NBS TECHNICAL NOTE

458

Activation Analysis Section:

Summary of Activities July 1967 to June 1968

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

UNITED STATES DEPARTMENT OF COMMERCE
Maurice H. Stans, Secretary
NATIONAL BUREAU OF STANDARDS • A. V. Astin, Director

TECHNICAL NOTE 458

ISSUED MARCH 1969

Activation Analysis Section:

Summary of Activities July 1967 to June 1968

Edited by Philip D. LaFleur

Activation Analysis Section
Analytical Chemistry Division
Institute for Materials Research

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C., 20402 - Price $1

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 have now issued these summaries for all of our sections. The following is the second annual report on progress of the Activation Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

During the period covered by this progress report the separation between the Radiochemical Analysis Section and the Activation Analysis Section became complete by the appointment of different Section Chiefs for each section.

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 high inherent accuracy, the very high sensitivity for many elements, the lack of a reagent "blank" in most analyses, and the fact that there are few sources of systematic error associated with the technique that are difficult to evaluate.

During this past year, the Section has become more involved with the application of activation analysis in biological and medical problem areas, and the first steps of what is hoped will be a fruitful relationship with the National Institutes of Health, especially The National Institute of Arthritis and Metabolic Disease, have begun. In connection with these problems, the Section has taken a leading role in the development of Standard Reference Materials for application to analytical problems in medicine and horticulture. Standards of botanical material and freeze-dried blood serum, which are carefully characterized for their trace element content, are being developed now, and a Standard of freeze-dried tissue (liver) will be developed in the near future.

The Activation Analysis Section is composed of three groups that are oriented to a specific source of nuclear radiation; the reactor, LINAC, and Cockcroft-Walton generator groups, and a fourth group for the development of radiochemical separations. This method of division serves the administrative needs. More important is the fact that 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 8. 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

TABLE OF CONTENTS

TABLE OF CONTENTS (cont.)

TABLE OF CONTENTS (cont.)

LIST OF FIGURES

LIST OF FIGURES (cont.)

LIST OF TABLES

LIST OF TABLES (cont.)

ACTIVATION ANALYSIS: COCKCROFT-WALTON GENERATOR, NUCLEAR REACTOR, LINAC

July 1967 through June 1968

Edited by Philip D. LaFleur

ABSTRACT

The facilities used by the reactor, LINAC and neutron generator groups for activation analysis are described. Proposed installation of four new irradiation terminals and a new pneumatic transfer tube system are outlined.

A new 2.5-mA neutron generator has been installed and the biological shield, pneumatic transfer system and the detector assembly modified. Studies of blank problems for oxygen determination and self-absorption corrections in photopeak analysis have resulted in greatly improved precision for Standard Reference Materials. Halide in photographic emulsions, using 14-MeV and 2.6-MeV neutrons, have been determined.

Considerable emphasis has been placed on the development of group radiochemical separations, SRM steel and high purity zinc samples have been analyzed using this technique.

Eighteen different SRMs were analyzed for a variety of elements and a variety of service analyses were performed.

The self-absorption effects of the matrix on irradiation photons were studied and calculations of sensitivities for photon activation analysis were made. Carbon in sulfur, yttrium in rare earth oxides and oxygen in sodium were determined by photon activation.

The extraction of metals by bis(2-ethylhexyl) orthophosphoric acid has been studied, and distribution coefficients are given for many of the transition metals. The results indicate enhanced applicability of this reagent for radiochemical separations.

Updated keys for computer literature searching and a sample output are included.

KEY WORDS:

Activation analysis, Cockcroft-Walton neutron generator, computer literature searching, extraction, group separations, homogeneity testing, hydrogen bis(2-ethylhexyl) phosphate, matrix effect, molybdenum, NBS LINAC, NBS reactor, photon activation analysis sensitivities, Standard Reference Materials, zinc.

1. INTRODUCTION

During the past year the activation analysis technique has become more and more important in the certification of Standard Reference Materials (SRM). The number of elements which we are capable of analyzing without significant developmental work has increased markedly during this year. The capability of all of the projects has been greatly extended during this time.

As mentioned in last year's report, one of the most serious limitations of the activation analysis technique is in the difficulty in approaching the rapid multi-element analytical capability that is characteristic of emission spectroscopy or spark-source mass spectrometry. Past efforts at survey type analyses have been made with the use of nondestructive techniques and computer resolution of the complex gamma-ray spectra that result. This technique has been only moderately successful and has, in several cases, led to serious questioning of the value of nuclear activation analysis.

We are attempting to achieve the multi-element analysis capability through the application of group radiochemical separations as outlined below.

Except in unusual circumstances, e.g. high accuracy at trace concentration levels, we do not believe that activation analysis is apropos for survey analyses, especially qualitative, since emission and spark-source mass spectrometry are much more versatile for this purpose.

With the advent of high resolution solid state gamma ray detectors, many people have felt that radiochemical separations were no longer needed in activation analysis, that all analyses could be performed using instrumental techniques and computer data reduction. Our philosophy is to use nondestructive activation analysis whenever it is feasible and whenever it gives high accuracy and precision. In cases where nondestructive analysis meeting these criteria

is not possible, we believe very strongly in the utilization of radiochemical separations.

Because stable carriers can be added prior to radiochemical separations, some workers have employed sloppy chemical techniques using the excuse that "I can always determine the yield later." Often these yields are determined using precipitates, etc., which are poorly characterized. The resulting poor precision of analysis has led some workers in the field of activation analysis to blame chemistry for this lack of precision and to devote themselves wholly to instrumental analysis. It is also more expensive to do activation analysis when yield determinations are necessary, since you are essentially analyzing the sample twice. When adequate separations are not available in the literature, we strive to develop separations which are rapid, give very high yields, preferably quantitative, and are as simple as possible. There is no substitute for good chemistry!

The ideal technique is the marriage between nondestructive analysis and analysis with chemical separations. This technique may be referred to as the group separations method in which groups of elements, 1 to 4 or more, are separated together. These groups generally can be resolved readily using high resolution gamma-ray spectrometry. It is this technique, group radiochemical separations, that is receiving the greatest emphasis within the radiochemical separations project.

As always, the evaluation of systematic and random errors has been paramount in the efforts of all the projects in the section. The installation of a new neutron generator having a vastly improved neutron flux level has enabled the analysis of macro constituents in metallo-organics and of oxygen in metals with precisions approximating those of non-nuclear techniques. Using this new generator facility, the studies of the evaluation of systematic errors resulting from

self-absorption and degradation of neutrons during irradiation and of gamma rays during counting, have been completed. This technique allows extrapolation of correction factors between matrices and has been instrumental in allowing analysis of metallic elements in metallo-organics to be performed.

The National Bureau of Standards Reactor (NBSR) achieved criticality in December of 1967, but low power start-up tests are still continuing. It is anticipated at this time that operation in excess of 100 KW will occur in October of 1968 enabling the reactor neutron activation analysis project to utilize the reactor here at the Bureau of Standards rather than having irradiations performed at other reactor centers. In spite of this handicap the reactor neutron activation project has been very fruitful in terms of number of analyses performed during this year.

The photonuclear analysis project has continued to operate whenever time was available at the LINAC. During this year the work on the analysis of carbon in sodium metal has been completed and another project, also of great interest in the fast-breeder reactor program, that of the determination of oxygen in sodium metal, using the $^{16}O(\gamma,n)^{15}O$ reaction has also been completed. There has been no change in the LINAC operating schedule and we are still irradiating approximately one day a week for an eight hour irradiation period. All laboratory facilities in the reactor building, with the exception of the new pneumatic tube facilities, have been completed and we now do all work, with the exception of reactor irradiations, here at the National Bureau of Standards.

2. LIAISON AND GENERAL FACILITIES

A. Liaison

Although the NBS Reactor achieved criticality in December 1967, usable power levels are not yet available for experiments. Because of this, the use of the NBSR facilities for activation analysis by scientists outside the Bureau has not yet been realized.

B. General Facilities

The start-up of the NBS reactor in December, 1967, created a need for efforts in the design and installation of new multi-routing pneumatic transfer systems, suitable handling facilities for highly radioactive samples and for the preparation of irradiation guides for the experimenter. A major proportion of this work has been completed. Subject to final approval by the Hazards Committee, these facilities should be made available during fiscal year 1969.

All of the facilities in the laboratory wing of the NBSR have been completed, with the exception of the pneumatic tube facilities discussed below, and are now in daily use by the personnel of the Section. We are, in addition, still using the irradiation facilities of the NBS LINAC and other reactors, especially the Naval Research Laboratory Reactor.

Efforts have also been expended on the design of a small hot-cell facility in which up to 50 curies of 1 MeV gamma-ray activity can be handled safely. This facility is expected to have the provision for remote handling of the sample for rapid decontamination of the sample from undesirable matrix activity.

An exhaustive draft covering regulations for irradiations in the NBSR has been completed. This guide includes sample irradiation requirements for all available and planned facilities. Over 500 elements and matrices have been included. At the present time the proposed guide is being evaluated for possible acceptance by the Reactor Hazards Committee.

C. Pneumatic Tube System

At the time of construction the NBSR was equipped with a pneumatic tube system consisting of four terminal positions in the reactor and a send/receive location for each tube located in rooms C001 and C002 (fig. 1). The expected flux levels at 10 MW indicate a thermal flux 7.3×10^{13} n·cm^{-2}·sec^{-1} for the tube closest to the core and a thermal flux of 3.8×10^{13} n·cm^{-2}·sec^{-1} with a fast flux of $.16 \times 10^{13}$ n·cm^{-2}·sec^{-1} for the tube farthest from the core.

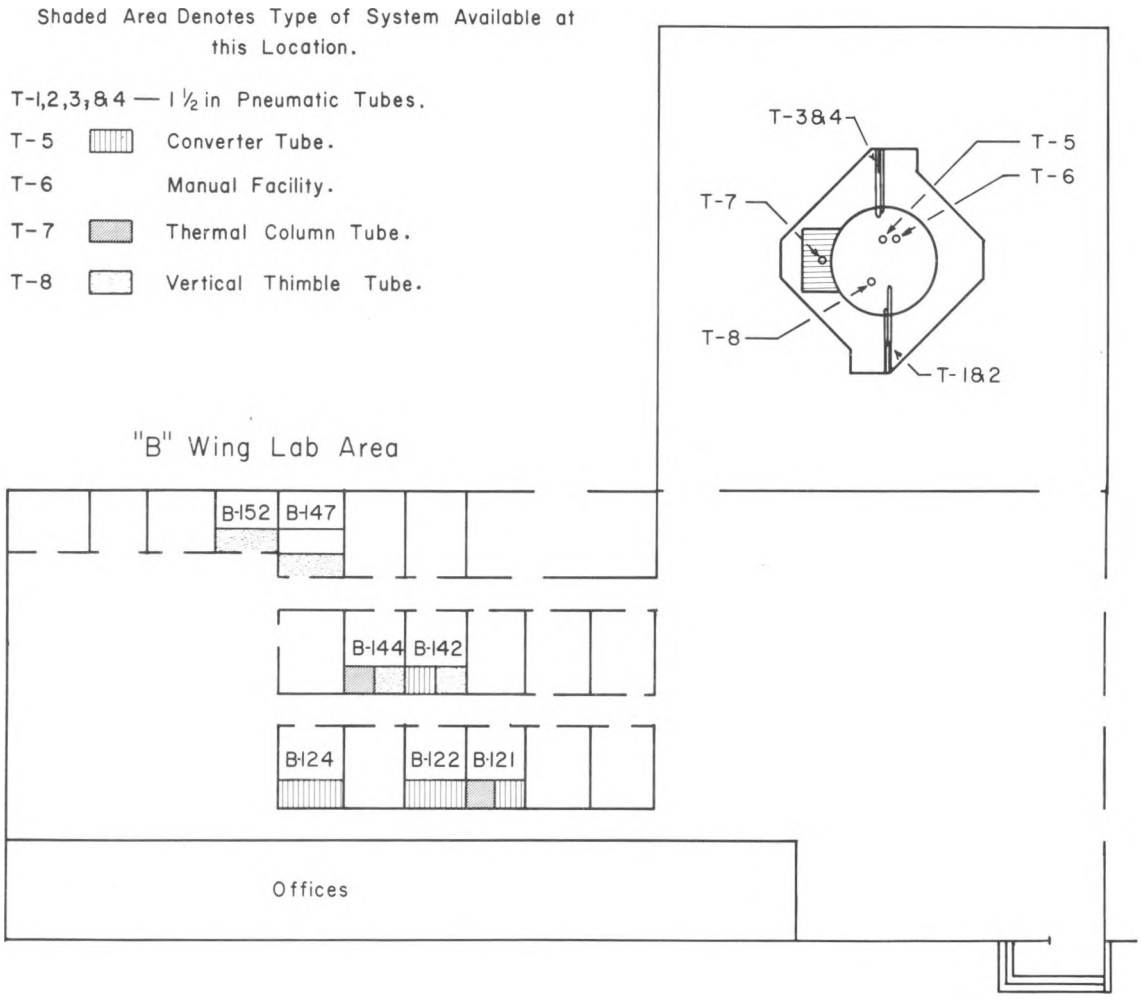

Figure 1. Terminal locations of new pneumatic tube systems.

In order to expand these capabilities, 4 new irradiation terminals are currently under construction. One of the terminals will be constructed entirely of graphite and will be located in the thermal column of the reactor. Using a 1 1/2 in. i.d. pneumatic tube system, laboratories B-144, B-121, and C002 will have access to an essentially pure thermal neutron flux of about $3x10^{11}$ $n.cm^{-2}.sec^{-1}$.

The remaining three terminals will be located in the reactor core. Two of these will be coupled to 7/8 in. i.d. pneumatic tubes, while access to the remaining terminal will be manually from the top of the reactor on the control room level. This manual irradiation facility will be used when samples must be irradiated for a longer period of time than can be allowed in the pneumatic tube location because of radiation damage and heating of polyethylene rabbits. Since it is less affected by the high levels of gamma heating and radiation damage which are to be expected at this location the sample containers will be made of high purity graphite. An irradiation of one reactor cycle (18 days) should produce an NVT of approximately $3x10^{20}$ neutrons in this irradiation facility.

The two 7/8 in. in-core facilities will consist of a vertical irradiation terminal similar to the four tubes orginally installed, and a fast neutron convertor terminal. The fast neutron convertor system will allow irradiation in an essentially pure fission spectrum flux of about $3.5x10^{13}$ $n.cm^{-2}.sec^{-1}$, and will have send/receive stations located in laboratories B-142, B-121, B-124 and C002. The flux in the vertical terminal will be much the same as the manual irradiation system, however, it will be used for short irradiations (probably 3 min. or less) and will serve laboratories B-142, B-144, B-147 and C001.

When the new system is completed the sample irradiation capability of the NBSR will have been expanded to a total of 8 irradiation positions and 22 send/receive locations which

will service 8 different laboratories within the reactor building (fig. 1).

1. Sample Vehical (Rabbit) High density linear polyethylene sample containers will be used in the 7/8 in. system. On special occasions, however, high purity graphite or beryllium containers of the same configuration could be used.

The 7/8 in. and 1 1/2 in. rabbits which will be used in the pneumatic tube system, and the graphite bucket for use with the manual irradiation facility, are shown in figure 2.

Figure 2. Sample carriers for use in NBSR.

2. Instrumentation In order to monitor traffic from the 22 send/receive locations to the 8 irradiation terminals, an instrumentation system has been developed to prevent the insertion of more than one sample in any one tube. An interlock system also has been incorporated whereby only one sample may be in transit at one time. This serves to prevent the insertion, or withdrawal of several samples simultaneously. Since many of the tubes pass through laboratories or work areas, a visual warning system has been built which will be activated in the event a sample becomes lodged in a tube. The alarm will be sounded when a sample has exceeded the preset maximum transit time from the reactor to the receiving station.

In the event of a major scram of the reactor, or a power failure, an emergency system has been developed, using an independent supply of CO_2 propelling gas, which will automatically return all samples in the irradiation terminals to a central, shielded location. This system circumvents the possibility of samples remaining in the core and the rabbit and/or sample container melting during a scram or power failure.

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

3. ACTIVATION ANALYSIS WITH 14 MeV NEUTRONS

A. Introduction

Primary emphasis in this program has been given to research on new approaches toward the improvement of the precision and accuracy of 14 MeV neutron activation analysis. The use of the dual sample-biaxial rotating sample assembly has improved precision by neutron flux homogenization, especially in oxygen analyses, by about a factor of ten better than by other normalization techniques. The NBS system gives results limited in precision chiefly by counting statistics and permits the analyst to determine both neutron and gamma-ray attenuation in dense samples. An outline is given of the careful studies which substantiated the expected exponential dependence of the attenuation correction factor on the calculated attenuation coefficient difference between the sample and the standard. Empirically determined calibration curves as a function of sample diameter can be used to predict attenuation correction factors for oxygen in other matrices than steel.

The more general case of analyses for elements other than oxygen, in which gamma rays of less than 4.8 MeV result from nuclear level transitions or positron annihilations, was also the subject of a detailed research study. Such factors as reaction threshold effects on neutron attenuation and photon energy dependency on attenuation correction factors were evaluated.

Since capsule blanks can cause major difficulties in the determination of trace amounts of oxygen, a method for precisely establishing the capsule contribution was developed. This method corrects for the geometrical configuration of the sample within the capsule. Experimental results are in good agreement with theory.

A highly promising research study was also made on the determination of halogens in a silver bromide matrix in photographic emulsions. Since a knowledge of chloride and iodide composition is essential to the evaluation of the primary light-sensitive properties of such emulsions, rapid and accurate methods were needed. It was found that accurate chloride analyses could be made with a relative standard error of 1% at the 200 mg level. The use of 2.8 MeV neutrons produced by the $^{2}H(^{2}H,n)^{3}He$ reaction, which eliminated undesirable radioisotopes induced above this reaction threshold, allowed the accurate determination of iodine to 1% relative standard error at the 420 mg level.

By the use of a new high flux neutron generator (2.5mA maximum output) plus improvements in shielding, pneumatic tube system and detector, analyses of Standard Reference Materials have been possible with higher orders of precision and accuracy. The elements nitrogen, fluorine, magnesium, silicon, phosphorus, cobalt and silver have been determined (singly) in thirty Standard Reference Materials. Some of the more interesting analyses will be described.

(S. S. Nargolwalla)

B. Status of the 14 MeV Neutron Activation Facility

1. Installation of High Flux Neutron Generator

The flux limitation of the old facility has been eliminated by the installation of a new high flux neutron generator rated at 2.5 mA maximum deuteron beam output, and capable of accelerating monoatomic deuterons up to 200 keV. A gain of about a factor of ten in flux has been realized. The neutron generator, shown in figure 3 is operated from outside the biological shield. The operating console and other equipment are shown in figure 4. Aside from the flux, the new machine differs from the older model in that the design of the tritium target holder includes Freon cooling instead of water and is replaceable for rapid and safe target changes. The generator

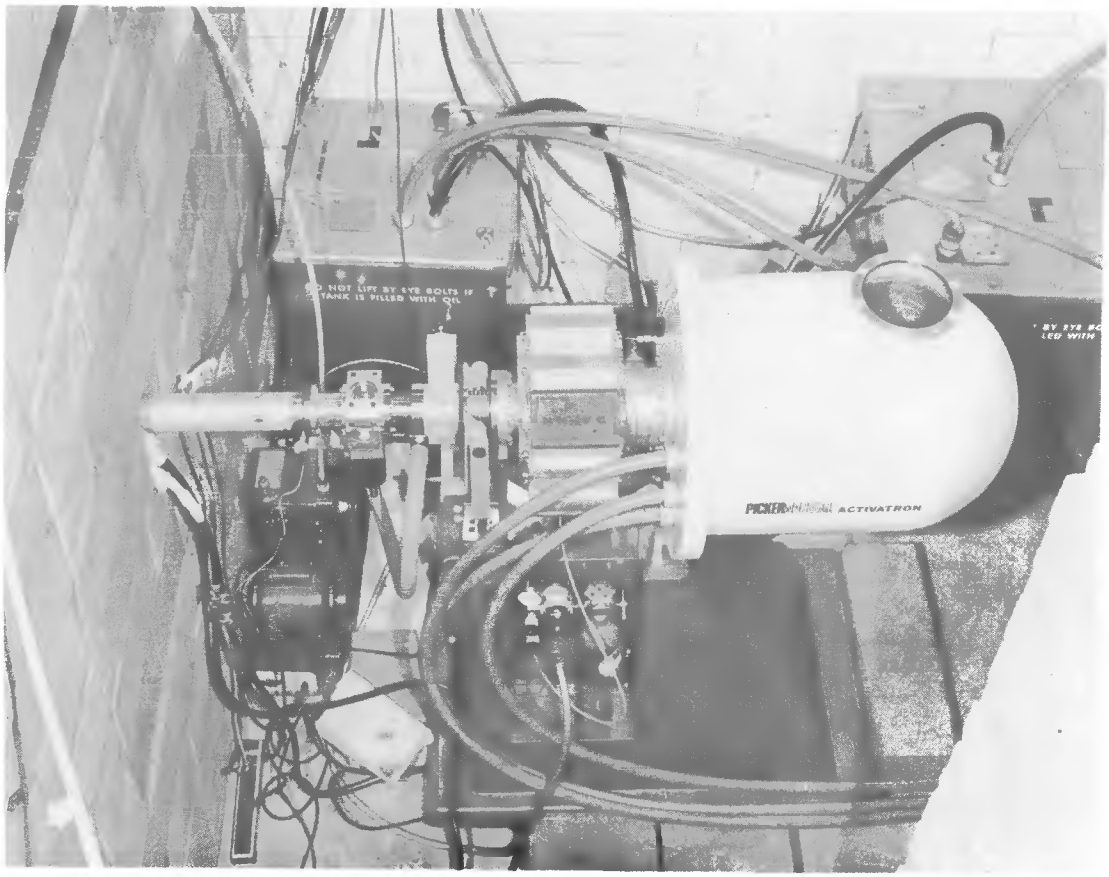

Figure 3. 2.5 mA neutron generator.

also has beam focusing capability and a remote mechanical deuterium leak. The beam stability of this accelerator is comparable to the 500 μA machine previously used [1].

