[redacted]

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0349492 0

ORNL-1563
Progress

AEC RESEARCH AND DEVELOPMENT REPORT

LABORATORY RECORDS
1954

STABLE ISOTOPE RESEARCH AND PRODUCTION DIVISION SEMIANNUAL PROGRESS REPORT FOR PERIOD ENDING MAY 20, 1953

CLASSIFICATION CHANGED TO: DECLASSIFIED
AUTHORITY OF: AEC 11-23-59
D. D. Bamberg 2-25-60

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

LIBRARY LOAN COPY

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

UCC

POST OFFICE BOX P
OAK RIDGE, TENNESSEE

[redacted]

[redacted]

[redacted]

ORNL-1563

This document consists of 38 pages
Copy 4 of 99 copies. Series A

Contract No. W-7405-eng-26

STABLE ISOTOPE RESEARCH AND PRODUCTION DIVISION SEMIANNUAL PROGRESS REPORT

For Period Ending May 20, 1953

C. P. Keim, Director

DATE ISSUED

DEC 16 1953

OAK RIDGE NATIONAL LABORATORY
Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

[redacted]

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0349492 0

[redacted]

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-11. Central Files
12. Central Files, ORNL R. C.
13. C. E. Larson
14. W. B. Humes (K-25)
15. L. B. Emlet (Y-12)
16. A. M. Weinberg
17. E. H. Taylor
18. E. D. Shipley
19. R. C. Briant
20. F. C. VondeLage
21. J. A. Swartout
22. S. C. Lind
23. F. L. Culler
24. A. H. Snell
25. A. Hollaender
26. M. T. Kelley
27. G. H. Clewett
28. K. Z. Morgan
29. J. S. Felton
30. A. S. Householder
31. C. S. Harrill
32. C. E. Winters
33. D. W. Cardwell
34. E. M. King
35. D. D. Cowen
36. P. M. Reyling
37. C. P. Keim
38. S. Lawrence
39. J. M. Herndon
40. R. S. Livingston
41. F. W. Hurd
42. P. E. Normand
43. C. R. Baldock
44. J. R. McNally, Jr.
45. Boyd Weaver
46. G. C. Williams
47. P. M. Uthe

EXTERNAL DISTRIBUTION

48-53. Argonne National Laboratory
54-55. Atomic Energy Commission, Washington
56-58. Brookhaven National Laboratory
59-60. Carbide and Carbon Chemicals Company (K-25 Plant)
61-64. Carbide and Carbon Chemicals Company (Y-12 Plant)
65. Chicago Patent Group
66. Chief of Naval Research

[redacted]

[redacted]

[redacted]

67-69. duPont Company, Augusta
70. General Electric Company, Richland
71. Hanford Operations Office
72. Iowa State College
73-74. Knolls Atomic Power Laboratory
75. Los Alamos Scientific Laboratory
76. Naval Research Laboratory
77-78. New York Operations Office
79. Patent Branch, Washington
80. Savannah River Operations Office, Augusta
81. duPont Company, Wilmington
82-84. University of California Radiation Laboratory, Berkeley
85-90. Technical Information Service, Oak Ridge

[redacted]

[redacted]

Reports previously issued in this series are as follows

Y-497	July 1, 1949 to September 30, 1949
Y-550	October 1, 1949 to December 31, 1949
Y-586	January 1, 1950 to March 31, 1950
Y-636	April 1, 1950 to June 30, 1950
Y-685	July 1, 1950 to September 30, 1950
Y-723	October 1, 1950 to December 31, 1950
Y-765	January 1, 1951 to March 31, 1951
Y-797	April 1, 1951 to June 30, 1951
Y-821	July 1, 1951 to September 30, 1951
ORNL-1228	October 1, 1951 to December 31, 1951
ORNL-1298	January 1, 1952 to March 31, 1952
ORNL-1356	April 1, 1952 to June 30, 1952
ORNL-1434	July 1, 1953 to September 30, 1952
ORNL-1483	Period Ending December 31, 1952

[redacted]

[redacted]

CONTENTS

	PAGE
ISOTOPE ANALYSIS METHODS LABORATORY	1
Introduction	1
Nuclear Resonance	1
Project NR-1 - table of nuclear moment data	1
Project NR-2 - nuclear resonance analytical applications	1
Project NR-3 - nuclear magnetic resonance equipment development	2
Microwave Spectroscopy	2
Project M-1 - microwave spectrum of vinyl fluoride	2
Project M-2 - microwave spectrum of vinyl acetylene	3
Project M-3 - microwave spectrometer equipment development	3
Infrared Spectroscopy	4
Project IR-1 - infrared spectra of lithium alkyls	4
Optical Spectroscopy	4
Project OS-1 - plane-grating monochromator	4
Project OS-2 - spectroisotopic assay of lithium	4
Project OS-3 - photodetector investigations	5
Project OS-4 - helium spectra	6
Project OS-5 - Xe^{135}	6
Project OS-6 - hyperfine structure of U^{235}	6
Project OS-7 - Zeeman spectroscopy	7
Spectrochemistry	7
Project SC-1 - general spectrochemical analysis	7
Project SC-2 - spectrochemistry of stainless steels and other reactor materials	8
Project SC-3 - spectrochemical analysis of rare earths	8
Project X-1 - uranium analysis by x-ray absorption	8
Project X-2 - x-ray diffraction analysis	9
Special Projects	9
Project SP-1 - the evaporator	9
Project SP-2 - automatic data accumulation	9
Project SP-3 - calutron filament-life experiments	10
Publications	10
MASS SPECTROMETER LABORATORY	11
Introduction	11
High-Temperature Analyses	11
Isotopic assay	11
Uranium tetrafluoride analysis	11
Biological investigations	11
Low-Temperature Analyses	11

[redacted]

[redacted]

PAGE

Sample summary 11
Argon 12
Hydrogen equilibration 12
Deuterium abundance 12
Hilsch tube experiments 13
Laboratory Equipment 13
New mass spectrometer tube (MSB-2) 13
Ion source gate circuitry 13
Gas-handling equipment 13
Mercury-diffusion pumps 14
Electropolishing 14
Publications 14

RESEARCH AND DEVELOPMENT STABLE ISOTOPES 15
Metal Reduction and Related Work 15
Hilsch Tube 16

