths

The photonuclear activation analysis technique for the determination of yttrium without chemical separation described in last year's report [1] has been applied to the determination of yttrium in several rare earth oxides. The determination of yttrium is difficult using thermal neutron activation analysis because the product nucleus decays exclusively by beta emission and must be separated from chemically similar elements.

We use the nuclear reaction $^{89}Y(\gamma,n)^{88}Y$ for this determination. ^{88}Y has a half-life of 108 days and decays by emission of 898 keV and 1827 keV gamma rays in coincidence. The threshold for the reaction is 12.0 MeV, the energy of maximum cross section is 16.3 MeV, the value of this maximum cross section is 191 millibarns and the width at half-height of the cross section curve is 3.8 MeV.

Some results obtained on rare earth oxides are given in table 34.

Table 34. Results of Yttrium Determination for Some Rare Earth Oxides

Sample	Y_2O_3. (ppm)
Nd_2O_3	16,17,17
Pr_2O_3	421,408,430
Sm_2O_3	17,19
Gd_2O_2	26,25
Tb_2O_3	171,180
Dy_2O_3	175,165,176

Two potential sources of systematic error were investigated to assure that they did not interfere with the determination. At least one of each of the rare earth samples in the table was counted two or three times over a period of several months and compared with its standard. The apparent concentration of yttrium did not change and one may infer from this that there are no interferences in counting.

The possibility of differences in self-shielding during counting was examined by spiking inactive rare earth oxide and yttrium oxide samples with known amounts of ^{88}Y. These samples were made into the configuration of the counting samples and counted under identical conditions. The ratio of counting rates was within one percent of the ratio of ^{88}Y added.

For the general determination of yttrium in a variety of materials by this nuclear reaction, a cursory examination of the problem of interfering nuclear reactions was made.

The potential interfering reactions are

$$^{93}Nb(\gamma,\alpha n)^{88}Y$$

$$^{90}Zr(\gamma,np)^{88}Y$$

$$^{90}Zr(\gamma,2n)^{88}Zr \xrightarrow{\varepsilon} {}^{88}Y$$

Samples of niobium, zirconium and yttrium were irradiated at 35 MeV and the relative amount of flux received by each sample monitored with copper foils. A few days after irradiation the niobium sample was examined with a Ge(Li) detector. No ^{88}Y was observed and an upper yield limit of about 10^{-5} for the production from niobium relative to that from yttrium on an equal weight basis was obtained. The zirconium sample was examined a few hours after irradiation and again after several weeks. A few hours after irradiation, a small amount of ^{88}Y was observed and an equivalent upper yield limit of about 10^{-4} was obtained. Several weeks later, ^{88}Y had grown in from ^{88}Zr to such an extent that the count rate relative to the monitor and weights of zirconium and yttrium was of the order of one percent of the yttrium. Thus if zirconium is known or suspected to be present in a given sample, it is necessary to separate the Y from Zr if the sample is not to be counted promptly.

5. Carbon and Oxygen in Sodium

A substantial effort has continued on the determination of carbon and oxygen in sodium. We have cooperated and are discussing cooperation with other laboratories on the comparison of results from samples drawn from the same lot.

In photon activation analysis the nuclear reactions and half-lives of the products of interest are

$^{12}C(\gamma,n)^{11}C$	20.5 minutes
$^{16}O(\gamma,n)^{15}O$	2.1 minutes

Both radionuclides decay by positron emission. Their half-lives are of sufficient length to permit a simple separation.

There are two major advantages in accomplishing these analyses by photonuclear activation analysis. These advantages are frequently available in most activation analysis. One is the ability to etch the sample after irradiation, but before separation and counting, thus eliminating reagent blanks and the possibility of contamination of the sample thereby obtaining an analytical result truly representative of the bulk sample. Our samples are etched in a solution of ethyl alcohol containing about ten percent water. The etching process is shown in figure 43. It is apparent

Figure 43. Etching of sodium in alcohol-water mixture

from the figure that the evolution of hydrogen bubbles assures the removal of surface impurities from the sample. Generally, three or four such etches are made for each sample. In the case of oxygen, if there is a substantial amount of sodium hydroxide and sodium carbonate on the surface, it is useful to etch prior to irradiation so that the post irradiation etch does not require excessive time.

The second advantage of activation analysis is that the final "analytical signal," the counting of the separated activity, decays at a rate characteristic of the nuclide produced. Since many of the isotopes produced by photon activation decay by positron emission, separations for the element of interest must be clean as well as be completed in a time commensurate with their half-lives. They also must be quantitative or amenable to yield determination.

The separation of carbon has been described [26]. The technique utilizes the "low temperature combustion" method. The apparatus is shown in figure 44. Oxygen enters the assembly via the three-way stopcock at the top center of the photograph. The irradiated and etched sodium sample with

Figure 44. Combustion of sodium for carbon determination

about 100 mg of inactive sodium carbonate in a quartz crucible is heated with a gas burner. When the sodium melts, the heating is stopped and the stopcock directly below the Kjeldahl bulb is closed. One to two seconds later combustion occurs. The sodium is burned to sodium oxide and the carbon is converted to sodium carbonate. As seen in the figure, sodium oxide diffuses above the combustion. The closed stopcock prevents the oxide from coming in contact with the carbon dioxide liberated later. When the crucible has cooled, acid is added via the three way stopcock to liberate the radioactive carbon as CO_2. Boiling under vacuum refluxes the acid solution throughout the combustion vessel and neutralizes sodium oxide which has diffused to the walls. The exit gas is scrubbed in a solution of sulfuric and boric acids to remove radiofluorine produced by the reaction $^{23}Na(\gamma,\alpha n)^{18}F$. The CO_2 is trapped in a sodium hydroxide solution. The activity in this solution is counted by measuring the 511 keV radiation from position annihilation. The two annihilation quanta are emitted at 180° angles and are detected with two 4 in. x 4 in. NaI(Tl) detectors and a coincidence apparatus. The coincidence unit, scaler and pulse height analyzer are shown in figure 45. Background with this detection apparatus is typically 0.2 cpm.

Figure 45. Coincidence unit for positron annihilation counting

The apparatus for the separation of oxygen in sodium is shown in figure 46. With joint J open, irradiated and etched sodium is dropped into distillation flask A. The flask contains 25 ml of water in which six grams of sodium hydroxide has been dissolved to temper the reaction rate of the sodium with the water. Nitrogen introduced via stopcock S1 flushes the hydrogen from the system.