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

2. Biological Shield

In order to house the new high-flux machine, the existing biological shield had to be modified considerably. A general layout (fig. 5) and the cut-a-way drawing (fig. 6) indicate the extent of the modifications in terms of additional high density (180 lb/ft^3) shielding and the construction of a small target room. A closed-circuit T.V. camera can be accom-

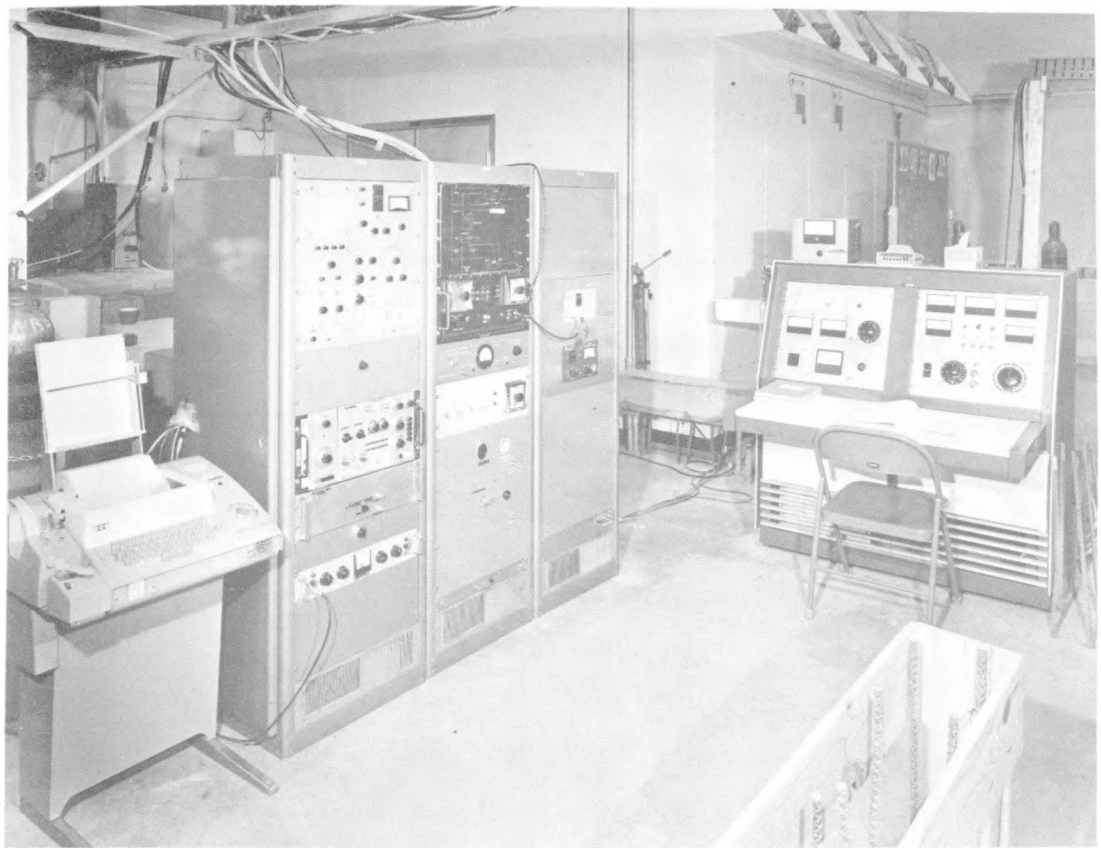

Figure 4. Pulse height analyzer and sequence programmer with associated electronics and neutron generator operating console.

modated in the target room to view the beam for alignment purposes. Preliminary dose measurements made by the Health Physics unit indicate that the shielding of the new structure is equivalent to that of the previous shield for a flux ten times greater than obtained with the 500 μA generator.

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

3. Pneumatic Transfer System

To accommodate the location of the accelerator with respect to the modified biological shield, the pneumatic tube system had to be redesigned. An improved high-speed transfer facil-

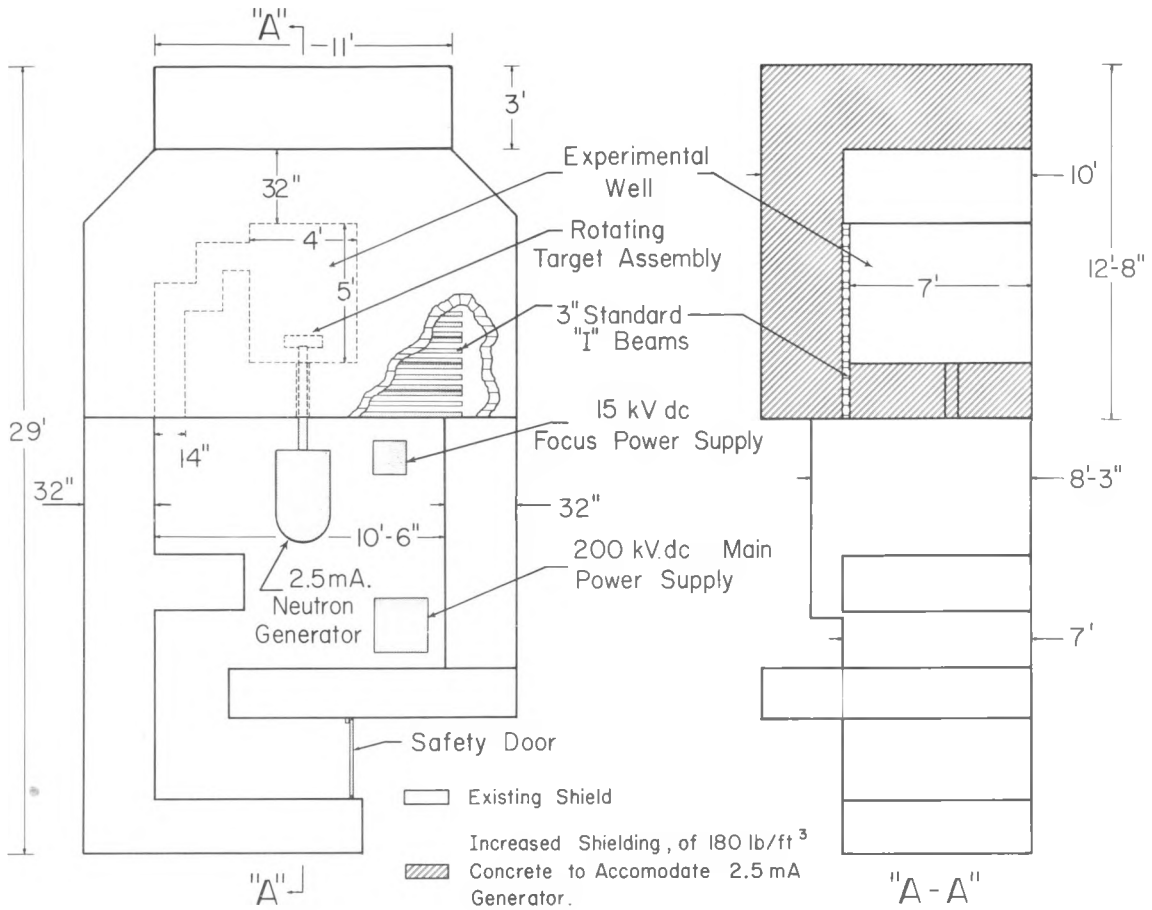

Figure 5. Plan view showing modification to existing biological shield. A=top view, A-A=side view.

ity constructed from 3/4 in. i.d., 1/8 in. wall polyethylene tubing was installed. More efficient air-operated routing switches at the loading and sample-routing stations insured a completely closed system, ideal for trace oxygen determinations in which the propelling gas is nitrogen. The arrester pin and sample spinning assemblies described previously [2] have been eliminated. Reproducible sample placement between the two scintillation detectors is achieved through close-tolerance design of the sample receiver. A schematic diagram showing the general layout of the pneumatic tube facility is illustrated in figure 7.

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

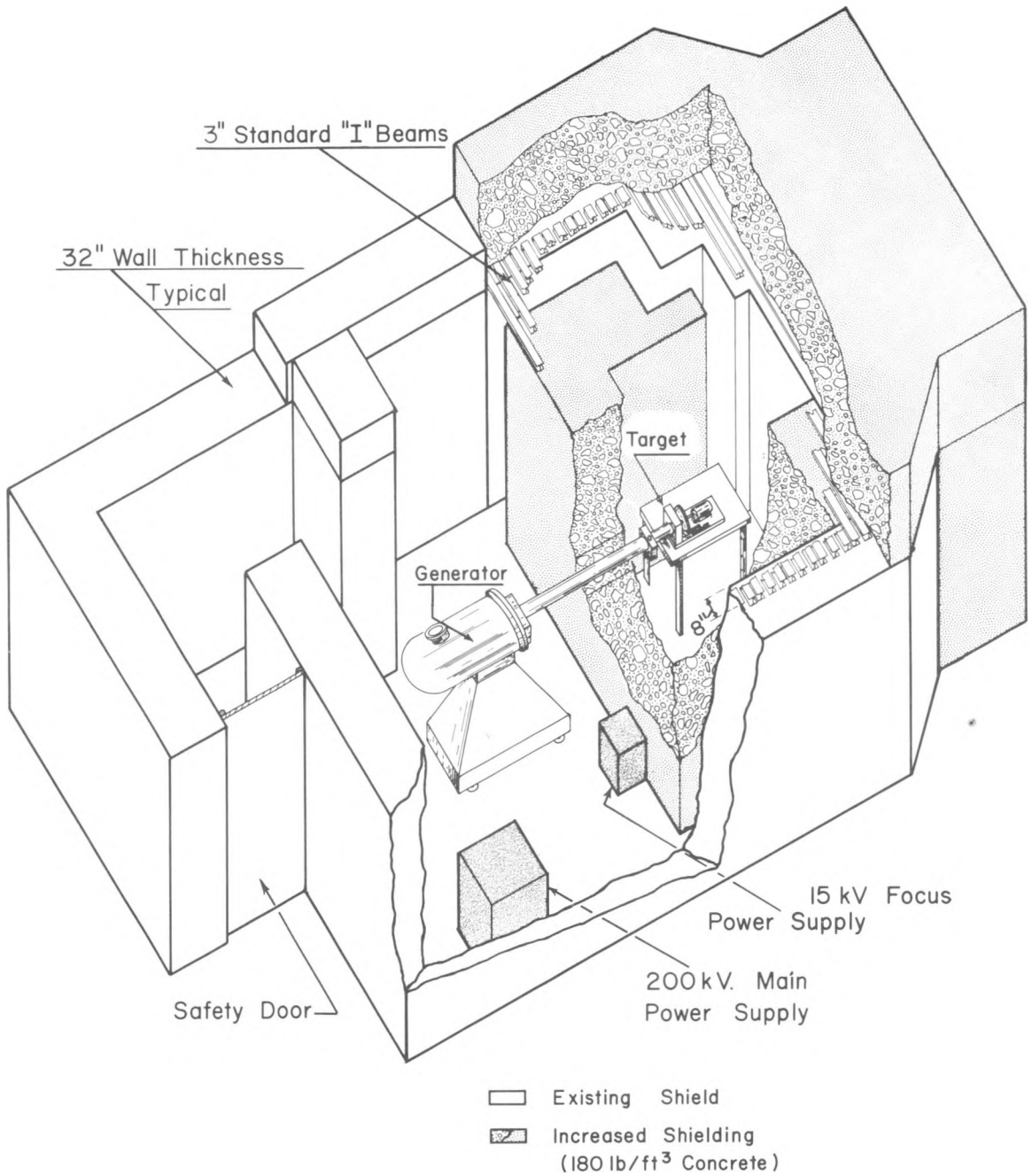

Figure 6. Cutaway drawing showing the location of the neutron generator in the biological shield.

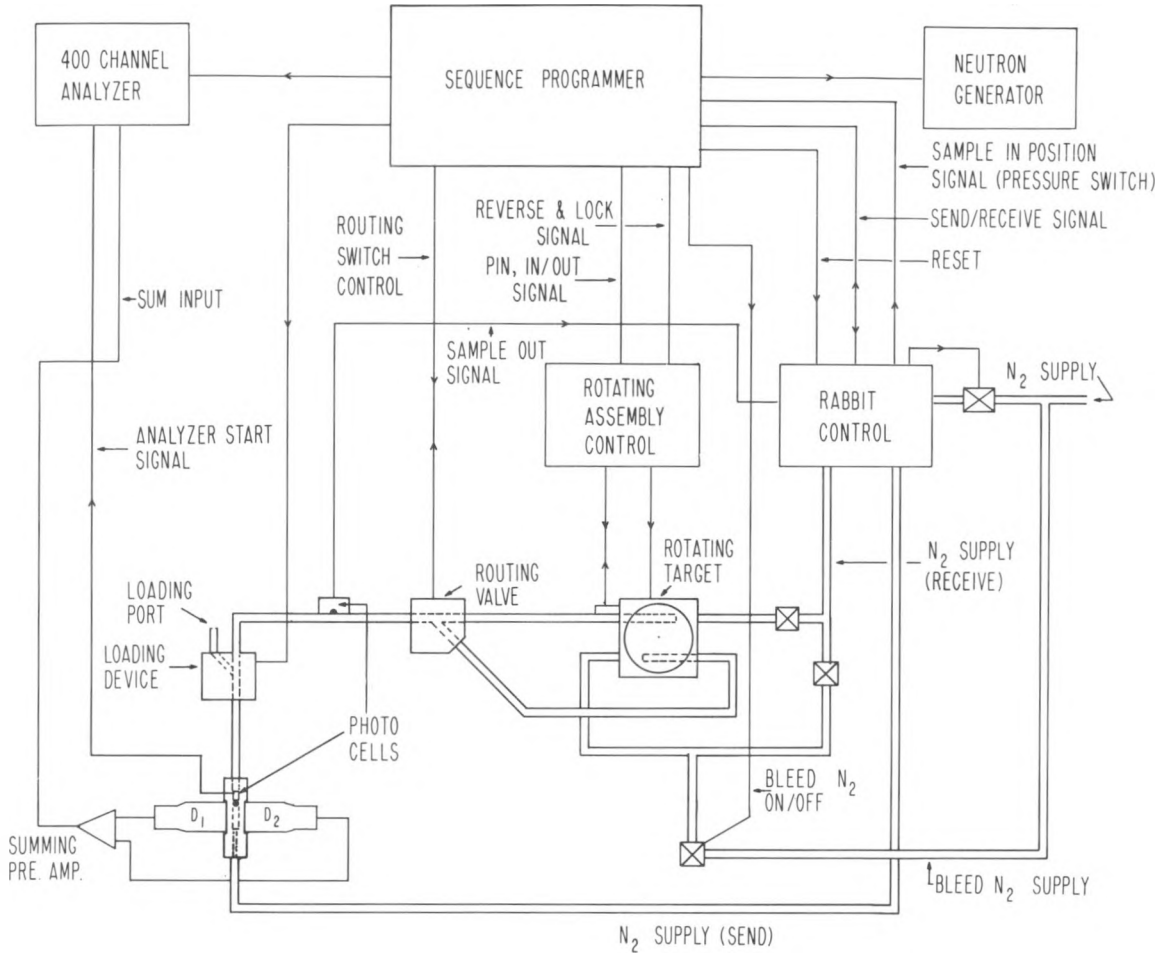

Figure 7. Schematic of pneumatic tube transfer system.

4. Detector Assembly

Two 4 in. x 3 in. NaI(Tl) scintillation detectors, each mounted on a 5-in diameter photomultiplier tube, form the basis of the detection system. These detectors are matched for gain, gain-shift and resolution to within 0.25% of one another. In our earlier work [2] it was found that the detector shield was slightly underdesigned with respect to neutron shielding, and activation of the detectors was observed. The new shield is located 12 ft further from the neutron source and the concrete and paraffin layers were doubled in thickness. Little or no activation of the detectors has been

observed. The locations of the detectors inside the shield showing the sample receiver are illustrated in figure 8.

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

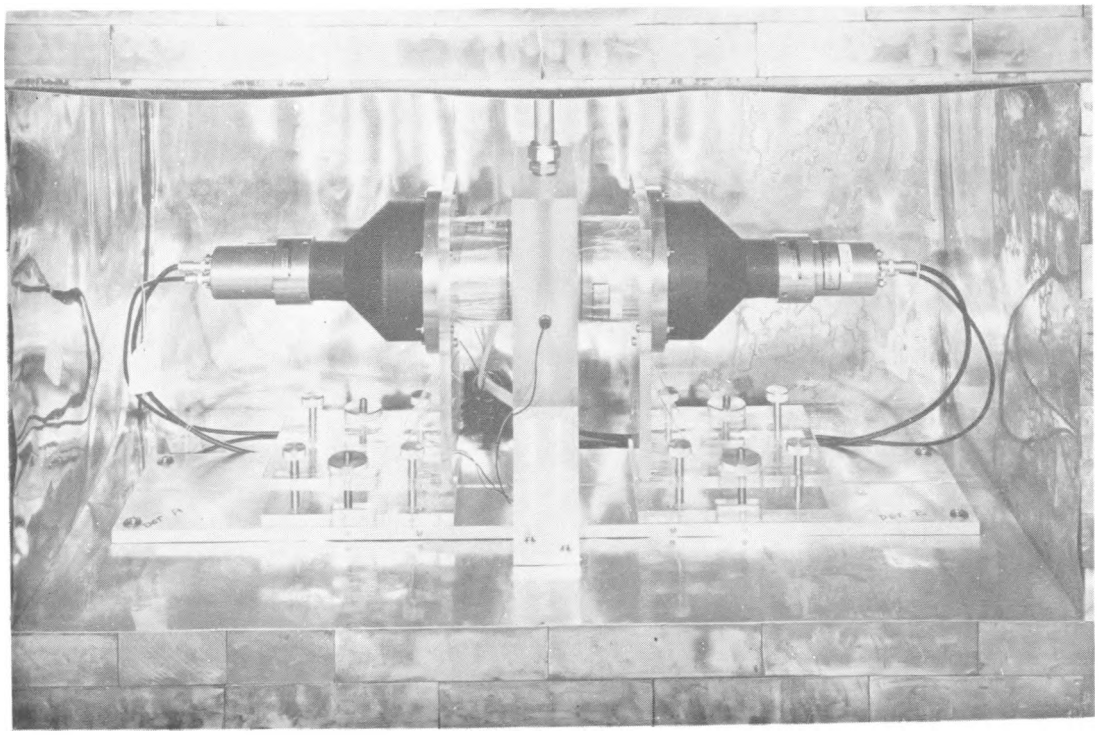

Figure 8. Inside view of detector shield.

5. Sequence Programmer

Major modifications in the earlier unit were made in order to adapt the apparatus to the new sequence of operations. The new experimental sequence can be followed with the aid of the schematic diagram shown in figure 7 and the circuit diagram illustrated in figure 9. The basic principle of sequencing action is identical to that described previously [2]. A step-by-step description of the individual operations is given in appendix 1.

(F. C. Ruegg and M. Stalbird, Radiochemical Analysis Section, J. E. Suddueth and S. S. Nargolwalla)

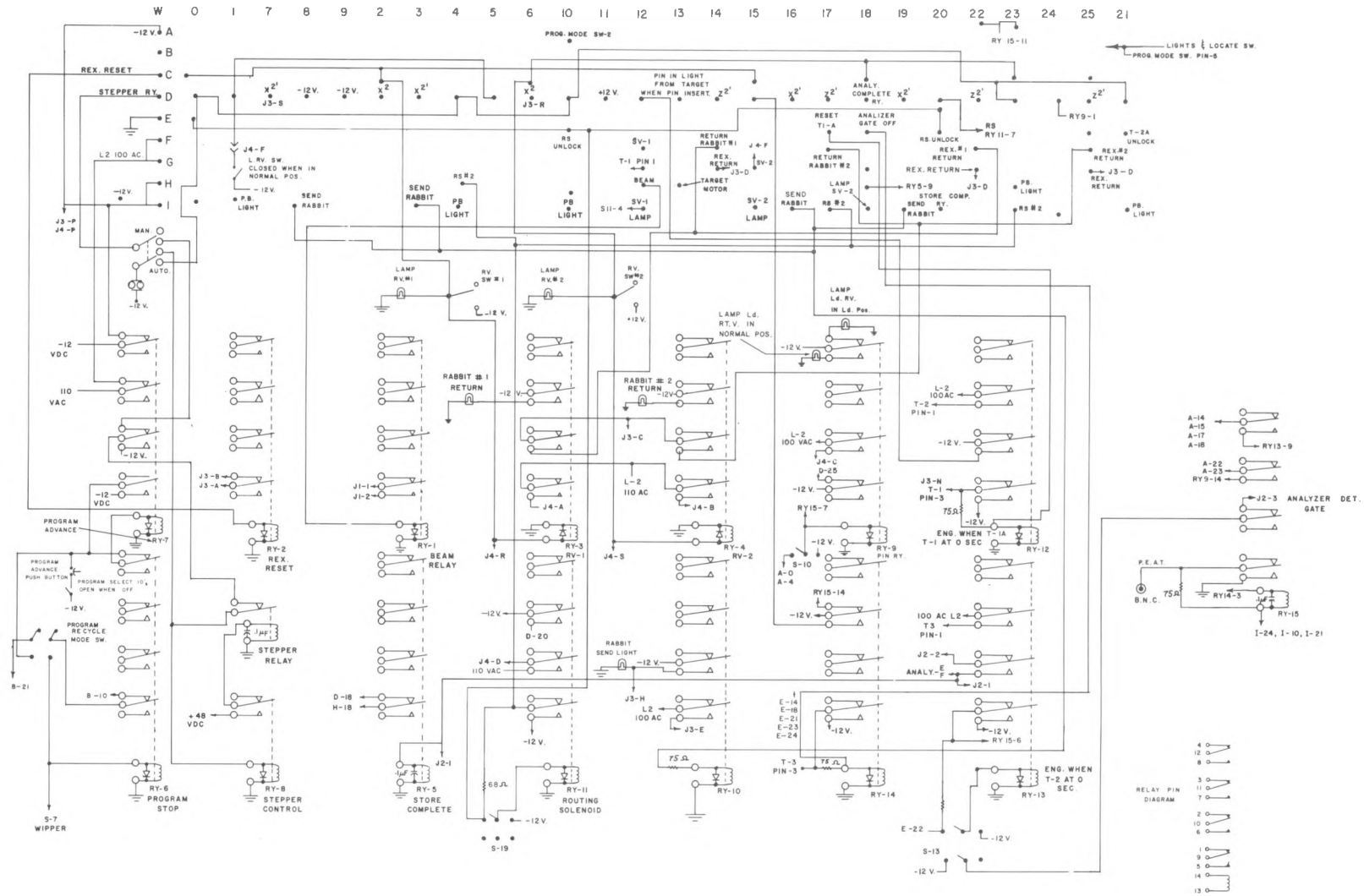

Figure 9. Circuit diagram of sequence programmer.

6. Photo-electric Trigger Circuit

This trigger circuit (fig. 10) is used to sense the capsules as they pass through the pneumatic transfer system. When a capsule interrupts the light beam, the photocell resistance becomes large and transistor T-1 is driven into its "on" state. The tunnel diode D-1, which is used as a discriminator, turns transistor T-2 off which produces a fast positive pulse. This pulse is used to trigger a monostable described previously [2] which activates a relay.