STABLE ISOTOPE SEPARATION RESEARCH AND CALUTRON OPERATIONS 20
Introduction 20
Collections 20
Silicon, Series GC-XBX 20
Lithium, Series GD-XBX 20
Lithium, Series GE-XBX 20
Boron, Series GF-XAX 21
Palladium, Series GG-XBX 21
Platinum, Series GH-XBX 22
Neodymium, Series GI-XAX 22
Development 22

STABLE ISOTOPE CHEMISTRY, RESEARCH, AND PRODUCTION 23
Introduction 23
Special Projects 23
Calutron Services 23
Chemical Refinement 24
Separation of Rare Earths 24
Publications 26
Isotope Shipments and Requests 27
Preparation for shipment 27

[redacted]

STABLE ISOTOPE RESEARCH AND PRODUCTION DIVISION SEMIANNUAL PROGRESS REPORT

ISOTOPE ANALYSIS METHODS LABORATORY

J. R. McNally, Jr., Department Head

INTRODUCTION

The work of the Isotope Analysis Methods Laboratory in the field of spectroscopic investigations of elements and isotopes is being reported on a project basis. This is a departure from the usual form which has been used previously, but it is felt that persons not directly acquainted with the work will thereby obtain a more complete picture of the over-all purpose, objectives, and activities of the department projects. Specific fields of investigation covered are nuclear resonance, microwave and infrared spectroscopy, optical spectroscopy, spectrochemistry, and x-ray absorption and diffraction.

NUCLEAR RESONANCE

Project NR-1 - Table of Nuclear Moment Data (H. E. Walchli). The general objective of Project NR-1 is to collect all pertinent published and unpublished information on the nuclear magnetic moments of isotopes. The specific objectives are as follows (1) the compilation of nuclear magnetic resonance frequencies, nuclear spins, measurement methods, frequency ratios determined, chemical compounds used, precision of measurement, and other information, (2) the construction of working tables of diamagnetically corrected nuclear magnetic moments and standardized frequency ratios; and (3) a review of the status of chemical shielding effects.

The background information is scattered throughout the scientific literature, and existing tables of nuclear magnetic moments do not give complete data on the conditions of observation, precision, and diamagnetic corrections. The experimental quantities (frequency ratios, compounds, precision, etc.) are basically important for proper evaluation of nuclear magnetic moment measurements in this laboratory.

A preliminary tabulation was distributed to about 20 laboratories for review and recommendations with regard to the correctness and completeness of the project The data have been incoprorated into a report[1] that is complete through April 1, 1953 and which is designed to permit the addition of new data as they become available Except for the maintenance of an up-to-date laboratory copy on new material, the project is essentially complete with the issuance of this report. It is possible that supplementary listings of new material will be made available at a later time.

Project NR-2 - Nuclear Resonance Analytical Applications (H. E. Walchli). The general objective of Project NR-2 is to determine the feasibility of nuclear resonance as an analytical tool The specific objectives are the investigation of the lithium isotopic content of solutions of propylene diamine and the evaluation of hydrogen as occluded HF in UF_6.

Previous work[2] done in this laboratory on the isotopic determinations of Li^6 and Li^7 in solutions indicated that signal distortion and insensitivity prevented reproducible determinations of abundance ratios from the nuclear

(1) H E Walchli, *A Table of Nuclear Moment Data*, ORNL-1469 (April 1, 1953)

(2) *Quarterly Progress Report, Stable Isotope Research and Production Division, July 1, 1951 to September 30, 1951*, Y-821, p 25

magnetic resonances. Further investigations of other solutions and the improvement of signal response were therefore necessary The K-25 laboratory is interested in a routine analytical tool for the determination of the occluded HF in UF_6 Nuclear resonance measurements in which the proton signal is used would appear to be suitable, since the requirement is a minimum sensitivity of only about 1 mole of HF per mole of UF_6.

Measurements have been made on Li^7 in several samples of propylene diamine, but the results were no better than those obtained with aqueous solutions of lithium chloride. Signal-to-noise ratios for the Li^7 resonance in various solutions of lithium chloride in propylene diamine are given in Table 1.

TABLE 1. SIGNAL SENSITIVITY OF Li^7 RESONANCE IN PROPYLENE DIAMINE SOLUTIONS OF LITHIUM CHLORIDE

LiCl SAMPLE SIZE (mg)	CONCENTRATION (mg/ml)	SIGNAL-TO-NOISE RATIO
456	57	>100
150	17	10
73	9	3
0	0	~0

Measurements on a sample of K-25 material with 2 to 5 moles of HF per mole of UF_6 were made with the spectrometer. Proton resonances were observed, but the background proton level from the polyethylene spectrometer head unit was too large to permit the two contributions to be distinguished. Revisions of the spectrometer electrical equipment are continuing, a proton-free fluorothene head is to be constructed, and the HF sample will be reinvestigated.

Project NR-3 - Nuclear Magnetic Resonance Equipment Development (H. E. Walchli, O. B. Rudolph). The general objective of Project NR-3 is to increase the sensitivity and the linearity of the nuclear resonance equipment. The specific objectives are as follows (1) to obtain an r-f sensitivity of 1 to 5 μv, to obtain complete linear amplification of the signal, and to introduce increased magnetic field stability, (2) to detect the nuclear magnetic moment of U^{235} by using a fixed-frequency spectrometer and to extend the application to other isotopes with low nuclear gyromagnetic ratios, and (3) to re-evaluate the analytical applications of nuclear resonance equipment.

At present, the equipment sensitivity is of the order of 50 to 100 μv In addition, the output to the recorder is extremely nonlinear, and the magnet field regulation, which uses a temperature-sensitive wire-wound resistor for a current standard, is limited to 1 part in 20,000

A water-cooled, precision, magnet-current resistor has been designed to give temperature resistance stability to 1 part in 100,000 and should permit magnetic-field regulation to the same magnitude The Varian spectrometer has been revised, the audio section is now linear, and the acceptance range of this section extends from 27 μv to 15 volts in several subranges, with suitable oscilloscope monitoring points now available. Design of an r-f amplifier section with a sensitivity of about 3 to 5 μv is about 75% complete After the equipment development is finished, the sensitivity and frequency ranges will permit a search for the U^{235} resonance for which $(\mu/I) \cong 0.26$ nuclear magnetons,[3] as well as for resonances of numerous other isotopes with small gyromagnetic ratios

MICROWAVE SPECTROSCOPY

Project M-1 - Microwave Spectrum of Vinyl Fluoride (H W. Morgan, J H. Goldstein[4]) The general objective

