

NATL INST OF STAND & TECH

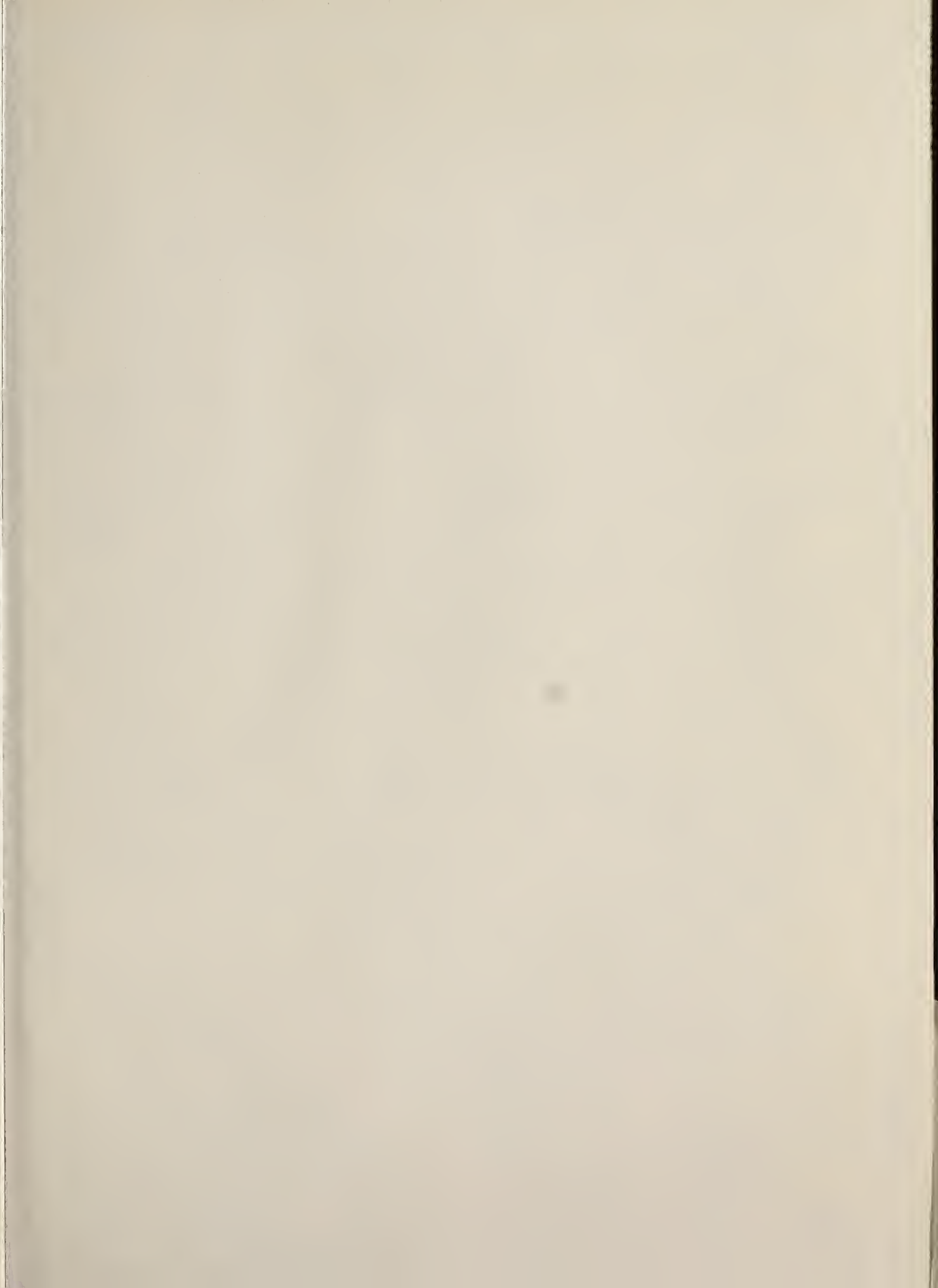


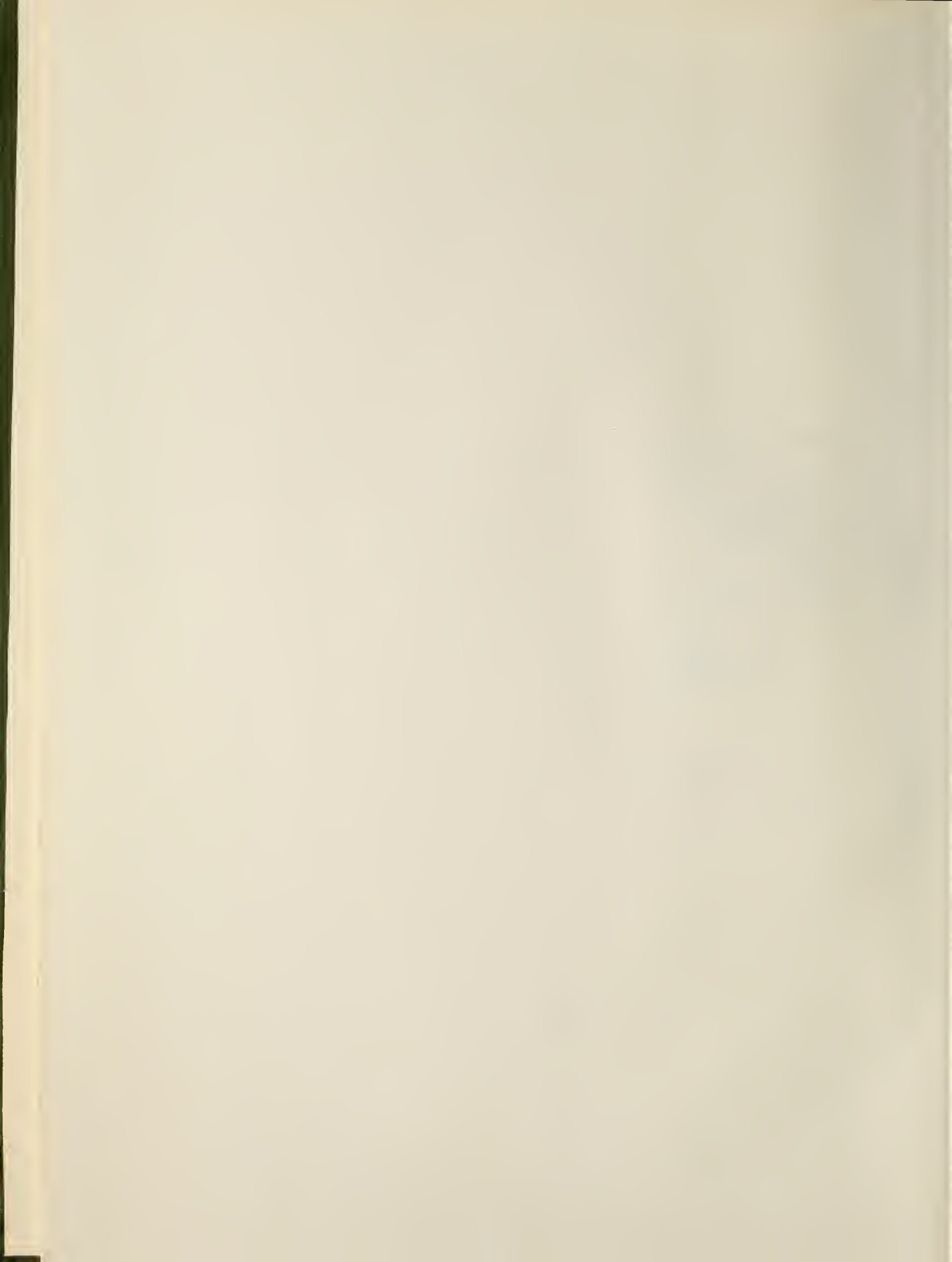
A11107 230371











FEB 3 1969



TECHNICAL NOTE

NATIONAL BUREAU
OF STANDARDS
LIBRARY

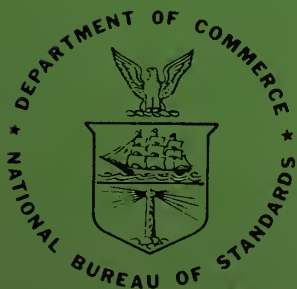
MAR 6 1973

111705

456

Analytical Mass Spectrometry Section:

Summary of Activities
July 1967 to June 1968



U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards¹ was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in three broad program areas and provides central national services in a fourth. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, and the Center for Radiation Research.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Standard Reference Data and a group of divisions organized by the following areas of science and engineering:

Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Cryogenics²—Radio Physics²—Radio Engineering²—Astrophysics²—Time and Frequency.²

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to methods, standards of measurement, and data needed by industry, commerce, educational institutions, and government. The Institute also provides advisory and research services to other government agencies. The Institute consists of an Office of Standard Reference Materials and a group of divisions organized by the following areas of materials research:

Analytical Chemistry—Polymers—Metallurgy — Inorganic Materials — Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides for the creation of appropriate opportunities for the use and application of technology within the Federal Government and within the civilian sector of American industry. The primary functions of the Institute may be broadly classified as programs relating to technological measurements and standards and techniques for the transfer of technology. The Institute consists of a Clearinghouse for Scientific and Technical Information,³ a Center for Computer Sciences and Technology, and a group of technical divisions and offices organized by the following fields of technology:

Building Research—Electronic Instrumentation — Technical Analysis — Product Evaluation—Invention and Innovation—Weights and Measures — Engineering Standards—Vehicle Systems Research.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center for Radiation Research consists of the following divisions:

Reactor Radiation—Linac Radiation—Applied Radiation—Nuclear Radiation.

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

² Located at Boulder, Colorado 80302.

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

UNITED STATES DEPARTMENT OF COMMERCE
C. R. Smith, Secretary
NATIONAL BUREAU OF STANDARDS • A. V. Astin, Director



TECHNICAL NOTE 456

ISSUED NOVEMBER 1968

Analytical Mass Spectrometry Section:

**Summary of Activities
July 1967 to June 1968**

Edited by William R. Shields

Analytical Mass Spectrometry 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.

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 45 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. In 1968 we plan to issue these summaries for all of our sections. The following is the third annual report on progress of the Analytical Mass Spectrometry Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

The basic function of the Analytical Mass Spectrometry Section is to establish high accuracy absolute isotopic ratio standards. To this end the section is concerned with developing instrumentation and devising analytical techniques which will improve the precision of isotope ratio measurements; and at the same time it has the responsibility of developing the chemical procedures necessary for the preparation of the calibration standards necessary to convert the analytical precision statement to an accuracy statement.

The atomic weight that can be calculated from the absolute abundance ratio is of course our most important by-product. For the first time since this laboratory became fully operational we will go two years without completing a new atomic weight determination. During the past two years the wedding of chemistry and mass spectrometry has produced absolute abundance ratio standards for two elements, lead and boron, both of which vary in nature hence no atomic weight statement can be made. The attempt for an atomic weight statement on nickel was not successful. A quantitative method for preparing the calibration standards was developed but a sufficiently precise mass spectrometric procedure has eluded us. Virtually by definition each succeeding atomic weight becomes more difficult.

In order to specify adequately the 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.

William R. Shields, Chief
Analytical Mass Spectrometry Section

TABLE OF CONTENTS

	<u>PAGE</u>
1. MULTI-STAGE MASS SPECTROMETER	1
A. Introduction	1
B. Operation	1
1. Mechanical	1
2. Electronic Systems	5
C. Organization	8
1. Amplifier and Discriminator Unit	8
2. Dual Scaler Unit	8
3. Shift Register Timer	12
4. Control Unit	12
5. Data Transfer Unit	16
6. Calculating System	16
7. Automatic Operation	18
D. Construction and Design	22
1. Amplifier Design and Construction	22
2. Timer Unit Design	25
3. Control Unit Design	25
4. Data Transfer Unit Design	26
E. Ion Multipliers	27
2. CHEMISTRY	28
A. Introduction	28
B. Boron	31
C. Fluorspar	32
D. Lead	32
1. Lead Isotopic Standards	32
2. Archaeological Samples	33
E. Nickel	34
F. Plutonium	35
1. Chemical Standard	35
2. Isotopic Standard	37
G. Uranium	37
3. MASS SPECTROMETRY	39
A. Boron	39
B. Lead	40
1. Lead Isotopic Standards	40
2. Archaeological Isotopic Studies	43
C. Nickel	43
D. Plutonium	43

	<u>PAGE</u>
4. PERSONNEL AND ACTIVITIES.	45
A. Personnel Listing	45
B. Publications.	45
C. Talks	46
D. Committee Activities.	46
5. REFERENCES.	47

LIST OF FIGURES

FIGURE NO.