(F. C. Ruegg, Radiochemical Analysis Section)

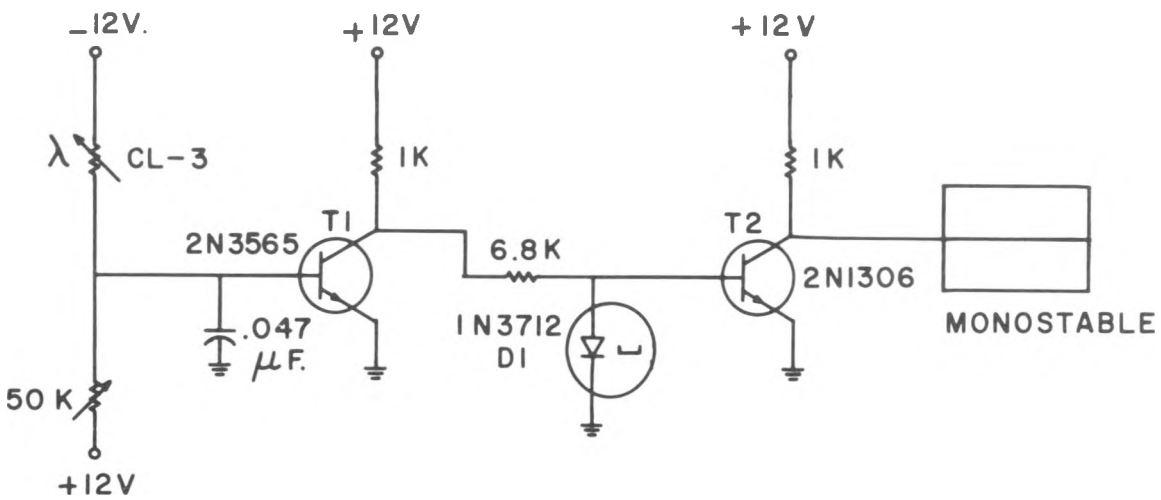

Figure 10. Photoelectronic trigger circuit.

C. Research Activities

1. Dual Sample-Biaxial Rotating Assembly

The high degree of precision obtained as a result of flux homogenization by the dual sample-biaxial rotating sample assembly has indicated the absolute need for such devices [3] for meaningful analysis using 14 MeV neutrons. We have realized that neutron flux perturbation is the most important factor affecting reproducibility, since beam control is very limited. For this reason, most normalization procedures lead

to either ambiguous or incorrect analyses. Beam jitter or beam wander is particularly undesirable when short-lived species are being produced; the determination of oxygen by the $^{16}O(n,p)^{16}N$ reaction is a prime example. The dual sample-biaxial rotation is achieved by a special gear mechanism. This assembly allows reproducible placement, as determined by irradiating and counting carefully prepared identical capsules of benzoic acid, and permits both sample and standard to be exposed to an identical neutron flux as a result of biaxial rotation. An optimum rotation speed was determined and target displacements of one-half inch in all directions were found to have negligible effect. By the use of standard statistical procedures, it was found that the analytical precision, which is now most often limited by the total number of counts accumulated, is about ten times better than that which most normalization techniques can provide. The system permits the analyst to determine both neutron and gamma-ray attenuation in dense samples. This irradiation assembly is currently being utilized for the accurate and precise determination of oxygen and other elements in NBS Standard Reference Materials.

(S. S. Nargolwalla and F. A. Lundgren)

2. Evaluation of Systematic Errors

The evaluation of systematic errors in the analysis for oxygen was a major objective of further research [4] and methods were developed whereby accurate absorption correction factors could be experimentally determined with a high degree of precision. In comparative 14-MeV neutron activation analysis for oxygen, the neutron and gamma-ray attenuation differences in the sample and standard introduce systematic errors. The neutron attenuation process utilizes the concept of total removal cross section (Σ_R) as a more accurate measure of the matrix attenuation of 14-MeV neutrons, while the gamma-ray attenuation takes the usual meaning of the total linear attenuation coefficient (μ_o). Equations are then derived for the

total attenuation correction factor. The equipment used and experimental procedure including sample selection and preparation are outlined in detail [4]. The experimentally determined correction factor for both the neutron and gamma-ray case shows an exponential dependence on the calculated difference between the respective attenuation coefficients for sample and standard. Within the range of sample diameters tested, preliminary data indicate that the slope of each calibration line is linearly dependent upon the sample diameter. For comparable diameters, the magnitude of the slope for neutron attenuation is approximately ten times greater than for gamma attenuation. Such calibration lines, for a given generator system, allow an experimental relationship to be generated which will permit the evaluation of absorption errors to give correction factors for other matrices. The general technique can be adapted to other light elements as well. Some typical analyses of Standard Reference Materials, corrected for attenuation, illustrate the high degree of accuracy and precision obtained.

(S. S. Nargolwalla and M. R. Crambes)

3. Self-Absorption Corrections in Gamma-Ray Photopeak Analysis

Success with the application of the above research prompted us to extend the work to the general case of analysis in which the measurement of gamma radiation is made by counting the area under the photopeak [5]. A study was then initiated to determine the photon self-absorption relationships for the general case of photopeak analysis of gamma-ray energies resulting from nuclear level transition and positron annihilation.

By the judicious selection of appropriate samples and standards, the reaction threshold effect on the previously determined neutron attenuation correction relationship [4] and the photon energy dependency on the attenuation correction factor were evaluated. For positron emitters, careful sample

selection and preparation permitted a study of effects due to differences in density and positron energy or both. The experimental technique used consisted of simultaneously irradiating a sample and standard in a dual sample-biaxial rotating assembly and sequentially counting between two 4 in x 3 in NaI(Tl) scintillation detectors coupled to a 400-channel pulse height analyzer system. This technique and the method of data processing have been described in previous work [3,4]. A comparison of photon attenuation correction factors as a function of the differences in the linear attenuation between sample and standard for the three possible cases is shown in figure 11. Under a given set of irradiation and counting conditions the slope representing the general case of photopeak analysis is independent of gamma energy and approximately twice that of 4.8- to 8.0 MeV range used for oxygen analysis. This is due to the reduction in efficiency for photopeak counting when compared to counting between the 4.8- to 8.0 MeV range. Since the photon attenuation correction factors

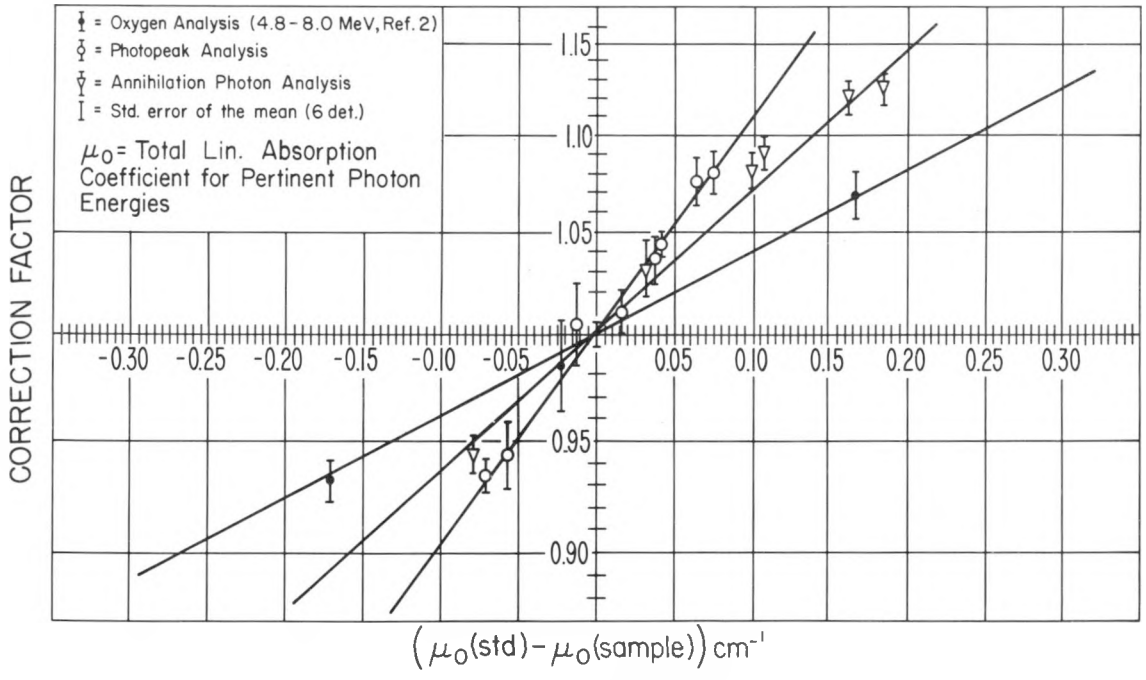

Figure 11. Gamma ray attenuation correction factor calibration curve.

can only be determined from prior knowledge of the neutron attenuation characteristics, it is now confirmed that neutron attenuation is best approximated by the removal cross section concept and thus independent of the reaction threshold. The straight line relationship observed for positron emitters show that the correction factor is independent of density and positron energy differences. However, the small reduction in the slope when compared to that obtained for the general case, can be attributed to bremsstrahlung contribution in the photopeak region. Both of these factors would increase the efficiency of counting with corresponding reduction in the observed photon attenuation.

The accurate determination of self-absorption systematic errors has enhanced the applicability of 14-MeV neutrons to the accurate and matrix-independent analysis of O, N, F, Na, Mg, Si, P, Co and Ag for the Standard Reference Materials certification program.

(M. R. Crambes, S. S. Nargolwalla and J. E. Suddueth)

4. Analysis of Photographic Emulsions

This project involved the application of fast neutron activation analysis of halogens to bulk photographic emulsions. Bulk emulsions consist of three major components: a silver halide, gelatin and water. The proportions of these components vary somewhat, depending upon the use anticipated. For example, x-ray films have a higher silver halide-to-gelatin ratio than do fine grain microfilms.

The primary light-sensitive properties of a photographic emulsion are determined by the composition of the silver halide component in so far as the ratio of chloride, bromide and iodide are concerned. For example, an emulsion containing 1 mole percent iodide and 99 mole percent bromide has much higher sensitivity to light than a pure silver bromide emulsion or an emulsion containing chloride and bromide. Thus, the composition of the silver halide component of an emulsion

establishes its basic photo-sensitive properties. Furthermore, second-order modifications in the light-sensitive properties can be achieved by changes in the technique of precipitation of the silver halide and the incorporation of various other materials which are known sensitizers or desensitizers.

Therefore, there exists a strong need to have accurate rapid methods of analysis for the halides in photographic emulsion matrices. Present chemical and physical methods, however, fall short of this goal. There are two methods which are commonly used for these analyses. One is a coulometric argentometric titration of the halides which is reasonably accurate but is rather long and laborious. The method is cumbersome because it requires removal of the silver by zinc reduction prior to titration. The halides are separated by differential oxidation. One operator is capable of carrying out six determinations in an eight-hour day. The method is, however, applicable to any mixture of chloride, bromide and iodide. The second method used is x-ray fluorescence. This method is reasonably good for the measurement of iodide, but suffers from severe self-absorption errors when used for bromide and chloride. The soft x-rays from these two elements are greatly attenuated by the matrix and slight changes in the matrix composition cause a change in the attenuation.

Fast neutron activation analysis appear to offer several possible solutions to the problem. In general, matrix attenuation problems are considerably smaller with the higher energy gamma rays as compared with the soft x-rays used in the x-ray fluorescence technique. This makes activation analysis more generally applicable. It is highly possible that very accurate chloride analyses can be carried out directly on emulsions, using a sodium iodide detector and irradiating the sample with 14-MeV neutrons. The determination of bromide and iodide may require the use of the higher resolution germanium detectors since the most abundant gamma rays are not separated sufficiently in energy for complete resolu-

tion with a sodium iodide detector. Another alternative which could be investigated is the irradiation of the samples with 2.8 MeV neutrons produced by the reaction $^{2}H(^{2}H,n)^{3}He$. This would eliminate some of the undesirable reactions with reaction thresholds greater than 2.8 MeV which result in complex spectra that are difficult to resolve.

A nondestructive neutron activation technique for the analysis of chloride and iodide in a silver bromide matrix was developed. Chlorine was measured after activation with 14.7 MeV neutrons. The 3.1 MeV gamma rays from ^{37}S were measured without interference. Calibrations were carried out using photographic emulsions containing 10- to 200 milligrams of chlorine. The relative standard error of a single determination at the 10 milligram level was 5%; at the 200 milligram level it approached 1%.

Iodine was measured via ^{128}I produced by n,γ activation with 2.8- MeV neutrons. A straight line calibration curve was established for 2- to 420 milligrams of iodine. The relative standard error of a single determination at these two levels was 20% and 1% respectively.

This technique offers an attractive alternate to existing chemical and instrumental methods for the determination of iodide and chloride in silver halide mixtures since it has the potential for providing rapid analyses with reasonably good precision. A manuscript describing this study has been prepared for publication.

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

5. Blank Problems in the Analysis of Trace Oxygen

A major difficulty in the accurate and precise determination of trace amounts of oxygen by 14-MeV neutron Activation analysis is the contribution of oxygen from the sample capsule. Errors as large as ca. 25% in blank correction and more than 100% in the final result can be experienced

if the count from the oxygen in the capsule is merely subtracted from the total sample-in-capsule count.

From our recent investigations, a procedure for precisely establishing the capsule contribution to the total count from the encapsulated sample has been defined. This procedure takes into account the attenuation of the capsule activity due to the presence of the sample in it. It also includes correction for the geometrical configuration of rods of different diameters within the capsule. For metal rods, a "flow-through" capsule (fig. 12) propelled with nitrogen in the pneumatic transfer system has been used to eliminate any oxygen contribution from the void volume of the capsule. Experimental results are in good agreement with those calculated on the basis of theory. This work has been submitted for publication.

(S. S. Nargolwalla, E. P. Przybylowicz and J. E. Suddueth)

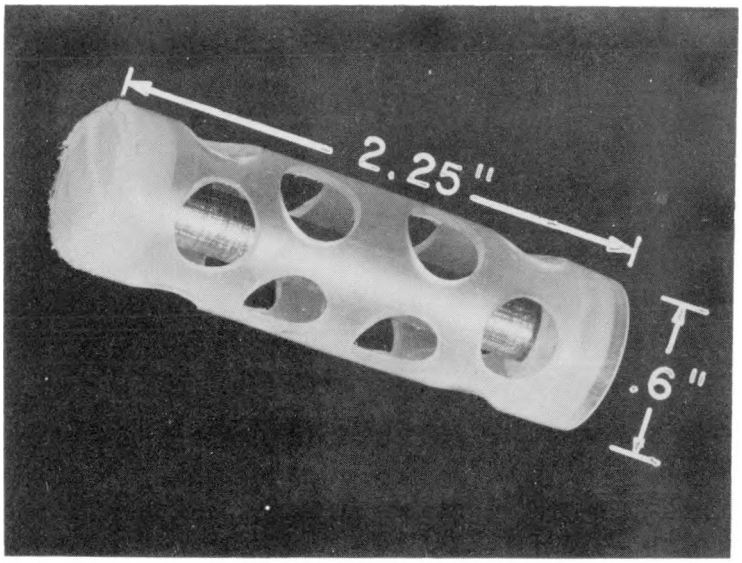

Figure 12. Flow-through capsule.

D. Role of 14-MeV Neutrons in the Activation Analysis of Standard Reference Materials

During the past year, over thirty Standard Reference Materials have been analyzed. Elements such as O, N, F, Mg, Si, P, Co and Ag have been determined. Our main contribution to the certification program has been in the trace oxygen analysis in ferrous and nonferrous materials and in the macro analysis for the metallic component in a number of organo-metallic compounds. Some of the more interesting analyses are described.

1. Determination of Oxygen in Ferrous and Non-ferrous Metals

Five different steels and two titanium alloys were analyzed for trace oxygen. The concentrations of oxygen varied between 30 and 3000 ppm. Usually about six rods from each type of sample were analyzed, and between 6 and 8 determinations were made on each rod.

In most cases the rods were supplied in 4-inch lengths. The rod diameters varied between 1/4 and 1/2 inch. Each sample was cut with a clean hacksaw and a 2-inch length was cleaned for five minutes in an ultrasonic bath charged with trichloroethylene. The samples were rinsed in deionized water and immediately dried in a dry nitrogen atmosphere. Each rod was encapsulated, in our low-oxygen polyethylene irradiation containers in a nitrogen atmosphere. The samples were transported to the irradiation site inside a clean polyethylene bag filled with nitrogen. In spite of the great care taken during encapsulation and transportation, a small percentage of the samples suffer from air leaks either during the sealing process or during transportation. To remove this source of error, a new approach was tried. The method employed was discussed briefly in Section C. Part 5 of this report.

The samples were irradiated for about thirty seconds with a standard in our dual sample-biaxial assembly, and the oxygen content determined by a method recently described [3,4]. The results are shown in table 1. The uncertainties* of the mean values shown in table 1 (and table 2) are

$$\frac{tS_B}{\sqrt{k}} \qquad \text{where:}$$

$t = t_{1-\alpha/2}$ for k-1 degrees of freedom
in table A-4 of NBS Handbook #91

$\alpha = 0.05$ for the 95% confidence interval.

$$S_B = \left(\frac{(\bar{y}_1 - \bar{\bar{y}})^2 + (\bar{y}_2 - \bar{\bar{y}})^2 + \ldots (\bar{y}_k - \bar{\bar{y}})^2}{k-1} \right)^{1/2}$$

$\bar{y}_i$ = weighted mean for n determinations per sample.

$\bar{\bar{y}}$ = mean of weighted means.

k = number of samples.

The analytical error in most cases is believed by us to be insignificant relative to the imprecision due to counting statistics. Statistical tests indicate that some degree of inhomogeneity is induced in most samples, though insufficient data are available to determine the degree of inhomogeneity precisely.

In addition to the ferrous materials, macro oxygen in cycsint (SRM 143b) was determined. Two batches of this material were analyzed. The result, 26.28±0.30%* oxygen, are in good agreement with the stoichiometric value of 26.63% stipulated for this high purity material.

---

*This treatment of the uncertainty of the results was suggested by B. L. Joiner of the NBS Statistical Engineering Section (205.03).

Table 1. Analysis of Oxygen in Ferrous and Non Ferrous Materials

Sample	No. of Samples	No. of Determinations Per Sample	Oxygen Concentration ppm: 14-MeV Neutron Activation Analysis	Oxygen Concentration ppm: Vacuum and Inert Gas Fusion Methods
1. Vacuum Melted Steel [SRM 1092]	6	8	27.8±5.4[a]	28±2[b]
2. Stainless Steel [SRM 1091]	6	6	132.0±7.6	131±8
3. Ingot Iron [SRM 1090]	6	6	492±29	484±14
4. Medium Carbon Steel [SRM 1041]	1	12	225±13[d]	170
5. Valve Steel	7	8	60.0±5.2	N.D.[c]
6. Titanium [SRM 355]	6	6	2896±44	3031±57
7. Titanium Alloy [SRM 356]	6	6	1279±28	1332±77

[a] Uncertainties are $\frac{t\ S_B}{\sqrt{k}}$

[b] Uncertainties refer to standard deviation (1 sigma) which include analytical precision and irreproducibility due to inhomogeneity.

[c] Not determined.

[d] Standard deviation of the average of 12 determinations.

Table 2. Analysis of Organometallic Compounds

Compound	Element Determined	No of Samples	No. of Determinations per Sample	Concentration %: 14-MeV Neutron Activation Analysis	Concentration %: Certified Values
Cobalt Cyclohexanebutyrate [SRM 1055a]	Cobalt	4	4	14.62±0.10[a]	14.83[b]
Silver 2-ethylhexanoate [SRM 1077]	Silver	4	4	42.26±0.40	42.4±0.42
Magnesium Cyclohexanebutyrate [SRM 1061a]	Magnesium	3	4	6.69±0.04	6.8±0.42
Octaphenylcyclohexanesiloxane [SRM 1066]	Silicon	1	6	14.16±0.11	14.1±0.14

[a] Uncertainties are $\frac{t\ S_B}{\sqrt{k}}$

[b] Certified value on SRM #1055a calculated for $C_{20}H_{34}CoO_4$ (M.W., 397.40)

2. Analysis of Organometallic Compounds

These standards provide oil-soluble materials of known, reproducible composition. They are primarily issued for the transportation industry and the U. S. Department of Defense for the analysis of lubricating oils to determine engine wear. The 14-MeV neutron activation technique has proven to be a highly accurate and precise method for macroconstituent analyses [4]. The organometallics are extremely well-suited for this technique since besides the metal component, the only other activated specie is oxygen. Two minutes after irradiation, ^{16}N from $^{16}O(n,p)^{16}N$ ($T_{1/2}$=7.2 sec) decays and the activated product of the metal component can be measured free from interference. A number of SRM renewals in this series of compounds have been analyzed using the general method of simultaneous irradiation of sample and standard followed by sequential counting of the gamma-ray of interest. The results of analyses are shown in table 2. Although the self-absorption corrections necessary to relate the sample to the standard were as high as 14% in some cases, the final results are in close agreement with the certified values. The work with the organometallics has provided an opportunity to verify much of our research pertaining to evaluation of self-absorption errors in cases where photopeak counting is done.

3. Analysis of Silicon

Silicon in Silica Brick (SRM 102) and Borosilicate glass (SRM 93) was determined. The activation analysis results, 43.74±0.78%* Si and 37.51±0.45%* Si, compare favorably with the certified values 43.91% and 37.68%, respectively. The nuclear reaction $^{28}Si(n,p)\ ^{28}Al$ Eγ=1.78. MeV, $T_{1/2}$=2.31 min) was used.

(S. S. Nargolwalla, J. E. Suddueth, M. R. Crambes, E. P. Przybylowicz and Gilbert W. Smith)

*Standard deviation of the average of 4 determinations on one sample.

4. ACTIVATION ANALYSIS WITH A NUCLEAR REACTOR

A. Introduction

The main emphasis in the Reactor Activation Analysis Project has been the development of the capability to perform analyses of a variety of elements in essentially any matrix rapidly and with the highest possible accuracy and precision. We now have this capability for many elements, and will continue our methods development during the coming year. Some of the methods developed are given in the following pages. Much of our research has been involved with analysis of constituents of NBS Standard Reference Materials.

B. Research Activities

1. Group Separations for Activation Analysis of Steels

Since many of the Bureau's Standard Reference Materials are steels a major effort was devoted to the development of rapid group separations by means of which a number of elements could be determined in steels, rapidly and with high precision and accuracy. The elements for which group separation procedures have been developed are W, Mo, Ni, Cu, As, Cr, Co, Sb, and Ga.