[3] *Stable Isotope Research and Production Quar Prog Rep Dec 31, 1952*, ORNL-1483, p 17

[4] Consultant, Emory University

of Project M-1 is the investigation of the microwave absorption spectrum and the Stark effects of vinyl fluoride The specific objective is the evaluation of the molecular rotational energy levels, the moments of inertia, the molecular asymmetry parameter K, and the electric dipole moment of the molecule, CH_2 CHF. The examination of this compound completes the study of the vinyl halides In addition to these halides, vinyl acetylene and vinyl cyanide have also been studied

The J = 0 to 1 and J = 1 to 2 groupings have been observed and measured in the regions about 19,500 and 39,000 megacycles, respectively The asymmetry parameter K is approximately -0.95, which indicates that vinyl fluoride is nearly a prolate symmetric rotor molecule. In addition, the Stark-effect characteristics and the temperature dependence of many other lines are being measured and studied. These lines arise from both μ_a and μ_b Q-type transitions of vinyl fluoride, as well as from impurities in the sample. Precise Stark-effect measurements have been made on the J = 0 to 1 transition for the determination of the electric dipole The experimental work is currently being stressed and will continue until sufficiently accurate data are obtained to interpret the molecular parameters and to identify impurity lines.

Project M-2 - Microwave Spectrum of Vinyl Acetylene (H. W. Morgan, J. H Goldstein) The general objective of Project M-2 is the examination of the microwave spectrum and the Stark effects of the vinyl acetylene molecule The specific objective is a precise evaluation of the moments of inertia, the asymmetry parameter K, the dipole moment, and the centrifugal distortion correction parameters of vinyl acetylene. This molecule is the first pure hydrocarbon to be observed in the microwave region It is also of interest because of its slight asymmetry, very few studies have been made of near-symmetric tops.

The J = 1 to 2, J = 2 to 3, and J = 3 to 4 transitions were observed and measured, and parameters that have previously been reported[5] were evaluated Attempts to observe the J = 0 to 1 transition have been unsuccessful The J = 1 to 2 and J = 2 to 3 transitions can be fit perfectly by these parameters, but the J = 3 to 4 group shows differences well beyond the limits of experimental error. Attempts to interpret these discrepancies on a theoretical basis have so far been unsuccessful. Measurements will be made of the J = 3 to 4 transition frequencies for vinyl cyanide to determine whether similar discrepancies exist in this comparable molecule. If this proves to be the case, the study will be continued, and a separate study will be made of the centrifugal distortion effects.

Project M-3 - Microwave Spectrometer Equipment Development (H. W. Morgan) The general objective of Project M-3 is to increase the sensitivity, reliability, and versatility of the existing spectrometer. The specific objectives are to decrease noise in the system from external sources and to decrease radiated signals which interfere with other laboratory equipment. At present, there are serious limitations in the search for and measurement of weak microwave absorption signals because of cross-interference with other electrical equipment

A relay rack cabinet housing the frequency standard oscillator and frequency multipliers has been specially treated with copper metal to reduce extraneous radiation. A copper shielding box is being constructed to house the Hallicrafters receiver

A new and reliable frequency tripler has been designed (it uses a 4X150A tube) and has been partially completed

---

[5] *Op cit*, ORNL-1483, p 18

by the shops. Other units of the frequency standard have been modified so that they can be operated continuously to achieve maximum frequency stability. Upon completion of the work on the frequency standard, the following projects will be undertaken double shielding of the 100-kc square-wave generator, installation of a new vacuum line, and construction of a low-noise 100-kc preamplifier.

INFRARED SPECTROSCOPY

Project IR-1 - Infrared Spectra of Lithium Alkyls (P. A. Staats, J. H Goldstein). The general objective of Project IR-1 is to obtain the infrared molecular absorption spectra of lithium alkyls The specific objectives are to obtain pure samples of lithium alkyls, to examine the characteristics of the Li-C bond, and to investigate the Li^6-C and Li^7-C stretching frequencies

Isotope shifts in molecules are large in the infrared region, they are of the order of 150 cm^{-1} for the Li-H bond and decrease to about 40 cm^{-1} for the Li-C bond. The infrared spectrometer being used at present can resolve 3 cm^{-1}, and if the Li-C stretching frequency is a strong absorber, it is possible that infrared assay methods can be developed [6]

Lithium butyl and lithium isopropyl of questionable purity have been prepared and their infrared spectra have been run. Attempts to purify these alkyls by fractional crystallization have failed. Lithium butyl has been successfully distilled in a high-vacuum short-path still which gives a product of high purity. Qualitative information as to the heat stability of the afore-mentioned alkyls has been determined. As soon as the spectra of several pure lithium alkyls have been obtained, an attempt will be made to identify the Li-C stretching frequency and, where possible, to make complete vibrational assignments for the molecules. The short-path distillation method looks promising, and all subsequent liquid samples will be purified in this manner.

OPTICAL SPECTROSCOPY

Project OS-1 - Plane-Grating Monochromator (G. K. Werner). The general objective of Project OS-1 is to develop a high-resolution, high-intensity, plane-grating monochromator for application to spectroisotopic analysis. For the specific objectives, the monochromator is to satisfy the following requirements spectrum resolution of 200,000 or better, coarse spectrum displacement by grating rotation, fine spectrum-displacement control by auxiliary means, and adaptability to scanning and/or integrating photoelectric methods.

The feasibility of spectroisotopic assay of numerous elements important in atomic energy work has been well established. The instrument under design will utilize the Ebert type of mounting[7] and will incorporate a Bausch and Lomb 8-in plane grating and two concave mirrors on a 16-ft lathe bed mounted on vibration isolators.

The engineering design is practically complete, however, the concrete piers and electrical outlets to the monochromator have already been installed. A novel double-flexure mirror mounting for focussing and and scanning the spectra is to be tested in the monochromator. Sensitivity to wavelength peaking is to be of the order of 1 mA or better.

Project OS-2 - Spectroisotopic Assay of Lithium (D. D Smith, Z. Combs). The general objectives of Project OS-2 are the development and

(6) See application to C^{12} and C^{13} in CO_2 by J C Kluyver, Thesis, Drukkerij v/h Kemink en Zoon N V - Domplein 2, Utrecht

(7) W G Fastie, *J Opt Soc Amer* **42**, 641 (1952)

the application of the hollow-cathode source to the analysis of Li^6 and Li^7 relative abundances. The specific objectives are to investigate the extension of the single hollow-cathode source to a multiple source and to perform lithium isotopic assays for the Stable Isotope Division and others

Hollow-cathode excitation of lithium for isotopic analysis was developed in this laboratory and has been reliably applied to the analysis of high-concentration Li^6 samples for the Stable Isotope Division. The precision at low Li^6 levels and the sampling time require still further development.