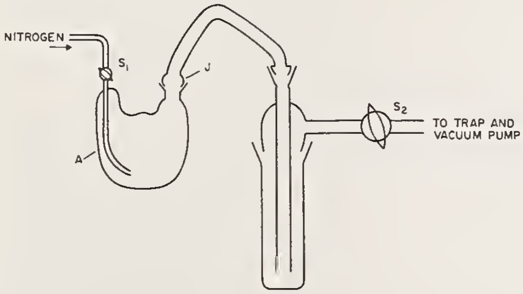

Figure 46. Apparatus for separation of oxygen from sodium

The oxygen, present as Na_2O^* after activation, is converted to sodium hydroxide upon dissolution and the radioactive oxygen exchanges with oxygen in the water. After dissolution, joint J is connected, stopcock S2 is closed and stopcock 2 is opened to vacuum. The distillation flask is heated with a blast burner and about one half of the water is distilled into the liquid nitrogen cooled trap. After distillation, the quantity of water distilled is measured, diluted to a constant volume and the annihilation radiation counted. Some results are shown in table 35.

Table 35. Oxygen in Sodium Results

Reagent Grade Sodium - Lot I	90,77,82 ppm
Reagent Grade Sodium - Lot II	51,42,47 ppm
Reagent Grade Sodium - Lot III	100,105,110,100 ppm
Sodium Correction Loop Experiment	29,22,20 ppm

6. RADIOCHEMICAL SEPARATIONS

A. The Use of Hydrated Antimony Pentoxide (HAP) for Separation of Elements in Irradiated Materials

1. Introduction

In the neutron irradiation of many materials, such as those of biologic origin, geological specimens, glass, etc., for which activation analysis is a useful tool, the large amounts of sodium present result in very high levels of gamma activity. This activity can cause a radiological health hazard, as well as serious problems in the analysis of the gamma spectra for other nuclides present.

Girardi and co-workers at ISPRA [12] reported the use of hydrated antimony pentoxide (HAP) for the selective, quantitative removal of radiosodium from mixtures of radionuclides. A study of the use of HAP as applied to the NBS activation analysis program was started by attempting to repeat some of the work reported by Girardi. First, the retention of sodium-22 in 12<u>M</u> HCl on HAP was measured. Quantitative removal was observed. However, difficulty in the handling of the HAP was encountered. The HAP proved to be very fragile, i.e., it continually broke into extremely fine particles, even after sieving and slurrying with HCl or water to remove the "fines."

The HAP was used in 11mm diameter columns. If the filtering and supporting media at the bottom of the HAP column were not retentive enough some of the "fines" came through with the eluant, carrying appreciable quantities of the sodium along. If the filtering and supporting media were too retentive, the "fines" plugged it up and little or no flow through the column resulted. After trials with quartz-wool plugs as recommended by Girardi gave very poor results, course fritted filter discs, selected by trial and error were found to be satisfactory. Figure 47 shows a column found to be useful for quantities of HAP up to 9 grams and solutions up to 50 ml.

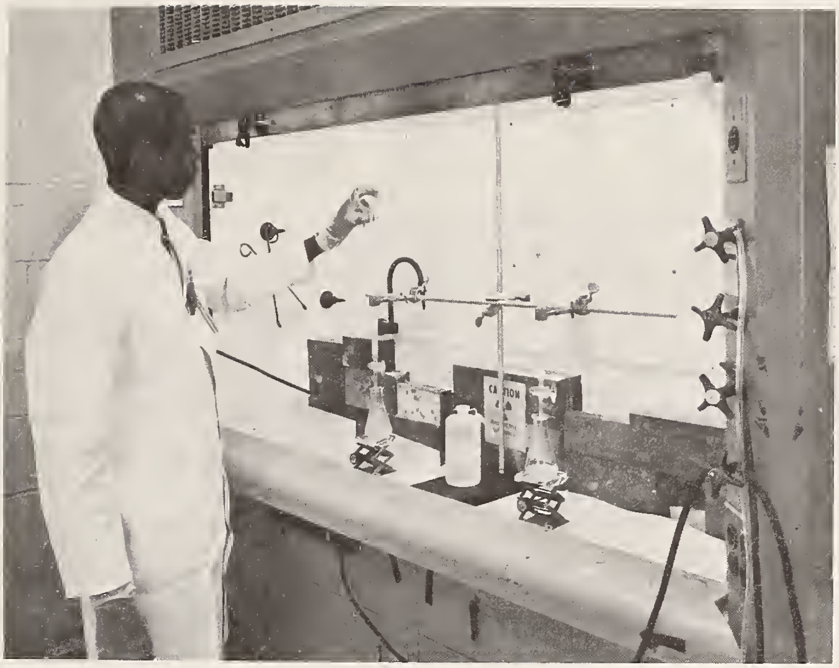

Figure 47. Sodium removal on a HAP column

2. Experimental

a. Retention of ^{22}Na on HAP from 12M HCl. One half ml of ^{22}Na solution and 15 ml 12M HCl, with from 0 to 70 mg NaCl as carrier were added to a 2 oz. polyethylene screw-top bottle, and counted on a 3 in. x 3 in. NaI(Tl) crystal connected to a 1024 channel analyzer. This was the standard counting procedure for all samples.

The solution was then passed through a 3 gm column of HAP prepared as above, and the eluant collected in a clear 2 oz. polyethylene bottle and counted. The flow of the solution through the HAP column was assisted as necessary by light air pressure applied to the top of the column. Flow rate was held to 2-3 ml/min. In all cases, retention of the ^{22}Na on the HAP column was quantitative. The columns were then washed with two successive 15 ml portions of 12M HCl, and the eluates caught and counted separately. In all cases, only small fractions of a percent of the ^{22}Na showed in the eluates.

b. Separation of ^{22}Na and ^{110m}Ag in 12M HCl Solution. Two hundred and fifty μl of the ^{22}Na solution, 0.5 ml of a solution of ^{110m}Ag and 15 ml 12M HCl were added to a 2 oz polyethylene bottle and counted. The solution was then passed through a 3 g column of HAP, the eluate collected and counted as above. The ^{22}Na was quantitatively retained on the HAP, and 92% of the ^{110m}Ag was present in the eluate. The HAP column was rinsed with 15 ml 12M HCl, which was collected and counted as above. A trace of ^{22}Na and the remainder of the ^{110m}Ag were present. The HAP column was rinsed with a second 15 ml portion of 12M HCl. Again, a trace of ^{22}Na was present.