The basic procedure is as follows: The sample of steel or cast iron is dissolved in a mixture of HNO_3 and $HClO_4$ with strong fuming of $HClO_4$ to remove carbon and to oxidize As and Sb to the +5 state and prior to fuming. The separation procedure, which is shown in figure 13, consists of three solvent extraction steps. Tungsten and molybdenum are extracted from 3N HCl using α-benzoinoxime in chloroform. Antimony, gallium, and the bulk of the iron matrix are extracted into isopropyl ether from 7.5N HCl. Nickel is extracted from basic citrate solution using dimethylglyoxime in chloroform. Copper, arsenic, chromium and cobalt remain in the aqueous phase and can be determined quantitatively using a Ge(Li) detector to resolve the 511 keV annihilation radiation of ^{64}Cu from the 560 keV γ-ray of ^{76}As and to resolve the ^{60}Co γ-rays from any remaining traces of ^{59}Fe.

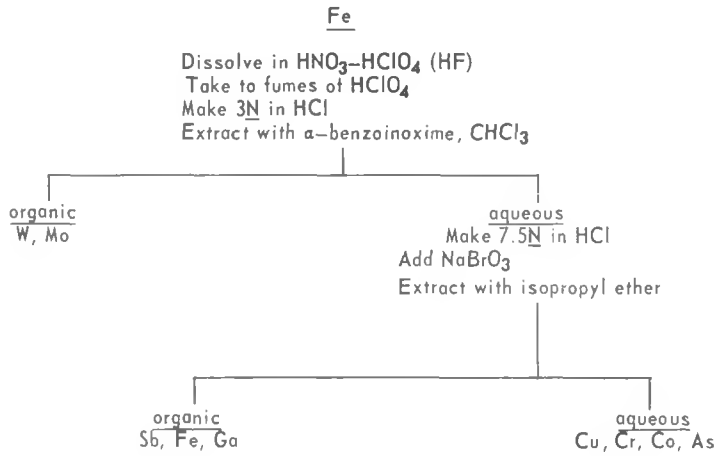

Figure 13. Flow sheet for group separations from iron and steel matrices.

The separation is very rapid; six replicates can be carried through the entire scheme in about two hours after dissolution. The scheme has been applied to the analysis of a variety of cast iron and steel samples including some containing up to 4% C and 4% Si. Uncertainties of less than 5% at the 95% confidence level can be obtained with 6 determinations. By counting all the fractions, an element, whose presence might not have been suspected, can be determined quantitatively.

A manuscript describing this work has been submitted for publication.

(B. A. Thompson and P. D. LaFleur)

2. Determination of Impurities in High Purity Zinc by Neutron Activation Analysis

Analyses were requested of three grades of high purity SRM zinc, two nominally 99.999% Zn and one nominally 99.9999% Zn. The determination of as many elements as possible at the ppb level was desired. To achieve this end, both nondestructive and destructive analyses were performed. The number of elements which could be determined nondestructively was limited by the intense radioactivity of the zinc matrix ($T_{1/2}$ of 14 h and 265 d) and of the copper-64 and copper-67 radio-

activities formed by the (n,p) reactions on the zinc matrix ($T_{1/2}$ of 12.9 h and 61 h, respectively).

In the nondestructive analyses, no impurities were seen, but upper limits were obtained for aluminum, vanadium, rhodium, indium and manganese.

For destructive analysis, various approaches were considered, including electrodeposition, amalgam exchange, solvent extraction and precipitation. Group separation methods were desired to minimize the total analyses time.

The method developed was primarily based on solvent extraction and is shown in figure 14. Silver, which was present at the ppm level in most of the samples, was precipitated as AgCl and removed by filtration. Tungsten and molybdenum were extracted into $CHCl_3$ with α-benzoinoxime; antimony, gold, gallium and selenium were extracted into isopropyl ether as the chloride complexes; $SnCl_2$ was added and the arsenic and iridium chlorocomplexes were extracted into isopropyl ether.

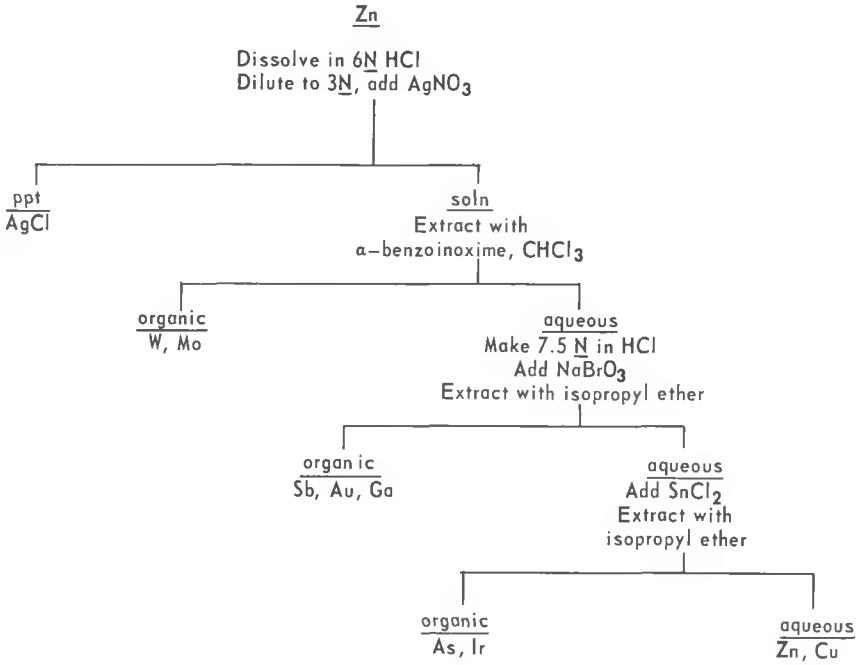

Figure 14. Flow sheet for group separations from a zinc matrix.

Only Ag, Sb and Au were actually detected but upper limits at the ppb level were determined for the other elements. For these group separations, a Ge(Li) detector usually was required for the resolution of the gamma rays of the elements of interest from those of remaining traces of Zn and Cu activities.

A separate procedure was developed for the determination of sodium and potassium. In this case, the zinc and copper matrix activities were separated from the possible sodium and potassium impurities. The zinc was precipitated as zinc ammonium phosphate and the copper as the sulfide. Several precipitations were made with large quantities of holdback carriers. No, Na or K was observed, but lower limits were determined for Na at the sub-ppb level and K at the sub-ppm level.

(B. A. Thompson and D. A. Becker)

3. Determination of Molybdenum by Activation Analysis

Molybdenum is one of the elements which is very often certified in SRM steel samples at the Bureau of Standards. In addition, this element has been shown to be essential in higher plants and animals, where it is present in the enzymes nitrate reductase [6] and xanthine oxidase [7] respectively. The levels at which molybdenum is normally found in biological samples requires a very sensitive procedure, while the maximum precision possible is required for application to the SRM program.

A number of procedures have been published for the determination of molybdenum by activation analysis, commonly using α-benzoinoxime [8], cupferron [9], ion-exchange [10], etc. Most of the published data indicate that these procedures suffer from poor precision.

The reagent hydrogen bis(2-ethyl-hexyl) phosphate (HDEHP) has been shown to be an excellent extractant for fission product molybdenum [11] and has been applied for the various sample matrices here at the National Bureau of Standards.

a. Experimental

The samples analyzed included SRM steel samples 5ℓ and 6g, kale samples obtained from Dr. H. J. M. Bowen [12] and lyophilized liver samples. In all cases the samples were sealed in quartz ampoules prior to irradiation. Standards used were MoO_3 also sealed in quartz ampoules. Samples and standards were irradiated with flux monitors for flux normalization. Irradiations were performed in the glory tube facilities at the Naval Research Laboratoary Reactor at a nominal flux of $8x10^{12} n \cdot cm^{-2} \cdot sec^{-1}$ for 1 to 5 hours.

After irradiation the samples were dissolved in HNO_3-$HClO_4$ mixtures. In the case of the steel samples, HF was added prior to $HClO_4$ fuming to drive off most of the silica.

After sample decomposition, the residue was taken up in 3M $HClO_4$ and extracted into 0.75M HDEHP in petroleum ether for 1-2 min. The use of mechanical shaking machines is often frowned upon when extracting intensely radioactive solutions, since the ground glass stoppers of separatory funnels often become unseated during the extraction and the radioactive contents of the funnels are thrown about the laboratory area. To circumvent this problem, separatory funnels were modified by replacing the standard taper stopper system with tubing having threads to accommodate screw closures with conical polyethylene lines. Examples of these funnels are shown in figure 15. Using these funnels no leakage problems have occurred.

After extraction, the samples are washed twice with 20-ml portions of 3M $HClO_4$ for 15-30 seconds each. The Mo is then back extracted with 3 15-ml portions of 10M HNO_3 containing ~3% H_2O_2. Five milliters of $HClO_4$ are added to the combined back extracts in a 200-ml erlenmeyer flask and the sample evaporated to fumes of $HClO_4$. The sample is transferred to a 40-ml centrifuge tube, 10 mg of Fe^{+++} carrier is added, and $Fe(OH)_3$ is precipitated with NaOH to scavange any activities that may have accompanied the Mo. The $Fe(OH)_3$ is centri-

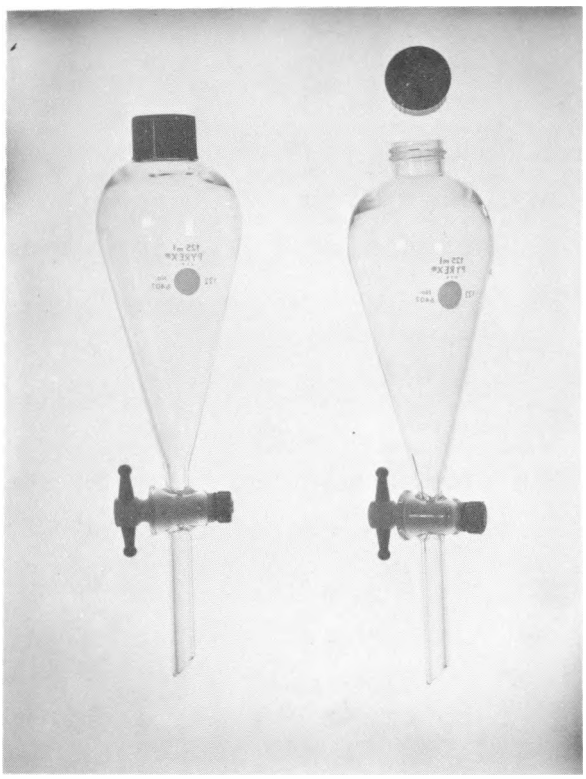

Figure 15. Separatory funnels modified with screw-top closures.

fuged off, and the supernatant liquid is counted for ^{99}Mo after allowing 24 hours for ^{99m}Tc equilibration. A 3 in. x 3 in. NaI(Tl) detector and a 400-channel pulse height analyzer is used and the 140-keV photopeak is integrated.

b. Results and Discussion

The results of the analyses are shown in table 3. Using the procedure described, eight samples may be prepared for counting in less than 3 hours (after dissolution).

Using this separation technique it has been possible to perform analyses at great sensitivity and with excellent precision for molybdenum. Current studies are being undertaken to apply this technique to samples of rocks, ores, and clays.

Table 3. Results of Molybdenum Analyses

Sample	Mo Found[a]	Mo Present
SRM 5ℓ	0.019±0.002%[b]	0.02%[c]
SRM 6g	0.038±0.001%[b]	0.035%[c]
Kale	2.55 ±0.08 ppm[d]	2.59±0.23 ppm [9]
		2.33±0.47 ppm [12]
Liver	3.40 ±0.08 ppm[d]	

[a]All errors are given at $ts/\sqrt{n}$ at the 95% confidence level

[b]6 samples

[c]NBS certified value

[d]8 samples

(P. D. LaFleur)

C. Analysis of Standard Reference Materials

1. Activation Analysis of Copper and Nickel in Clay Standard Reference Materials

Microgram amounts of copper and nickel were determined in SRM clays 97a and 98a by neutron activation analysis. Radiochemical procedures were used for the separations of copper and nickel from the complex matrix.

a. Experimental

Samples of SRM clays weighing 500 mg and of asbestos weighing 100 mg were encapsulated in 2/5-dram polyethylene snap-cap vials. Standards of copper and nickel foil weighing about 10 mg each were fixed on top of the vials and the samples were irradiated at a neutron flux of approximately $8 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$ for two hours in the glory tube facilities of the Naval Research Laboratory Reactor.

After irradiation the clay samples, with 20 mg of Cu and 1 mg of Ni carriers, were fused for 20 minutes with 2 g of sodium peroxide in a zirconium crucible. During fusion the

crucible was swirled from time to time to expedite the dissolution. After fusion the crucible containing the cooled mass was placed in a beaker containing 100 ml of 2 M HCl and heated to dissolve the fusion cake. Occasionally a turbid solution was obtained which was clarified by addition of 2 ml of 48% HF. Therefore, 2 ml of HF was added routinely to the samples after they were dissolved in HCl.

The asbestos samples together with 1 mg of nickel carrier were dissolved by heating with 10 ml of concentrated H_2SO_4. The residue was dissolved in 50 ml of 2 M HCl.

Copper and nickel standards were dissolved in 5 ml of concentrated HNO_3 and diluted to 25.0 ml.

Copper. To the clay solution 10 ml of a 5% thioacetamide solution was added and it was heated for about 5 minutes to precipitate copper sulfide. After cooling the precipitate was filtered, washed twice with water and mounted for counting.

Nickel. The filtrate was heated to remove excess H_2S. Then 10 ml of a 50% ammonium citrate solution was added and the excess acid was neutralized with ammonium hydroxide. After cooling, the solution was made slightly alkaline with ammonium hydroxide and transferred to a 25-ml separatory funnel. Five milliliters of a 1% dimethylglyoxime solution was added and the nickel complex was extracted by shaking with 15 ml of chloroform. An additional 10-ml portion of chloroform was used to extract any remaining nickel complex. The two chloroform portions were combined and the volume was reduced to about 5 ml by evaporation.

Immediately after separation, the activities of the nickel fraction and the standard were measured with a 3 in. x 3 in. NaI(Tl) crystal and a 1024-channel pulse height analyzer. The 1.49 MeV peak of ^{65}Ni was used for the analysis.

The activities of the copper sample and the standard were measured with a 30-cm^3 Ge(Li) detector and a 4096-channel pulse height analyzer. The 511-keV annihilation radiation

of ^{64}Cu was used for the copper analysis. The gamma-ray spectrum of the copper sulfide sample was found to have peaks at 0.56 MeV, 0.66 MeV and 1.22 MeV which were due to ^{76}As. These peaks, however, did not interfere in the determination of copper, as they were completely resolved from the annihilation peak.

b. Results

The results of the analysis of copper and nickel in SRM 97a and 98a are shown in table 4. The yields of the radiochemical separation procedures was determined using radioactive tracers of nickel and copper. The chemical recoveries of copper and nickel were found to be 94±2* and 95.5±2* respectively.

(I. H. Qureshi)

Table 4. Copper and nickel in SRM clays

Sample		Amount of Cu (ppm)	Amount of Ni (ppm)
SRM 97a (1)		17.4	75.4
" (1)		20.0	81.8
" (3)		23.0	69.6
" (3)		23.8	78.4
" (5)		20.2	82.2
" (5)		19.2	83.4
	Mean	20.6±2.4[a]	78.4±5.2[a]
SRM 98a (2a)		208.4	172.4
" (2a)		217.4	174.4
" (6b)		206.2	173.4
" (6b)		194.6	181.4
" (4e)		186.6	156.6
" (4e)		189.8	176.8
	Mean	200.6±12[a]	176.6±8.4[a]

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

*$ts/\sqrt{n}$ at the 95% confidence level.

2. Determination of Gold in SRM Platinum

A redetermination of gold in high purity platinum SRM was requested. Since the gold level was known to be of the order of a few ppm, some chemical separation from the platinum matrix was necessary. The determination is also subject to interference from the large amounts of ^{199}Au formed by decay of ^{199}Pt. Killick [13] has described a method of reducing this interference by use of a lead and plastic absorber. This preferentially absorbs the low energy gamma rays from ^{199}Au while absorbing a much smaller percentage of the ^{198}Au.

a. Experimental

The procedure employed for the analysis was as follows: Two 100 mg platinum samples were irradiated for 4 hours in the NRL reactor. Gold standards were irradiated at the same time. After irradiation the samples were dissolved in aqua regia and made up to a volume of 100 ml. Gold was separated chemically from six aliquots of each sample by extraction into isopropyl ether using HBr. The chemical yield was 95.4%. The ether fractions were counted with a 3 in. x 3 in. NaI(Tl) detector using the lead and plastic absorber mentioned above. The dead time was further reduced by raising the lower level discriminator to a point just below the 0.41 MeV ^{198}Au photopeak.

b. Results

The results of the twelve determinations are given in table 5.

Table 5. Gold in SRM 681 (Platinum)

(Results are in ppm)

8.05	8.13
8.23	8.32
8.34	8.33
8.44	8.87
8.27	8.70
8.37	8.95

$\bar{X}$	s	$ts/\sqrt{n}$ (95%)
8.42	0.28	±0.18

These results are comparable to those obtained by other methods.

(B. A. Thompson, and G. W. Smith)

3. Nondestructive Determination of Manganese and Vanadium in Iron and Steel Standard Reference Materials 5k, 5ℓ, 6g, 101e, 101f, 101g, 196 and 342a.

Eight iron-based SRM's were analyzed for their manganese and vanadium content. Their type and composition are listed in table 6. Besides the two elements of interest, the SRM's had additional added elements up to a maximum of 13 per SRM, averaging about 10. These added elements ranged in concentration from <0.1% to over 3% (except for the 70% chromium in the ferrochrome SRM.

Similar samples have been previously analyzed for vanadium in this laboratory [1,2]. In most cases the procedures were essentially the same. Only where the procedures vary significantly will they be discussed here.

Table 6. Information on samples analyzed

SRM	Type	Elemental content (%) Manganese	Vanadium
5k	Cast iron	0.536[a]	0.014[a]
5ℓ	Cast iron	0.70[b]	0.034[b]
6g	Cast iron	1.05[b]	0.054[b]
101e	Cr18-Ni9	1.77[a]	0.043[a]
101f	-	unknown	unknown
101g	-	unknown	unknown
196	Ferrochrome	∿0.1[b]	∿0.1[b]
342a	Nodular iron	0.28[b]	0.018[b]

[a]Certified values, as reported in NBS Misc. Publ. 260 (1968 Edition). These samples were to be used as control samples.

[b]These values were aim composition or heat analyses.

a. Experimental

The techniques used for the analysis of these samples varied significantly from the references given above in the following two ways. First, a small volume portable lithium-drifted germanium detector was used to verify the gamma-ray purity of several of the samples, in addition to the normal half life determination. A 3 in. x 3 in. (7.6 cm x 7.6 cm) sodium iodide detector was used for the analyses to improve counting statistics. Second, since manganese was also to be determined in these samples, the complement subtraction technique was not used. Instead, a known amount of manganese was added to the vanadium standard approximately equal to the amount of manganese found in the sample. Thus, the standard consisted of both manganese and vanadium in essentially the same ratio found in SRM's. In this way any interference by the high manganese activity would affect both the sample and the standard the same way. This technique allowed the analysis for both manganese and vanadium with a single irradiation and a single counting period. It also eliminates some subtle difficulties such as inaccurate live-time corrections due to large differences in the dead time between samples and standards.

b. Results and Discussion

The results from these analyses are presented in table 7. Because there is some question as to the accuracy of the results obtained, the technique was thoroughly investigated. For the vanadium analyses, it was shown that the results were not changed when the complement subtraction technique was compared with the technique described above. For the manganese analyses, a second set of 5ℓ samples were irradiated for a longer period of time in a higher neutron flux position, allowed to decay for 10 hours, and then the 1.81 and 2.11 MeV gamma-rays counted and data calculated. These new results agreed with the previous results at the 95% confidence level. In addition, for this second set of samples, the manganese

Table 7. Manganese and vanadium in SRM cast iron samples

	Manganese			Vanadium		
SRM No.	No. Samples	Mean (%)	ts* $\sqrt{n}$	No. Samples	Mean (%)	ts* $\sqrt{n}$
5k	6	0.591	.019	3	.0165	.0025
5ℓ	6	0.699	.006	6	0.036	.003
6g	6	1.05	.02	6	0.059	.003
101e	3	1.69	.27	3	0.0345	.0035
101f-1	4	0.0934	.0156	4	0.0318	.0048
101g-8	3	0.0959	.0072	3	0.0309	.0055
101g-5	5	0.0917	.0025	5	0.0290	.0007
101g-6	3	0.0913	.0055	3	0.0283	.0007
342a	7	0.0291	.0074	7	0.019	.0017
196-1	4	0.283	.011	4	0.117	.003
196-2	6	0.284	.008	6	0.116	.003
196-4	5	0.281	.014	5	0.117	.004
196-6	4	0.280	.006	4	0.116	.005

*The $ts/\sqrt{n}$ numbers given are at the 95% confidence level.

standard used was a different chemical compound obtained from a different manufacturer. This was done in order to eliminate any possible bias due to an insufficiently characterized standard. The vanadium standard used was a solution freshly made from vanadium metal which had already been rigorously evaluated as to purity and reliability.

The apparent lack of precision in some of the results given in table 7 is at least in part due to a proven inherent inhomogeneity for trace and minor constituents in many of the iron and steel SRM's for samples ca. 100 mg. This characteristic can readily be seen in the vanadium contents of the 101 series. The apparent precision of the 101g samples are considerably better (1.0-2.1%) than the precision of the 101e and 101f samples (4.0-9.4%).

4. Analysis for Cobalt in Lithium-Boron-10 Glass Using a Pre-dissolution Technique

Several scientists connected with the NBSR have developed a new SRM for the measurement of thermal neutron fluxes. In brief, the method utilizes the activation of a 1/V activator (in this case, cobalt) in a glass bead (∿1 mm radius) which has been made black to thermal neutrons through the incorporation of 10% lithium oxide and 40% boron oxide (92% enriched boron-10). The cobalt content was known to be approximately 9%.