A simple hollow-cathode source permitting rapid change of samples for single-type analyses has been developed. Reproducibility at the low level of 13.93% Li^6 has been improved. The limit of error at the 95% confidence level of any one of the 30, 1-min exposures to the same cathode operated at different currents was investigated, and data are given in Table 2. The major source of isotopic assay error is spectrum drift caused by atmospheric changes This drift effect is shown in the data of Table 3. The major problem associated with the 21-ft grating spectrograph is the spectrum drift Attempts to eliminate the drift by using a helium line as a spectrum position monitor have been only partially successful. The problem will be investigated further

Project OS-3 – Photodetector Investigations (G. K. Werner, O B. Rudolph) The general objective of Project OS-3 is to improve measuring techniques in general spectrophotometric work. The specific objectives are to select the most sensitive phototubes for lithium spectroisotopic assay and to investigate other measurement methods which will give higher ratios of signal-to-phototube noise variations

TABLE 2. REPRODUCIBILITY OF LITHIUM SPECTRA, Li^6 and Li^7, AT 6707 A

HOLLOW-CATHODE CURRENT (ma)	REPRODUCIBILITY OF 13 93% SAMPLE (Limit of error, %)	DRIFT* (%)
60	±1 3	-1 3
50	±1 0	-1 1
40	±0 46	-0 36
30	±0 24	-0 08

*As measured by average of first ten readings compared with last ten readings

TABLE 3. ASSAY RESULTS ILLUSTRATING SPECTRUM DRIFT ON REPLICATE SAMPLES

SAMPLE NO	Li^6 DETERMINATION (%)	DEVIATION (%)
1	15 92	+0 49
2	15 80	+0 37
3	15 58	+0 15
4	15 44	+0 01
5	15 32	-0 11
6	15 13	-0 30
7	15 43	0 00
8	15 13	-0 30
9	15 43	0 00
10	15 09	-0 34
Average	15 43	±0 22

The present direct-reading equipment introduces dark-current compensation through periodic subtraction operations of 1-sec duration following each 1-sec exposure period Reproducibility of the system to constant light intensity is considerably better than variations caused by actual source conditions. Choice of phototubes for this type of operation depends on high sensitivity and on small variations in dark current.

Numerous phototubes have been tested at a wavelength of 6707 A for sensitivity, dark current, and dark-current variations Of those tested, the 1P21 was best suited to the requirements of operation Since the actual light

level is low and is quite comparable to dark current in certain investigations, the fatigue effects in the photomultiplier are small. The present light-measuring system for lithium assay is adequate Pending improvements in the light source and in the spectrum line-peak setter, no changes are contemplated. In anticipation of future limitations of the photoelectric equipment, tests will be made on English and German photomultipliers, tube refrigeration, image converters, S-1 sensitivity photocells, heat-treated photocells, and the lead sulfide type of cell.

Project OS-4 - Helium Spectra (K. L Vander Sluis, O. C. Yonts). The general objective of Project OS-4 is to investigate the spectra of He^3 and He^4. The specific objective is to re-examine the reported pressure and isotope shifts[8] in He^3 and He^4.

Relatively large pressure effects for the isotope lines and an isotope pressure effect (of the order of 0.003 cm^{-1}) have been reported for helium In addition, the anomalous isotope shifts for the helium lines warrant further investigation

Spectra of He^3 and He^4 have been excited by radiofrequency (2450 megacycles) in liquid-nitrogen-cooled electrodeless discharge tubes and in a small, atomic beam source Line widths were comparable, depending on the amount of power input, to the Doppler widths of sources at temperatures greater than 77°K. An improved atomic beam source of helium atoms is to be constructed, and liquid-hydrogen cooling of the discharge tube may be tested. An attempt may also be made to observe the resonance singlet transition at 580 A under high resolution.

Project OS-5 - Xe^{135} (K. L. Vander Sluis). The general objective of Project OS-5 is to study the hyperfine spectrum of Xe^{135} The specific objective is to determine the nuclear spins and magnetic moments of Xe^{135} and its decay products.

Xenon-135 decays by 9-hr beta emission to Cs^{135}. Xenon-135 has 81 neutrons and is expected to have a ground-state spin of 1/2. The very large cross section of Xe^{135} indicates that hyperfine data may reveal important information about the state of the nucleus. Normal xenon has been investigated in an effort to find a suitable carrier gas for excitation and dilution, and a 10% xenon mixture, with neon as the carrier, appears to be most favorable. Tests are to be made to determine optimum photographic conditions for the sensitive hyperfine lines.

Project OS-6 - Hyperfine Structure of U^{235} (K. L Vander Sluis). The general objective of Project OS-6 is to obtain improved hyperfine data on the U^{235} nucleus. The specific objective is to investigate, under high resolution, the structures of the 4915 A neutral atom line and the 4515 A ionized atomic line of U^{235}.

The spin, nuclear magnetic moment, and quadrupole moment of U^{235} have been previously reported[9] as $I = 5/2$, $\mu = +0\ 66$, and $Q = -8 \times 10^{-24}$ cm^2. Since Q is a measure of the asymmetrical shape of the nucleus and is of importance in fission theory, it is desirable to obtain as exact a number for this term as is possible. Hyperfine splitting of the 4915 A line has been obtained with a resolution of about 700,000 by using a liquid-air-cooled hollow-cathode source. Intensity and operating conditions were not constant and introduced difficulties in reproducing and improving the resolution. Attempts were made to excite the spectrum by using radiofrequency excitation, but they were

(8) M Fred, F S Tomkins, and J K Brody, *Phys Rev* **79**, 212 (1950)

(9) G L Stukenbroeker and J R McNally, Jr , *J Opt Soc Amer* **40**, 336 (1950), *Stable Isotope Research and Production Quar Prog Rep Dec 31, 1952*, ORNL-1483, p 22

unsuccessful. Further investigations will be made of the electrodeless discharge method.