c. Separation of ^{22}Na and ^{110m}Ag from Solutions of $HClO_4$ Since many of the samples analyzed in the Section's program are processed in $HClO_4$, a study of the behavior of $HClO_4$ solutions of various radionuclides on HAP columns was initiated. The ^{22}Na solution containing ^{110m}Ag and ∿50 mg NaCl in 15 ml of 12M, 6M or 3M $HClO_4$ respectively were counted.

d. 12M $HClO_4$. The solution was passed through a 3 gm HAP column and the eluate was collected and counted as above. Approximately 68% of the ^{22}Na and no ^{110m}Ag were present in the first eluate. The HAP column was rinsed with 15 ml 12M $HClO_4$. Eluate #2 showed ∿32% of the original ^{22}Na present, and no ^{110m}Ag. The HAP column was rinsed with a second 15 ml 12M $HClO_4$. Eluate #3 showed <1% of the original ^{22}Na and no ^{110m}Ag. These results were extremely interesting, since Girardi had reported that he was unable to remove sodium from HAP with any of the acids and solvents that he had tried.

e. 6M $HClO_4$. The solution was passed through a 3 gm HAP column and the eluate collected and counted as above. No ^{22}Na or ^{110m}Ag were detected. The HAP column was rinsed with two separate 15 ml portions of 6M $HClO_4$, and the eluates collected and counted separately. No ^{22}Na was detected in either eluate, and only trace amounts of ^{110m}Ag were observed.

The HAP column was then rinsed with 15 ml of 12M HCl. The eluate contained no ^{22}Na and ∿15% of the ^{110m}Ag. The HAP column was then rinsed with a second 15 ml of 12M HCl, and the eluate ∿2.5% of the ^{110m}Ag and ∿3% of the ^{22}Na were present.

f. 3M $HClO_4$. The solution was passed through a 3g HAP column. No detectable amounts of ^{22}Na or ^{110m}Ag were in the eluate. The HAP column was rinsed with 15 ml of 3M $HClO_4$. The eluate again showed no ^{22}Na or ^{110m}Ag activities. The HAP column was rinsed with 15 ml 12M HCl. The eluate contained no ^{22}Na but ∿70% of the ^{110m}Ag was present. It was attempted to rinse the column with a second 15 ml portion of 12M HCl, but the column clogged and only about 10 ml could be passed through. The eluate contained no ^{22}Na, but significant amounts of ^{110m}Ag, which could not be measured quantitatively.

In further studies, after refinement of the HAP column preparation procedure, it was shown that the ^{22}Na and ^{110m}Ag could be recovered sequentially and quantitatively from HAP columns on which they had been deposited from 3M $HClO_4$ solutions, using successive eluations with 12M $HClO_4$ and 12M HCl. However, varying amounts of the ^{110m}Ag, from zero to 15% came through with the original 3M $HClO_4$ fraction.

g. Separation of ^{198}Au, ^{110m}Ag and ^{22}Na with HAP. Using a solution of ^{198}Au, ^{110m}Ag and ^{22}Na in 3M $HClO_4$, and the eluation procedures described in (a) above, it was found that the gold came through quantitatively in the first two 3M $HClO_4$ eluates, 96% in the first and the rest in the second eluate. The ^{110m}Ag and ^{22}Na were then separated by successive eluations with 12M HCl and 12M $HClO_4$ as described in (c) above.

h. Separation of Radioactive Sodium from Glass. One hundred and forty mg of MG GCA-41 glass (not irradiated) and 0.5 ml ^{22}Na solution were dissolved in HF, HNO_3 and $HClO_4$, taken to dense fumes of $HClO_4$, and, very carefully, to dryness. The residue was then dissolved in 12M HCl and counted.

The solution was passed through a 3g HAP column, and the eluate collected and counted as above. Approximately 0.3% of the ^{22}Na showed up in the eluate.

A number of such HAP columns were then prepared and given to Dr. Barbara Thompson, who used them to separate ^{24}Na from solutions of irradiated glass samples.

Two aliquots of a solution of irradiated glass 40-B, obtained from W. D. Kinard, were diluted to 15 ml with 3M $HClO_4$, and passed through separate 3g HAP columns. Each column was rinsed with two 15 ml portions of 3M $HClO_4$, which were collected and counted separately. The sodium was retained quantitatively on the HAP columns. Gold-198 came through quantitativley in the first eluate. Other radionuclides present, not completely identified, came through the first and second eluates in approximately equal proportions, and in lesser, but significant amounts in the third eluate. From this preliminary work it would appear that 3M $HClO_4$ is not the ideal medium for initial passage of a complex mixture of radionuclides through HAP. A medium which would allow either quantitative passage of all or most of the radionuclides through the HAP, or which would permit quantitative retention of all or most of the radionuclides on the HAP would be most desirable. The former exists, e.g., 12M HCl as reported by Girardi. The latter will be a goal of further investigation here, along with means of selectively eluting the absorbed radionuclides.

3. Results and Discussion

Studies have shown that hydrated antimony pentoxide (HAP) as reported by Girardi and Sabbioni [12] at ISPRA, is very effective in removing sodium from solutions. Further, these preliminary studies have shown that by use of suitable solvents, namely different acids of various concentrations, with HAP, selective absorption and elution of a mixture of radionuclides may be effected. Further investigative efforts along these lines will be carried out, possibly in conjunction with studies of other inorganic ion exchangers, such as SnO_2, which have been reported in the literature.

(W. F. Marlow)

B. The Application of the Antibiotic, Tetracycline, to Chemical Separations

1. Introduction

The group of antibiotics called the tetracyclines have found wide application in the field of medicine since the early 1950's. The group includes such antibiotics as tetracycline (achromycin), oxytetracycline (terramycin), and chlorotetracycline (aureomycin). Tetracycline is the generic name for 4-dimethyl amino-1,4,4a,5,5a,6,11,12a-octahydro-3, 6,10,12,12a-pentahydroxy-6-methyl-1,11 dioxo-2 naphthacene carboxamide. It is a yellow crystalline compound having the formula $C_{22}H_{24}N_2O_8$ and a molecular weight of 444.43. The structure of the tetracycline molecule is shown in figure 48.