1. Amplifier-discriminator mounting.	2
2. Circuit diagram of amplifier-discriminator.	3
3. Improved air-operated beam valve.	6
4. Data and control system flow chart.	9
5. Computer-control system	10
6. Control unit.	11
7. Shift input timer block logic	13
8. Control unit block logic.	14
9. Data transfer unit block logic.	17
10. Generalized single ratio program.	20
11. Tunnel diode characteristics.	24
12. Micro anion-exchange column for separation of plutonium from americium and uranium.	36
13. Furnace for ignition of uranium oxides.	38

LIST OF TABLES

TABLE NO.

1. Control registers command constants	18
2. Program registers command constants	19
3. NBS Atomic Weights accepted by the ICAW	29
4. Analyses of SRM 79b, fluorspar.	32
5. Summary of absolute isotopic ratios	41
6. Absolute isotopic ratios for the three standard samples	42

ANALYTICAL MASS SPECTROMETRY SECTION: SUMMARY OF ACTIVITIES
JULY 1967 TO JUNE 1968

Edited by William R. Shields

ABSTRACT

This report describes the advances in instrumentation and the research activities of the Analytical Mass Spectrometry Section during the period July 1967 to June 1968.

Advances in instrumentation include the construction of the electronic interface automating both the control of the multistage instrument, and the digital readout and data reduction. A new and improved beam valve is also described.

Elements studied during this period include: B, Ni, Pb, Li, U, and Pu. Chemical procedures are given for B, Pb, CaF₂, U, and Pu; mass spectrometric procedures are given for B.

Key words: Mass spectrometry, instrumentation, procedures, isotopic analyses.



1. MULTI-STAGE MASS SPECTROMETER

A. Introduction

The first two stages of a projected three stage mass spectrometer had been designed, constructed, and made operational at the end of last year. This instrument has been subjected to extensive testing during the past year to determine the operational feasibility of certain components. In addition, the interfacing to a small digital computer has been completed, various programs written and tested, and operation of the instrument under complete computer control has been achieved.

B. Operation

1. Mechanical

a. General - The instrument as presently constructed is a two stage, 90° sector field instrument with the two stages joined in an off-axis "S" configuration. At the junction of the two stages is a conventional faraday cage arranged so that it may be removed from the beam path completely. Thus the instrument may be used as a single section 12 inch radius instrument or, by removing the cage, as a two stage spectrometer. The detector for the second stage is an ion multiplier, the output of which is fed to an amplifier-pulse height discriminator mounted on the multiplier housing. The amplifier-pulse height discriminator is described below (see also figures 1 and 2).

Preliminary experiments with the "S" configuration indicate that a spectral purity has been obtained such that the contribution of the leading edge of a peak at mass 235 at the half mass position (i.e., mass 234.5) is 1 part in 5.0×10^5 and of the tail of the same peak at mass 235.5 is 1 part in 1.125×10^6 .

b. High Vacuum Beam Valve - Immediately behind the source region of the first stage is a high vacuum beam valve which has been previously described [1]. Extensive experience

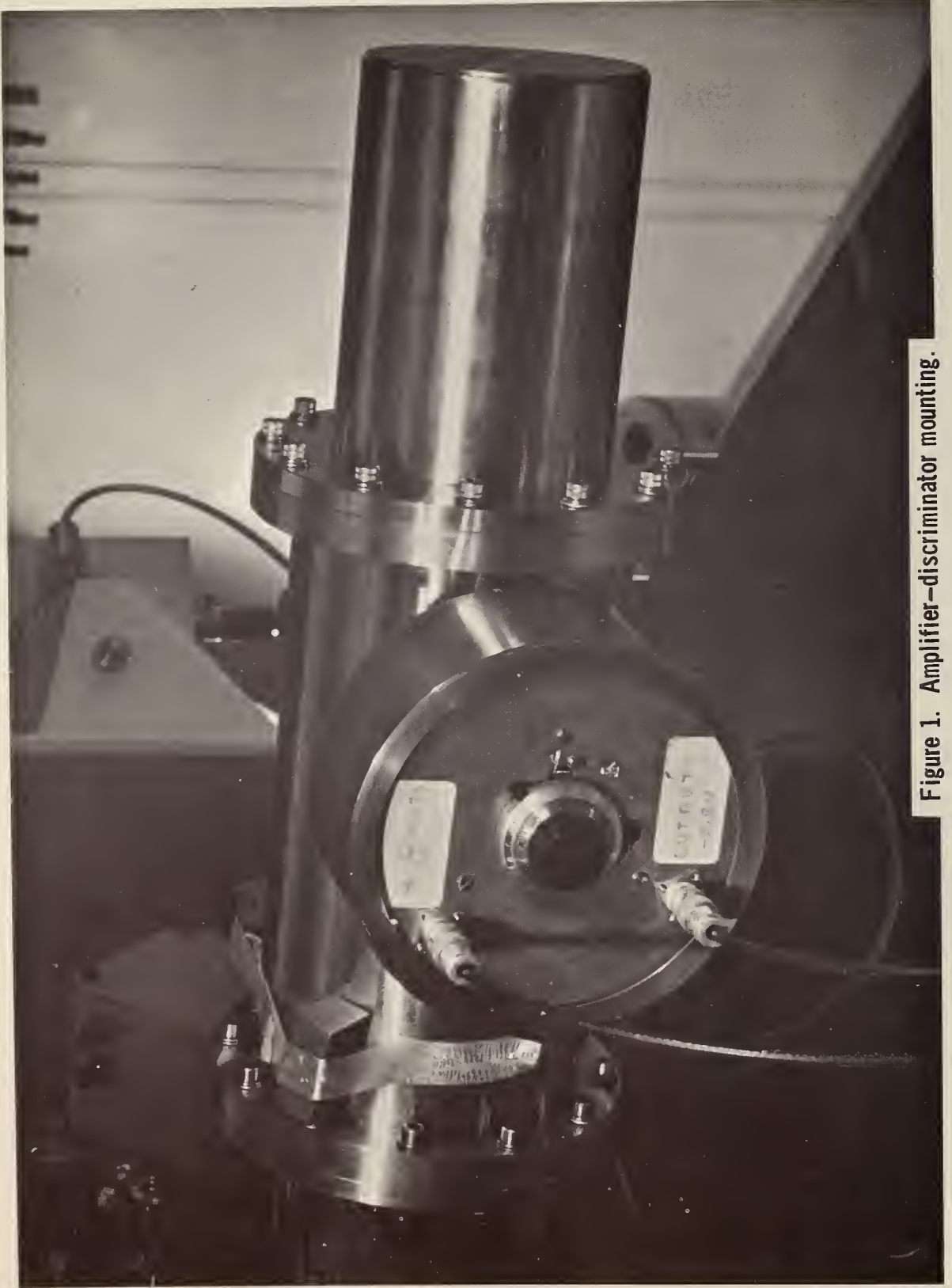
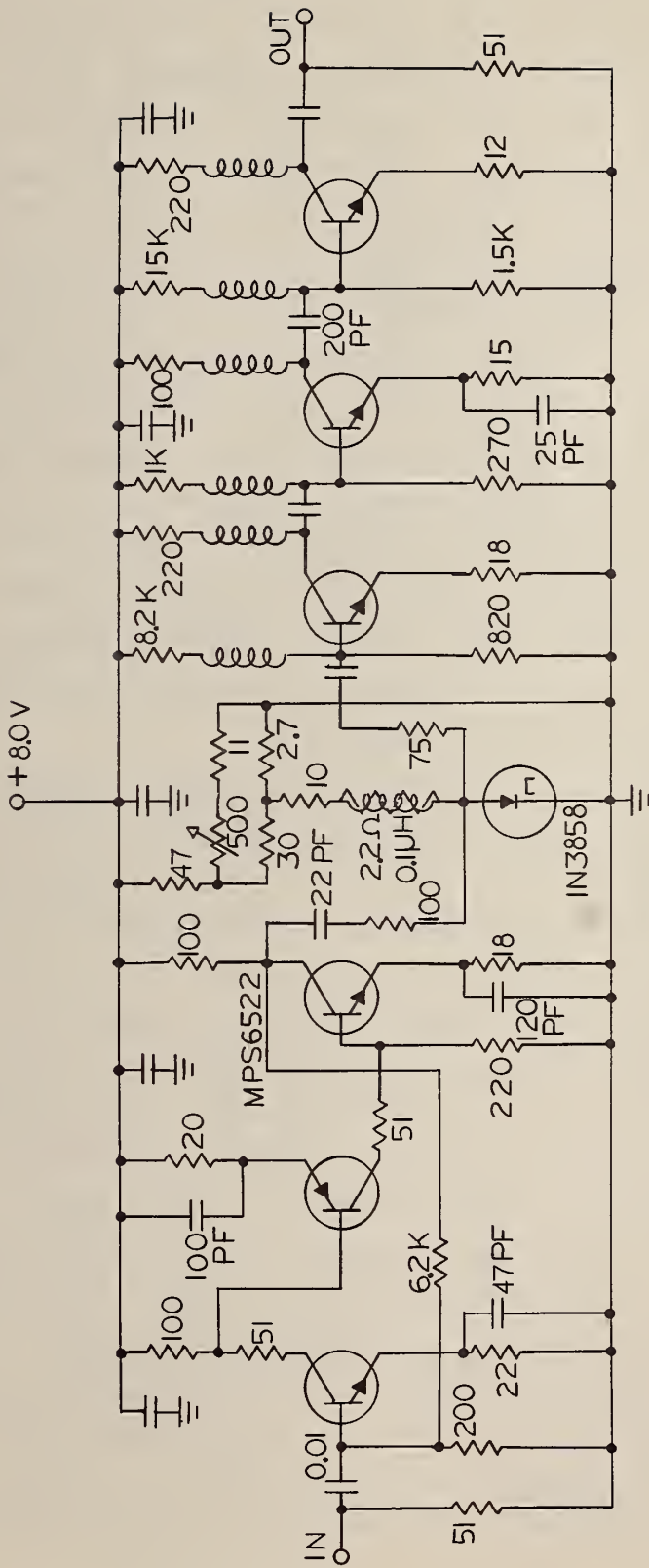


Figure 1. Amplifier-discriminator mounting.



ALL TRANSISTORS NOT MARKED 2N2865
 ALL CAPACITORS NOT MARKED 0.01MFD
 ALL INDUCTORS NOT MARKED 1.5 UH

Figure 2. Circuit diagram of amplifier-discriminator.

with this valve during the past year has lead to the rejection of the design even though it has proven to be an excellent vacuum valve. As mentioned in the above reference it has proven impossible to prevent the shearing of the Teflon plastic insert during normal operation. This leads to the production of small shreads or shards of plastic which extend into the valve opening. Experiments have shown that shards as small as 1/16" long by 1/32" wide extending into the beam opening (.375 × .750 inches) may shut off the beam almost completely due to static charging of the plastic. More important, however, is the loss of beam definition (i.e., loss of peak shape) before the beam is completely stopped. This can lead to serious analytical errors which may go unnoticed.

Although it is possible that a carbon loaded plastic insert might be a successful replacement, both to prevent shredding and static charging in the event that it did take place, this alternative also was rejected.

It was suspected that a very small but still finite amount of O₂ was leaking into the flight tube of the instrument around the packing gland of the valve. It was not possible to measure this leak with conventional vacuum gauges but its effect was determined in the following manner:

It has been demonstrated over a period of years that if a careful low temperature analytical procedure is followed, the $^{235}\text{U}/^{238}\text{U}$ ratio shows a bias of 0.45% that can be controlled at the 0.1% level or better. Results obtained on either of two instruments equipped with the above type of plastic insert valves showed an average bias of approximately 0.2% but which could be controlled only at about the 0.25% level. A series of experiments with identical samples (U-500) on two instruments identical except for the inclusion in one of a beam valve showed that the erratic results could be traced directly to the valve.