Project OS-7 - Zeeman Spectroscopy (P. M. Griffin, O C. Yonts). The general objectives of Project OS-7 are to obtain the Zeeman spectra of some of the heavy elements and to use these data as an aid to the extension of the classification of the spectra of these elements. The specific objectives are to develop safe and adequate methods of exciting and photographing the spectra of uranium and plutonium atoms in a uniform magnetic field, to deduce the total angular momentum quantum numbers J_1 and J_2, and to calculate, when possible, the Landé g factors associated with the two levels involved in the transitions

The Zeeman spectrum of uranium has been quite thoroughly studied at wavelengths below 5500 A by research teams at the Massachusetts Institute of Technology, the U S Bureau of Standards, and the Zeeman Laboratorium at the University of Amsterdam [10] However, no results of Zeeman structure in U II lines above 5600 A have been reported Although the status of the classification of the spectra of U I and U II is fair, as evaluated by Meggers, many problems still remain unresolved, such as which of two systems of low-lying levels in U II involving 5*f* electrons is more tightly bound Zeeman data on lines in the near infrared region up to 12,000 A would facilitate the solution of these problems

Because of the similar complexity of the plutonium spectrum, no significant progress can be expected without the aid of Zeeman data The most serious difficulty encountered so far on both projects (uranium and plutonium) has been the development of sources which give adequate excitation when operated in a magnetic field, but which still, in the case of plutonium, prevent any escape of the highly toxic sample. Sources have been developed to burn uranium metal electrodes in an atmosphere of helium Exposures up to 1 hr are possible by operating eight sources successively for 7 min each. A source for plutonium has been built which is safe as far as health hazards are concerned Testing of this source for sufficient excitation of plutonium is not complete Much of the electrical and optical equipment used in connection with this project has been redesigned and rebuilt to facilitate more dependable operation when plutonium is run

The final exposures for uranium Zeeman spectra are to be made within the next month Final testing of the plutonium source and the actual plutonium Zeeman spectra are to be completed shortly thereafter Reduction of data and the application of the resulting information to the classification of the spectra will proceed as scheduled.

SPECTROCHEMISTRY

Project SC-1 - General Spectrochemical Analysis (M R Skidmore, J. A Norris) The general objective of Project SC-1 is the improvement of the "universal" method of general sample analysis The specific objectives are to improve sensitivity of analysis for certain elements, to remove interferences in present standards, and to prepare various standards with added matrix for improved accuracy.

A graphite-matrix method has been in use for the spectrochemical analysis of isotope materials and for the general survey of unknown samples This method is subject to bias when large quantities of alkalies are present in the sample Standards for

(10) J J Katz and E Rabinowitch, *The Chemistry of Uranium*, NNES VIII-5, chap 2, McGraw-Hill, New York, 1951

analysis by this method are approximately seven years old and need revision. Except for the investigation of the alkali suppression effects, no thorough study of this procedure has been attempted. New and regrouped standards are to be prepared to match the sample types, and various classes of matrices are to be studied in connection with line interferences and excitation effects

Project SC-2 - Spectrochemistry of Stainless Steels and Other Reactor Materials (S J. Ovenshine, J. A Norris) The general objective of Project SC-2 is to determine the chemical constituents of various stainless steels and other construction materials used in reactor development. The specific objectives are to identify rapidly and uniquely the types of stainless steels, to analyze precisely for the chemical constituents, and to perform surface penetration studies of corrosion test specimens

Numerous analytical methods which have been developed for the testing of routine steels are not, in general, applicable to the samples received for analysis However, use is made of reported line pairs, and, in some cases, specific procedures and methods of excitation have been adopted The solution methods utilizing porous electrodes are being used, since they permit ready addition of internal standards and a wider freedom in the choice of line pairs Standards for corrosion studies are being prepared by using chromium, nickel, molybdenum, columbium, and zirconium Attempts will be made to determine and reduce the causes of the present plate-to-plate variation, as compared with the within-plate precision

Project SC-3 - Spectrochemical Analysis of Rare Earths (J J. Mundzak, J A. Norris) The general objective of Project SC-3 is to improve and extend the method of rare-earth analysis developed in this laboratory.

The method for analysis of the rare earths in chemically concentrated samples has been published.[11] It consists of a porous-cup procedure and gives a precision of ±10% of the rare-earth concentration at the 99 5% confidence level, 50 rare-earth determinations can be performed per man-day. Recent work has emphasized the maintenance and improvement of the sensitivity for the various constituents, and the method has been extended to all the rare earths, with the exceptions only of promethium (not naturally occurring) and the very rare species, thulium and lutetium Should the scope of the rare-earth separation program be enlarged, it will be necessary to give serious consideration to photoelectric analysis methods.

Project X-1 - Uranium Analysis by X-Ray Absorption (W. F. Peed, H W Dunn, W B. Wright, Jr.,[12] J E Brown[12]). The general objective of Project X-1 is to improve uranium analysis techniques involving x-ray methods The specific objectives are to improve the present method, to develop process-control x-ray analysis methods, and to investigate a double-beam x-ray absorption approach.

The basis of the x-ray absorption method has been discussed previously [13] Evaluation of the method by the Y-12 Analytical Laboratory indicated ready applicability to routine problems of handling impure, as well as pure samples The method has been successfully developed for the concentration range of 100 to 30,000 ppm (uranium in water matrix), with impurities present as high as 4% by weight of the matrix. Most of the changes recommended in the 1952

(11) J A Norris and C E Pepper, *Anal Chem* 24, 1399 (1952)

(12) On part-time loan from Y-12 Production Plant

(13) W F Peed and H W Dunn, *Preliminary Investigation of Monochromatic X-Ray Absorption as a Method of Analysis for Uranium*, ORNL-1265 (April 8, 1952)

report have been introduced Investigation of the double-beam method and test application to process control will continue

Project X-2 - X-Ray Diffraction Analysis (H. W. Dunn) The general objective of Project X-2 is to obtain x-ray diffraction data on chemical compounds The specific objectives are to obtain a file of x-ray diffraction data on compounds of importance to the reactor and corrosion groups, to identify compounds and relative abundances, and to pursue the investigation of diffraction analysis methods (e.g., the phase diagram for the Li-Na-K fluochromate series and the solubility studies of uranyl phosphates).