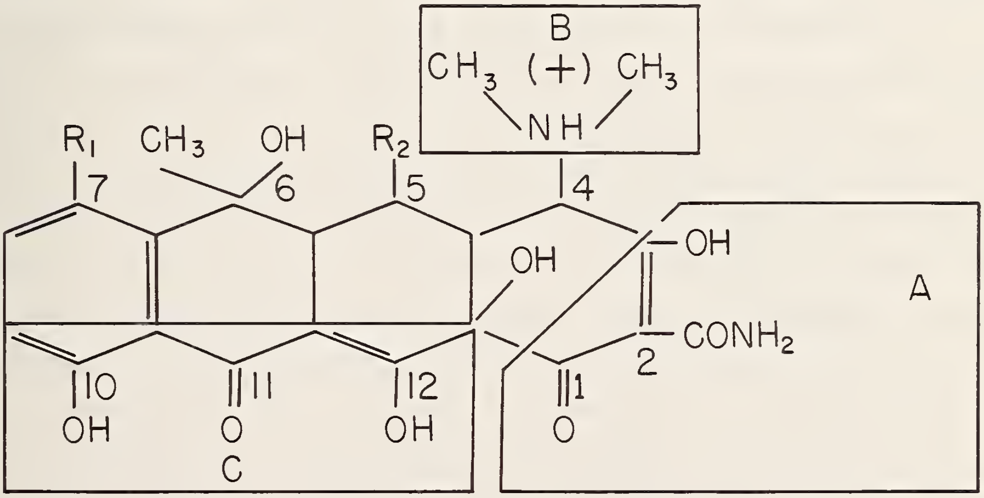

Figure 48. Structure of the tetracyclines

Oxytetracycline	R_1=H, R_2=OH
Cyclotetracycline	R_1=Cl,R_2=H
Tetracycline	R_1=H, R_2=H

The groups A, B, and C illustrate the three distinct acid groups of the molecule, the tricarbonylmethane system A, the ammonium cation B, and the phenolic diketone system C. The three thermodynamic pka values have been assigned by Leeson [27] et at. as pK, (system A)=3.30, pK_2 (system C)=7.68, and pK_3 (system B)=9.69.

Tetracycline has been recognized for some years as an excellent chelating agent for various inorganic ions. Its action as an antibiotic has been attributed to its strong chelating properties [28].

Albert [29,30] has calculated stability constants for the interaction of many metal ions with tetracycline .HCl, oxytetracycline .HCl, and chlorotetracycline .HCl, and has found many to form stable complexes. Maxwell et al. [31] have determined the stability constants of magnesium, calcium, and strontium with tetracycline. Other studies have postulated that tetracycline facilitates the elimination of strontium from bones in mice [32,33], although Maxwell, et al. dispute that this enhancement is due to a strontium-tetracycline complex since calcium forms a more stable complex with tetracycline than does strontium.

Ibsen and Urist [34] have postulated the positions of chelation of the molecule with calcium to be between the oxygens at carbon positions 10 and 11, 11 and 12, the oxygen at carbon 1 and the NH_2 at carbon 2., and the oxygens at carbons 2 and 3. Ishidate and Sakaguchi [35] have studied the chlorotetracycline complexes of various metals in order to predict the point of chelation in the molecule. Baker and Brown [36] have concluded that chelation with cobalt and nickel takes place through two oxygens of the 1,2,3 tricarbonmethane system, the amide oxygen at C_2 and the hydroxyl at C_1 or C_3.

Although much work has been done with tetracycline in structural determinations of stability constants, no one had previously applied tetracycline to chemical separations, although one would postulate from the structural studies previously mentioned that it may be useful in that capacity.

The first application of tetracycline for an analytical separation was a solvent extraction produced for the determination of strontium-90 in environmental grass samples [37].

A study was then conducted to determine the feasibility of a comprehensive examination of the extraction of the metallic elements using tetracycline. The metals chosen for this preliminary study were titanium, scandium, iron, nickel, yttrium, niobium, thallium, and lead.

2. Experimental

The tetracycline used in this study was supplied by Charles Pfizer and Co.* as the hydrochloride. Benzyl alcohol was chosen as the organic solvent because it readily dissolves the tetracycline and is immiscible with water. In preparing the solution the tetracycline-benzyl alcohol mixture was heated slightly to facilitate solution and was cooled to room temperature before use in the extraction studies.

The procedure used in this study consisted of adding aliquots of gamma emitting isotopes of titanium, scandium, iron, nickel, yttrium, niobium, thallium and lead to small volumes of distilled water. The pH of these solutions was adjusted to various values with dilute HCl or NaOH. The solutions were then extracted for one minute with an equal volume of tetracycline in benzyl alcohol ($4.5\text{x}10^{-3}$M). The mixture was centrifuged to guarantee complete separation of the layers. The layers were drawn off and the individual phases counted with a sodium iodide detector connected to a scaler and automatic sample changer. Curves of percent extraction into the organic phase versus pH were plotted.

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* See disclaimer in Preface.

The percent extracted in the diagrams are for one extraction with tetracycline in benzyl alcohol. Because of the hydrolysis of the tetracycline, if more than one extraction is desired, it may be necessary to readjust the pH of the aqueous phase. For this reason extraction studies will be conducted for some metals using buffered solutions.

3. Results

Figure 49 shows the extraction curves obtained for the metals investigated in the preliminary study. Thallium (III) extracted much more readily than the other elements but this extraction can not be attributed to the formation of a thallium tetracycline complex since thallium extracted equally well into the solvent, benzyl alcohol. The extraction of the other elements shown in figure 49 are attributable to the formation of tetracycline complexes which were soluble in benzyl alcohol since they did not extract into benzyl alcohol. Those ions with charges of three or greater extract more readily than lead or nickel.