Previous to our work, wet chemical analyses were performed on the cobalt content of this glass, and the results showed an apparent inhomogeneity at small sample sizes, and a cobalt content of 9.23%. Since the purpose of these beads was to determine a neutron flux with an accuracy and precision approaching 1%, and a great deal of time and effort had been put into making the glass, these results required verification before acceptance. Thus, the object of our analyses was to verify these findings. The use of a completely different analytical technique, such as neutron activation analysis should tend to eliminate any systematic errors and produce a clear-cut answer to the homogeneity problem. However, due to the severe neutron self-shielding problem involved, the absolute cobalt number obtained may have a negative bias. This bias should not affect the precision of the analysis and the homogeneity results should still be valid, providing certain precautions are taken to insure exactly the same amount of self-shielding for all the samples.

a. Experimental

The samples, in the form of small chips of glass, were weighed and transferred to tared polyethylene snap-cap vials. There were seven samples, with weights varying from 1.519 mg to 3.660 mg. The samples were then dissolved in the polyethylene vials using small amounts of perchloric and hydrofluoric acids. After complete dissolution, the solutions

were diluted with de-ionized water until the sample weight was 1g, and the vials closed and heat sealed. The standards were made from pure cobalt metal, which was dissolved and diluted in exactly the same manner as the samples. All samples and standards had copper foil flux monitors attached for flux normalization.

The 10.5 min ^{60m}Co was used for the analyses. The vastly improved sensitivity at short irradiation times for small samples over the long-lived ^{60}Co more than offset the disadvantage of having to count the low-energy 59 keV isomeric transition photons. It was felt that, since the samples and standards were to be diluted and counted in exactly the same way, any gamma-ray absorption present would be identical for all standards and samples. One other problem may be present; that is the neutron self-shielding within a sample due to the high lithium and boron-10 content. Dilution of the sample by almost a factor of 1000 will decrease the neutron self-shielding to a small value. In addition, since all samples have exactly the same configuration in the dilute form, samples of equal weight will have identical neutron self-shielding. Thus a plot of specific activity versus sample weight should reveal any neutron self-shielding still present.

The procedure for analysis was as follows: the samples were irradiated for one minute in the south pneumatic tube facility of the Naval Research Laboratory Reactor, and were allowed to decay for two and one-half minutes. Then the samples were counted for five minutes using a 400-channel pulse height analyzer and a 3 in. x 3 in. NaI(Tl) detector. In all cases approximately 1,000,000 counts were accumulated in the 59-keV peak after subtraction of background. Appropriate corrections were made, including flux normalization.

b. Results and Discussion

The results obtained averaged 9.17±0.12% cobalt (± value is $ts/\sqrt{n}$ at the 95% confidence level). These results indicate that the maximum inhomogeneity present is of the order of 1.5%. However, since the precision of the technique, even with great care, is approximately 1%, it is not definite whether an actual inhomogeneity does exist. The cobalt concentration observed is slightly less than the wet chemistry results, however, the values overlap.

Concerning the possible problem of neutron self-shielding, a comparison of samples having over a factor of two difference in glass content showed no trend toward a decrease in specific activity with an increase in sample weight. This indicates that no significant neutron self-shielding was present at these dilutions.

(D. A. Becker)

5. Copper and Arsenic in SRM Cast Iron Samples

As part of the Standard Reference Materials certification program at the National Bureau of Standards, we determined the copper and arsenic content in cast iron SRM's 5ℓ and 6g, and nodular iron SRM 342a. Copper and arsenic are easy to separate together as acid sulfides, and, using a Ge(Li) detector, the 511-keV annihilation radiation from the ^{64}Cu is easily resolved from the 560 keV principal gamma ray from the ^{76}As.

a. Experimental

Samples of the SRM's were weighed out (ca. 100 mg) into polyethylene snap-cap vials; copper flux monitors were attached, and the samples, along with standards of As_2O_3 (primary standard) and copper metal, were irradiated for one hour in the glory tube facilities of the NRL reactor. The samples were dissolved in 15 ml of 1:1 HNO_3-$HClO_4$ + 10 mg Cu carrier. When fumes of perchloric acid were visible, the samples were cooled slightly and about 3 ml of 48% HF was added and the samples were fumed to incipient dryness to drive off the

silica as SiF_4. The samples were then taken up in 20 ml of 1 N HCl and heated to boiling. About 50 mg of KI was added to assure reduction of the As to As(III), and copper and arsenic precipitated as the sulfides with about 10 ml of 5% thioacetamide in water. The samples were kept at or near the boiling point for about 3 minutes, and allowed to cool. The precipitates were filtered through glass-fiber filter pads, washed, dried with acetone, and counted using a 30-cc Ge(Li) detector in conjunction with a 4096-channel pulse height analyzer.

b. Results

The results are summarized in the following table:

Table 8. Copper and arsenic content of SRM cast iron samples

SRM	Sample	Cu content (%)	As content (%)
51	1	1.015	0.00098
	2	0.982	0.00136
	3	1.010	0.00112
	4	0.996	0.00096
	5	0.982	0.00092
	6	1.017	0.00091
	mean	1.004±0.019[a]%	0.00104±.00018[a]%
6g	1	0.521	0.0430
	2	0.524	0.0428
	3	0.507	0.0422
	4	0.517	0.0426
	5	0.526	0.0445
	6	0.526	0.0414
	mean	0.520±0.008[a]%	0.0428±0.0011[a]%
342a		0.1468	Not determined (<10 ppm)
		0.1448	
		0.1432	
		0.1390	
		0.1420	
		0.1438	
	mean	0.1433±0.0029[a]%	

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

(P. D. LaFleur)

6. The Determination of Cu and Sb in Solder

The Activation Analysis Section was requested to participate in the certification of SRM 127b which is a 40% Sn - 60% Pb material. The elements requested were Cu, Sb, and As. It was decided to use an acid sulfide separation in the presence of HF (to complex the Sn and prevent its precipitation) and use a high resolution Ge(Li) detector to resolve the gamma rays of the Cu, Sb and As.

a. Experimental

The solder (ca. 100 mg) was weighed into polyethylene snap-cap vials, Cu flux monitors were attached, and the samples and appropriate standards of Cu, As, and Sb were irradiated for one hour in the glory tube facilities of the NRL Reactor. The samples were dissolved in approximately 10 ml of concentrated H_2SO_4, 10 mg Cu carrier was added, the samples were cooled, and transferred quantitatively to 40-ml conical centrifuge tubes. The samples were centrifuged and the supernatant liquid transferred to erlenmeyer flasks The $PbSO_4$ precipitates were washed once with a 5% Na_2SO_4 solution, centrifuged, and the wash added to the samples. The precipitate was discarded. The samples were then heated to boiling, KI added to reduce the As to As(III), about 3 ml of 48% HF and 15 ml of 5% thioacetamide solution were added. The samples were kept at or near the boiling point for about 3 minutes, then were removed from the hot plate and allowed to cool. The precipitates were filtered through glass-fiber filter pads, washed, and dried with actone. The samples were then counted using a 30 cc Ge(Li) detector in conjunction with a 4096-channel pulse height analyzer.

b. Results

Examination of the gamma-ray spectra showed that the activity of the ^{76}As was so low, compared to the high Sb activity, that the peak could not be totally resolved from the Sb peak. To remove the possibility of bias from the As

on the Sb results, the 687 keV peak of ^{122}Sb was used for the analyses, along with the 511 keV annihilation radiation for the Cu. A rapid method for separating the Sb from the As is presently being developed. The results for Cu and Sb are given below:

Table 9. Copper and Antimony content of SRM 127b (solder)

	Cu content (%)	Sb content (%)
SRM 127b	0.0098	0.409
	0.0095	0.431
	0.0113	0.457
	0.0104	0.380
mean	0.0103±0.0013[a]%	0.419±0.052[a]%

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

(P. D. LaFleur)

7. Activation Analysis of SRM Urea, Creatine and Uric Acid

The NBS Office of Standard Reference Materials is in the process of characterizing the above clinical materials in preparation for issuance as Standard Reference Materials (SRM's). One aspect of this characterization was to be a survey of these specially purified materials for impurities, especially enzyme poisons. For this purpose, the Activation Analysis Section was asked to examine these materials for trace elemental impurities.

a. Experimental

The samples were irradiated in the in-core facility at the NRL reactor for 1 hour at a neutron flux of approximately $8 \times 10^{12} n.cm^{-2}.sec^{-1}$. After irradiation, the samples were returned to the NBSR for nondestructive counting and for group separation procedures. In addition, some short irradiations were made in the NRL pneumatic rabbit irradiation positions for short half-life radioisotopes. These samples were counted at NRL with no chemical separation; but with transfer to clean non-irradiated containers before counting.

b. Results and Discussion

A number of elements were found to be present in trace quantities in these biological materials. They included chlorine, manganese, copper, gold, aluminum and zinc at the sub-ppm level and sodium, which was present at levels of ~1-150 ppm. In addition, arsenic and antimony were looked for but not found.

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

8. Determination of the Homogeneity of SRM Clays Nos. 97a and 98a: Analyses for Sodium and Scandium

Two renewal SRM clays were received for homogeneity studies, No. 97a, Flint Clay, and No. 98a, Plastic Clay. Three different cuts of the finely powdered material were received.

These six clay samples were examined by nondestructive neutron activation analysis to determine which elements, if any, could be easily used for a study of the inhomogeneity in trace element content. The two elements selected, sodium and scandium, were excellent for a homogeneity study, because of their different chemical characteristics and their ease of determination by nondestructive techniques.

a. Experimental

Irradiations were made in the glory tube facilities of the NRL Nuclear Reactor. Samples of approximately 100 mg were heat-sealed in polyethylene snap-cap vials before irradiation. After irradiation, the samples were quantitatively transferred to clean, non-irradiated poly vials for counting.

Counting equipment used included a 3 in. x 3 in. NaI(Tl) detector and a large volume Ge(Li) semiconductor detector. The germanium detector was used to verify that only one γ-ray peak was in the area of interest, then the sodium iodide detector was used to obtain a large number of peak counts to minimize the error due to counting statistics.

b. Results and Discussion

The results are given in Tables 10 and 11. Since only the homogeneity was of interest, the numbers were calculated relative to each other. Corrections were obtained and made for flux variations within the irradiation position, both vertically and horizontally.

Since the value of a homogeneity test is directly related to the precision of measurement, considerable time was expended in the evaluation of random and systematic errors on such precision. Experimental work with the same and similar type samples showed that with considerable care, we could routinely obtain precisions of the order of 1%. Thus, the values shown are estimated to have a precision of 1-2%.

The calculated ± values (S_o of average) are 1.0% and 1.3% for the scandium and 2.4% and 2.8% for the sodium, for 97a and 98a, respectively. This indicates no apparent inhomogeneity for the scandium distribution. However, since the standard deviation of 2.4% and 2.8% are significantly above the precision of the technique, there does seem to be a small inhomogeneity in the sodium distribution among the three cuts.

(D. A. Becker)

D. Service Analyses

1. Nondestructive Neutron Activation Analysis of Impurities in Several Quartz Samples with a Lithium-Drifted Germanium Semiconductor Detector

Four samples of quartz were submitted to the Activation Analysis Section for determination of their impurity content. The samples had been obtained from various sources of supply, and were to be examined for absolute and relative impurities, in order to select the best source for the specific requirements at hand.

Table 10. Results of Homogeneity Studies of SRM Clay #97a

Sample Cut	Relative[a] Scandium Concentration	Average Scandium	Relative[b] Sodium Concentration	Average Sodium
1	1.034		1.068	
	0.998	1.008	0.972	1.020
	0.991		1.021	
3	1.011		1.015	
	0.999	1.000	0.993	1.006
	0.991		1.009	
5	0.986		0.965	
	1.004	0.992	1.005	0.974
	0.987		0.951	
Average =				
	1.000±0.010[c]		1.000±0.024[c]	

[a] Absolute Scandium concentration (Relative conc. ≡ 1.000) is 34.4 ppm on a dry basis.

[b] Absolute Sodium concentration was not determined. The ratio of the two sodium concentrations was: $\frac{[Na]\ 95a}{[Na]\ 97a} = 1.986$

[c] ± Values are standard deviation of the average.

NOTE: Sample sizes ranged from 85 mg to 135 mg with an average of 120 mg. All samples were dried several days @ 110°C before weighing. Cut numbers are those of the Office of Standard Reference Materials.

Table 11. Results of Homogeneity Studies of SRM Clay #98a

Sample Cut	Relative[a] Scandium Concentration	Average Scandium	Relative[b] Sodium Concentration	Average Sodium
2a	1.018		1.013	
	1.006	1.011	0.950	0.995
	1.011		1.029	
4c	1.005		1.001	
	0.999	0.984	0.999	0.979
	0.949		0.937	
6b	1.002		1.034	
	1.012	1.006	1.069	1.026
	1.004		0.975	
Average =				
	1.000±0.013[c]		1.000±0.028[c]	

[a]Absolute Scandium concentration (Relative conc. ≡ 1.000) is 39.1 ppm. on a dry basis.

[b]Absolute Sodium concentration was not determined. The ratio of the two sodium concentrations was: $\frac{[Na]\ 98a}{[Na]\ 97a} = 1.986$

[c]± values are standard deviation of the average.

NOTE: Sample sizes ranged from 90 mg to 142 mg, with an average at 117 mg. All samples were dried several days at 110°C before weighing.

a. Experimental

Since considerable care had been used in the packaging, samples were analyzed as received, except in one case where the sample was too large. In order to reduce the size to that required, the large single piece was placed inside a section of clean thick-walled polyethylene tubing, the ends clamped shut with hemostats, a hammer used to break up the quartz and a fragment was selected for analysis. The quartz did not cut through the polyethylene, so no contamination should occur through this process.

The samples were irradiated in precleaned polyethylene vials, for 1 hour in the NRL Nuclear Reactor. They were then brought back to NBS, transferred to clean, non-irradiated vials, and counted on a 30cc lithium drifted germanium detector.

b. Results

The results obtained are found in table 12. Since high precision and accuracy was not required, and since the primary interest was in the relative impurity concentrations between the four samples for one element, multiple samples were not analyzed.

c. Discussion of Results

The results shown in table 12 indicate a great range in impurity contents of the four quartz samples, approaching three orders of magnitude in one case. No one sample is lowest in all impurities, which means that the source selected would have to be on the basis of which impurities would interfere the least in the planned utilization of the finished material.

(Donald A. Becker)

2. Nondestructive Analysis for Silver, Chlorine, Bromine, Sodium and Potassium in Quartz

The absorption and exchange of molten silver bromide and silver chloride in contact with quartz surfaces was being evaluated and the Activation Analysis Section was asked to

Table 12. Impurities in Quartz Samples

Sample No.[a]	Sample Weight(g)	Concentrations of Impurities Found (ppm)[b]						
		Gold	Zinc	Arsenic	Antimony	Manganese	Sodium	Potassium
1	0.102	<0.0007	130	<0.005	0.276	0.302	20.4	73.7
2	0.106	0.0005	9.4	0.081	0.342	0.0089	1.20	1.6
3	0.0756	0.0231	<0.3	0.177	0.793	0.017	0.391	<0.4
4	0.152	<0.0001	<0.2	<0.003	<0.006	0.0197	7.71	4.08

[a]Sample Identification is as follows:

1. Brazilian Rock Crystal
2. Clear Fused Quartz
3. Brazilian Quartz
4. Quartz - USA

[b]See discussion of accuracy and precision in the text.

analyze quartz tubing samples for silver, chlorine, and bromine. During the course of the analyses it became known that the sodium and potassium concentrations in the quartz were important also, and could be obtained, in most cases, with little extra effort on our part.

We received a total of four sets of samples, which included quartz tubing which had been in contact with the molten salts as well as non-contacted samples. They were analyzed as received, with no additional cleaning. Care was taken in the transporting and storage as well as during the irradiations so that no contamination of the samples occurred. The product nuclides used for the analyses were silver-110, chlorine-37, bromine-82, sodium-24, and potassium-42. The concentrations found ranged from less than 0.1 to over 400 ppm.

Additional information and specific results can be obtained from the publication by K. Stern [14].

(D. A. Becker and E. D. Anderson)

3. Analysis of Nickel and Manganese in Standard Asbestos Samples

The National Center for Urban and Industrial Health, U.S. Public Health Service, Cincinnati, Ohio, prepared a number of asbestos samples for their industrial health standards program. These samples had been analyzed for several elements by two laboratories, one using activation analysis, the other atomic absorption spectrometry. In the case of the Mn and Ni content of these samples, the two laboratories disagreed markedly. The Activation Analysis Section was asked to provide reference analyses for these two elements.

a. Nickel

The experimental technique was the same as that described in Section C, Part 2 of this report.

The results we obtained, together with the results of the other laboratories are given in table 13. Our values agree well with those of the atomic absorption technique

Either inhomogeneity of the sample or, more likely, interference from ^{56}Mn if nondestructive activation analysis was used, may be the cause of disagreement between the two laboratories. Due to the limited quantity of samples received, any inhomogeneity could not be investigated.

Table 13. Nickel content of asbestos samples.

Sample	Amount of Ni (ppm) in Asbestos Samples		
	Lab H (Activation Analysis)	Lab C (Atomic Absorption)	NBS (Activation Analysis)
Crysotile 0-991	-	1970	1506
Crysotile 0-010	<200	795	659
Crocidolite 0-014	8700	13	12
Crocidolite 0-993	-	139	84
Amosite 0-007	1500	34	25
Anthrophyllite 0-016	1900	424	488

(I. H. Qureshi)

b. Manganese

Nondestructive manganese determinations were made by neutron activation analysis on samples of about 100 mg each. After irradiations of 10 minutes in the NRL rabbit and 3 hours decay, gamma-rays from the 2.58 hour ^{56}Mn were counted using a sodium iodide detector.

Results are shown in table 14. Relatively large amounts of sodium (probably milligrams) were found in the Crocodilite samples II, III and VI, and the induced ^{24}Na was removed by complement subtraction. The agreement with either Lab H or Lab C is good in the case of samples I and III and fair in the case of VI. Because only 100 mg of each sample was furnished, no estimates could be made of sample inhomogeneity

Table 14. Manganese results on asbestos samples.

Sample No.	Description	ppm Mn Based on 0.845MeV Peak	ppm Mn Based on 1.81MeV Peak	Quoted Cincinnati Analyses ppm Mn Lab A A.A.	Quoted Cincinnati Analyses ppm Mn Lab B Atomic Absorption
I	Chrysotile 0-991	866	843	-	868
II	Crocodilite I 0-992	675[1]	-	-	924
III	Crocodilite II 0-993	1018[1]	-	-	950
IV	Amosite 0-994	5188	4852	-	3988
V	Amosite 0-007	12321	11794	15000	13900
VI	Chrysotile "B" 0-010	584	568	510	443
VII	Crocodilite 0-014	1042[1]	779[1]	870	864
VIII	Anthophyllite 0-016	1473	1450	1200	988

[1] ^{24}Na subtracted from spectrum by complement subtraction.

(Gilbert W. Smith)

4. The Determination of Copper in Serum and Urine

In cooperation with the National Institute of Arthritis and Metabolic Diseases at the National Institutes of Health, we determined the copper levels in blood serum and urine taken from a patient suffering from Wilson's Disease. Wilson's Disease is a hereditary disease in which the patient's metabolism is unable to control the trace element copper. We received samples of serum and urine taken prior to treatment with penacillamine and after treatment was well established.

a. Experimental

One milliliter samples of serum were transferred to weighed quartz ampoules which had been rigorously cleaned with HNO_3 and distilled water. The ampoules were sealed, and the contents weighed by difference. Copper flux monitors were attached, and the samples were irradiated in the glory tube facilities of the NRL reactor for one hour. The ampoules were carefully opened and the samples transferred with 10 mg Cu carrier to erlenmeyer flasks quantitatively. The samples were ashed with HNO_3 - $HClO_4$ and the residue taken up with about 25 ml of 1 N HCl. The samples were heated to boiling and 10 ml of 5% thioacetimide solution was added. The samples were held at or near boiling point for about 3 minutes then removed from the hot plate and allowed to cool. The precipitate was collected on a glass-fiber filter pad, washed with water, and dried with acetone. The samples were then counted using a 3 in. x 3 in. (7.6 cm x 7.6 cm) NaI(Tl) detector in conjunction with a 400 channel pulse height analyzer. The 511-keV annihilation radiation of ^{64}Cu was used for the analysis.

b. Results

The results are summarized in table 15.

Table 15. Copper content of human serum and urine

Serum

Taken 2/26/68	3.4 ppm Copper
Taken 3/5/68	3.7 ppm Copper

Urine

Taken	Total Volume	Cu Content (ppm)	Total Cu Excreted
2/25 - 2/26/68	1710 ml	1.9	0.33 mg
3/4 - 3/5/68	3000 ml	6.4	1.92 mg

These results agree with the results of atomic absorption spectrometry.

(P. D. LaFleur)

5. Preparation of DNO_3 for the NBS Reactor

In order to minimize corrosion of the primary coolant system in the NBSR, it is desirable to maintain the pD of the system at or near the neutral point. During operation, the pD slowly rises, so it is necessary to add acid to the system periodically. To avoid adding light hydrogen (protium) to the heavy water system, we were asked to make some heavy nitric acid by the Reactor Operations Section of the Reactor Radiations Division, using the method utilized by R. L. Tromp [15] at the National Reactor Testing Station. The method used is the classical method of preparing a low-boiling point acid from a salt of the acid and a higher boiling acid.

a. Experimental

A 2-lb. ampoule of Sulfan* stabilized SO_3 (liquid) is sealed into an all-glass system consisting of the ampoule, and a condenser which terminates in a tube long enough to extend slightly below the surface of 180 ml of D_2O in a 500-ml glass stoppered reagent bottle. The bottle is vented to the air through a drying tube containing $Mg(ClO_4)_2$. The SO_3 is distilled into the D_2O (which is resting in an ice bath), slowly at first, then more rapidly as the concentration of the D_2SO_4 being formed increases, using infra-red heat lamps. When nearly all of the SO_3 has been distilled, the 500-ml reagent bottle containing the D_2SO_4 is removed and quickly stoppered.

Another all-glass system is prepared consisting of a 3000-ml round bottom flask containing 4 lbs of $NaNO_3$, which has been dried at 120° C for at least 24 hours, and about 1500-ml of D_2O, connected through a condenser to a 4 liter reagent bottle. The boiling flask is in a heating mantle which is on top of a large magnetic stirrer, and a 3/8-in x 2-in Teflon

---

*See disclaimer in preface.

stirring bar is in the flask. One neck of the boiling flask has a dropping funnel in it through which the D_2SO_4 is added. The flask is heated with stirring to prevent bumping and D_2SO_4 is added slowly. The DNO_3 produced is distilled into the reagent flask at about 120° C. Using the system described, DNO_3 of 11 M was produced.

(P. D. LaFleur)

5. ACTIVATION ANALYSIS WITH THE NBS LINAC

A. Introduction

Useful beam from the NBS electron linear accelerator has been available for about 18 months. Our efforts during this time have been divided roughly equally between the methodology of photon activation analysis including flux monitoring, evaluation of systematic error and calculation of sensitivities, and determinations for which photon activation is particularly suited. These included the determination of carbon and oxygen in sodium, yttrium in rare earths and cast iron, and carbon in sulfur.