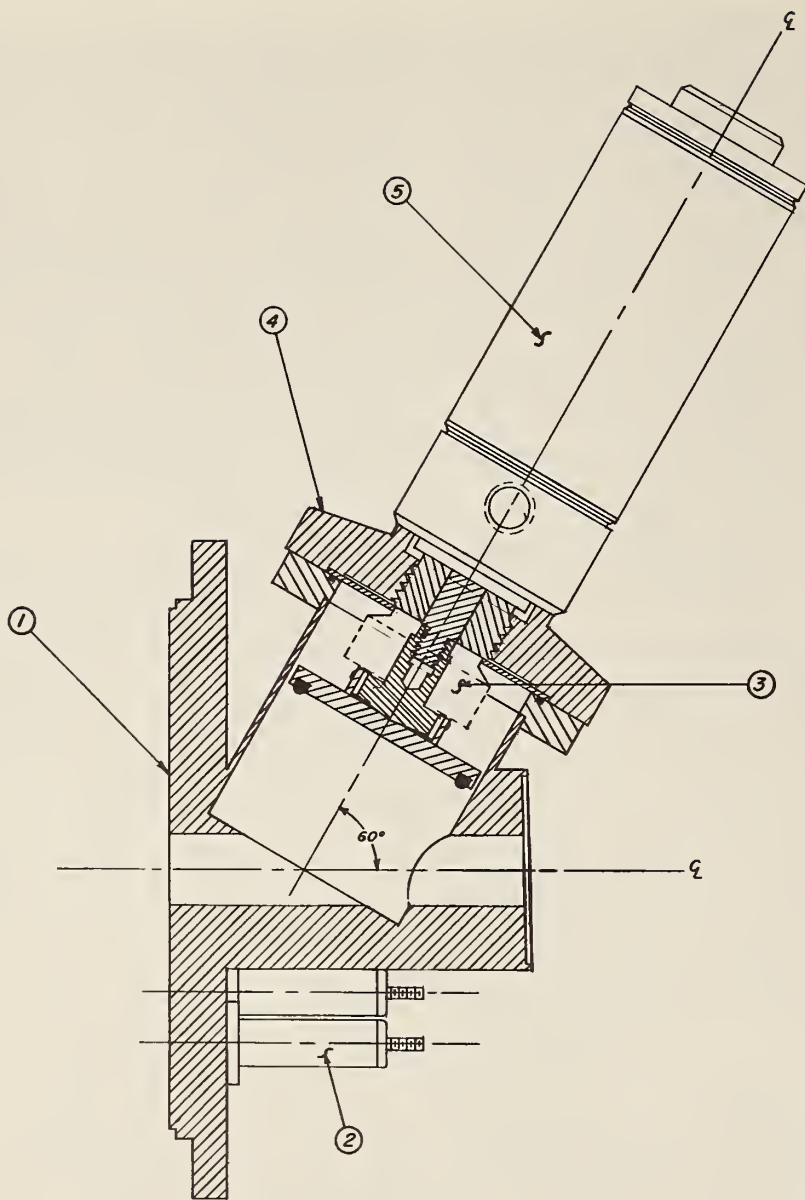
It is postulated that the very small amount of O₂ entering through the packing of the valve is sufficient to react with the ionizing filament, causing the formation of UO⁺ ions and changing the instrumental bias. The UO⁺ ions are detectable and this signal is invariably larger in the valve equipped instrument. Further, if the packing nut is tightened carefully it is possible to obtain consistent results at the 0.1% level until the valve has been operated from 6 to 10 times.

Due to these problems the valve has been redesigned to completely enclose the valve mechanism. The air-operated valve and source flange are shown in figure 3.

c. Filament Posts - During the above experimental work a phenomenon was regularly encountered which had been only rarely observed in the past. This was an extreme instability in the filament signal. The cause of this instability was finally traced to the presence of huge (i.e., more than 3×10^{-10} A) alkali ion signals which were present even after the filaments had been previously baked under vacuum for several hours. An examination of the vacuum feed-throughs normally used for filament posts showed that the center pin of these posts was manufactured using a nickel-iron alloy instead of the iron-chrome alloy (Type 446) usually supplied by the manufacturer. The thermal conductivity of the nickel-iron alloy is nearly twice that of the usual material (.0300 vs .0500) and, apparently, was sufficiently high to permit excessive heating of the glass insulating material which released alkali elements which were subsequently ionized. Type 446 stainless steel is now specified for the feed-throughs supplied to this laboratory.

2. Electronic Systems

The design and construction of a number of components required to interface a small digital computer to the spectrometer has been completed and the system is now in operation. The organization and construction details are described below.



1	SOURCE FLANGE / BEAM VALVE	NBS DWG 310.06 D-1607
2	RING & FEEDTHRU TERMINAL	NBS DWG 310.06 B-213-3
3	BELLOWS ASSEMBLY WITH	ULTEK MODEL 40-352
5	AIR DEVICE (8'O'RINGS)	
4	BONNET	ULTEK PART # C 50039200

Figure 3. Improved air-operated beam valve.

A number of significant advances have been made in the analog instrumentation used to measure the integrated ion current in mass spectrometers and, in general, reliable results have been achieved. However, the need to achieve greater sensitivities for samples of diminishing size or to span wider ratios forces the decision to adopt a technique fundamentally less limited in dynamic response. Counting the individual pulses generated at the target by each ion is such a technique.

The output of a pulse detector is a discrete number and therefore digital techniques may be used. For this a counting system consisting of an amplifier and discriminator followed by a scaler and a precision timer is used.

To be of practical value the amplifier, discriminator, and scaler must be very fast (a system capable of 30 nsec pulse pair resolution has a coincidence loss error of $\sim 1\%$ at a 500 KHz pulse rate). At the same time very few spurious pulses can be tolerated and the response of the system must be very uniform (total system background count rate must be $\ll 1$ ct/sec if an accurate value is to be obtained at high ratios). The scaler must be capable of holding a large number (8 decades) to handle counts due to high count rates during practical time periods. The timer must be capable of a relative accuracy and resolution several orders of magnitude better than the highest ratios to be measured to avoid degradation of the measurement since the end value of a determination is a series of averages in which a systematic time error would be enhanced. To relieve the experimenter of the tedious burden of copying large numbers and to reduce the possibility of human error in computing results, two further additions seem practical. These are a teletypewriter to provide a typed copy as well as a visual display for the eight digit scalers and the inclusion of a small digital computer to process the data. The digital computer can serve to provide programmable instructions to the timer, scalers,

and auxiliary functions and to give hard copy data readout through its own printer, as well as data reduction and closed loop control.

C. Organization

The digital data control system now in operation has eight major components as follows: (see figures 4, 5, and 6)

1. Amplifier and discriminator
2. Dual 8 digit 100 mega-hertz scaler
3. 7 digit shift register timer
4. Control unit
5. Data transfer unit
6. Computer/Calculator
7. Auxilliary program and storage unit (APS)
8. Teletypewriter readout

The dual scaler and the computer systems are commercially available items. Owing to the specific nature of the requirements, the other items listed were designed and constructed in part by this laboratory.

1. Amplifier and Discriminator Unit

The amplifier and discriminator unit (figures 1 and 2) is a design modification based on an original design by F. H. Sawada [2] then modified by A. B. Hance and L. R. Hanrahan [3]. The final version provides a higher sensitivity (~ 1 mV) coupled with a more stable tunnel diode trigger circuit. The tunnel diode trigger circuit exhibits none of the hysteresis effects due to high counting rates found in the earlier designs. This is a very important aspect since the unit is to be used in an automatic system where if the discriminator were to "lock up" during operation, without an attendant on hand to adjust the condition, an entire run of data would be lost.

2. Dual Scaler Unit

The dual eight digit scaler is a commercially available item. Its general specifications include: operation to

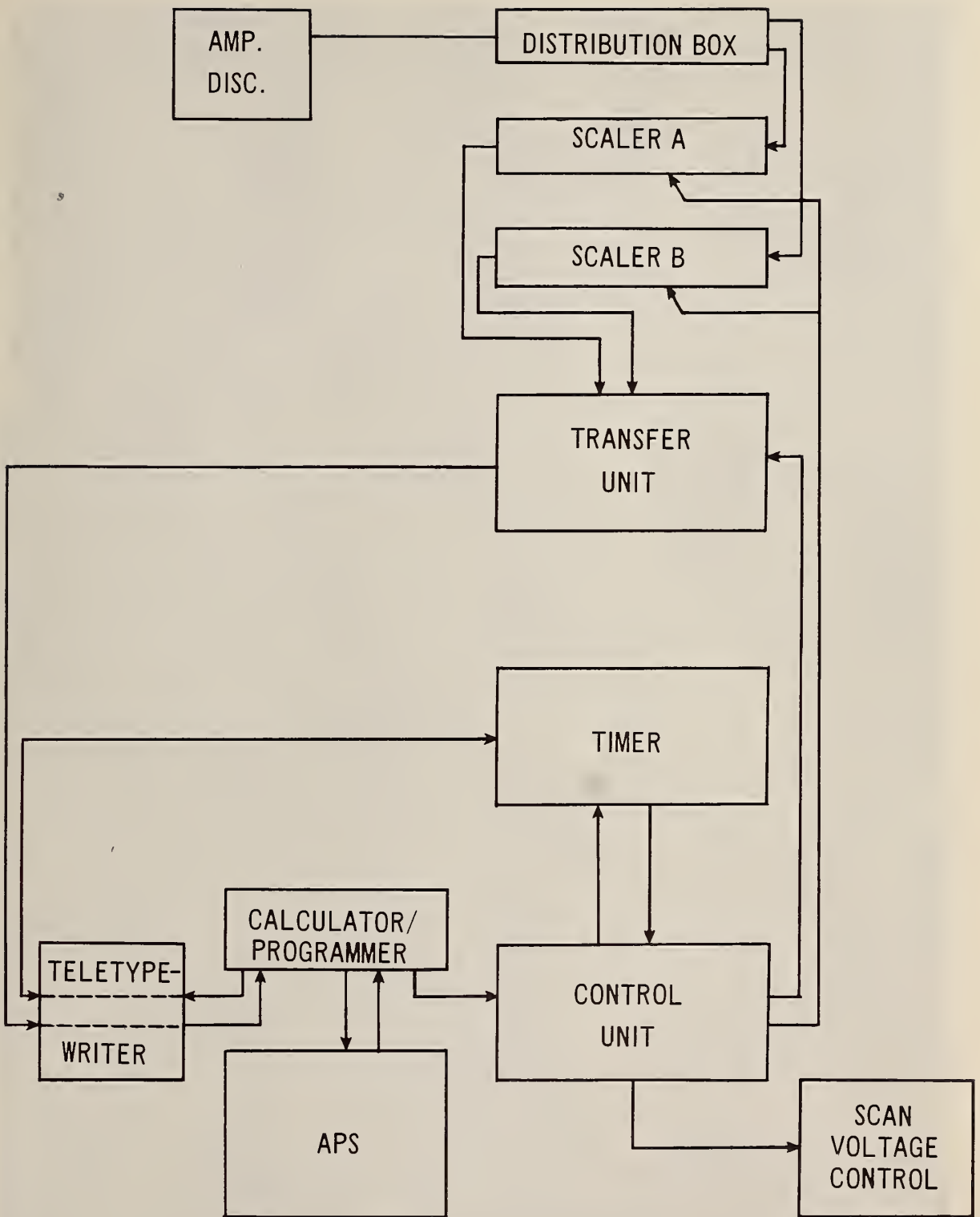


Figure 4. Data and control system flow chart.



Figure 5. Computer-control system.



Figure 6. Control unit.

100 mega-hertz, independent start, stop and reset gates, and independent electrically buffered outputs for data readout.

The next three units are, respectively, timing, control, and interfacing units and embody the special aspects of the design philosophy expressed earlier.

3. Shift Register Timer

The first of these units is a seven digit count down timer (figure 7) which can provide time intervals from .001 sec. to 9999.999 sec. in increments of .001 sec. and with a time resolution and precision of ~ 1 μ sec. Two methods of entering the timing interval are provided. In the first a digital number representing the time interval in milliseconds is transferred into the timer's shift register from the computer memory. The second method of setting time is done by entering 10^N milliseconds into the time register where N is between zero and six. Separate range switches relate the "A" time selection to scaler "A" and the "B" time to scaler "B". When both scalers are started together only the "A" time selection is obeyed. The second method has the advantage over the first that the time can be entered instantaneously and can result in true "dead timeless" operation. The timer can also be started, stopped, reset, or have time entered in either fashion manually from front panel switches. Two independent time pulse outputs are provided at the rear apron. One is 100 KHz not gated, and the other is a 1 KHz signal gated with the start-stop command of the timer.