X-ray diffraction studies of reactor materials and corrosion products have resulted in numerous new data on chemical compounds. Considerable data have been accumulated on the various phases of Li-Na-K fluochromates which result from selective leaching of the chromium from stainless steel loops that are used for circulating liquid metal Except for a few boundary points of the solid-solution areas of the phase diagram, quite complete data are now available for these compounds. Studies were carried out on the compounds formed by different uranyl phosphates in solution The fluochromate and uranyl phosphate interplanar spacings will be measured, and intensities will be recorded so that data may be available to other laboratories.

SPECIAL PROJECTS

Project SP-1 - The Evaporator (O C. Yonts, K. L. Vander Sluis). The general objective of Project SP-1 is to build a vacuum evaporator for metal and dielectric films. The specific objective is to fill the immediate need for an evaporator to produce aluminum and silver films for interferometer plates and concave mirrors.

In order to obtain maximum resolution from the Fabry-Perot etalon, it is necessary that the highest possible reflectivity be obtained from the coated surface In the case of silver, this can only be obtained from fresh surfaces, since corrosion reduces reflectivity and increases absorption rapidly with age

The evaporator consists of a 14-in.-dia pyrex dome fitted to a carefully ground, mild-steel base plate. The base plate contains eight spark plugs of the Phillips ion-gage type, four spark plugs of the β-K lead type, and two spark plugs of the coaxial type The high-vacuum system is built of 4-in pyrex pipe with a roughing line of 2-in pyrex pipe Koroseal gaskets are used throughout, and a 4-in. DPI type MF-300 diffusion pump supplies high vacuum, a Kinney VSD-556 is used as a roughing and forepump The whole system is mounted on a unistrut table covered with plywood A Pirani gage is located in the forevacuum line, and a 35-ton ion gage is used in the high-vacuum line The evaporator has been used to coat etalon plates with silver and aluminum, and the coated plates have been obtained in approximately 1 hour It is planned to recoat an echelle with aluminum in the near future, also, some additional construction is planned with regard to a dome-handling device

Project SP-2 - Automatic Data Accumulation (W F Peed, H E Walchli) The general objective of Project SP-2 is to develop instrumentation and methods for rapidly accumulating and recording data The specific objectives are as follows to improve the data accumulation method for x-ray uranium absorption analysis, to develop a printer-timer unit with a range of approximately 0 to 100 sec, to the nearest 0.01 sec, and to develop automatic repeat-operation controls for application to multiple-station hollow-cathode operation.

A large portion of the personnel and equipment time is consumed in read-out and repeat operations. Economical read-out methods are desirable for routine testing, as well as for analytical investigations Preliminary testing of an IBM typewriter, which was converted to automatic data recording from time-storage units, has been done, the tests indicate that a read-out and sequential operation system is feasible The automatic data accumulator will be constructed, and actual field tests will be given.

Project SP-3 - Calutron Filament-Life Experiments (O C. Yonts). The general objective of Project SP-3 is to study the processes causing erosion of the calutron filament The specific objective is to increase the useful filament life in calutron ion sources

One of the problems involved in the stable-isotope separation program since its inception has been the frequent trouble with short filament life in the calutron Only on few occasions has filament life approached that achieved in the uranium-production plant Average filament life with uranium was about 120 hr (Alpha plant), with a 150-hr life not too uncommon. Stable-isotope production runs have had filament life varying from 10 to 15 hr for material such as titanium and 200 hr for mercury, but with most elements, the filament life has been between 30 and 50 hours

The work of this project has been concerned with the operation of the ion source in the manner of a gas-filled diode. True diode operation greatly reduces both ion output and filament erosion Since the output loss cannot be tolerated, a so-called "modified diode operation" has been investigated This type of operation results in a twofold increase in filament life, with no serious loss in output Production runs have been made on silicon and lithium, and experimental runs have been made on titanium. In the case of silicon, average ion output was about 10% less, the decrease was only about 1% for lithium, whereas in the case of titanium, output was approximately 15% greater for the modified diode run. Further studies of the geometrical and electrical source conditions will be made in an attempt to optimize all source conditions

PUBLICATIONS

Reports and papers in preparation or submitted for publication

1. G K Werner, "Semi-Automatic Recording of Wavelength Data," to be published in the *Journal of the Optical Society of America*
2. H W Morgan and J. H. Goldstein, "The Microwave Spectrum of Vinylacetylene."
3. H. W. Morgan and J. H Goldstein, "The Microwave Spectrum and Molecular Structure of Vinyl Fluoride."

Reports published and papers presented

1. G L Stukenbroeker and J. R. McNally, Jr , "Isotope Shifts in Thorium - Th 230 and Th 232," *J Opt Soc Amer* **43**, 36 (1953).
2. E. J Spitzer and D D Smith, "Spectrochemical Analysis of Zirconium Oxide," *Appl Spectroscopy* **6**, No. 5, 9 (1952)
3. H E Walchli, *A Table of Nuclear Moment Data*, ORNL-1469 (April 1, 1953).
4. W. F Peed, W. B Wright, Jr , and G L Rogosa, *Application of X-Ray Fluorescence to Analysis of Zirconium in Uranium*, ORNL-1419 (December 6, 1952).
5. G K Werner, "Photoelectric Applications in Spectroscopy," paper presented at Southern Association of Spectrographers, spring meeting, Oak Ridge, April 1953.
6. J. A Norris, "Physical Principles of Excitation," paper presented at Southern Association of Spectrographers, Spring Meeting, Oak Ridge, April 1953

7. H. E. Walchli, "Nuclear Magnetic Resonance Measurements of Selenium," *Phys Rev.* **90**, 331 (1953).
8. H. W. Morgan and J. H. Goldstein, letter to the editor "The Microwave Spectrum of Vinylacetylene," *J. Chem. Phys.* **20**, 1981 (1952).
9. O. C. Yonts, *Filament-Life Extension in High-Intensity Ion Sources*, ORNL-1525 (April 27, 1953).

MASS SPECTROMETER LABORATORY

Russell Baldock, Department Head

INTRODUCTION

The high-temperature oven for vaporization of solid materials in the mass spectrometer has been successfully applied to the isotopic analysis of molybdenum and boron. Quantitative tests were completed on the time-integration method of analysis of UF_4 for UO_2F_2. Investigations were made on 96 samples by using the G-E mass spectrometer. The ion source gate circuitry for appearance potential studies has been completed.