B. Facilities

The target and pneumatic transfer facility described in previous progress reports continues to function in a satisfactory manner. The fluorescent screen is of great assistance to the accelerator operators in positioning the electron beam properly. Figure 16 shows a photograph taken on closed circuit television of the electron beam striking the screen. The beam approximately fills a circle of one inch diameter. In the

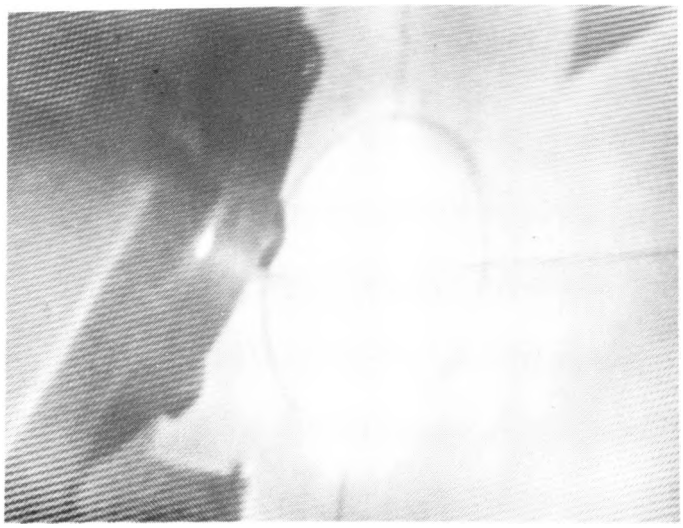

Figure 16. Photograph of electron beam from LINAC striking fluorescent screen

foreground the beam pipe which carries the electron beam may be seen.

A second rabbit terminal has been installed directly behind the original terminal. This is used for production of isotopes for decay scheme studies, Mossbauer spectroscopy, and tracers for radiochemical separations research.

C. Carbon and Oxygen in Sodium

The determination of carbon and oxygen in sodium is a problem of substantial concern in the technology of liquid-sodium cooled reactors and one for which photon activation analysis is uniquely suited.

Classical methods for these determinations are subject to error because of the possibility of contaminating the surface of the sample before an analysis of the bulk of the sample can be accomplished. In addition, reagent and equipment blanks may be large relative to the amount of the non-metal to be determined.

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

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

Both radionuclides decay by positron emission. Their half-lives are of sufficient length to permit a simple separation. After irradiation, the samples are etched to remove approximately 25% of the sample before separation. The separation of carbon has been described [16]. The separation of oxygen consists of dissolving the sample in 6M NaOH under a stream of nitrogen. The radioactive oxygen is converted to hydroxide which exchanges with the water. A portion of the water is rapidly distilled and the positron anhillation radiation counted by coincidence spectrometry. Yields of 40-50% are usually obtained and the time from the end of irradiation to

beginning of counting is usually about four minutes. Sensitivities of a few ppm are possible.

(G. J. Lutz and D. A. DeSoete)

D. Matrix Effect

A general source of systematic error in activation analysis is the difference in absorption of the bombarding particles between sample and standard. Serious error can arise through neglect of differences in self-shielding. We have evaluated the extent to which these errors can occur in our photon activation facility.

Since the mean free path of the photons in the sample is large compared to the dimensions of the sample one may write

$$\frac{f}{fo} = e^{-t\Sigma\mu\rho} \qquad (1)$$

where fo = photon flux with zero attenuation (photons/cm^2- sec)

f = photon flux after attenuation (photons/cm^2- sec)

$\Sigma\mu\rho$ = The sum over all elements in the sample of the density of each element (cm^{-1})

t = Thickness of the sample (cm)

Since the activity per unit weight of an element in the sample produced during irradiation is proportional to the flux we may replace fluxes with A and Ao

$$\frac{A}{Ao} = e^{-t\Sigma\mu\rho} \qquad (2)$$

Since μ is energy dependent, for complete rigor the right side of the equation should be replaced with a sum of terms over all photon energies. For ease in computation and without significant loss in accuracy one may consider an average energy and use the gamma ray absorption coefficients corresponding to this energy. A logical choice is the energy of maximum cross section.

In our facility, samples are cylindrical in shape and have a diameter of 0.95 cm. The photon beam is perpendicular to the axis of the cylinder and thus travels a circular cross section of the sample.

Samples of MgO, PbO and carefully blended mixtures of the two compounds to give variations in photon absorption properties were irradiated and the specific activities of ^{24}Na and ^{202}Pb produced for the reactions $^{25}Mg(\gamma,p)^{24}Na$ and $^{204}Pb(\gamma,n)^{203}Pb$ were measured. The results were fitted to the logarithmic form of equation (2).

$$\ln A = -t\Sigma\mu\rho + \ln Ao$$

The value of t was experimentally determined to be 0.32±.02 cm. This is in reasonable agreement with the estimated value which would be 0.785 x radius or 0.38 cm.

(G. J. Lutz)

E. Sensitivities in Photon Activation Analysis

A new radiator for the photon activation analysis facility has been designed. It was considered worthwhile to estimate the photon flux to be expected from this target and calculate sensitivities for determination of the elements.

Estimates have been made of specific activities to be expected from bremsstrahlung produced by an electron accelerator. The photon flux distribution from electrons striking a 0.6cm. tungsten target at different energies and included in the cone described by a five degree angle from the forward direction has been calculated. Flux times cross section for photonuclear reactions of analytical utility was integrated and disintegration rates of the reaction products for most of the elements under conditions of different electron energies and irradiation times were calculated. Relative values for the specific activities were calculated and compared with the experimental results of Oka and co-workers [17].

The comparison of measured and calculated (γ,n) yields was made under the irradiation conditions of 20 MeV electrons and a 0.2 mm platinum radiator. Since Oka's paper did not specify the angle subtended by his samples, it was possible only to compare relative yields. Our calculated results were normalized to 2×10^6 reactions/mole for the $^{55}Mn(\gamma,n)^{54}Mn$ reaction to coincide with the values found by Oka. The calculated results are plotted along with those of Oka in figure 17. The agreement is satisfactory.

(G. J. Lutz)

F. Carbon in Sulfur

A request was made by the Office of Standard Reference Materials for the determination of carbon in intermediate purity sulfur. A sample of the sulfur had previously been irradiated with thermal neutrons and no gamma-emitting products had been observed. A preliminary irradiation with 35 MeV photons yielded, as expected, a prodigious amount of 2.5 minute, positron emitting, ^{30}P produced via the reaction $^{32}S(\gamma,np)^{30}P$. When this had decayed, the only activity observed was the 20.5 minute, positron annihilation gamma of ^{11}C produced via the reaction $^{12}C(\gamma,n)^{11}C$.

A matter of concern in the determination was extraneous contamination. Since the lumps of sulfur obtained powdered to a great extent from the shock of travelling by compressed air to and from the irradiation position, the commonly used technique in AA of removing the surface after irradiation and before counting was not practical.

Since a bulk analysis was desired, approximately one-quarter inch of material was skimmed from all surfaces of the sample which were irregular lumps of about one inch dimensions. In all the pre-irradiation manipulations, only tools and container of glass and stainless steel along with the irradiation containers to be described were allowed to come in contact with the surfaces.

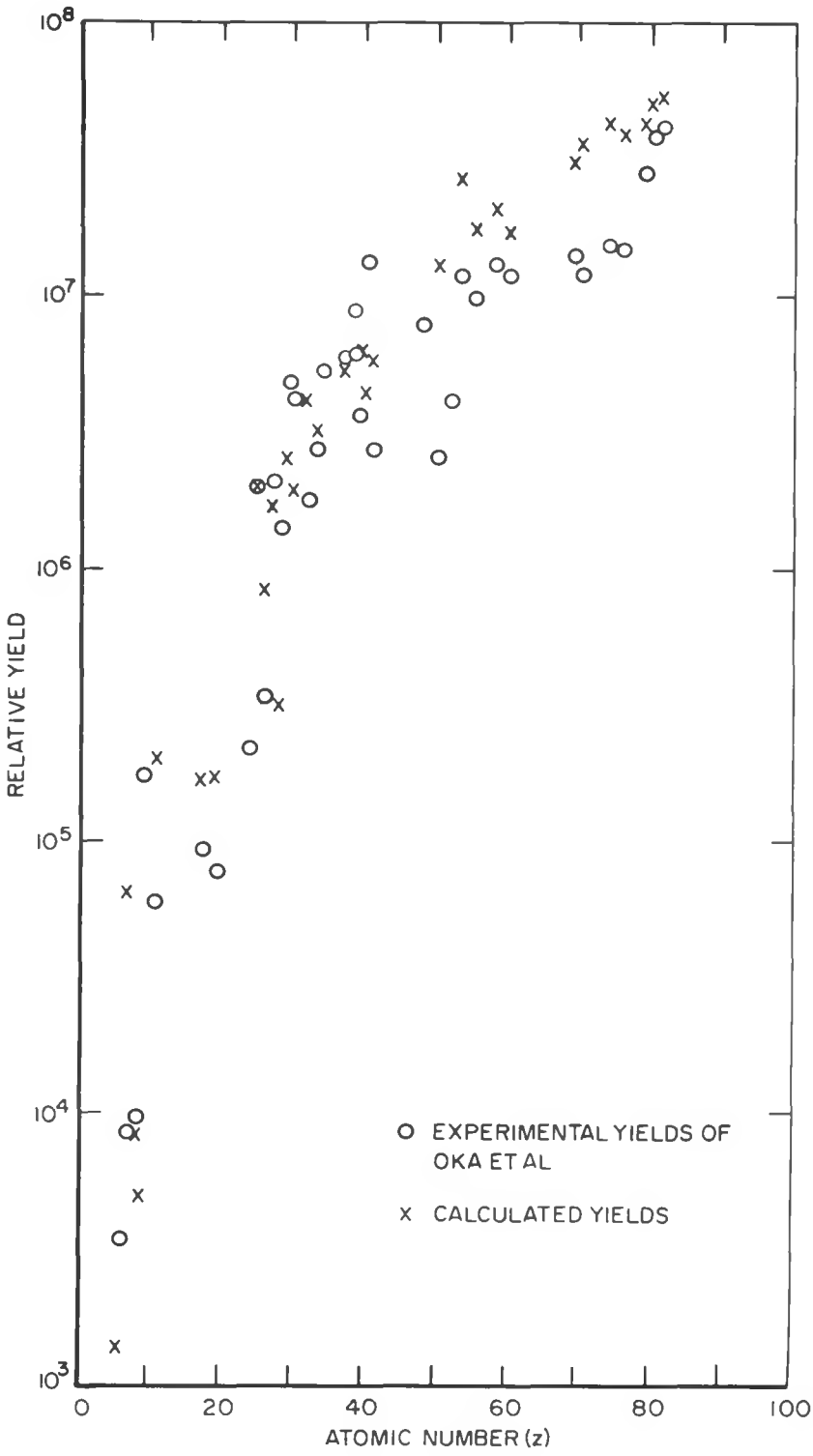

Figure 17. Normalized results of sensitivity calculations shown with experimental results of Oka et al.

In our facility samples are usually encapsulated in snap cap polyethylene vials which are placed in large, aluminum rabbits for irradiation. Because of concern over recoil ^{11}C atoms from the polyethylene containing the sample, small aluminum vials, fabricated in the shop, were used for encapsulation. After the removal of the surface of the sulfur, it was pulverized in a glass mortar and samples were encapsulated. Discs of polyethylene were taped to each end of the aluminum vials as flux monitors. Powdered graphite was used as a standard.

The samples were irradiated for 20 minutes with a beam of 30 μamps and an electron energy of 35 MeV. After irradiation, the samples were allowed to decay for about 30 minutes and then were transferred to clean vials and the positron annihilation radiation decay followed for about 30 minutes.

Results obtained are given in table 16.

Table 16. Carbon content in intermediate purity sulfur.

Lot Number	C content (ppm)
1	73,80,60,72
2	68,82,76
3	69,50,62
4	59,78,65,77

(G. J. Lutz and D. Setlock)

G. Yttrium in Rare Earths

Yttrium has been determined in a variety of rare earths by the reaction $^{89}Y(\gamma,n)^{88}Y$. The product nuclide decays with emission of 0.90 and 1.83 MeV gammas in cascade. Samples were measured by counting the 1.83 MeV gamma ray with a 30-cm^3 lithium-drifted germanium detector or a 3 in. x 3 in. NaI detector, with two 4 in. x 4 in. NaI detectors using coicidence counting.

An analysis of relative sensitivities is shown in table 17. The first column shows the detector system used. The next column shows background; for the 3x3 NaI and Ge(Li) detector, this is the region of the 1.83 MeV photopeak. Using the method of Currie [18] for calculating detection limits for 20 hours of counting background and 20 hours of counting sample, the minimum detectable count rate is shown in the next column. The fourth column shows detection efficiency which is based on irradiation as well as counting conditions. The irradiation conditions are a two hour irradiation with an electron energy of 35 MeV and an average beam current of about 30μA The optimum counting geometry is used in all cases. The fifth column is the ratio of the third and fourth columns and shows the maximum mass of yttrium detectable. Coincidence counting is somewhat superior to the other two methods. Since several grams of sample can be accommodated, a sensitivity of a few tenths of a ppm is possible.

A manuscript describing this investigation is being prepared for submission to a scientific journal for publication.

Table 17. Comparison of sensitivities for yttrium using various detector systems.

Detector	Background (Counts/hr)	Minimum Detectable Activity (Counts/hr)	Detection Efficiency (Counts/hr - μg Y)	Minimum Mass of Y Detectable (μg)
30 cm^3 Ge(Li)	1.5	1.5	.3	5.0
3-in x 3-in NaI(Tl)	200	15	8.5	1.9
Two 4-in x 4-in NaI(Tl) in coincidence	1.5	1.5	1.6	.9

6. EXTRACTION OF METALS BY BIS(2-ETHYL-HEXYL) ORTHOPHOSPHORIC ACID

Solvent extraction studies using bis(2-ethyl-hexyl) orthophosphoric acid (HDEHP) as the extractant, are being made with the ultimate aim of developing group chemical separation procedures. The extraction behavior of Ti, Cr, Mn, Zr, Nb, Mo, Tc, Hf, Ta, W, So, Y, and the lanthanides from 1 to 11M solutions of hydrochloric, perchloric and nitric acids into a 0.75M HDEHP solution (diluted with cyclohexane or n-heptane) has been studied.

The group IVB elements and scandium exhibit high extraction which is independent of hydrogen ion concentration; the group VIIB elements are essentially unextracted. The extraction of some elements of group VB and VIB and of the lanthanides reaches a minumum and then increases with increasing acidity.

The log of the distribution ratios of the group III-VIIB elements and the lanthanides have been plotted as a function of acid concentration in figures 18 to 21.

In order to get more information on the extraction mechanism further investigations were carried out on the extraction of molybdenum. Solutions containing different amounts of HDEHP were used to study the influence of solvent concentration in the organic phase on the extraction of molybdenum from 3M and 9M nitric acid solutions. A log-log plot of the distribution ratios versus HDEHP concentrations, shown in figure 22 exhibits a straight line with an approximate slope of 1, which indicates 1:1 solvent dependency for molybdenum extraction.

Solutions containing semi-gross quantities of molybdenum were used to study the effect of molybdenum concentration on the distribution ratio. The distribution ratio was found to increase with increasing molybdenum concentration in the aqueous phase and levels off at a concentration of approximately 5 mg of Mo/ml. The distribution ratios in 9M HNO_3

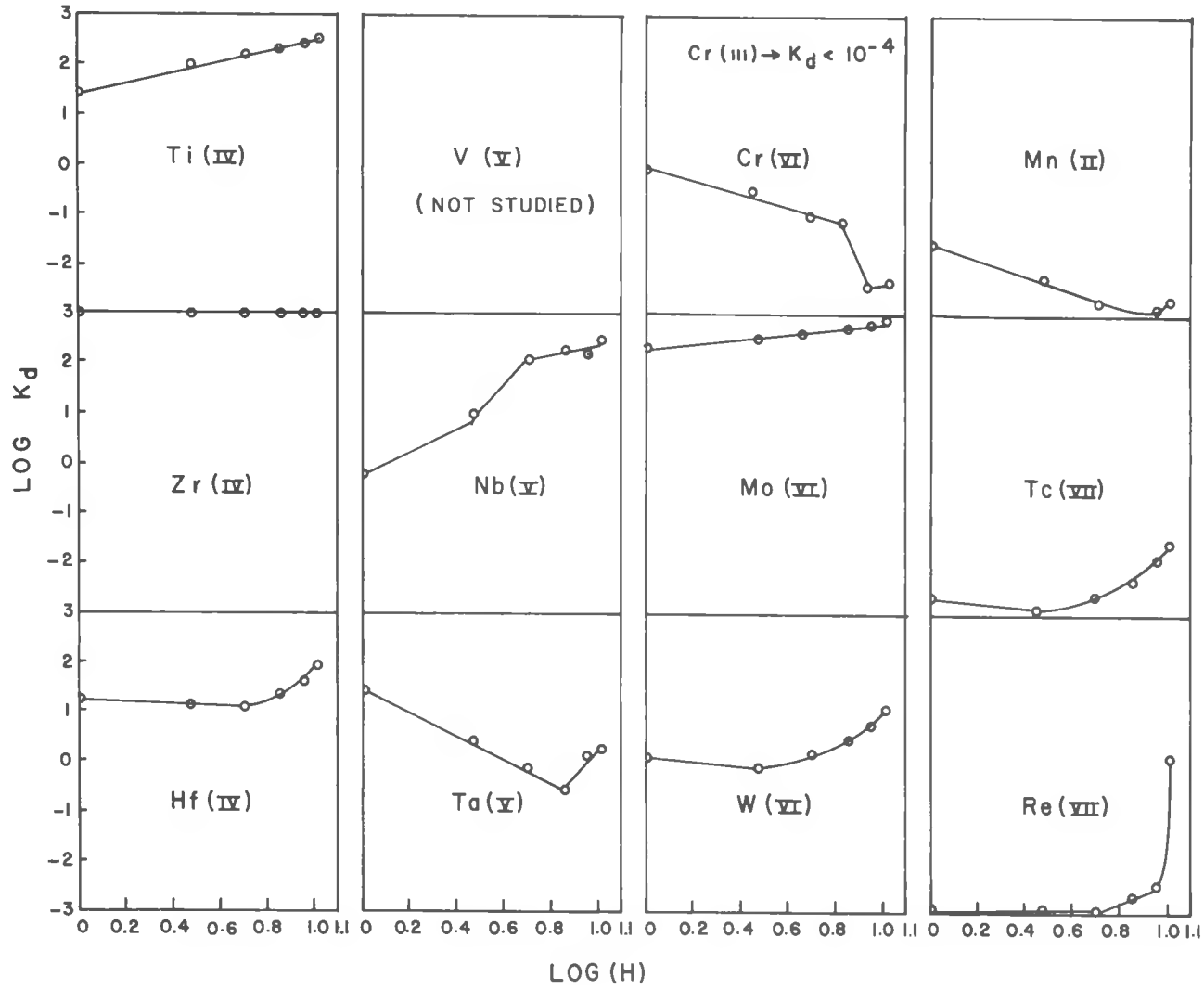

Figure 18. Plot of log Kd as a function of $HClO_4$ concentration.

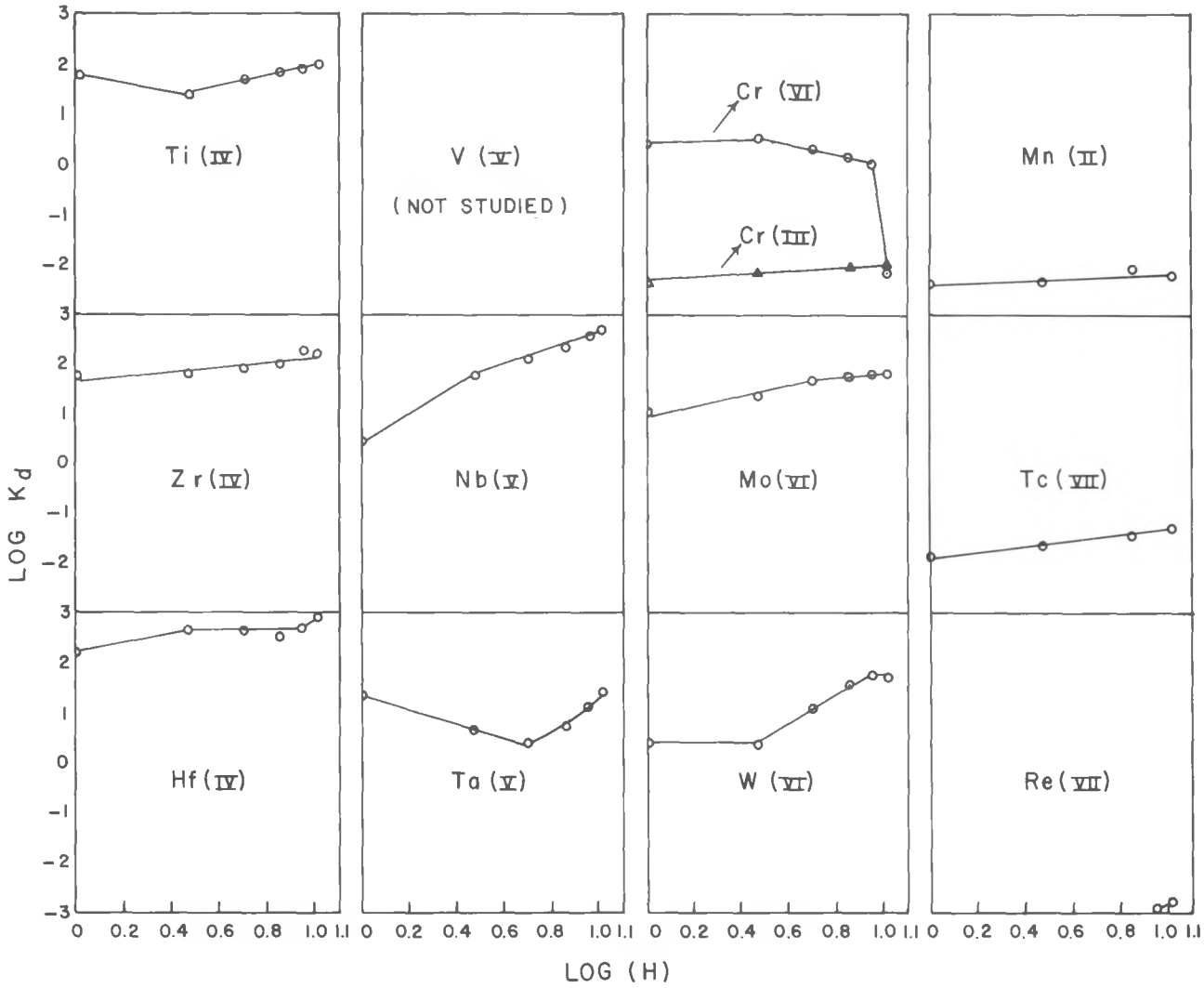

Figure 19. Plot of log Kd as a function of HNO_3 concentration.