4. Control Unit

The second of the specially designed data system units is the control unit. The system design centers about the control unit (Figure 8) which receives coded instructions from the computer and performs the necessary gating and logic functions to operate the scalers, timer, transfer unit, and voltage control. Allowance has been made for the possibility of breakdown and some form of operation can be maintained

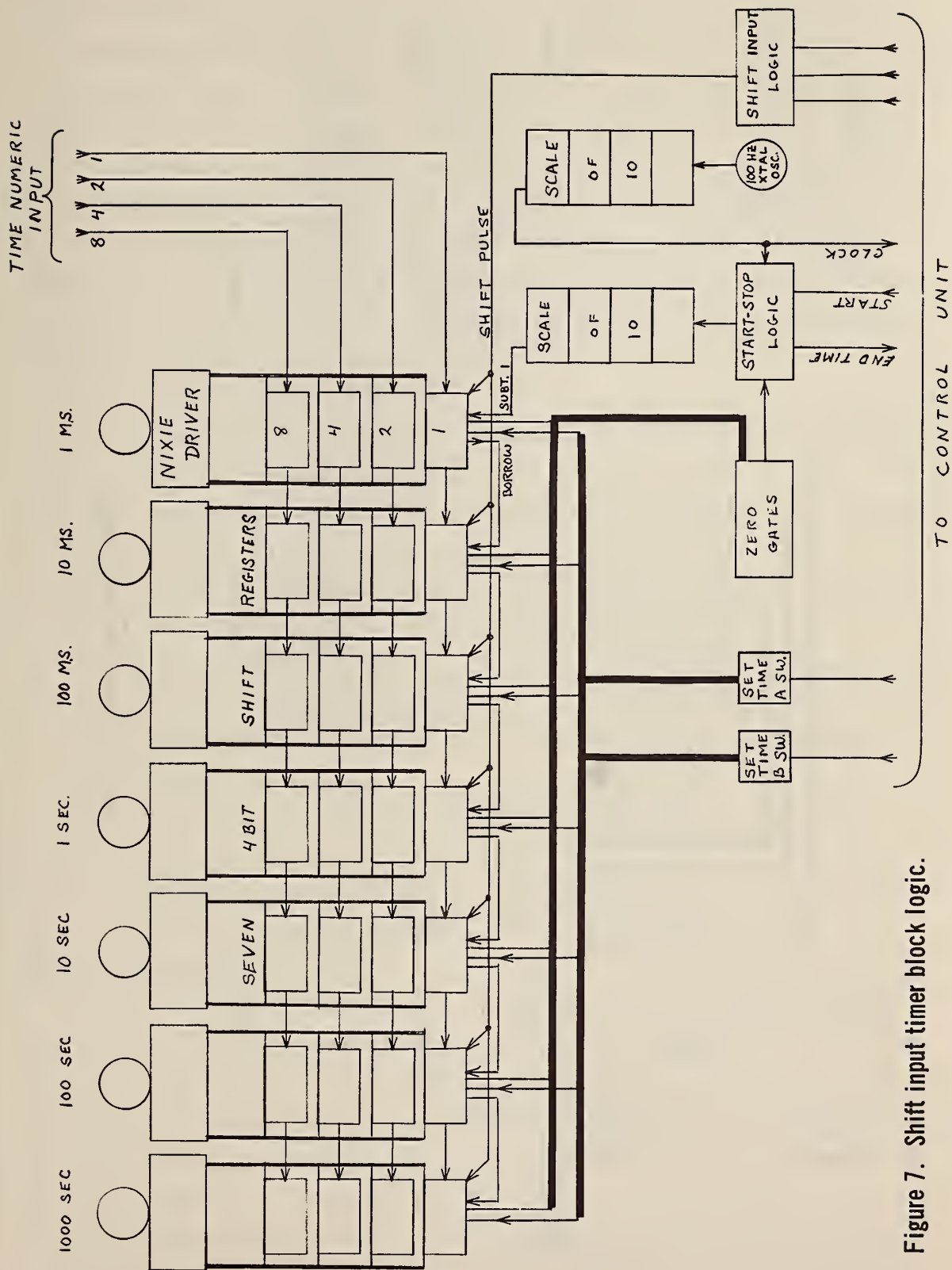


Figure 7. Shift input timer block logic.

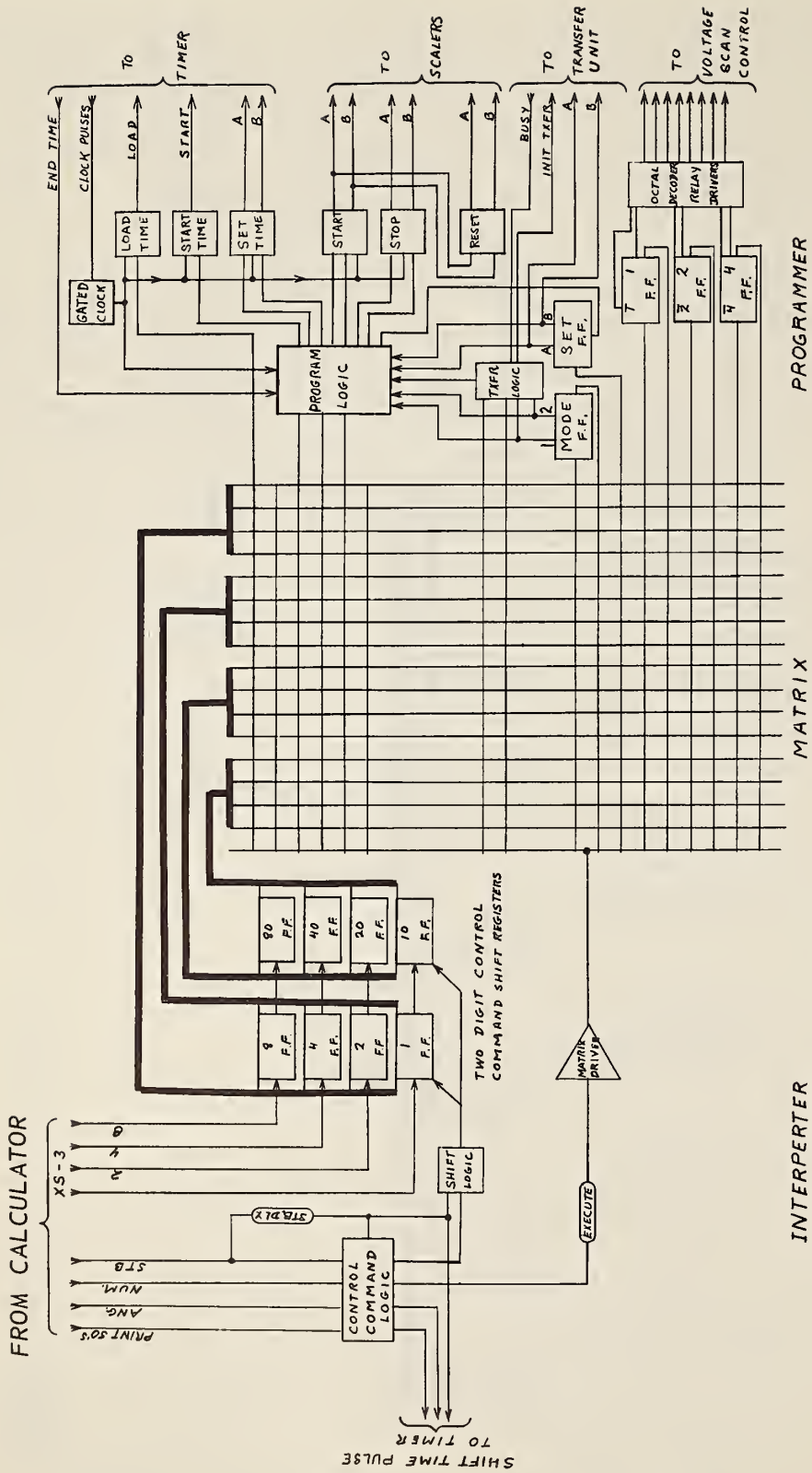


Figure 8. Control unit block logic.

after removing any individual unit with the sole exception of the dual scaler. For example, even if the timer is removed, one scaler can be used to provide time interval gating in the preset count mode. The interpreter section of the control unit accepts control commands in EXCESS 3 (XS-3) code issued by the computer and translates them into logical operations to be executed by the programmer sections. The XS-3 code instruction is displayed in binary form on the control units front panel. The logical operations performed by the programmer section include in Mode 1:

- Starting the timer,
- Starting either or both scalers A and B simultaneously with the timer start,
- Stopping the scalers with the time equal zero command issued by the timer
- Transferring the contents of either or both scalers into the computer or programmed command.
- Resetting each scaler at the beginning of a run.
- Resetting all functions on programmed command.
- Setting the timer at start command in the prompt time entry mode.
- Loading the timer shift register with a numeric output from the computer.
- Setting the voltage control output into any one of eight possible states.

MODE 2 operation.

The mode 2 operation of the programmer operates independently of the computer once it is begun. This is a dead timeless (no time lapse between the stop of one and the start of the next cycle) recycle mode where scaler A is started and run for the time period "A" (prompt entry) at the conclusion of which scaler B is started and run for time period "B". At this time A is started again on a repeating cycle. The operation is entirely dead timeless unless the transfer of data from the stopped scaler takes longer than the time period

set for the running scaler. In such a case the timer waits for the transfer cycle to be completed before continuing. This mode can be run with or without data transfer.

5. Data Transfer Unit

The third special unit designed for the data and control system is a transfer unit. (see figure 9) The purpose of this unit is to transfer the data produced by either of the eight digit scalers into the teletypewriter input peripheral of the computer. The transfer is done on command from the control unit or manually by front panel push buttons. Suppression of leading zeros is also controlled by a front panel switch. An auxilliary provision is included in this unit for a preset count stop mode. Selectable by front panel switches, a stop command can be generated when one of the two scalers reaches a preset number. If in this mode of operation the other scaler is connected to count the time pulses and the number recorded is the time interval necessary to count a specific number of pulses or the inverse of sample intensity. This mode of operation can produce ratios based on numbers of equal statistical significance.

6. Calculating System

The last three components of the system operate as a single functional unit. The calculator used for this system is a desk top computer/calculator (Mathatron 8-48) having eight 9-digit storage registers which include sign and a two digit exponent. It also has a 48 step program register which can perform each of the basic arithmetic functions +, -, ×, ÷ and can recall, print from or store in any of its registers. The auxilliary program and storage unit (APS) extends the capabilities of this machine to include 48 storage registers and 480 program steps. The 480 program steps are divided into 10 loops of 48 steps each. The individual loops can be programmed to automatically loop, branch and return, and skip. Independent variable entry points can also be accommodated.

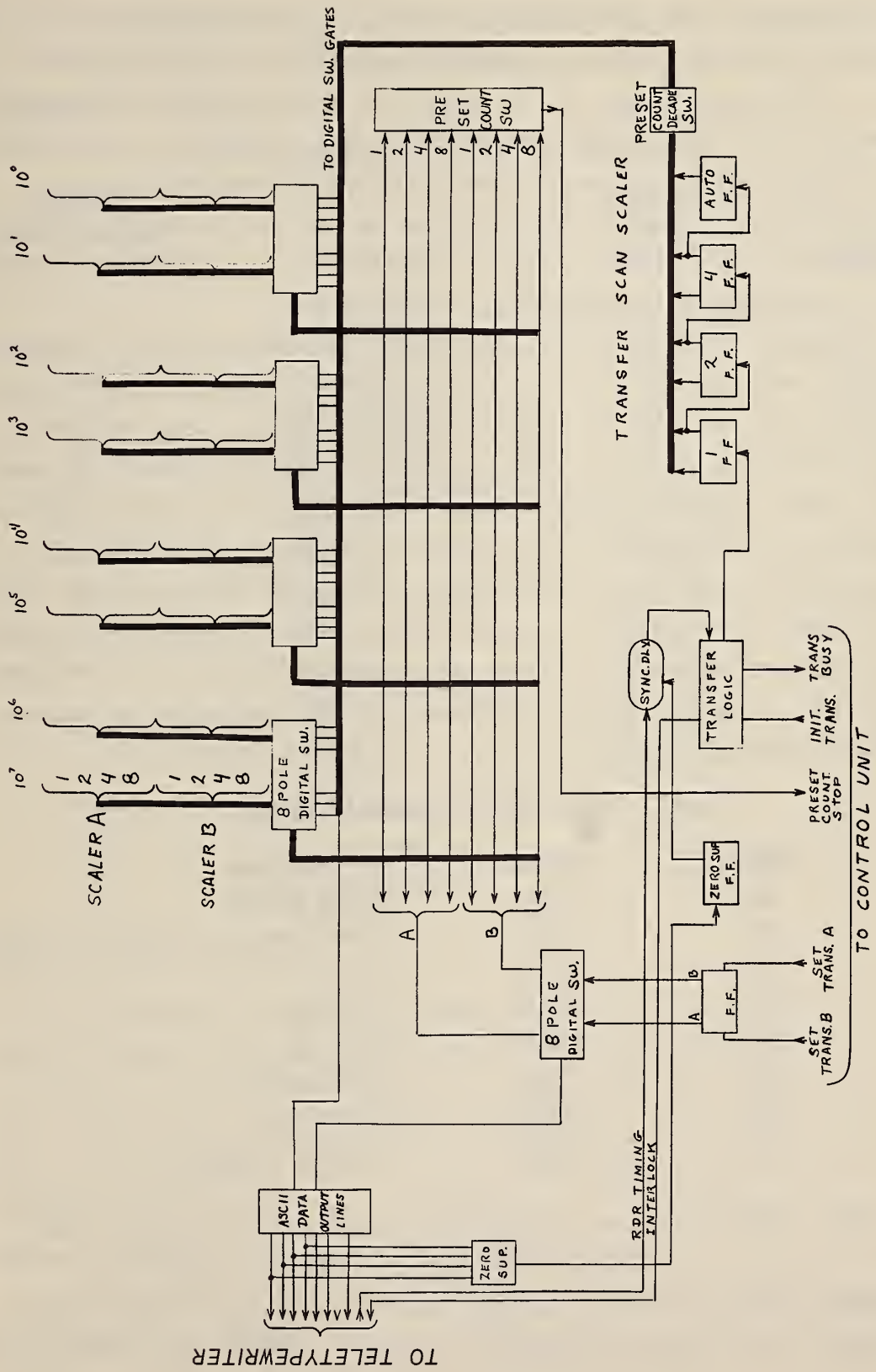


Figure 9. Data transfer unit block logic.