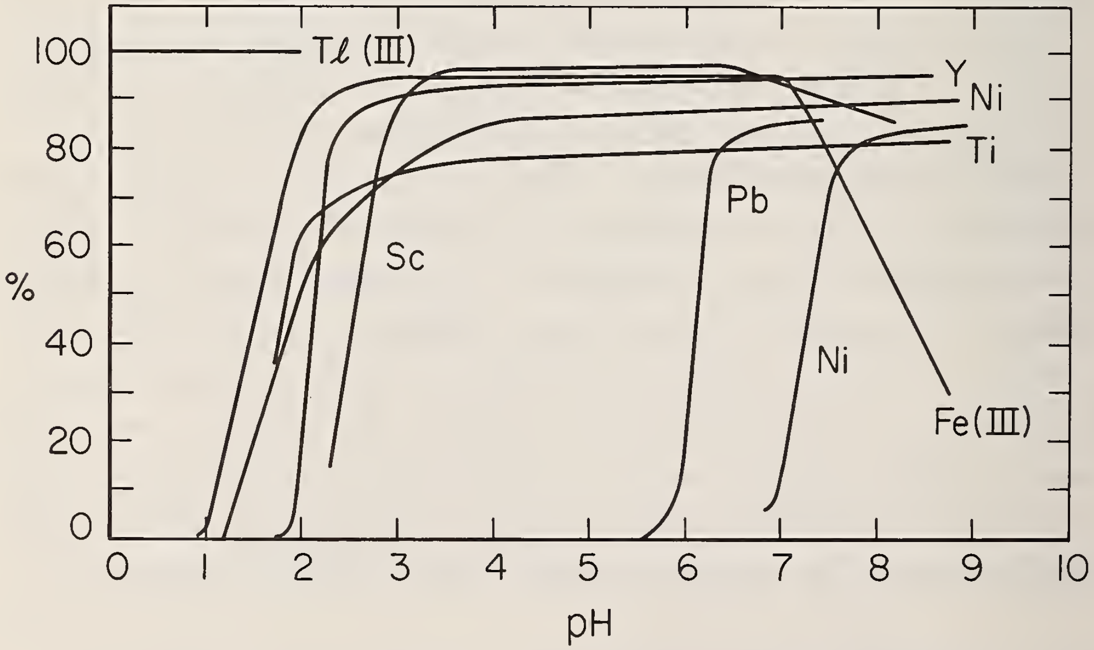

Figure 49. Extraction curves with tetracycline

The difference in the extraction of thallium and iron in different oxidation states is illustrated in figure 50. The higher oxidation states of thallium and iron extract much more efficiently.

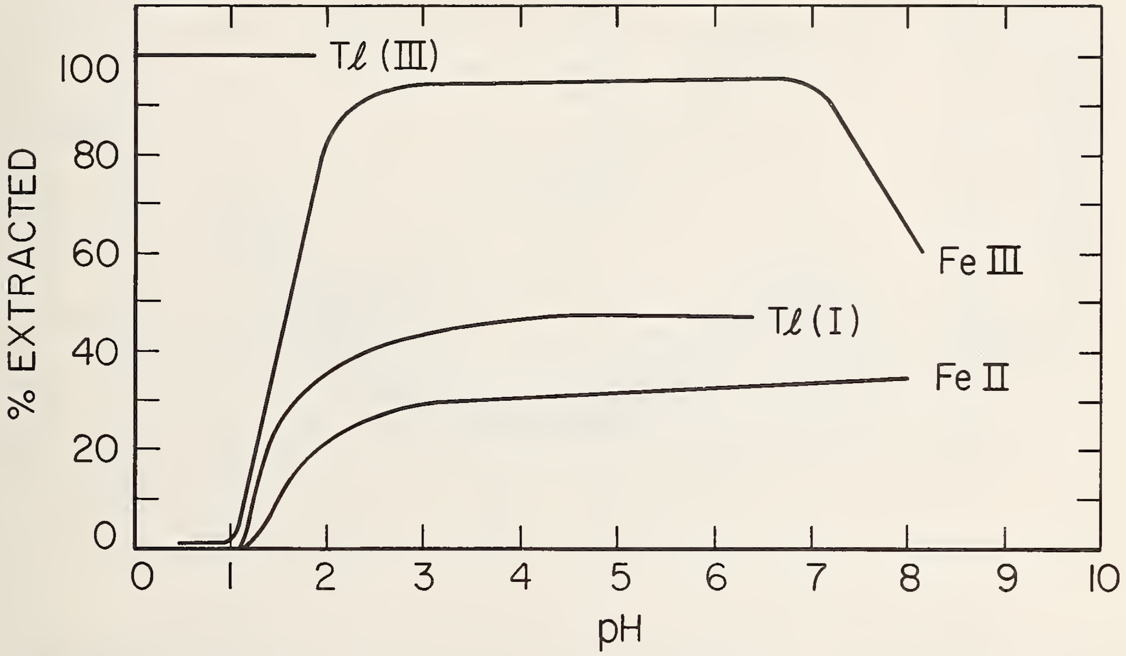

Figure 50. Extraction of iron and thallium at various oxidation states

Since some of the metals which extract in the lower pH range could not be separated from one another by a pH adjustment, the possibility of differential complexation through the addition of a complexing agent was investigated. The extraction of yttrium, scandium, iron and niobium were studied with EDTA, citric acid, and tartaric acid added. The concentrations of these complexing agents were varied from .01M to 1M. EDTA proved to be such a strong complexing agent that none of these metals were extracted at any pH value.

Figure 51 shows the extraction curves obtained in the presence of .01M citric acid. Higher citric acid concentrations did not significantly change the shape or position of

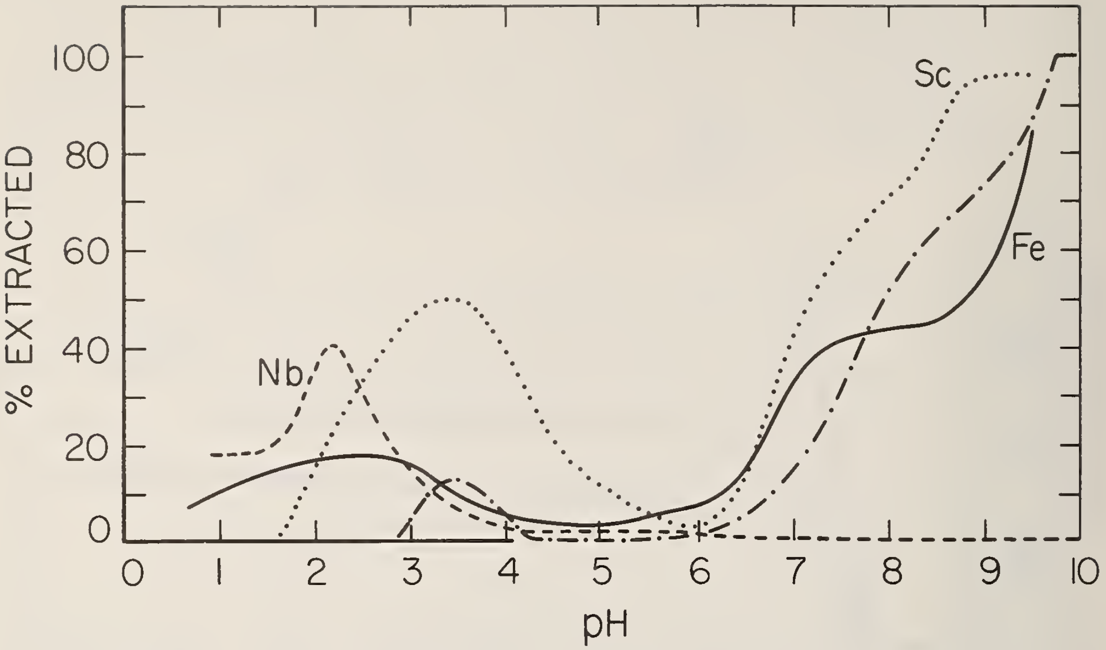

Figure 51. Extraction with citric acid added.

the curves. At pH 9.5 scandium, yttrium, and iron (III) can be separated from niobium by the addition of citric acid but no separation of scandium, yttrium, and iron was attained.