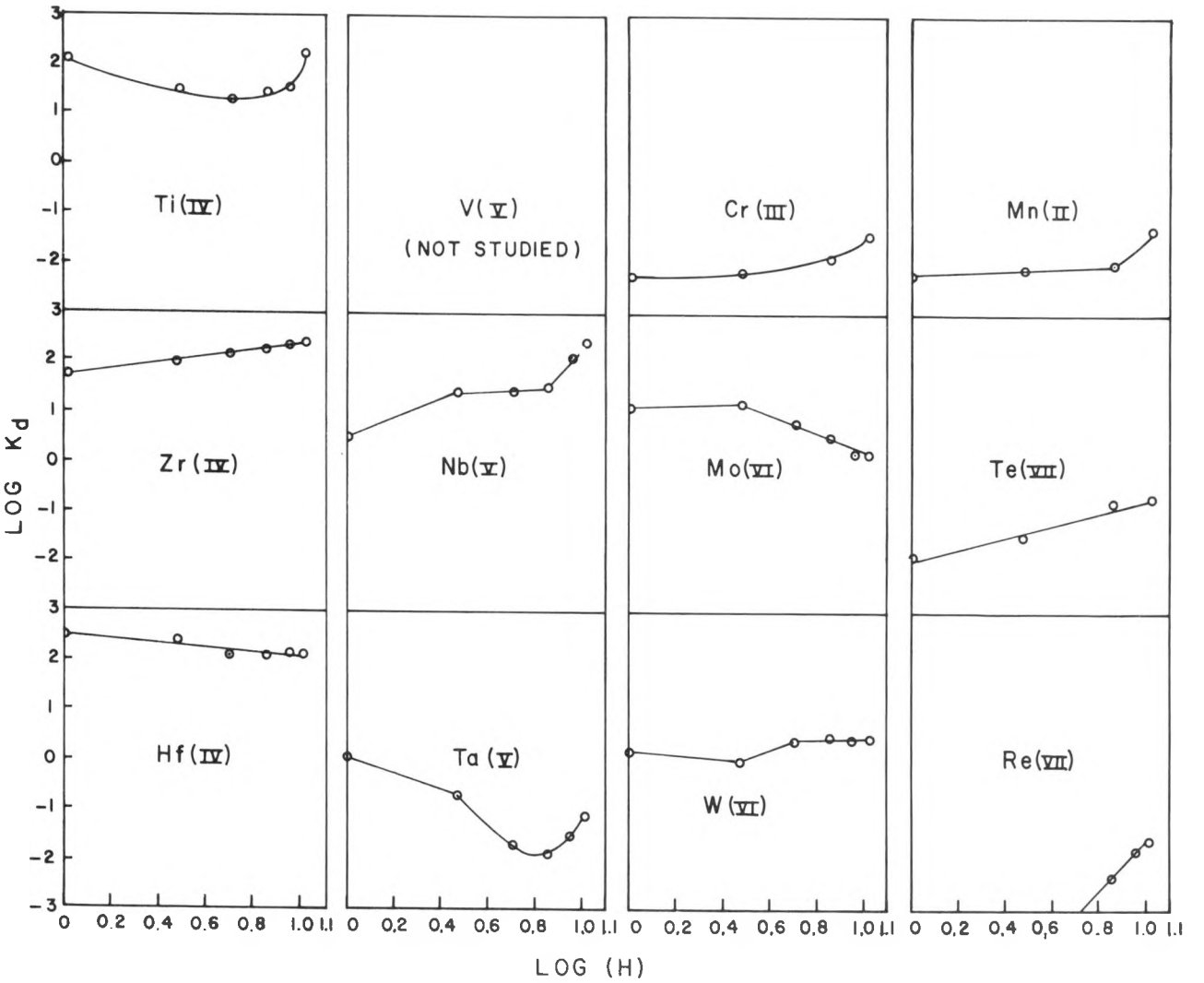

Figure 20. Plot of log Kd as a function of HCl concentration.

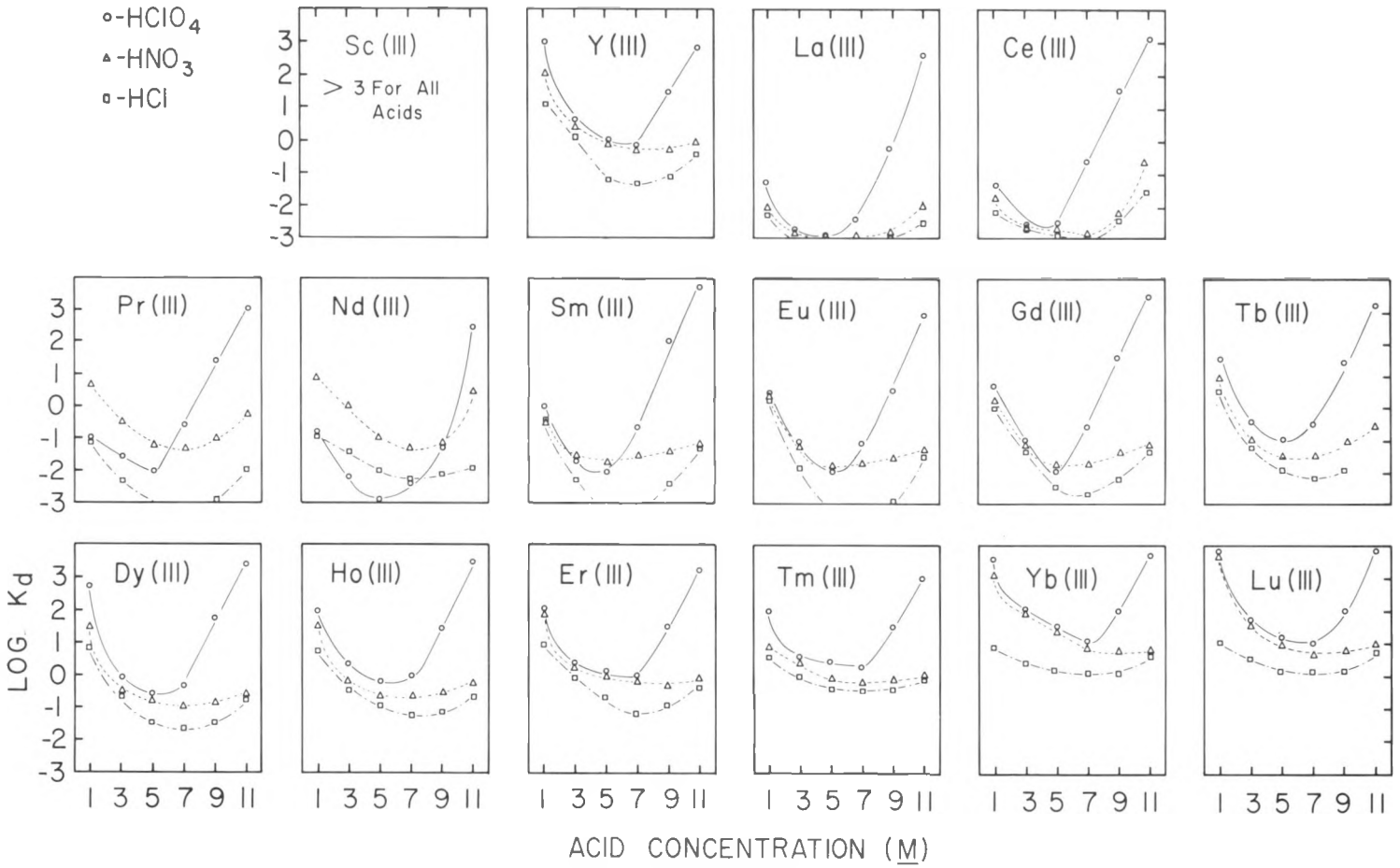

Figure 21. Plot of log Kd as a function of acid concentration for the lanthanides.

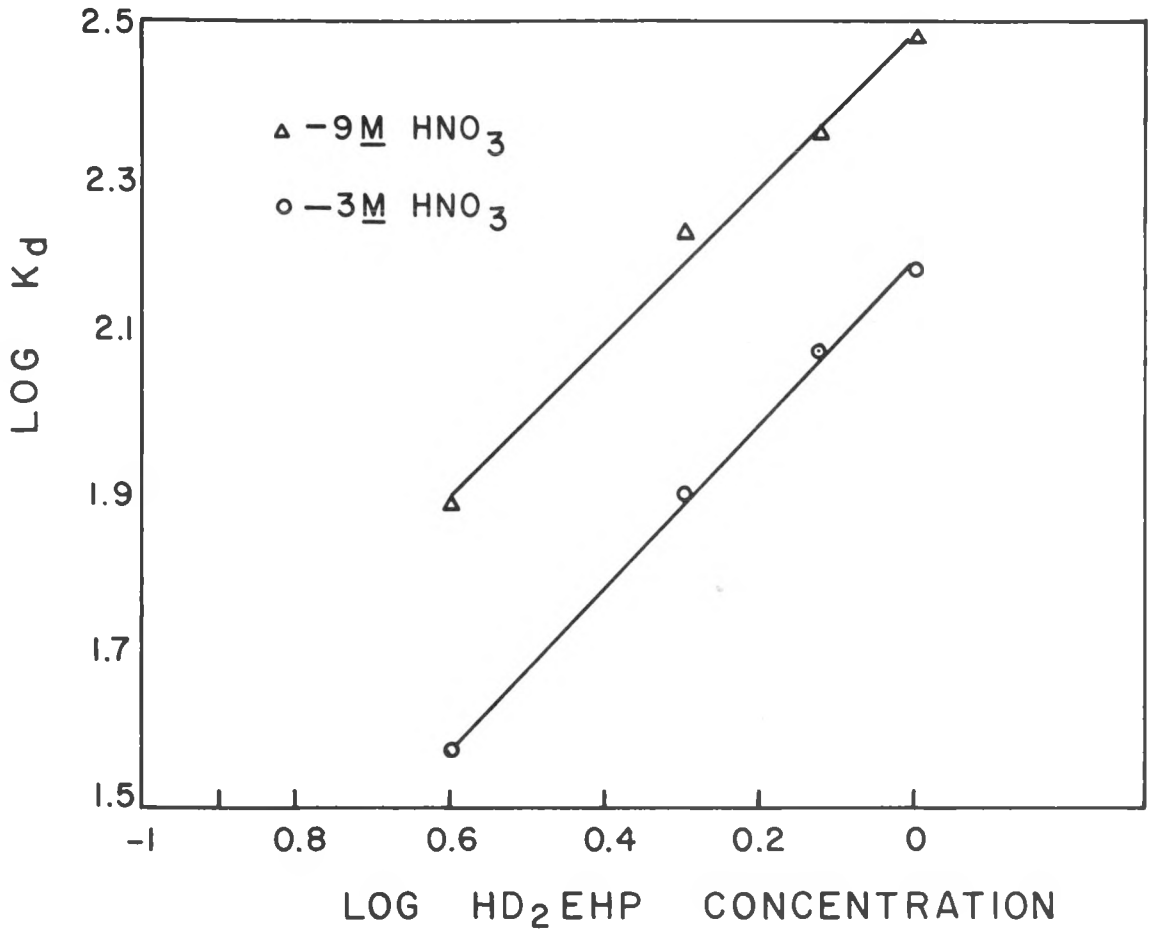

Figure 22. Plot of log Kd for molybdenum as a function of HDEHP concentration.

were found to be higher than that in 3M HNO_3. The extraction remains quantitative even when 10 mg of Mo/ml or a total of 100 mg of Mo, was in the aqueous phase.

According to the solvent dependency studies, one mole of HDEHP should be required for the extraction of one mole of molybdenum from the solution. However, HDEHP was found to extract more than stiochiometric amounts of molybdenum which indicates that a high molybdenum concentrations polymerization in the organic phase may take place. Infra-red studies also indicate a change in the character of the organic species and the possibility of polymerization at high molybdenum

concentrations. Formation of chain polymers has been observed by Baes, et al. [19] in the extraction studies of uranium by HDEHP.

The extraction of metals from acid solutions greater than 5M HDEHP appears to be complex. At high aqueous acid concentrations, interactions similar to those observed in TBP [20] involving the acid, or its anion, may be operative in the extraction. Therefore, the extraction of hydrochloric, perchloric and nitric acids into 0.75M HDEHP was studied. Several solutions of three acids were equilibrated with solutions of HDEHP by mechanically shaking for 2 minutes. The two phases were separated by centrifugation and the aqueous phase was titrated with a 0.5M sodium hydroxide solution to determine the amount of acid extracted into the organic phase. The distribution of the acids between the organic and aqueous phases is shown in figure 23. It may be seen from the figure that for nitric and perchloric acids, the amount of acid extracted varies linearly with the initial aqueous acid concentration up to about 9M original acid concentration. Above 9M the curves become asymptotic, indicating saturation of the organic phase.

Infra-red spectra of the equilibrated organic phases show the presence of nitrate and perchlorate absorption bands in the organic phase with aqueous acid concentrations greater than 4M. The intensities of these absorption bands increases with the acidity of the aqueous phase up to about 9M aqueous concentration confirming the titration data. However, infra-red spectra of HDEHP solutions which were equilibrated with aqueous solutions containing 6M nitrate or perchlorate ions (3M NO_3^- as $NaNO_3$ in 3M HNO_3 or 3M ClO_4^- as $CaClO_4$ in 3M $HClO_4$) do not show the absorption band for nitrate or perchlorate ions. This observation indicates that the entire acid molecule may be extracted rather than only the anions to form species of the type HNO_3.HDEHP and $HClO_4$.HDEHP.

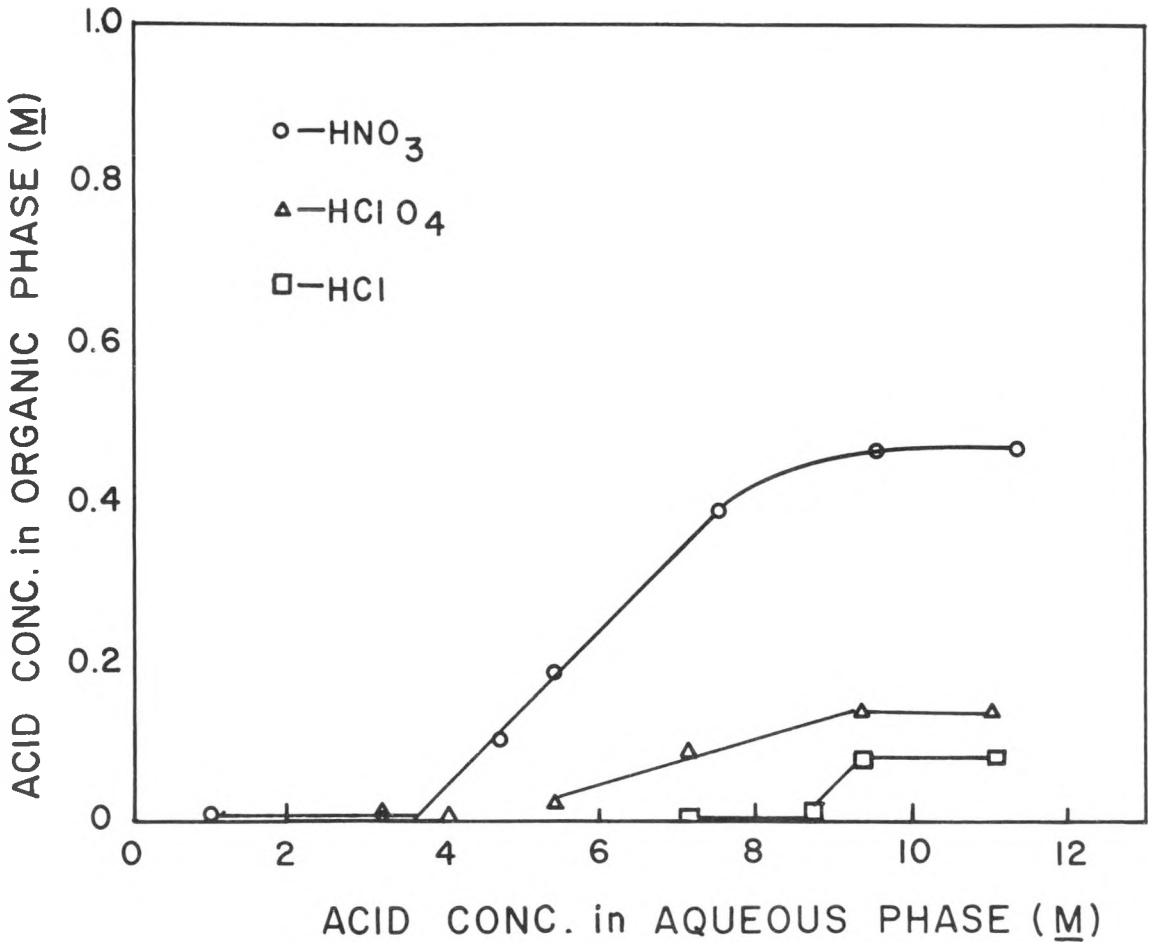

Figure 23. Extraction of $HClO_4$, HNO_3, and HCl by HDEHP.

Further studies are in progress to attempt to elucidate the mechanism or mechanisms of the extraction of metals into HDEHP from strong acid solutions.

(I. H. Qureshi, L. T. McClendon and P. D. LaFleur)

7. ACTIVATION ANALYSIS LITERATURE SEARCHING FILE

The Analytical Chemistry Division of the National Bureau of Standards has, for several years, maintained a file for the activation analysis literature. Each of the some four thousand books, journal articles, reports, theses and conference proceedings in the file is keyed to each (if appropriate) of the following five categories

I. Element Determined
II. Matrix Analyzed
III. Technique Used
IV. Nature of publication, language and country of origin
V. Scope of publication

The specific keys for each category are given in Appendix 2.

The title, authors and location in the literature along with an identifying number and the appropriate keys, are entered on magnetic tape. Subsequently a computer search to identify these items included in a key of a category or combination of keys in the various categories can be accomplished. A portion of a typical readout is shown in figure 10. For this listing the following keys were requested: Key 1 - all, Key 2 - 88, Key 3 - all, Key 4 - all.

It is intended to publish in October, 1968, a complete bibliography of activation analysis identifying all items in the literature associated with the specific keys of the first three categories.

(G. J. Lutz)

NBS-IMR ACTIVATION ANALYSIS SEARCH NO. 132

I1 105
I2 MAHONY, J.D.
I3 REACTIONS OF HE-3 WITH LIGHT ELEMENTS APPLICATIONS TO ACTIVATION ANALYSIS.
I4 UCRL-11780 (PH.D. THESIS), 62P., JANUARY 1965. (ENGLISH), UCRL, BERKELEY, CALIF

I1 130
I2 DE, A.K. * MEINKE, W.W.
I3 ACTIVATION ANALYSIS WITH AN ANTIMONY-BERYLLIUM NEUTRON SOURCE.
I4 ANAL. CHEM., 30, 1474-1482 (1958). (ENGLISH). DEPT. OF CHEM., UNIV. OF MICHIGAN, ANN ARBOR, MICH.

I1 208
I2 HALL, T.A.
I3 CHEMICAL ELEMENT ANALYSIS OF RADIOACTIVE MIXTURES IN BIOLOGICAL MATERIALS.
I4 NUCLEONICS, 12, NO. 3, 34-35 (1954). (ENGLISH). SLOAN-KETTERING INSTITUTE FOR CANCER RESEARCH, NEW YORK, N.Y.

I1 211
I2 HAMAGUCHI, H. * HASHIMOTO, J. * HOSOHARA, K. * NARUSAWA, Y.
I3 A NEW APPLICATION OF NEUTRON ACTIVATION ANALYSIS TO THE POLAROGRAPHY OF HOLMIUM.
I4 BULL. CHEM. SOC. JAPAN, 33, 562-563 (1960). (ENGLISH). DEPT. OF CHEMISTRY, FACULTY OF SCIENCE, TOKYO UNIV. OF EDUCATION, BUNKYO-KU, TOKYO, JAPAN.

I1 344
I2 MEINKE, W.W. * ANDERSON, R.E.
I3 ACTIVATION ANALYSIS USING A LOW LEVEL NEUTRON SOURCE.
I4 ANAL. CHEM., 25, 778-783 (1953). (ENGLISH). CHEMISTRY DEPT., UNIV. OF MICHIGAN, ANN ARBOR, MICH.

I1 544
I2 YAKOVLEV, Y.V. * KULAK, A.I. * RYABUKHIN, V.A. * RYTCHKOV, R.S.
I3 THE DETERMINATION OF TRACE IMPURITIES IN PURE MATERIALS BY RADIOACTIVATION ANALYSIS.
I4 SECOND UNITED NATIONS INTERNATIONAL CONFERENCE ON PEACEFUL USES OF ATOMIC ENERGY, P/2023, 496-505 (1958). (ENGLISH). RUSSIA.

I1 589
I2 KUSAKA, Y.
I3 ACTIVATION ANALYSIS OF SILVER USING RADIUM PLUS BERYLLIUM NEUTRON SOURCE.
I4 BUNSEKI KAGAKU, 8, 111-115 (1959). (JAPANESE) (ENGLISH SUMMARY). DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, KONAN UNIVERSITY, JAPAN.

I1 662
I2 YAKOVLEV, Y.V. * KULAK, A.I. * RYABUKHIN, V.A. * RYTCHKOV, R.S.
I3 THE DETERMINATION OF TRACE IMPURITIES IN PURE MATERIALS BY THE RADIOACTIVATION ANALYSIS.
I4 PROGRESS IN NUCLEAR ENERGY SERIES IX, VOL. I-ANALYTICAL CHEMISTRY, PERGAMON PRESS, 145-162, 1959. (ENGLISH TRANSLATION). RUSSIA.

Figure 24. Typical readout of computer literature search.

8. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Activation Analysis Section
- Philip D. LaFleur, Section Chief (1/4)
- James R. DeVoe, Section Chief (3/4)*
- Betty E. Dawson, Secretary (3/4)
- Patricia A. Snyder, Secretary - Transferred (1/4)
- Ramona Roberts (Summer Worker, Youth Opportunity Program)

Activation Analysis, Reactor
- P. D. LaFleur, Project Leader (1)
- D. A. Becker, Project Leader - Special Project (1)
- E. D. Anderson - Transferred (1/4)
- T. E. Gills (1)
- W. D. Kinard (1)
- F. A. Lundgren (1/4)
- W. P. Reed - Transferred (3/4)
- G. W. Smith (1)
- B. A. Thompson (3/4)
- Patricia Brady (Summer Worker, Youth Opportunity Program)

Activation Analysis, Cockcroft-Walton Generator
- S. S. Nargolwalla, Project Leader and Assistant Section Chief (1)
- M. R. Crambes - Terminated (1/2) NBS Contract, France
- Paul Black - Terminated (1/4)
- E. P. Przybylowicz (1/3) Industrial Research Associate, Eastman Kodak Company
- Sheryl Birkhead (Summer Worker, Youth Opportunity Program)

Activation Analysis, LINAC
- G. J. Lutz, Project Leader (1)
- D. A. DeSoete - Terminated (1/6) NBS Contract, Belgium
- Diane Setlock - Terminated (1)
- Moneta Sherin (Summer Worker, Youth Opportunity Program)

Radiochemical Separations
- P. D. LaFleur, Project Leader
- L. T. McClendon - Transferred (3/4)
- I. H. Qureshi (1), NBS Contract, Pakistan

---

*Section Chief of Radiochemical Analysis Section

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

B. Publications

G. W. Smith and D. A. Becker, "The Preparation of an NBS Biological Standard Reference Marerial for Trace Element Analysis," Proceedings of the Symposium on Nuclear Activation Techniques in the Life Sciences, International Atomic Energy Agency, Vienna, 1967 pp. 197-207.

S. S. Nargolwalla, M. R. Crambes and J. R. DeVoe, "A Technique for the Evaluation of Systematic Errors in the Activation Analysis for Oxygen with 14 MeV Neutrons," Anal. Chem. 40 666 (1968).

F. A. Lundgren and S. S. Nargolwalla "Use of a Dual-Sample-Biaxial Rotating Assembly with a Pneumatic Tube Transfer System for High Precision 14-MeV Neutron Activation Analysis," Anal. Chem. 40, 672 (1968).

G. J. Lutz and D. A. DeSoete, "Determination of Carbon in Sodium by Photon Activation Analysis," Anal. Chem. 40 820 (1968).

C. List of Talks

P. D. LaFleur, "The Application of Activation Analysis to Biomedical Problems," Armed Forces Radiobiology Research Institute, Bethesda, Maryland, September, 1967.

P. D. LaFleur, "The Application of Activation Analysis to Biomedical Problems," National Institutes of Arthritis and Metabolic Diseases Seminar, National Institutes of Health, Bethesda, Maryland, October, 1967.

S. S. Nargolwalla, "A Technique for the Evaluation of Systematic Errors in the 14 MeV Neutron Activation Analysis for Oxygen," Conference on Chemistry and Spectroscopy, Anaheim, California, October, 1967.

G. J. Lutz, "Non-Reactor Methods of Activation Analysis," (Panel Discussion) Oak Ridge National Laboratory, Gatlinburg, Tennessee, October 1967.

G. J. Lutz, "Photon Activation Analysis," Greater Washington Area Activation Analysis Council, Washington, D. C., November, 1967.

J. R. DeVoe, "Standard Reference Material for Trace Analysis in the Life Sciences," Oak Ridge National Laboratory, Tennessee, November, 1967.

G. J. Lutz, "The Determination of Carbon in Sodium by Photon Activation Analysis," (G. J. Lutz and D. A. DeSoete American Chemical Society, San Francisco, Calif. April, 1968.

P. D. LaFleur, "The Determination of Molybdenum by Activation Analysis," American Chemical Society, San Francisco, Calif. April, 1967.

B. A. Thompson, "Rapid Group Radiochemical Separation in the Activation Analysis of Steels," (B. A. Thompson, P. D. LaFleur) American Chemical Society, San Francisco, April, 1968.

J. R. DeVoe, "The Determination of Fluorine by 14-MeV Neutron Activation Analysis," (J. R. DeVoe and S. S. Nargolwalla), American Chemical Society, San Francisco, April 1968.

S. S. Nargolwalla, "Evaluation of NBS 1090 Series for Oxygen and Nitrogen Content by Several Methods," Ann. Meeting Div. I, Committee- E-3, ASTM, NBS, Gaithersburg, Maryland, April, 1968.

P. D. LaFleur, Chairman, General Papers (two sessions), Division of Nuclear Chemistry and Technology, American Chemical Society, San Francisco, Calif, April, 1968.

S. S. Nargolwalla, "Current Status of Activation of Trace Oxygen," a Panel Discussion, 14th Annual Meeting of the American Nuclear Society in Conjunction with the Canadian Nuclear Association, Toronto, Canada, June, 1968.

S. S. Nargolwalla, "Self-Absorption of Gamma Photons from Nuclear Emission and Positron Annihilation in 14 MeV Neutron Activation Analysis." 14th Annual Meeting of the American Nuclear Society in Conjunction with the Canadian Nuclear Association, Toronto, Canada, June, 1968.

9. ACKNOWLEDGMENTS

The Activation Analysis Section wishes to thank Dr. Keith Marlow, Mr. E. Bebbs, Mr. L. Harris and Mr. R. Vogt of the Naval Research Laboratory Reactor Facility for making the irradiation of samples possible. We also wish to acknowledge the assistance of the NBS Health Physics staff who have helped us with the safe handling of these samples.

We wish to express our thanks to Dr. R. S. Carter and his staff of the Reactor Radiations Division for their cooperation in making arrangements for our use of the facilities in the NBS Reactor Building. 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 also wish to express our appreciation to Professor J. Hoste, University of Ghent, Belgium, and Dr. Usmani for making possible the visit of Doctors DeSoete and Qureshi, respectively.

This section acknowledges Mrs. J. R. Gossard for her assistance in preparing this report.

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

10. LIST OF REFERENCES

[1] DeVoe, J. R., editor, NBS Technical Note 404 (1966).

[2] DeVoe, J. R., editor, NBS Technical Note 428 (1967).

[3] Lundgren, F. A. and Nargolwalla, S. S., Anal. Chem. 40 762 (1968).

[4] Nargolwalla, S. S. Crambes, M. R. and DeVoe, J. R., Anal. Chem. 40, 666 (1968).

[5] Crambes, M. R., Nargolwalla, S. S. and Suddueth, J. E. Transactions, American Nuclear Society, 11, No. 1, 97 (1968).

[6] Nicholas, D. J. D., and Nason, A., Plant Physiol. 30, 135 (1955).

[7] Totter, J. R., Burnett, W. T., Monroe, R. A., Whitney, I. B. and Comar, C. L., Science 118, 555 (1953).

[8] Thompson, B. A. Strause, B. M. and Leboeuf, M. B., Anal. Chem. 30, 1023 (1958).

[9] Livingston, H. D. and Smith, H., Anal. Chem. 39, 538 (1967).

[10] Webster, P. O., Brune, D. and Samsahl, K. Inst. J. Appl. Rad. Isot. 15, 59 (1964).

[11] LaFleur, P. D., PhD Thesis, University of Michigan (1967).

[12] Bowen, H. J. M., Analyst 92, 124 (1967).

[13] Killick, R. A., Talanta 8, 793 (1961).

[14] Stern, K., J. Phys. Chem. in press.

[15] Tromp, R. L., Idaho Nuclear Corp., Idaho Falls, Idaho, private communication.

[16] Lutz, G. J. and DeSoete, D. A., Anal. Chem. 40, 818 (1968).

[17] Oka, T. Kato, Nomura, K. and Saito, T., Bull. Chem. Soc. Japan, 40, 575-579 (1967).

[18] L. A. Currie, Anal. Chem. 40, 586 (1968).

[19] Baes, C. F. Jr., Zingaro, R. A. and Coleman, C. F., J. Phys. Chem. 62, 129 (1958).

[20] Hesford, E. and McKay, H. A. C., J. Inorg. Nucl. Chem. 13, 156 (1960).

APPENDIX 1

Sequencing Action of Programmer

After presetting (a) gas pressures on the main nitrogen and bleed nitrogen supplies (b) irradiation timer and (c) total multiscaling time on the analyzer clock timer, the samples are ready for loading.

Position Home (H). In this position the loading-routing valve (Ld. RV - fig. 7) is in the "load" position, the sample routing valve (RV - fig. 7) is in sample position #1 and the trigger device (REX) is reset. The programmer is advanced manually to position #1 on the front panel.

Position #1. The valve (Ld. RV) is released and returns to its normal position. A microswitch indicates when this position is secured and advances the programmer to the next step.

Position #2. The (REX) is reset and advances the programmer to position #3.

Position #3. The first rabbit is loaded and propelled into the irradiation assembly. Its arrival there is sensed by a mercury pressure switch which advances the programmer to the next step.

Position #4. The valve Ld. RV is switched to "load" position and valve RV is switched to sample position #2. The second sample is manually loaded and the programmer is manually advanced to position #5.

Position #5. In this step the Ld. RV is released and its return to normal is sensed by the microswitch which advances the programmer to position #6.

Position #6. The trigger (REX) is reset and the programmer is advanced to position #7.

Position #7. The second sample is injected into the second location in the dual-axis irradiation assembly where its arrival is sensed by a mercury pressure switch and advances the programmer to the next step.

Position #8. Valve RV is switched to sample position #1 and the programmer advances to step #9.

Position #9. Advances to position #10.

Position #10. The motor "start" button is pressed. This initiates the rotation of the irradiation assembly. The programmer is manually advanced to position #11.

Position #11. Advances to position #12.

Position #12. In this position the neutron beam is turned on, the irradiation timer starts the countdown and nitrogen gas at approximately 10 lb f/in^2 is bled into the rotating-sample assembly. Termination of the preset irradiation time advances the programmer to position #13.

Position #13. The beam is turned off, and the rotating sample assembly is given a signal to reverse the motor and index the assembly to the proper orientation for rabbit return. The bleed nitrogen is turned off and the irradiation timer is reset. When the indexing operation is completed the programmer receives a "pin-in" signal and advances to position #14.

Position #14. The first rabbit is returned and the photoelectric gas trigger (PEGT) cuts off the return gas supply and advances the programmer to position #15. The signal for gas cut-off is given a fraction of a second before the rabbit actually arrives at the receiver to reduce damage to the receiver by heavy samples.

Position #15. The photoelectric analyzer trigger (PEAT), located at the point of rabbit arrival in the receiver, initiates the counting of the first sample and the trigger (REX) is reset. After termination of the preset counting time, the programmer is advanced to the next step.

Position #16. The detector gate of the analyzer is closed and the first sample is returned to the irradiation position. The pressure switch cuts off the gas supply and advances the programmer to the next position.

Position #17. The valve RV is switched to sample position #2 and the second sample is returned for counting. The PEGT turns off the gas and advances the programmer to position #18.

Position #18. The PEAT initiates the counting of the second sample for the remaining time on the analyzer clock. At termination of this count the programmer advances to the next step.

Position #19. The second sample is returned to the irradiation site, the pressure switch turns off the gas and advances the programmer to position #20.

Position #20. The valve RV is returned to sample position #1 and the programmer advances to position #21.

Position #21. The automatic sequence ends at this point. The samples can be either unloaded by advancing through steps #21-to-Home or can be re-irradiated by switching the "recycle" switch to the recycle mode which causes the programmer to return to position #10. To remove the samples, the programmer is manually advanced to position #22.

Position #22. Sample #1 is returned and the PEAT turns off the gas and advances the programmer to position #23.

Position #23. The valve Ld. RV is switched to the load-unload position, the valve RV is switched to sample position #2. The first sample is manually ejected (via REX) and then the programmer is manually advanced to position #24.

Position #24. The valve Ld. RV is switched to the normal position and the programmer advances to position #25.

Position #25. Sample #2 is returned and the PEAT turns off the gas and advances the programmer to Home.

Position Home. The valve Ld. RV switches the load-unload position and sample #2 is ejected manually. The programmer is now ready for a new cycle operation.

(F. C. Ruegg and M. Stalbird, Radiochemical Analysis Section, J. E. Suddueth and S. S. Nargolwalla)

APPENDIX 2

Keys for Computer Literature Searching

KEY 1 (ELEMENT TO BE DETERMINED)

1.	Actinium	Ac
2.	Aluminum	Al
3.	Americium	Am
4.	Antimony	Sb
5.	Argon	Ar
6.	Arsenic	As
7.	Astatine	At
8.	Barium	Ba
9.	Berkelium	Bk
10.	Beryllium	Be
11.	Bismuth	Bi
12.	Boron	B
13.	Bromine	Br
14.	Cadmium	Cd
15.	Calcium	Ca
16.	Californium	Cf
17.	Carbon	C
18.	Cerium	Ce
19.	Cesium	Cs
20.	Chlorine	Cl
21.	Chromium	Cr
22.	Cobalt	Co
23.	Copper	Cu
24.	Curium	Cm
25.	Dysprosium	Dy
26.	Einsteinium	Es
27.	Erbium	Er
28.	Europium	Eu
29.	Fermium	Fm
30.	Fluorine	F
31.	Francium	Fr
32.	Gadolinium	Gd
33.	Gallium	Ga
34.	Germanium	Ge
35.	Gold	Au
36.	Hafnium	Hf
37.	Helium	He
38.	Holmium	Ho
39.	Hydrogen	H
40.	Indium	In
41.	Iodine	I
42.	Iridium	Ir
43.	Iron	Fe
44.	Krypton	Kr
45.	Lanthanum	La
46.	Lead	Pb
47.	Lithium	Li
48.	Lutetium	Lu
49.	Magnesium	Mg
50.	Manganese	Mn
51.	Mendelevium	Md
52.	Mercury	Hg
53.	Molybdenum	Mo
54.	Neodymium	Nd
55.	Neon	Ne
56.	Neptunium	Np
57.	Nickel	Ni
58.	Niobium	Nb
59.	Nitrogen	N
60.	Nobelium	No
61.	Osmium	Os
62.	Oxygen	O
63.	Palladium	Pd
64.	Phosphorus	P
65.	Platinum	Pt
66.	Plutonium	Pu
67.	Polonium	Po
68.	Potassium	K
69.	Praseodymium	Pr
70.	Promethium	Pm
71.	Protactinium	Pa
72.	Radium	Ra
73.	Radon	Rn
74.	Rhenium	Re
75.	Rhodium	Rh
76.	Rubidium	Rb
77.	Ruthenium	Ru
78.	Samarium	Sm
79.	Scandium	Sc
80.	Selenium	Se
81.	Silicon	Si
82.	Silver	Ag
83.	Sodium	Na
84.	Strontium	Sr
85.	Sulfur	S
86.	Tantalum	Ta
87.	Technetium	Tc
88.	Tellerium	Te
89.	Terbium	Tb
90.	Thallium	Tl
91.	Thorium	Th
92.	Thulium	Tm

KEY 1 (ELEMENT TO BE DETERMINED) continued

93.	Tin	Sn
94.	Titanium	Ti
95.	Tungsten	W
96.	Uranium	U
97.	Vanadium	V
98.	Xenon	Xe
99.	Ytterbium	Yb
100.	Yttrium	Y
101.	Zinc	Zn
102.	Zirconium	Zr
103.	Rare earths	
104.	Actinides	
105.	Lanthanides	

KEY 2 (MATRIX ANALYZED)

1. Air, Atmosphere
2. Archaelogical specimens
3. Art
4. Biological, general, including virus
5. Biological, blood
6. Biological, urine
7. Biological, other fluids
8. Biological, soft tissue, including hair, nails, and hoofs
9. Biological, bone, teeth
10. Biological, fish
11. Biological, shell fish
12. Biological, seaweed
13. Biological, leaves, needles
14. Biological, wood
15. Biological, other botanical
16. Cellulose - Textiles
17. Cement
18. Chromatography and Ion Exchange - paper, resins, reagents, etc.
19. Clays
20. Coal
21. Corrosion Products
22. Detergents
23. Drugs
24. Dusts
25. Food
26. Forensic, general
27. Forensic, hair and fingernails
28. Forensic, poisons
29. Forensic, gunpowder residue
30. Forensic, trace identification
31. Glass
32. Inorganic Compounds (general)
33. In-stream Analysis
34. Isotopic Analysis
35. Liquids, excluding water and sea water
36. Metals and Alloys (general)
37. Meteorites and Tektites
38. Minerals
39. Ores
40. Organic Compounds
41. Organometallic Compounds
42. Particles
43. Pesticides
44. Petroleum and Derivatives
45. Photographic film and material
46. Plastics
47. Process control
48. Protein

KEY 2 (MATRIX ANALYSED) continued

49. Quartz
50. Reactor Materials
51. Reagents
52. Refractories and Ceramics
53. Rocks
54. Sediments, marine
55. Semi-conductor materials
56. Soils - fertilizers
57. Space applications, lunar
58. Stable tracers
59. Steel and Cast Irons
60. Surface analysis
61. Thin films
62. Water
63. Water, sea
64. Well logging
65. Lithium and its alloys and compounds
66. Ammonium compounds and alkali metals and their alloys and compounds (excluding lithium)
67. Beryllium and its alloys and compounds
68. Magnesium and its alloys and compounds
69. Calcium, strontium and barium and their alloys and compounds
70. Boron and its alloys and compounds
71. Aluminum
72. Aluminum alloys and compounds
73. Titanium and its alloys and compounds
74. Zirconium and its alloys and compounds
75. Hafnium and its alloys and compounds
76. Niobium and its alloys and compounds
77. Tantalum and its alloys and compounds
78. Chromium, vanadium and manganese and their alloys and compounds
79. Molybdenum and its alloys and compounds
80. Tungsten and its alloys and compounds
81. Iron and its alloys and compounds (excluding steels and cast irons)
82. Cobalt and its alloys and compounds
83. Nickel and its alloys and compounds
84. Copper and its alloys and compounds
85. Zinc and its alloys and compounds
86. Gallium, indium and thallium and their alloys and compounds
87. Cadmium and its alloys and compounds
88. Silver, Gold and Mercury and their alloys and compounds
89. Platinum and its alloys and compounds
90. Rhenium, Ruthenium, Osmium, Rhodium, Iridium and Palladium and their alloys and compounds

KEY 2 (MATRIX ANALYSED) continued

91. Carbon, graphite, diamond
92. Silicon and its alloys and compounds (excluding quartz)
93. Germanium and its alloys and compounds
94. Tin and its alloys and compounds
95. Lead and its alloys and compounds
96. Phosphorus and phosphates
97. Arsenic and Antimony and their alloys and compounds
98. Bismuth and its alloys and compounds
99. Sulfur
100. Selenium and Tellurium and their alloys and compounds
101. Rare earths and their alloys and compounds (including Sc + Y)
102. Halogens
103. Noble Gases
104. Uranium, Thorium and Plutonium and their alloys and compounds
105. Fission products

KEY 3 (TECHNIQUE USED)

1. Reactor - thermal neutron $(n,\gamma)_1$
2. Reactor - fast (n,p) (n,α) (n,n^1) (n,2n)
3. Reactor - epithermal
4. Isotope Source - neutrons
5. Generator - or sealed tube
6. Accelerator - neutrons
7. Photon Activation (includes Isotope Source)
8. Charge Particle (includes Isotope Source)
9. Secondary Particle
10.
11.
12.
13.
14.
15.
16.
17.
18.
19.
20.
21. Non-destructive
22. Chemistry - Dissolution Technique
23. Chemistry - Group Separations
24. Chemistry - General
25. Chemistry - Precipitation
26. Chemistry - Distillation
27. Chemistry - Solvent Extraction
28. Chemistry - Chromatography or Ion Exchange
29. Chemistry - Electrodeposition
30. Chmeistry - Isotope Exchange
31. Chemistry - Amalgam Exchange
32. Chemistry - Szilard-Chalmers
33. Chemistry - Substoichiometric
34. Chemistry - Automated
35. Chemistry - Absorption or Adsorption
36. Rapid Radiochemical Separation
37. Isotope Dilution
38.
39.
40.
41. Gamma Sepctrometry
42. Solid State Gamma Spectrometry
43. Beta and Alpha Spectrometry
44. Coincidence Spectrometry
45. Non-discriminatory counting (α, β, γ) but include half life and absorber measurements, autoradiography, emulsions.
46. Neutron Counting
47. Prompt Gamma Counting

KEY 3 (TECHNIQUE USED) continued

48.
49.
50.
51. Neutron Flux Determination, includes sample self-shielding and flux perturbations
52. Charge Particle Flux Determination, includes sample self-shielding
53. Photonuclear Flux Determination, includes sample self-shielding
54. Interfering Nuclear Reactions
55. Other errors associated with irradiation
56. Counting errors and corrections
57.
58.
59.
60.
61. Precision-accuracy discussed
62. Sensitivity tables
63. Preconcentration, contamination, collection and handling techniques
64. Irradiation techniques, sample handling and facilities, flux monitors
65. Activation analysis standards and standard reference materials
66. Computer applications and numerical methods
67. Data handling systems
68. Electronics in Activation Analysis
69.
70.
71.
72.
73.
74.
75.
76.
77.
78.
79.
80.
81.
82.
83.
84.
85.
86.
87.
88.
89.
90.

KEY 4

1. Abstract
2. Bibliography
3. Book or book chapter
4. Book review
5. Conference
6. Institute or Course
7. Journal (professional)
8. Journal (trade)
9. Patent
10. Press release (news)
11. Report
12. Thesis
13.
14.
15.

Language

16. English
17. English (translation)
18. German
19. French
20. Russia
21. Japanese
22. Chinese
23. Czechoslovakian
24. Dutch
25. Hungarian
26. Italian
27. Norwegian
28. Polish
29. Portugese
30. Serbo-Croatian
31. Spanish
32. Swedish
33. Rumanian
34. Hindi
35. Ukraninian
36. Arabic
37. Danish
38. Hebrew
39. Korean
40. Finnish
41. Greek
42. Others not listed

Work Done

43. USA
44. UK
45. Russia
46. France
47. Germany
48. Japan
49. Austria
50. Belgium
51. Canada
52. China
53. Czechoslovakia
54. Greece
55. Hungary
56. India
57. Israel
58. Italy
59. Korea
60. Mexico
61. Netherlands
62. Norway
63. Poland
64. Portugal
65. South Africa
66. South America
67. Spain
68. Sweden
69. Taiwan
70. Turkey
71. UAR
72. Yugoslavia
73. Australia
74. Switzerland
75. Rumania
76. Denmark
77. Philippines
78. Ukraine
79. Pakistan
80. New Zealand
81. Bulgaria
82. Finland
83. Vietnam

☆ U. S. GOVERNMENT PRINTING OFFICE : 1969—341-026/164