HIGH-TEMPERATURE ANALYSES

Isotopic Assay (J. R. Sites, G. A. Consolazio). The recently developed high-temperature filament oven for the vaporization of solid materials in the source of a mass spectrometer has been successfully applied to the assay of separated isotopes. The stable isotopes of two elements, molybdenum (in MoO_3) and boron (in H_3BO_3), have been checked by using both natural and previously assayed isotopically enriched material. In the mass cracking pattern of MoO_3, the MoO_2^+ ions are the most abundant and were used for the analysis. Corrections were made for the O^{18} contributions. The best ions for the boron analyses were $B_2O_3^+$ from the B_2O_3 material remaining after the dehydration of the H_3BO_3.

An analysis was made of a calcium-boron complex ($CaF_2 \cdot BF_3$) which is used as a source of the $B^{10}F_3$ used in neutron counters. The B^{10} concentration was found to be 96.1 ± 0.1%.

Uranium Tetrafluoride Analysis (L. O. Gilpatrick, J. R. Sites). Final tests were made on the time-integration method of analysis of UF_4 for UO_2F_2.[1] A known mixture was synthesized which contained 1.23 mole % of UO_2F_2 in purified UF_4, and when the mixture was analyzed by the time-integration method, a value of 1.40 mole % was obtained.

Biological Investigations (J. R. Sites, G. A. Consolazio). Two exploratory runs were made on biological materials. One run was made on a compound which was synthesized by B. L. Strehler and which has some physical properties similar to those of extracts of firefly tail luciferin, but the results were disappointing because the only ions that appeared were those of fragments of the parent compound.

Another run was made on an unashed sample of rat blood platelets to check the possibility of finding trace elements. The general background from the dissociating proteins prohibited any serious searching for trace-metal ions.

LOW-TEMPERATURE ANALYSES

Sample Summary (J. R. Walton). During the months of January through May 1953, 96 samples were investigated in the G-E mass spectrometer. A summary is given below

[1] *Stable Isotope Research and Production Quar Prog Rep Dec 31, 1952*, ORNL-1483, p 33

SAMPLE MATERIAL	NO OF SAMPLES RECEIVED	NO OF SAMPLES COMPLETED
Argon	4	4
Hydrogen and deuterium	26	18
Hilsch tube experiments	74	74
Carbon	2	
Total	106	96

Argon (J. R. Walton). Four samples of argon were received from the Y-12 Health Physics Group and were investigated for the impurities present (see Table 4). These argon samples were being used in radiation counting equipment. Two of the samples were taken from the manifold which transfers the gas from a cylinder to the counters, the remaining two samples were taken from a cylinder of compressed argon which was not in use at the time the manifold samples were taken.

Hydrogen Equilibration (J. R. Walton, G. A. Consolazio). Two samples of hydrogen plus deuterium were received from E. H. Taylor and J. A. Wethington, Jr., ORNL Chemistry Division, and four investigations were made. The purpose of these studies was to determine the effects of variable equilibration time at a temperature immediately below the equilibration temperature. The temperature was held constant and the equilibration periods were varied by 10, 15, 20, and 30 min, but only a slight change was noted in the equilibration time in these experiments.

Deuterium Abundance (J. R. Walton). Two samples of hydrogen produced from tap water were investigated for deuterium content to establish known calibration curves for samples of low deuterium concentration. Memory effects from previous samples containing larger amounts of deuterium made these determinations much too high. The deuterium content of natural water taken from Norris Lake is 0.0148%.[2]

Two samples of deuterium trapped in palladium were received from J. A. McLaren, ORNL Chemistry Division. The gas was transferred from the metal to a suitable gas-sample container by L. O. Gilpatrick. The mole per cent deuterium concentration of these samples was determined.

Three samples of deuterium produced from deuterium oxide furnished by J. W. T. Dabbs, Jr. and L. Roberts, ORNL Chemistry Division, were studied and the mole per cent abundance of deuterium was determined. The abundance agrees favorably with the assumed concentration reported at the source of the deuterium oxide.

Nine samples of deuterium have been studied to increase the precision of measurements and to reduce the memory effects. To reduce the memory effect, a portion of the sample being considered is flushed through the system three times before a spectrum is taken.

(2) I. Kirshenbaum, *Physical Properties and Analysis of Heavy Water*, NNES III-4A, McGraw-Hill, New York, 1951

TABLE 4. IMPURITIES PRESENT IN ARGON

IMPURITY	ARGON FROM THE MANIFOLD		ARGON FROM THE CYLINDER	
	Sample 166	Sample 167	Sample 168	Sample 169
H_2O	0.027 ± 0 001*	0 020 ± 0 002	0 025 ± 0 002	0 024 ± 0 002
$CO + N_2$	0 012 ± 0 002	0 001 ± 0 002	0 022 ± 0 000	0 003 ± 0 000
CO_2	0 005 ± 0 001	0 000	0 000	0 000

*These values are the ratio between the peak height of the impurity and the peak height of A^{40} in arbitrary units

Optimum focusing conditions are determined and these settings are used during the scanning operations. The peak heights of H_2 (mass 2), HD (mass 3), and D_2 (mass 4), in arbitrary units, are determined, and the following expression[3] is used in calculating the mole per cent abundance of high deuterium content in a sample

$$\text{Mole \% } D_2 = \frac{1290\left(\frac{D_2}{H_2}\right) + 194\left(\frac{HD}{H_2}\right)}{3.87\left(\frac{HD}{H_2}\right) + 12.9\left(\frac{D_2}{H_2}\right) + 1} .$$

For low deuterium concentrations, the following expression[4] has been used

$$\text{Mole \% } D_2 = 50 K_1' \frac{(HD)}{(H_2)} .$$

The factor K_1' is the equilibrium constant for the two-phase reaction $H_2O\ (l) + HD\ (g) \rightleftharpoons HDO\ (l) + H_2\ (g)$. The value for this constant at 25°C is 3.87.

Hilsch Tube Experiments (J. R. Walton, G. A. Consolazio). Seventy-four samples from Hilsch tube experiments were studied in the G-E mass spectrometer. An average of four spectrum scans was made of each sample – a total of 296 investigations. The early sampling techniques resulted in the introduction of water which caused inconsistent results, therefore, new sampling techniques were initiated which substituted mercury for the water. The mercury did not introduce interfering ion peaks in the mass range that was being investigated. Also, the deviation from the mean values of the peak-height ratios was lowered.