The punch tape and printer unit is a teletypewriter modified to operate as a computer peripheral input/output device. Although these units were not specifically designed to operate in such a system they were successfully adapted to receive data output signals from the data transfer unit as well as provide control logic commands to the control unit and numeric input to the timer.

7. Automatic Operation

Automatic operation of the system is achieved by programming the computer with step by step operational instructions to provide the automatic control, intermingled with instructions to sort or process data as it is being produced by the system. The computer memory has 48 memory locations, eight of which (50 through 57) are special in that logic signals can determine when one of the eight is being printed and the control unit interpreter is activated. These locations become command instructions and a set of seven constants are entered leaving one location blank for command manipulation purposes. The seven constants entered are as shown in Table 1.

Table 1. Control registers command constants.

Address	Constant	Function
50	Blank	To be derived
51	103	Load Time
52	206.0	Start A
53	307.0	Start B
54	408.0	Start AB
55	520.0	Transfer A
56	622.0	Transfer B
57	724.0	Transfer $A \cdot B/A + B$

These constants are a special set since (disregarding all but the last two digits before the decimal point) an arithmetic combination of proper pairs of numbers can result in forming all numbers between 1 and 32. There are thirty-two

possible command instructions available in the control unit although not all of them are used. A tabulation of commands is shown in table 2.

Table 2. Program registers command constants.

Number (last two digits before decimal point)	Command	Registers to generate command	XS 3 code displayed
00	Mode 1 (reset)		3·3
01	Mode 2	S53 – S52	3·4
03 ^a	Load time	S51	3·6
06 ^a	Start A & time	S52	3·9
07 ^a	Start B & time	S53	3·10
08 ^a	Start A & B & time	S54	3·11
11	Voltage 1	S51 + S54	4·4
12	Voltage 2	S52 + S52	4·5
13	Voltage 3	S52 + S53	4·6
14	Voltage 4	S53 + S53	4·7
15	Voltage 5	S53 + S54	4·8
16	Voltage 6	S54 + S54	4·9
17	Voltage 7	S55 – S51	4·10
18	Voltage 8	S57 – S52	4·11
20 ^a	Set A transfer	S55	5·3
22 ^a	Set B transfer	S56	5·5
24 ^a	Set A & B/A or B transfer	S57	5·7

^aIndicates stored constant.

The seven command constants stored permanently in the control registers are chosen to be the most frequently used in order to reduce the number of programming instructions for a given set of responses. Of course, for special programs where program space is at a premium, unused general command instructions can be replaced by a more convenient number to assist in design of the program.

The design of a simple Mode 1 single ratio program might be as shown in figure 10. To reduce program complexity the voltage setting constants can be written into the general

memory to be called into the command instruction locations (50's address) when desired. This also makes the program general since one can modify a voltage instruction without having to alter the program. The program which may be saved on punched tape, may be used repeatedly and, with modifications of the voltage and timing constants, can be fitted to most single ratio problems.

DEFINITIONS

Register	Constant	Function
S20	15.0	Set voltage for peak A
S21	18.0	Set voltage for peak B
S22	12800.0	Time B (12.8 seconds)
S23	2	Multiplier
S30	An	Counts for peak A
S31	An-1	
S33	Bn	Counts for peak B
S36	Rn	Ratio A/B = $\frac{A_n + A_n - 1}{B_n \times 2}$

PROGRAM

Loop 1	Program Step/s	Operation
	S20 S50 P50	Loads command for voltage A into transfer register (50) and sets voltage A
	P55	Sets transfer of contents of scaler A
	P52	Starts scaler A and timer
	N S30	Accepts contents of scaler A and prints number
	Automatic	Goes to Loop 2
Loop 2	S30 + S31/S33 x S23	Computes Rn
	S36 P36	Stores Rn in 36 and prints
	S30 S31	An becomes An - 1
	Automatic	Goes to Loop 3
Loop 3	S21 S50 P50	Sets voltage B
	P51 P22	Loads B time
	P56	Sets transfer of contents of scaler B
	P53	Starts scaler B and timer
	N S33	Accepts contents of scaler B and prints number
	S01	Command return to Loop 1

Figure 10. Generalized single ratio program.

The program as written will operate the mass spectrometer and collect the data necessary to compute ratios on a continuing basis until stopped. The present program does not contain automatic stop or other features necessary for a good general program such as for example subroutines that greatly optimize the program density. Nonetheless the program uses only 20% of the available memory and less than 15% of the available programming capabilities of the machine. Clearly very much more intricate programs can be written to solve larger and more complex routines. Time closed-loop operation can be achieved for mode 1 operation when the data produced is used to modify the time interval instructions for the various ratios involved. Operation of this type can be used to provide ratios of numbers of equal statistical significance without prior knowledge of the sample contents.

A series of operational programs have been written for the system which provide for four levels of data collection and reduction to be performed. These are:

- M1. Collects data and computes from one to four ratios on a repeat cycle basis for N times. (Note: This program is the least versatile but also requires the least time of operation and is particularly useful with very small samples where the signal may be decaying rapidly.)
- M2. Same as M1 except that it operates in a closed loop. After the first set of ratios is computed the program modifies the time for each dependent variable to provide unit ratios as the data are collected.
- M3. Same as M1 but computes a running average of each ratio, printing both the individual ratios and the averages for N times.
- M4. Incorporates M2 and M3 and therefore provides for up to four running averages as well as closed-loop operation and time corrected data for N times.

Mode 2 operation is done without command programming once the mode is initiated and it can be used either with or without data transferred to the printer. This mode of operation has proven to be most useful during the running of an entire spectrum and, as an example, permits the collection of data for 360 points at one second intervals over a spectrum of 6 mass units. A mass unit is typically 30 to 40 seconds wide giving excellent data resolution.

One last type of operation must be mentioned. In mode 1 operation two simultaneous signals may be measured. Such might be the case in comparing the response of an analog circuit to that of the pulse detector using a voltage to frequency converter to convert the analog signal to countable pulses. In this form of operation both scalers A and B can be started and stopped simultaneously by the timer. The data transfer unit automatically transfers the contents of first the A scaler and then the B scaler.

D. Construction and Design

1. Amplifier Design and Construction

The amplifier used is a three stage, D.C. coupled, complementary transistor, cascade circuit (figure 2). The open loop D.C. gain is held to a modest level by use of degeneration in each emitter circuit with minimum bypassing to improve rise time response. An overall feed back loop is used to maintain bias levels at the optimum current levels for each transistor to operate with its maximum gain-bandwidth product. This loop has little effect on the circuit gain and, in fact, this must not be allowed since the propagation delay of a pulse through the amplifier is on the order of 20 nanoseconds and an unbearable phase shift with accompanying distortion and instability would be produced if this loop were to be used as a gain limiting mechanism.

Since the amplifier is D.C. coupled, no coupling time constants exist and some considerable care was taken to insure that no other large capacitive time constants were present to affect the overload recovery. Since it is a complementary circuit, an oversized negative pulse drives each stage into cutoff, thereby avoiding the time constants of excess charge storage associated with saturated operation. The amplifier is essentially linear for pulses up to 40 mV input and then behaves with a minimum of undesirable overload characteristics for pulses up to 1 volt or more. For a 1 volt input pulse the amplifier recovered to within 3 % of its baseline in less than 100 nanoseconds.

The tunnel diode trigger circuit is coupled to the amplifier via a very short time constant which reduces the possibility of low frequency noise triggering. A rise rate of 5 mV/ns at the output of the amplifier is necessary to cause triggering. A load resistance of only 10 Ω is used in series with the load inductance of the tunnel circuit. This value of resistance provides a load line which has a slope steeper than the negative resistance characteristic of the tunnel diode (figure 11). A larger load resistor would increase the circuit recovery speed but it could also provide two stable intercepts (see dotted line, figure 11) where the high voltage point represents a "locked up" state of the discriminator. The lower value of load resistance makes it impossible for a second stable state to exist. One aspect of the steep slope load resistance is that by turning the discriminator up to the most sensitive region the discriminator will oscillate at a very high frequency which clearly defines the operational end point, or most sensitive setting, of the system. The load inductance necessary to permit this type of tunnel diode voltage switching is supplied by utilizing a 2.2 Ω 1 watt wire wound (type BW) resistor. The inductance of this resistor is about 0.1 μ H. The resistor has a very low capacitance, a high damping factor, and is extremely

stable. D.C. bias for the tunnel diode is supplied from a very low impedance (2.7Ω to ground) which is the bottom leg of a variable voltage divider controlled by the 10 turn potentiometer "discriminator level control". The circuit is intentionally non-linear with a quasi-logarithmic response over a range of about 30:1.

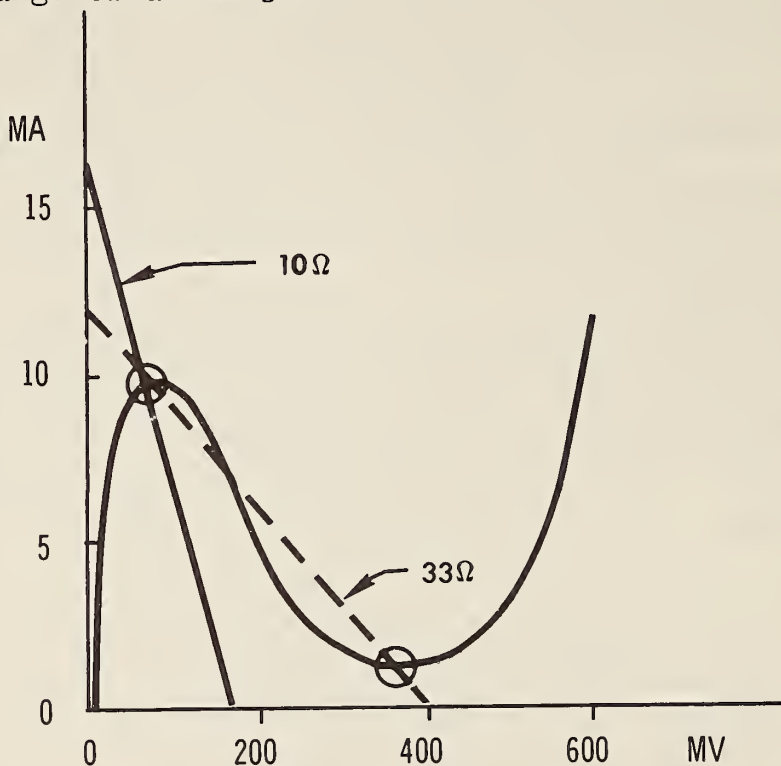


Figure 11. Tunnel Diode Characteristics
(with superimposed load limits)

The output of the tunnel diode circuit is capacitively coupled to a three stage amplifier which shapes and buffers the signal to drive the scaler with a pulse of very uniform height.

The system exhibits a nearly uniform response to input signals with rise times between 2 and 16 nanoseconds with its sensitivity dropping off rapidly for slower or faster rising pulses. The pulse pair resolution of the system is between 20 and 30 nanoseconds for input pulses less than 300 mV amplitude. The amplifier and discriminator circuits are

constructed on a double copper-clad glass epoxy laminate disc employing the "strip line" technique. The six transistors used in the circuit are arranged in a circular brass heat sink with the first three transistors used in the input amplifier and the last three are used for pulse shaping and output driver amplifiers with the tunnel diode trigger circuit mounted between the two circuits. The entire unit is constructed to mount conveniently at the end of the vacuum housing holding the ion multiplier (see figure 1).