Figure 52 illustrates the effect of tartaric acid as a complexing agent but again no separation of scandium, yttrium, and iron (III) could be realized.

Although it was not possible, using tetracycline, to isolate each of the elements studied, it was decided the results offered enough promise especially for the possibility of group separations, for the investigation with other elements to begin. These additional investigations are currently being conducted by studying the extraction of the transition elements. The data obtained thus far are summarized in figure 53.

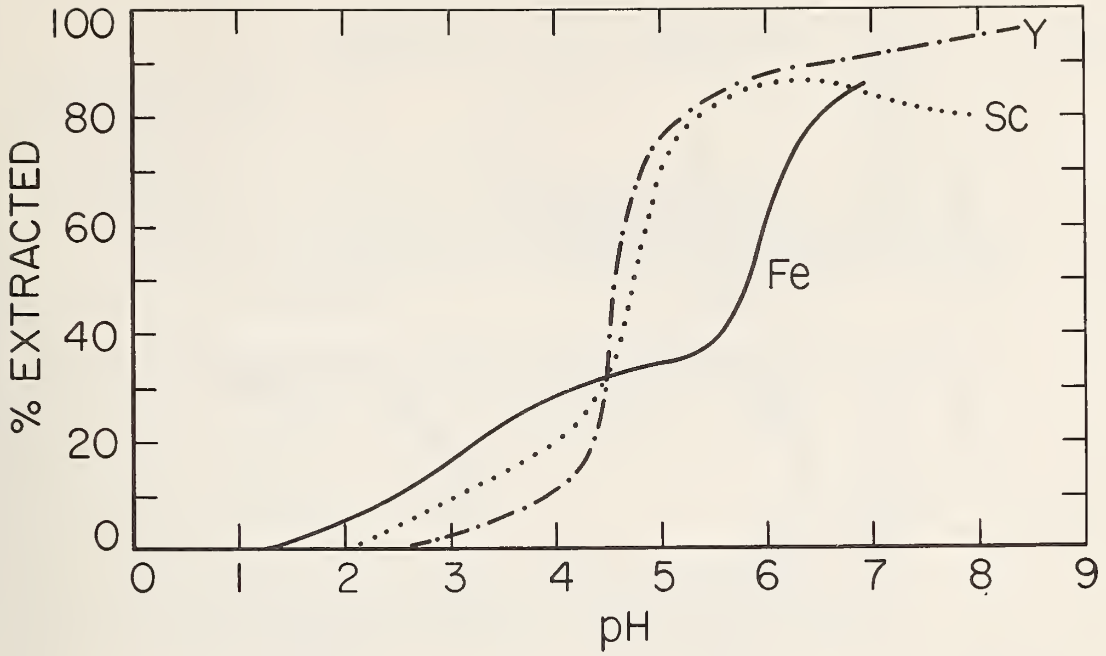

Figure 52. Extraction with tartaric acid added

Figure 53(a) illustrates the extraction of the group Ib elements (copper, silver, and gold). The extraction of Au(III) is due to the formation of an ion-associated complex with the benzyl alcohol. The partial extraction of silver, copper and gold were attributed to formation of tetracycline complex.

Interesting separations obtained within groups are mercury from zinc and cadmium, yttrium and scandium from lanthanum, niobium from tantalum, and molybdenum and tungsten from chromium.

4. Conclusions

On the basis of experimental work conducted thus far it would appear that tetracycline may be applicable to many chemical separations, both individual and group. The goal of this project is the study of the extraction of most of the elements in the Periodic Table with tetracycline. The use of buffered solutions will be investigated in some instances as will the effect of various different acids.