2. Timer Unit Design

The timer unit (figure 7) is basically a seven digit shifting register where the seven registers have been modified to count as well. Each of these registers is coupled to a "Nixie" display tube. A numeric sequence can be shifted into the register from the calculator printer unit only when the control logic shift input command is present. The timing pulses are provided by a crystal controlled oscillator operating at a frequency of 100 KHz and are counted down by a factor of 100 prior to being gated into the scaler. A 10 KHz pulse is routed to the control unit to insure synchronized gating of all command signals.

3. Control Unit Design

The control unit interpreter section (figure 8) has a two digit shift register into which command numbers from the computer are entered. Special logic is activated only when the Print Address 50's logic initiates a control transfer. The contents of the shift registers activate the 14×32 element matrix at the completion of the command cycle.

The programmer section of the control unit is activated by commands from the interpreter matrix and responds also to interlocking and gating signals from the timer and transfer units. Keyed clock pulses provide time gated parallel logic for all logical operations except for the scan high voltage control. The scan voltage relay control is a 3 bit register activated by the matrix and decoded into 8 relay driven outputs.

4. Data Transfer Unit Design

The data transfer unit (figure 9) makes use of a special logic module of the MAD-1 Series cards [4] called a digital switch. This card accepts eight lines from each of two sources and connects either, both or neither to the eight line output. Five of these controlled by a serializing register provide a digit serialized output from either scaler to drive the calculator printer input as though the teletypewriter unit were reading a punched tape.

The unit transfers data out of a scaler immediately at the completion of a run for which a data transfer is requested. Zero suppression is accomplished by stepping the serializing scaler at a fast rate until data is detected at the output at which time the scaler is synchronized with interlock pulses from the PTP unit. At the end of each transfer cycle one extra symbol is programmed to the PTP which restarts the computer program.

The three special data system components, timer, control unit, and data transfer unit were designed making use of modular logic boards. The MAD-1 Series cards, as they are designated, have 35 pin connectors and comprise a wide variety of logical elements for use in a "building block" logic. Up to 18 cards can be mounted in a single 8 1/2" x 19" rack mountable card cage along with its power supply. Manufacture of the cards, power supplies and hardware was done by a local company which also fabricated the three digital system units in accordance with our specifications.

The coupling of the data system to the computer could not be done in a straightforward manner since the logical outputs required were not all available in the standard output interface. The calculator system was not modified in its logic structure but considerable intrusion was done within the units with appropriate buffering circuits and some logic where necessary.

E. Ion Multipliers

The most essential part of any digital system used with a mass spectrometer is the ion multiplier. If very small samples are to be analyzed the multiplier is required to have nearly 100% ion to electron conversion efficiency, a minimum gain of 10^8 to 10^9 and the discriminator-multiplier combination must show background counts of less than one per ten seconds. Nineteen and twenty stage multipliers have been constructed with commercially available dynodes which are venetian blind dynodes of Be-Cu.

The multipliers have shown all of the above listed properties when first installed but have all failed completely after operation for periods ranging from 24 hours to 3 weeks. No apparent cause for these failures has been observed and the reasons for them are not understood. Work with these multipliers is continuing. In addition, a second commercially available multiplier is currently undergoing tests. This unit contains a Cu-Be venetian blind conversion dynode with a 17 stage electronic multiplier of the "Rajchman" structure.

(I. L. Barnes, W. A. Bowman, III, and R. W. Shideler)

A. Introduction

The chemical unit was started last year with the transfer of three chemists with over 50 years combined experience in high precision - high accuracy analytical chemistry from other sections of the Analytical Chemistry Division. One member of this unit, Mr. Murphy, spent about 8 months of the past year with the Office of Standard Reference Materials, so the burden of the year's work fell to the other members, Mr. Machlan and Mr. Sappenfield.

The work of the unit is centered around three projects, (1) the atomic weight of the elements by direct measure of their absolute isotopic abundance ratios, (2) nuclear isotopic standards, and (3) trace characterization by isotopic dilution analysis. The unit is responsible for the development of methods of analysis of sufficient precision and accuracy and the preparation of standards and samples for isotopic analysis of sufficient accuracy and purity so that the objectives of these three projects can be carried out. Generally, this involves the development of high precision - high accuracy methods for elemental analysis, the preparation of high accuracy isotopic standards, and the preparation of high purity samples for isotopic analysis.

The project dealing with the determination of atomic weights by direct measure of the absolute isotopic abundance ratios has been a highly successful program. The Report of The International Commission on Atomic Weights of the International Union of Pure and Applied Chemistry for 1967 points out the fact that the International Commission has adopted the NBS values for the atomic weights of bromine, chlorine, chromium, copper, magnesium, and silver (Table 3). Thus the NBS values for these elements are now the accepted world-wide atomic weights. Since silver, bromine, and chlorine were the key elements in the chemical determinations

of the atomic weights of other elements, their values are of added significance for the recalculation of the atomic weights of other elements.

Table 3. NBS Atomic Weights accepted by ICAW.

Element	Present value	Old value
Bromine	79.904 ± 0.001	79.909 ± 0.002
Chlorine	35.453 ± 0.001 ^a	35.453 ± 0.001 ^b
Chromium	51.996*	51.996 ± 0.001
Copper	63.546 ± 0.001	63.54
Magnesium	24.305*	24.312
Silver	107.868 ± 0.001	107.870 ± 0.003

* No uncertainty in last significant figure.

^a Independent measurement.

^b Based on silver.

During the past year work was completed on the absolute abundance ratios of three lead isotopic standards, common, equal atom, and radiogenic lead. These standards are available from the Office of Standard Reference Materials. As pointed out in last years "Summary of Activities" [1] the presently accepted ICAW value of 207.19 without limits leads to a false sense of security about the atomic weight of "common" lead. Six common leads were shown to vary in atomic weight from 207.184 to 207.241. Because of this variation of isotopic composition of lead in nature, it is imperative that an isotopic analysis be performed whenever the atomic weight of lead is of importance as in high precision - high accuracy lead chemistry.

Work was also completed on a high precision - high accuracy method for the assay of nickel solutions which will enable highly accurate isotopic standards of nickel to be prepared.

The second project deals with nuclear isotopic standards for mass spectrometry. This has been a highly successful program. The unit is responsible for the preparation of precise

and accurate isotopic composition standards from separated isotopes so that the absolute abundance ratios of standard materials of vital interest to the nuclear industry can be determined. To date, ten of the sixteen uranium isotopic standards have NBS certified values and the remaining six are being reevaluated. These standards are now being used as the primary standards for all AEC isotopic measurements, forming the quantitative basis for the current transfer of over \$80,000,000 of nuclear fuel from the AEC to private industry. These Standard Reference Materials are also accepted by EURATOM.

A high precision - high accuracy method for the assay of boric acid solutions has been developed and highly accurate isotopic standards of boron have been prepared for the certification of the absolute abundance ratio of boron in a standard boric acid.

The preparation of accurate calibration standards for plutonium is planned for the near future.

The third project has to do with trace characterization by isotopic dilution. Because of the shortage of personnel this unit has not been active in the trace range during the past year. However, the boron content of "Glass Beads for Neutron Flux Measurements" was determined by an isotopic dilution technique. The use of isotopic dilution mass spectrometry for the analysis of major constituents offers the advantage of accuracy (0.1%) to a non-quantitative system since once the isotopic spike has been added, none of the following chemical steps need be quantitative. We plan to use this technique for the analysis of major constituents in other materials.

The work briefly described in this introduction will be discussed in more detail in the following sections.

B. Boron

The determination of the isotopic composition and the percentage boron in the three glasses, "Glass Beads for Neutron Flux Measurements", submitted by the Office of Standard Reference Materials was completed. The glass beads contain Al_2O_3 , Li_2O , SiO_2 , and B_2O_3 in addition to a different activator (potentially radioactive via neutron absorption) for each glass. The three activators used were dysprosium, indium, and cobalt. The boron used in the preparation of these glasses was approximately 93% ^{10}B .

For the determination of boron isotopic composition, the samples of glass were fused with NaCO_3 , dissolved in water and made acid with H_2SO_4 . To the cobalt glass samples, SO_2 water was added to dissolve the cobalt and the solution was heated to expel most of the excess SO_2 . A double extraction was made with a chloroform-2-ethyl-1,3-hexanediol mixture. The organic layer was washed with dilute H_2SO_4 and the boron was back extracted into a NaOH solution. The NaOH solution was washed with chloroform and divided into three portions. One portion was titrated to determine the amount of boron present. The second was saturated with CO_2 and the third fraction was eluted through a cation ion exchange column and enough Na_2CO_3 was added to make a boron to sodium ratio of 1 to 1. Mass spectrometric analysis showed that the CO_2 saturated fraction was less satisfactory than that eluted through a cation exchange column.

For the determination of the percentage boron in the glass, water was added to dissolve the melt in the above procedure, and an amount of natural boron as boric acid (ANL II) was added to give a $^{11}\text{B}/^{10}\text{B}$ ratio of approximately one. With this exception, the above procedure was followed.

C. Fluorspar

The analysis of fluorspar, SRM 79b, submitted by the Office of Standard Reference Materials for the determination of CaF_2 has been completed. Two sets of four samples were analyzed with a value of 98.80 percent CaF_2 and a standard deviation of 0.03 percent. (See Table 4).

Table 4. Analyses of SRM 79b, Fluorspar.

Sample No.	Percent CaF_2		
	Set I	Set II	
1a	98.82		
2b		98.76	
3c	98.84		
4d		98.76	
5c	98.82		
6c		98.82	
7b	98.77		
8d		98.78	
Average	98.81	98.78	98.80
Standard deviation	± 0.029	± 0.026	± 0.030

The prescribed method of analyses was: a 0.5 g sample of fluorspar was digested in acetic acid containing CaCO_3 (0.025 g CaCO_3 in 375 ml of 10 percent acetic acid) and filtered. After this digestion and filtration the method of Dr. J. I. Hoffman as given on the Certificate of Analysis of Standard Sample 79, Fluorspar, was followed.

D. Lead

1. Lead Isotopic Standards

The calibration mixtures of separated lead isotopes which were described in last years "Summary of Activities" were used to obtain absolute values for the isotopic ratios of common, equal-atom, and radiogenic lead [5]. This paper also includes the details of the method for the high precision - high accuracy assay of lead solutions.

This high precision - high accuracy method for determining the concentration of lead in solution was tested on solutions containing known amounts of lead. Nine such solutions, in the approximate concentration of the solutions of the separated lead isotopes, were prepared from high purity lead containing less than 0.001% total detected metallic impurities. Four samples containing from 0.139 to 0.153 millimole (mM) of lead were withdrawn from each solution and the lead ion concentrations were determined as described [5].

Data resulting from the analysis of the nine lead solutions showed that (a) the concentrations of these solutions (as mM Pb/g soln) agreed to within 0.02% of the calculated (known) concentrations, (b) a slight positive bias of 0.01% was detected, (c) the method was independent of sample size or concentration for the range studied, and (d) the analyses of the nine solutions were of equal precision.

The extreme isotopic variability of natural lead results from the fact that ^{206}Pb , ^{207}Pb , and ^{208}Pb are continually being formed by the decay of ^{238}U , ^{235}U , and ^{232}Th , respectively. "Common" leads, thus, vary with geological age and environment. To convert the values obtained by the lead assay procedure from millimoles of lead to grams of lead it is necessary to know the isotopic composition of the particular lead used so that its atomic weight may be calculated. This can now be accomplished on an absolute basis using the standards certified by this project.

The combination of the high precision - high accuracy assay and the absolute isotopic composition allow the precise and accurate assay of lead metal and lead compounds.

2. Archaeological Samples

In the continuing cooperative effort with Dr. Robert H. Brill of the Corning Museum of Glass, the lead and/or copper were separated for isotopic analyses from bronze coins, paint pigments of paintings, lead pipes, ancient glasses, ores, and other artifacts.

The bronze coins, lead pipes, and ore were dissolved in dilute nitric acid, and the insoluble residue removed by filtration. Lead dioxide was then electrodeposited onto a platinum gauze anode, weighed and dissolved in a nitric acid - hydrogen peroxide mixture. The resulting solution was evaporated to dryness and the residue taken up in 2% HNO₃ so that the final solution contained 25 mg of Pb per ml.

The glasses were dissolved by repeated evaporations to dryness in hydrofluoric - nitric acid mixture and then dissolved in dilute HNO₃. The insoluble residue was removed by filtration and treated as above.