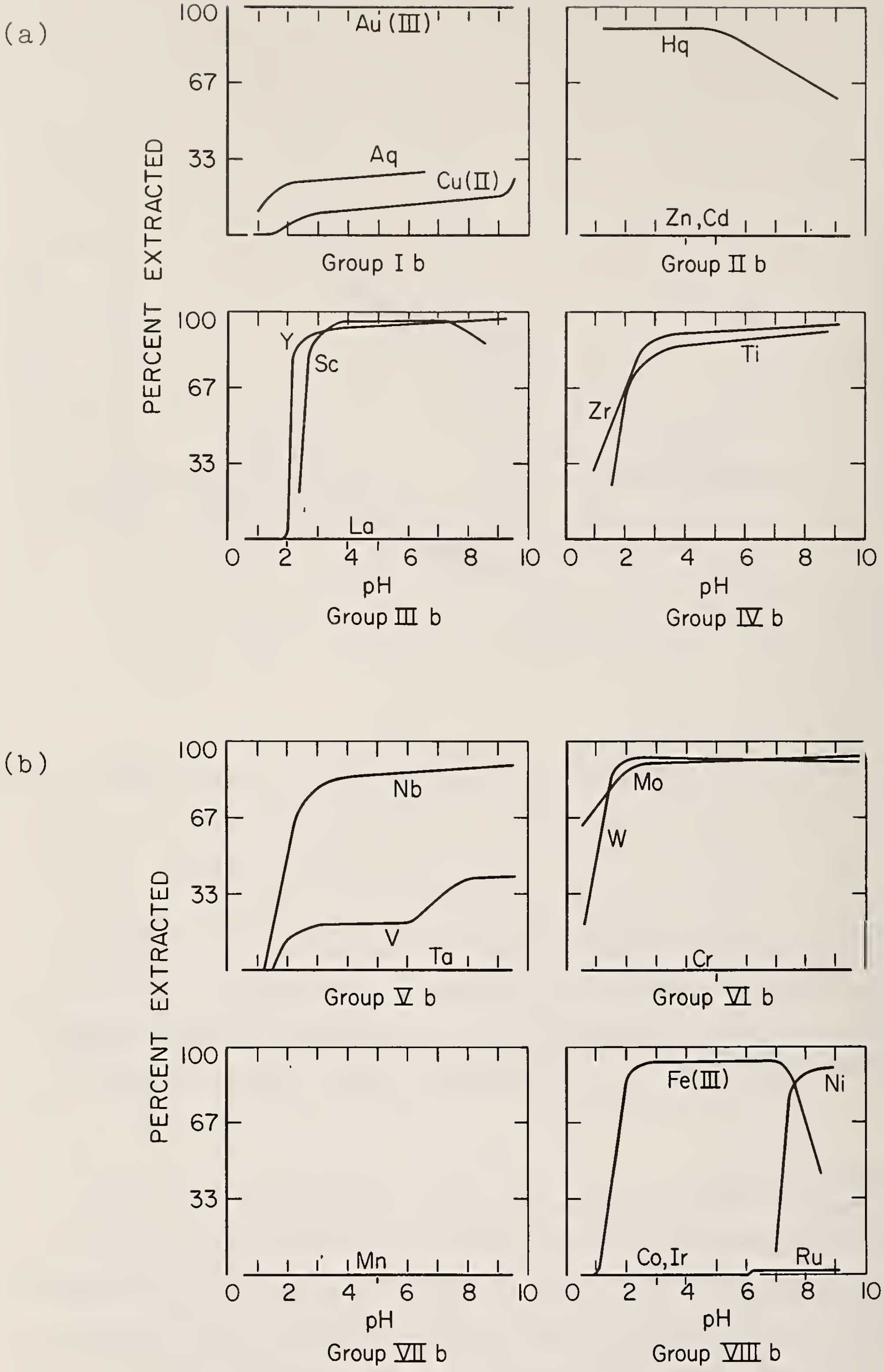

Figure 53. Extraction of transition elements with tetracycline

(L. W. Masters)

7. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Activation Analysis Section
- Philip D. LaFleur, Section Chief (1)
- Betty E. Crowther, Secretary (1)
- Wanda Collins (Summer Worker, Youth Opportunity Program)

Activation Analysis, Reactor
- P. D. LaFleur, Project Leader (1)
- D. A. Becker, Project Leader (1)
- T. E. Gills (1)
- W. D. Kinard (1)
- F. A. Lundgren (1)
- Paul Quittner, Guest Worker, Hungary
- G. W. Smith (on leave to IAEA) (1/4)
- B. A. Thompson (1/2)
- Kenzie DeLaine (Summer Worker, Youth Opportunity Program)

Activation Analysis, Cockcroft-Walton Generator
- S. S. Nargolwalla, Project Leader and Assistant Section Chief (1)
- J. E. Suddueth (1)
- Jerzy Niewodniczanski, Guest Worker, Poland
- E. P. Przybylowicz, Industrial Research Associate (1/6)
- Sheryl Birkhead (Summer Worker)

Activation Analysis, LINAC
- G. J. Lutz, Project Leader (1)
- L. W. Masters (1/2)

Radiochemical Separations
- B. A. Thompson, Project Leader (1/2)
- I. H. Qureshi, NBS Contract, Pakistan (1/3)
- W. F. Marlow, Guest Worker - USAEC (2/3)
- L. W. Masters (1/2)

Activation Analysis of Biological Materials
- D. A. Becker, Project Leader (1/2)

NOTE: Fractions in parentheses indicate fraction of the year in this position.

B. Publications

*R. E. Jervis, H. Al-Shahristani and S. S. Nargolwalla, "Fast Neutron Continuous Activation Analysis of Dilute Solutions," Proceedings of the 3rd International Conference, Modern Trends in Activation Analysis, National Bueau of Standards, Gaithersburg, Maryland, 1968, pp.

S. S. Nargolwalla, E. P. Przybylowicz, J. E. Suddueth and S. L. Birkhead, "Blank Considerations in 14-MeV Neutron Activation Analysis for Trace Oxygen," ibid, pp.

E. P. Przybylowicz, Gilbert W. Smith, J. E. Suddueth and S. S. Nargolwalla, "Activation Analysis of Chloride and Iodide in Photographic Emulsions Using 14.7- and 2.8-MeV Neutrons," ibid, pp.

S. S. Nargolwalla, E. P. Przybylowicz, J. E. Suddueth and S. L. Birkhead, "Solution of Blank Problems in 14-MeV Neutron Activation Analysis for Trace Oxygen," Anal Chem., 41, 168 (1969).

E. P. Przybylowicz, Gilbert W. Smith, J. E. Suddueth and S. S. Nargolwalla, "Activation Analysis of Halogens in Photographic Emulsions Using a Neutron Generator," Anal. Chem., 41, 819 (1969).

S. S. Nargolwalla and P. D. LaFleur, "Characterization of Standard Reference Materials for Industry and Research by Neutron Generator Activation Analysis," Proceedings of American Nuclear Society, Topical Meeting, Radiation and Isotope Technology in Latin American Development, San Juan, Puerto Rico, 1969, pp

L. W. Masters, A. B. Braun, A. Schwebel, "Determination of Strontium-90 in Environmental Samples After Extraction of Yttrium-90 and Barium-140 Using Tetracycline," Anal. Chem. (in press).

L. W. Masters, "The Separation and Determination of Strontium-90 in Environmental Samples Using Tetracycline," Master of Science thesis project submitted to the American University, Washington, D. C., June, 1968.

G. J. Lutz, Determination of Rare Earths by Photon Activatio Analysis," Talanta, (in press)

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* Work not done at NBS.

B. A. Thompson and P. D. LaFleur, "Rapid Group Radiochemical Separations for Activation Analysis in Steels," Anal. Chem., 41, 852 (1969).

B. A. Thompson, "Group Radiochemical Separations: A Practical Approach to Activation Analysis," Proceedings, 3rd International Conference on Modern Trends in Activation Analysis, National Bureau of Standards, Gaithersburg, Maryland pp 634-8 (1969).

G. J. Lutz, R. J. Boreni, R. S. Maddock, and W. W. Meinke "Activation Analysis: A Bibliography," NBS Tech. Note 467 (1968).

G. J. Lutz, "Self-Shielding Corrections in Photon Activation Analysis," Proceedings, 3rd International Conference, Modern Trends in Activation Analysis, National Bureau of Standards, Gaithersburg, Maryland, pp 829-34 (1969).

G. J. Lutz, "The National Bureau of Standards Automated Activation Analysis Information Retrieval System," Proceedings, 3rd International Conference on Modern Trends in Activation Analysis, National Bureau of Standards, Gaithersburg, Maryland, pp. 1128-30 (1969)

C. List of Talks

D. A. Becker, "Neutron Activation Analysis of Ultrapure Reagents: The Quest for an Absolute Blank," 156 Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1968.

W. D. Kinard, "The Determination of Indium and Copper in High Purity Gold by Neutron Activation Analysis," (P. D. LaFleur, W. D. Kinard and D. A. Becker) 156th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1968

T. E. Gills, "Neutron Activation Analysis of Impurities in Specially Purified Urea," (D. A. Becker and T. E. Gills) 156th Meeting of the American Chemical Society, Atlantic City, New Jersey, September 1968.

W. D. Kinard, "The Determination of Indium and Copper in High Purity Gold by Neutron Activation Analysis," (P. D. LaFleur, W. D. Kinard and D. A. Becker) 156th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1968.

G. J. Lutz, "Determination of Yttrium in Rare Earths by Photon Activation Analysis," (G. J. Lutz and P. D. LaFleur) 156th Meeting of the American Chemical Society, Atlantic City New Jersey, September, 1968.

G. J. Lutz, "The National Bureau of Standards Activation Analysis Literature File," 156the Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1968.

L. T. McClendon, "Radiochemical Separations Utilizing Hydrogen bis(2-ethylhexyl) Orthophosphate," (L. T. McClendon, I. H. Qureshi and P. D. LaFleur) 156th Meeting of the American Chemical Society, Atlantic City, New Jersey, Spetember, 1968.

B. A. Thompson, "Activation Analysis for Molybdenum in the Presence of Large Amounts of Tungsten," (B. A. Thompson, and P. D. LaFleur) 156th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1968.

B. A. Thompson, "Determination of Impurities in High Purity Zinc by Neutron Activation Analysis," (B. A. Thompson, and D. A. Becker) 156th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1968.

G. J. Lutz, "Self Shielding Corrections in Photon Activation Analysis," 3rd International Conference: Modern Trends in Activation Analysis, National Bureau of Standards Gaithersburg, Maryland, October 7-11, 1968.

G. J. Lutz, "The National Bureau of Standards Automated Activation Analysis Information Retrieval System," (G. J. Lutz, R. J. Boreni, R. S. Maddock and W. W. Meinke) 3rd Interantional Conference: Modern Trends in Activation Analysis, National Bureau of Standards, Gaithersburg, Maryland, October 7-11, 1968.

S. S. Nargolwalla, "Fast Neutron Continuous Analysis of Dilute Solutions," (J. E. Jervis, H. Al-Shahristani and S. S. Nargolwalla) 3rd International Conference: Modern Trends in Activation Analysis, National Bureau of Standards, Gaithersburg, Maryland, October 7-11, 1968.

S. S. Nargolwalla, "Blank Considerations in 14-MeV Neutron Activation Analysis for Trace Oxygen," (S. S. Nargolwalla, E. P. Przybylowicz, J. E. Suddueth and S. L. Birkhead) 3rd International Conference: Modern Trends in Activation Analysis, National Bureau of Standards, Gaithersburg, Maryland, October 7-11, 1968.

E. P. Przybylowicz, "Activation Analysis in Chloride and Iodide in Photographic Emulsions Using 14.7- and 2.8-MeV Neutrons," (E. P. Przybylowicz, Gilbert W. Smith, J. E. Suddueth and S. S. Nargolwalla) 3rd International Conference: Modern Trends in Activaiton Analysis, National Bureau of Standards, Gaithersburg, Maryland, October 7-11, 1968.

I. H. Qureshi, "Radiochemical Separations for Activation Analysis Using bis(2-ethylhexyl) Orthophosphoric Acid," (I. H. Qureshi, L. T. McClendon, and P. D. LaFleur) 3rd International Conference: Modern Trends in Activation Analysis, National Bureau of Standards, Gaithersburg, Maryland, October 7-11, 1968.

L. W. Masters, "The Application of the Antibiotic, Tetracycline to Chemical Separations," 4th Middle Atlantic Regional Meeting, American Chemical Society, Washington, D. C., February 12-15, 1969.

P. D. LaFleur, "Activation Analysis in Biology and Medicine," American Chemical Society Local Section Speaker's Tour:

a. Northeast Tennessee Section, Kingsport, Tennessee, March 10, 1969.

b. Chattanooga Section, Chattanooga, Tennessee, March 11, 1969.

c. Nashville Section, Nashville, Tennessee, March 12, 1969.

d. Wilson Dam Section, Muscle Shoals, Alabama, March 13, 1969.

e. Memphis Section, Memphis, Tennessee, March 14, 1969.

f. Auburn Section, Tuskeegee Institute, Alabama, March 13, 1969

g. Atlanta Section, Atlanta, Georgia, March 18, 1969.

h. Birmingham Section, Birmingham, Alabama, March 19, 1969.

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8. ACKNOWLEDGMENTS

The Activation Analysis Section wishes to thank Dr. Robert S. Carter, Mr. Tawfik M. Raby, Mr. James F. Torrence and the operating crews of the NBS Reactor for making the irradiation of samples possible. We also wish to acknowledge the assistance of Mr. Hugh E. DeSpain and the NBS Health Physics staff who have helped us with the safe handling of these samples. Further the assistance of Dr. J. E. Leiss and staff of the LINAC Radiation Division for arrangements to use the LINAC facilities is gratefully acknowledged. We also wish to thank Dr. Brian Joiner for assistance in the statistical analysis of experimental data.

We wish to thank the U. S. Atomic Energy Commission for making possible the visit of Mr. W. F. Marlow. We wish also to thank the International Atomic Energy Agency and the Academy of Mining and Metallurgy, Crakow, Poland, for making possible the visit of Dr. Niewodniczanski and the Ford Foundation and the Central Institute for Physics, Budapest, Hungary, for making possible the visit of Dr. Quittner.

This section acknowledges Mrs. R. S. Maddock for her assistance in preparing this report.

Special appreciation is expressed to Mrs. B. Crowther who typed the entire report and whose tireless efforts as section secretary has made our entire operation more efficient and effective.

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