E. Nickel

An assay method for nickel that will have an accuracy of approximately 0.01% is required for the assay of separated isotope solutions to be used in the preparation of isotopic standards for mass spectrometric calibration.

The dimethylglyoxime gravimetric method which has been used for the past 60 years, is generally reported to be good to about 0.1%. The present study is to determine if the accuracy of this method can be improved to 0.01% by utilizing very careful techniques.

Past experience has shown that the weighing error in glass fritted crucibles can be significant. To minimize this uncertainty, medium porosity, 15 ml glass crucibles were used and weighings were done on a microbalance. Repeated weighings, after washing with dilute ammonia solutions and drying at 150 °C, gave weights to within approximately 20 µg. If 100 mg of nickel were used this error in weighing would cause an error in the assay of about 0.004%.

Two homogeneous precipitation procedures, rather than the usual heterogeneous precipitation, were investigated. These procedures gave a denser nickel dimethylglyoxime which could be filtered on a 15 ml crucible. The first procedure [6], which utilized hydroxylamine hydrochloride and biacetyl

for the homogeneous precipitation, gave apparent recoveries of about 101%. Impure reagents, particularly the biacetyl, may have caused the high values. The second procedure [7] which utilized urea to give a homogeneous precipitation gave apparent recoveries of 100.1%. The urea may have been impure and caused the high results even though it had been filtered before using. A procedure similar to Bickerdike and Willard's [7] was used where ammonia was slowly added in place of using urea. This procedure, along with weighing on a microbalance and correcting for nickel in the filtrate gave results reproducible to about 0.01%. The procedure appears to give results biased about + 0.06%. Added impurities of iron, zinc, copper, cobalt, and manganese, each at the 0.1% level, resulted in no detectable interference, while at the 1% level, the apparent recovery was about 0.03% higher. Further investigation of the reason for the apparent high recoveries is planned.

F. Plutonium

1. Chemical Standard

a. Plutonium sulfate tetrahydrate - The plutonium sulfate tetrahydrate for the new assay standard, Standard Reference Material 944, was prepared at the New Brunswick Laboratory of the Atomic Energy Commission, New Brunswick, New Jersey. After preparation and assay of the material were completed at the New Brunswick Laboratory and the Los Alamos Scientific Laboratory, samples containing 0.5 g of plutonium were weighed for packaging at New Brunswick. One member of NBS Section 310.06 and two members of NBS Division 302 worked with New Brunswick personnel in weighing, bottling, sealing in plastic bags and packaging this standard in capped steel pipes. Samples were also taken for isotopic abundance measurements by mass spectrometry to determine the atomic weight of this sample.

b. Plutonium metal - The atomic weight of the plutonium metal assay standard, Standard Reference Material 949b, was determined from isotopic abundance ratios measured by mass spectrometry. The americium and uranium were separated from plutonium by anion-exchange. The sample was dissolved in 8N HNO₃ and added to a small column (figure 12) of AG 1 × 4 resin (1.3 cm high by 4.5 mm diameter). The americium and uranium were removed by elution with 8N HNO₃ and the plutonium was then removed with 0.3N HNO₃ [ref. 1, p. 34 and ref. 8, p.65]. The plutonium fraction was used for mass spectrometric measurements.

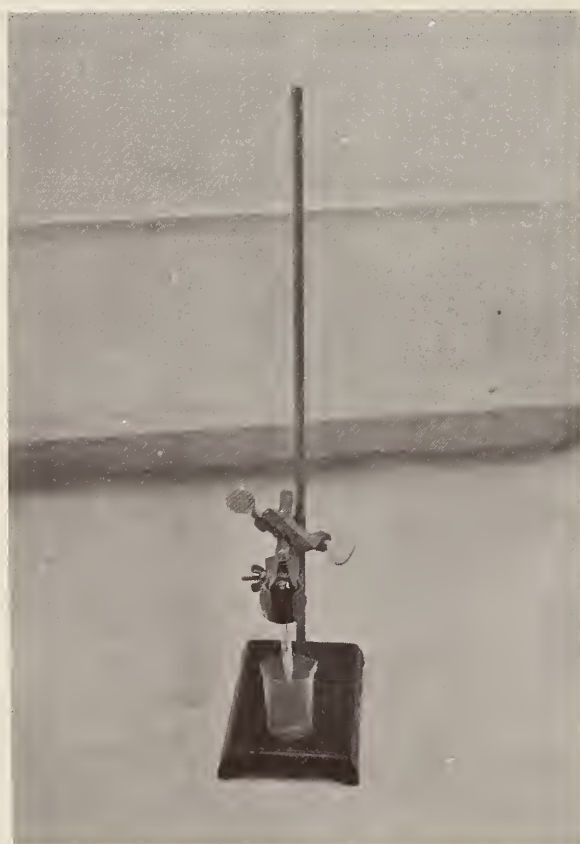


Figure 12. Micro anion-exchange column for separation of plutonium from americium and uranium.

Since the mass spectrometric measurements require a uniform matrix, this technique has been applied to submicrogram samples. The plutonium fraction was eluted into a teflon beaker and was evaporated to dryness. The plutonium residue was dissolved in a minimum of 5% HNO₃ and transferred to the filaments just before the mass spectrometric measurements were made.

2. Isotopic Standard

The evaluation of the half-life of ²⁴¹Pu was continued using the americium and uranium separation from plutonium procedure [ref. 1, p. 34 and ref. 8, p. 65] as above.

G. Uranium

Ten of the sixteen uranium isotopic standards now have NBS certified values. These values were determined by using accurately prepared mixtures of U-235 and U-238 separated isotopes to determine the mass spectrometer bias in the range of 10 to 90 percent ²³⁵U and by using U-233 for isotopic dilution to determine the ²³⁴U and ²³⁶U content [ref. 8, p. 63]. The ²³⁴U and ²³⁶U content of the remaining six standards have been determined but the mass spectrometer bias at the 0.5 to 5 percent ²³⁵U level has not been checked. Accurately known mixtures of U-235 and U-238 separated isotopes are being prepared to include this range.

Samples of the U-238 separated isotopes from 0.5 to 1 gram were ignited in order to give reproducible oxides. The oxides were ignited for one hour at 900 °C in air, overnight at 1050 °C in air, followed by one hour at 850 °C in oxygen (figure 13). The ignitions were conducted in a quartz tube and the samples were protected from water and carbon dioxide in the air during the ignition and also during the weighing [ref. 8, p. 61 and ref. 9, p. 68]. The U-235 samples will be ignited by the same procedure and after dissolving in diluted nitric acid, weighed aliquots will be added to the U-238 samples to give 0.5 to 5 percent ²³⁵U. Using these mixtures,

the mass spectrometer bias can be determined and values for uranium-isotopic standards U-005, U-010, U-015, U-020, U-030, and U-050 can be issued with NBS certification.

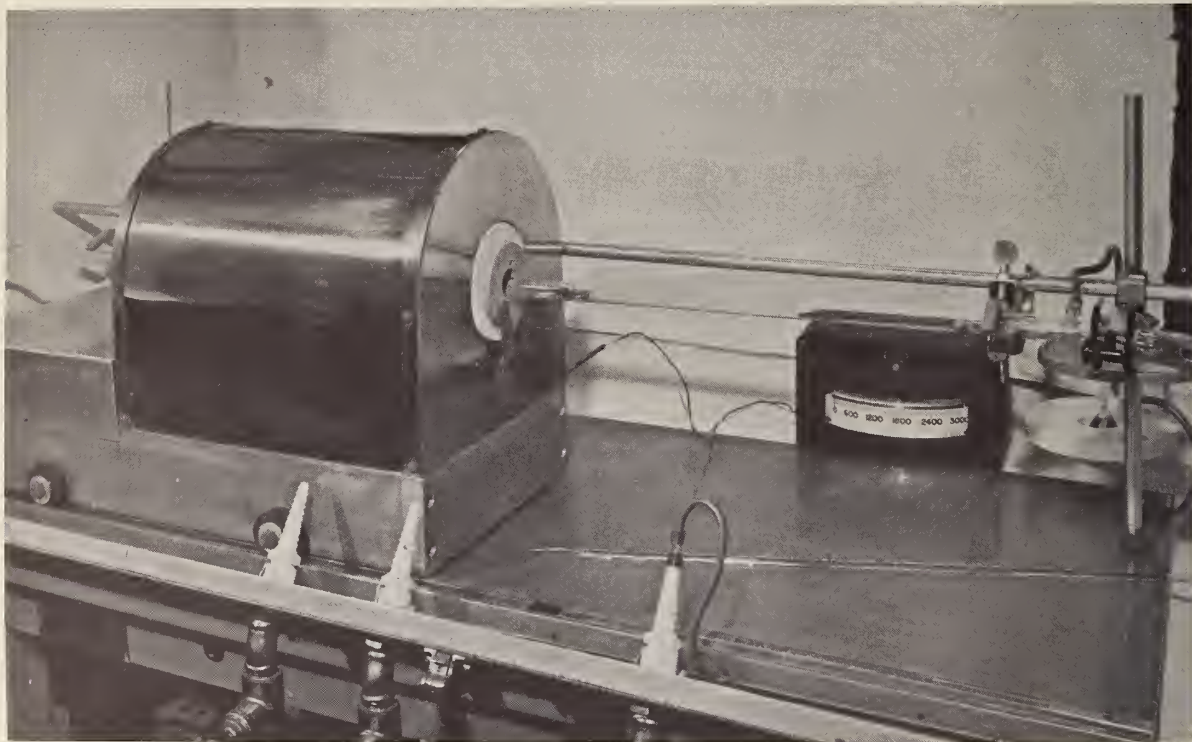


Figure 13. Furnace for ignition of uranium oxides.

(T. J. Murphy, L. A. Machlan, and K. M. Sappenfield)

3. MASS SPECTROMETRY

A. Boron

An analytical procedure for the isotopic analysis of boron has been developed and is an improvement of previous provisional procedures [ref. 10, p. 67; ref. 1, p. 40]. Surface ionization of Na_2BO_2^+ from a single filament tantalum ribbon (.001 × .030") is used. The sample is mounted on the filament as follows: one small drop of solution (~ 5 µg B) is dried by a heat lamp and a 1.2 A current for 5 minutes; the lamp is turned off and the electrical current is increased until the sample changes to a gray-white color; the current is maintained for 2 minutes after the color change.

For the mass spectrometric analysis the filament current is increased until the total boron signal on the transmission grid is barely detectable (1×10^{-13} A). During the next 18 minutes the signal will grow to a maximum and then decay to less than 2×10^{-12} A. The magnitude of the maximum intensity is a pre-determined analytical parameter and is held constant for all analyses. It is not necessary for two operators to use the same maximum intensity but it is essential that they be consistent. Maximum ion currents (grid) of 3×10^{-12} A and 6×10^{-12} A have been used by two different operators of this laboratory for extended periods and both appear to work equally well. When the signal fails to grow to the pre-determined maximum, or exceeds this intensity, the filament current is re-adjusted to achieve the desired intensity. Failure to be consistent will result in a loss of precision in the ratio determination because the filament bias is related to both the operating temperature and the manner in which the temperature is achieved.

After 18 minutes of heating the grid signal is increased to 6×10^{-12} A and it will decay for the remainder of the analysis. If the signal is less than 3×10^{-12} A after 30

minutes of heating, it is re-adjusted to 3.5×10^{-12} A. Data is taken between 42 and 55 minutes after the start of heating, as a decaying signal of $3 - 2 \times 10^{-12}$ A.

The emission stability is poor for some samples during the first minutes of heating but generally improves with time and is stable enough for a precise ratio measurement after 40 minutes of heating. The frequency of erratic emission is significantly greater for the relatively large sample size of 20 μ g than it is for the 5 μ g sample size. Use of the smaller sample size gives the same signal intensity without any significant difference in the experimental ratios.

The temperature of the filament is too cool for a precise determination with an optical pyrometer; only a faint red glow can be detected. The estimated temperature is approximately 750 °C (1.2 - 1.3 A).

This analytical procedure was used to determine the isotopic composition and the percentage of boron in an indium, a cobalt, and a dysprosium glass.

B. Lead

1. Lead Isotopic Standards

The absolute isotopic abundance ratios of six lead samples have been determined, using chemical and mass spectrometric techniques developed by this section [5].

The samples were studied in two groups. The first group consisted of three common lead samples which have for many years been used as interlaboratory reference samples. These are: NBS 200, galena from Ivigtut, Greenland, formerly distributed by the NBS; GS4, a lead sample distributed by the Isotope Geology Branch of the U.S. Geological Survey; and Cal. Tech. Pb, a lead sample distributed by the geochemistry group at the California Institute of Technology. The absolute isotopic ratios for these samples are given in Table 5. These samples were studied so that at least some of the previous work on common lead samples could be tied to an absolute scale.

Table 5. Summary of absolute isotopic ratios.

Sample	Absolute ratios		
	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
GS 4	0.061888 ± 0.000065^a	0.95342 ± 0.00036	2.2181 ± 0.0010
NBS 200	0.068353 ± 0.000072	1.00538 ± 0.00038	2.3675 ± 0.0011
C.I.T. Pb Std.	0.060151 ± 0.000063	0.93081 ± 0.00035	2.1835 ± 0.0010

^aOverall limit of error. The sum of the 95% confidence limits for the ratio determination and the terms covering effects of known sources of possible systematic error.

Uncertainty components (%):	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
95% confidence limits on ratio determinations of samples (n = 36)	± 0.01960	± 0.00933	± 0.01601
Bounds due to 95% confidence limits on ratio determinations of synthetics (n = 24)	± 0.00883	± 0.00442	± 0.00883
Bounds due to possible systematic error in chemical analysis	± 0.01247	± 0.00624	± 0.01247
Bounds due to possible error in separated isotopes	± 0.00753	± 0.00376	± 0.00753
Bounds due to possible systematic error in attenuator calibration	± 0.056558	± 0.01415	± 0.00000

The second group of samples studied was prepared by the NBS. This group includes a common lead and a radiogenic lead (^{206}Pb) purchased commercially, and an equal atom ($^{208}\text{Pb}/^{206}\text{Pb} \sim 1$) lead prepared at the Bureau by mixing appropriate quantities of the other leads. The absolute isotopic ratios are given in Table 6. These leads have been processed to >99.9% pure lead and have been drawn into 50 mil wire. They are being sold by the Office of Standard Reference Materials in 1 gram units sealed in glass ampules under argon.

Table 6. Absolute isotopic ratios for the three standard samples.

	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
Common Lead (SRM 981)	0.059042	0.91464	2.1681
Overall limit of error ^a	± 0.000037	± 0.00033	± 0.0008
Uncertainty Components:			
95% confidence limits on ratio determination (minimum = 0.00002)	± 0.000020	± 0.00007	± 0.0002
Bounds due to possible systematic error in chemical analyses	± 0.000005	± 0.00007	± 0.0002
Bounds due to possible systematic error in correction factor (including errors in separated isotopes)	± 0.000012	± 0.00019	± 0.0004
Equal-Atom Lead (SRM 982)	0.027219	0.46707	1.00016
Overall limit of error	± 0.000027	± 0.00020	± 0.00036
Uncertainty Components:			
95% confidence limits on ratio determination (minimum = 0.00002)	± 0.000020	± 0.00006	± 0.00007
Bounds due to possible systematic error in chemical analyses	± 0.000002	± 0.00004	± 0.00008
Bounds due to possible systematic error in correction factor (including errors in separated isotopes)	± 0.000005	± 0.00010	± 0.00021
Radiogenic Lead (SRM 983)	0.000371	0.071201	0.013619
Overall limit of error	± 0.000020	± 0.000040	± 0.000024
Uncertainty Components:			
95% confidence limits on ratio determination (minimum = 0.00002)	± 0.000020	± 0.000020	± 0.000020
Bounds due to possible systematic error in chemical analyses	± 0.000000	± 0.000006	± 0.000001
Bounds due to possible systematic error in correction factor (including errors in separated isotopes)	± 0.000000	± 0.000014	± 0.000003

^aThe overall limit of error is the sum of the 95 percent confidence limits for the ratio determinations and the terms covering effects of known sources of possible systematic error.

The diversity, purity, and source constancy of the NBS samples should allow them to supercede all previous lead isotope reference samples. Their universal use should allow all future isotopic studies of both common and radiogenic leads to be put on an absolute scale.

2. Archaeological Isotopic Studies

The study of lead and copper isotopes in archaeological samples, being conducted in cooperation with Dr. Robert H. Brill of the Corning Museum of Glass, is still in progress. Approximately 50 samples have been analyzed and significant correlations appear to be possible. The study should be completed by the end of this calendar year.

C. Nickel

The mass spectrometric analysis of nickel has not been successful. Although relatively strong stable ion signals can be obtained, studies with a 12-inch instrument have shown that there is a background peak approximately 0.05 mass units above the ^{58}Ni peak. This peak is approximately 0.5% of the ^{58}Ni peak; it is variable in size and increases during an analysis. Until a procedure is devised which eliminates this background peak, we will not be able to determine the atomic weight of nickel with suitable accuracy.

D. Plutonium

The increased transmission of the Z-lens source combined with cumulative analytical experience over the past 3 years has yielded an improved technique for plutonium analysis. Growing ion currents of $3 - 4 \times 10^{-11}$ A were obtained from 2 - 4 μg sample loadings. The atom ratios did not change significantly with time during the data taking period, although it was possible to cause serious fractionation by simply operating well above the normal sample-filament temperature (2.0 - 2.3 A).

The isotopic compositions of NBS plutonium standards 948 and 949b and a United Kingdom sample (UK-131) were determined. The composition of NBS 948 has been determined each year since 1964 as part of the program to evaluate the half-life of ^{241}Pu . This sample has a relatively low ^{241}Pu abundance of 0.597 atom percent (July 1967) and is changing to ^{241}Am at a rate of less than 1 ppm per day. Within the next 6 years it will be difficult to obtain the minimum $^{241}\text{Pu}^+$ ion current necessary for a 95% analytical limit of error statement at the 0.25% level, even with the increased transmission of the Z-lens source. The only other alternatives are to use ion multiplier deflection or to accept the larger limit of error statement that is expected from measuring ion currents of 1×10^{-13} A.

Sample UK-131 had a relatively large ^{241}Pu abundance of 2.9 atom percent (July 1967) and will be incorporated into the half-life program. Although the greater abundance is a distinct advantage for the mass spectrometric measurement, it also means that larger amounts of ^{241}Am will accumulate with the passage of time. Extra care will have to be taken to insure that essentially all of this americium is removed from the sample prior to the mass spectrometric analysis. Failure to reduce the americium to a level below about 5 ppm will cause a significant (positive) error in the calculated half life.

(E. J. Catanzaro and E. L. Garner)

4. PERSONNEL AND ACTIVITIES

A. Personnel Listing

William R. Shields, Section Chief

Joy J. Shoemaker, Secretary

Mass Spectrometry (absolute isotope ratio) --

Ernest L. Garner

Mass Spectrometry (isotope dilution) --

Edward J. Catanzaro

Mass Spectrometry (nuclear materials)

I. Lynus Barnes

Stoichiometry --

Thomas J. Murphy

Stoichiometry (nuclear materials) --

Lawrence A. Machlan

Separation and Purification --

Keith M. Sappenfield

Design and Fabrication --

William A. Bowman, III

B. Publications

1. Analytical Mass Spectrometry Section: Summary of Activities July 1966 to June 1967, NBS Technical Note 426, Ed. W. R. Shields, (1967).

2. E. J. Catanzaro, "Absolute Isotopic Abundance Ratios of Three Common Lead Reference Samples", Earth and Planetary Science Letters, 3, 343-346 (1968).

3. E. J. Catanzaro, T. J. Murphy, W. R. Shields, and E. L. Garner, "Absolute Isotopic Abundance Ratios of Common, Equal-Atom, and Radiogenic Lead Isotopic Standards", J. Res. NBS, 72A, 261-267 (1968).

C. Talks

1. E. J. Catanzaro, "Precision analysis by thermal emission", Federal Center, Denver, Colorado, August 1, 1967.
2. W. R. Shields, "Status of NBS isotopic abundance standards for lead, potassium, rubidium, strontium, and uranium", Federal Center, Denver, Colorado, August 2, 1967.
3. W. R. Shields, "Isotope ratio abundance measurements", Mass Spectrometry Discussion Group of Greater Washington, Alexandria, Virginia, December 18, 1967.
4. T. J. Murphy, "The Preparation of synthetic standards", Mass Spectrometry Discussion group of Greater Washington, Alexandria, Virginia, December 18, 1967.
5. E. J. Catanzaro, "Early Precambrian rocks in North America", Department of Agronomy, University of Maryland, College Park, Maryland, February 23, 1968.
6. E. J. Catanzaro, "Absolute isotopic abundance ratios of three lead isotope standards", American Geophysical Union Annual Meeting, Washington, D. C. April 10, 1968.

D. Committee Activities

L. A. Machlan

Member, Chemistry Panel of Interagency Board of Civil Service Examiners

T. J. Murphy

Member, Chemistry Panel of Interagency Board of Civil Service Examiners

Member, Meeting Arrangements Committee, Chemical Society of Washington

Member, Committee on Annual Report of Atomic Weights, American Chemical Society

Manager, Chemical Society of Washington

Member, Committee on Analytical Reagents of the American Chemical Society

5. REFERENCES

- [1] W. R. Shields, Editor, NBS Technical Note 426, (1967).
- [2] F. H. Sawada, "Design Technique for High Speed Pulse Circuitry for Surface Mass Spectrometer". IEEE Trans. on Nucl. Sci., NS-12 No. 1 February 1965 p. 374.
- [3] A. B. Hance, and L. R. Hanrahan, "Further Development of a High Speed Electron-Multiplier Discriminator for Mass Spectrometer Ion Detection", KAPL-3122, February 21, 1966.
- [4] P. G. Stein, Editor, NBS Technical Note 268, (1966).
- [5] E. J. Catanzaro, T. J. Murphy, W. R. Shields, and E. L. Garner, "Absolute Isotopic Abundance Ratios of Common, Equal-Atom, and Radiogenic Lead Isotopic Standards", J. Res. NBS, 72A, 261-267 (1968).
- [6] E. D. Salesin and L. Gordon, "Precipitations of Nickel Dimethylglyoximate from Homogeneous Solution", Talanta, 5, 81-85 (1960).
- [7] E. L. Bickerdike and H. H. Willard, "Dimethylglyoxime for Determination of Nickel in Large Amounts", Anal. Chem., 24, 1026 (1952).
- [8] O. Menis, Editor, NBS Technical Note 275, (1965).
- [9] O. Menis, Editor, NBS Technical Note 402, (1966).
- [10] W. R. Shields, Editor, NBS Technical Note 277, (1966).



NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, chemistry, and engineering. Comprehensive scientific papers give complete details of the work, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Illustrated with photographs, drawings, and charts.

Published in three sections, available separately:

● Physics and Chemistry

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, \$6.00; foreign, \$7.25*.

● Mathematical Sciences

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, \$2.25; foreign, \$2.75*.

● Engineering and Instrumentation

Reporting results of interest chiefly to the engineer and the applied scientist. This section includes many of the new developments in instrumentation resulting from the Bureau's work in physical measurement, data processing, and development of test methods. It will also cover some of the work in acoustics, applied mechanics, building research, and cryogenic engineering. Issued quarterly. Annual subscription: Domestic, \$2.75; foreign, \$3.50*.

TECHNICAL NEWS BULLETIN

The best single source of information concerning the Bureau's research, developmental, cooperative and publication activities, this monthly publication is designed for the industry-oriented individual whose daily work involves intimate contact with science and technology—for *engineers, chemists, physicists, research managers, product-development managers, and company executives*. Annual subscription: Domestic, \$3.00; foreign, \$4.00*.

*Difference in price is due to extra cost of foreign mailing.

NONPERIODICALS

Applied Mathematics Series. Mathematical tables, manuals, and studies.

Building Science Series. Research results, test methods, and performance criteria of building materials, components, systems, and structures.

Handbooks. Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications. Proceedings of NBS conferences, bibliographies, annual reports, wall charts, pamphlets, etc.

Monographs. Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

National Standard Reference Data Series. NSRDS provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated.

Product Standards. Provide requirements for sizes, types, quality and methods for testing various industrial products. These standards are developed cooperatively with interested Government and industry groups and provide the basis for common understanding of product characteristics for both buyers and sellers. Their use is voluntary.

Technical Notes. This series consists of communications and reports (covering both other agency and NBS-sponsored work) of limited or transitory interest.

CLEARINGHOUSE

The Clearinghouse for Federal Scientific and Technical Information, operated by NBS, supplies unclassified information related to Government-generated science and technology in defense, space, atomic energy, and other national programs. For further information on Clearinghouse services, write:

Clearinghouse
U.S. Department of Commerce
Springfield, Virginia 22151

Order NBS publications from:
Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

U.S. DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20230

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF COMMERCE

OFFICIAL BUSINESS