LABORATORY EQUIPMENT

New Mass Spectrometer Tube (MSB-2) (G. F. Wells). The frame and housing for the new mass spectrometer tube designed for handling radioactive materials has been received, and installation and connection of the tube and its appurtenances are now under way. This tube is designed to be operated from the mass spectrometer B power supplies in such a way that, while either tube is in operation, the other can be serviced and made ready for operation.

Ion Source Gate Circuitry (G. F. Wells). The mass spectrometer ion source gate circuitry[5] has been completed and delivered from the Y-12 Electronics Shop. The gating electrodes for the electron gun assembly[6] have been adapted for the existing high-temperature oven source and are being constructed at present. Tests of this equipment are being designed and will be carried out in the recently completed portable vacuum system which will provide simulated operating conditions except for the magnetic field. Testing in this manner before installation in the mass spectrometer will eliminate the considerable down time which would normally be encountered in carrying out these tests in the instrument itself.

Gas-Handling Equipment (L. O. Gilpatrick). The vacuum system in Room 22A was modified several times in the course of preparing a variety of gas samples for analysis on the mass spectrometer. The most extensive complement to the system was the construction of a water-decomposition apparatus that followed the designs of Brooks[7] and Johnson,[8] but included the addition of an automatic Toepler pump. This system allows the rapid collection of protium-deuterium

(3) C A Goodall and G J Alkire, *Mass Spectrometric Determination of Deuterium in Water*, HW-25258 (Aug 20, 1952)

(4) Kirshenbaum, *op cit*, p 206-210

(5) *Stable Isotope Research and Production Quar Prog Rep Dec 31, 1952*, ORNL-1483, p 38

(6) *Electron Gun Assembly*, Westinghouse Electric Corporation Research Laboratories, East Pittsburgh, Pa, Drawing No 56-A-5617

(7) T J Brooks, Trail Report 63 (Aug 28, 1944)

(8) H L Johnson, S A M Report 2XR-35 (March 1943)

mixtures from 5- to 20-mg samples of water. An automatic control provides either of three modes of operation continuous, timed, or manual half-cycle. The equipment is so designed that the decomposition of the sample is complete, and this avoids any possible fractionation of the hydrogen isotopes during the reaction with zinc. Twenty-three samples of hydrogen were prepared on this apparatus for examination in the mass spectrometer. Additional gas samples were prepared for examination in the mass spectrometer as follows normal butane, four, hydrogen from palladium, two, carbon dioxide, two, and hydrogen from hydrates, two.

Mercury-Diffusion Pumps (L. O. Gilpatrick). Two, 180-liter/sec, metal mercury-diffusion pumps were tested on a metal vacuum system and were found to perform well. One of these pumps, which was used as a replacement for an oil-diffusion pump, gave a much improved performance to the mass spectrometer.

Electropolishing (L. O. Gilpatrick). The high-current-density method of electropolishing[9] was applied to several mass spectrometer source assemblies which had been difficult to clean. The stainless steel parts were very beautifully polished in a matter of 30 to 60 sec at current densities of from 5 to 10 amp/in.^{2} in a bath of concentrated phosphoric and sulfuric acids.

(9) C L Faust, *Metal Finishing Guide Book and Directory*, 21 ed , p 234-245

PUBLICATIONS

Papers presented

1. Russell Baldock, J. R. Sites, L. O. Gilpatrick, and H. E. Carr, "Mass Spectrometer Investigation of Higher Valence Uranium Compounds," presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pennsylvania, March 2-6, 1953.
2. J. R. Walton, "High Temperature Mass Spectrometer Oven," presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pennsylvania, March 2-6, 1953.
3. Russell Baldock, J. R. Sites, L. O. Gilpatrick, and H. E. Carr, "Mass Spectrometer Analysis of UO_2F_2 in UF_4," presented at the American Physical Society, Durham and Chapel Hill, North Carolina, March 26-28, 1953.
4. J. R. Sites and B. L. Strehler, "Determination of Molecular Weight of Organic Compounds by Mass Spectrometry," presented at the American Physical Society, Durham and Chapel Hill, North Carolina, March 26-28, 1953.
5. Russell Baldock, "Analysis with the Mass Spectrometer," presented at the South Carolina section of the American Chemical Society, Aiken, South Carolina, May 12, 1953.

RESEARCH AND DEVELOPMENT STABLE ISOTOPES

P. S. Baker F. R. Duncan
H. B. Greene

METAL REDUCTION AND RELATED WORK

Activities during the current report period have been concerned with the following projects

1. the extension of previous developmental work on the thermal reductions of isotopically enriched lithium salts to the metal and the actual reduction of such salts to fulfill commitments,
2. service functions associated with calutron charge-material preparations,
3. the experimental investigation of isotope separation methods, other than electromagnetic, in such cases where that work could be interpolated in the regular program,
4. the investigation of some of the properties of enriched lithium isotopes.

The successful development of processes for the thermal reduction of lithium chloride in the presence of barium metal is covered in detail elsewhere.[1] The innovations forthcoming since December 1952 include the adaptation of the original batch-type process to an experimental scale, continuous production process, as well as improvements in the original method such as the use of a two-piece liner to facilitate metal recovery. These and other changes resulted from a more complete understanding of the mechanism of the entire reaction, which was gained from experiments suggested by a consideration of the phase diagram of $BaCl_2$-LiCl mixtures.

By utilizing these reduction methods, Li^6 metal (94.5% isotopic purity and over 94% chemical purity) was prepared. In addition, lithium metal was produced for use as an additive to the LiCl charge material regularly used in the calutron.

The equipment used in the lithium metal work has also been employed repeatedly to fuse finely divided $NdCl_3$ powder in order that it might be more effectively used as a starting material for the separation of neodymium isotopes. Associated with the general problem of finding a suitable neodymium charge material for the calutron, reduction of $NdCl_3$ to metallic neodymium was carried out successfully by using calcium metal as the reductant, as suggested by Spedding and Daane.[2]

Inasmuch as adequate amounts of Li^6 and Li^7 metal are available, the group has undertaken measurements of some of the physical and chemical properties, not only for the purpose of obtaining the data but also with the hope that characteristics suggesting potential separation methods might be uncovered or that information fundamentally affecting existing methods might be secured. The first such determination was the melting points of the two isotopes. Both isotopes were found to have a melting point of 179 ± 0.2°C, so apparently no difference in melting points exists within these limits. Chemical purification of some of the salts of these isotopes is currently under way so that the melting points of these compounds may also be ascertained.

A dependable and accurate technique for investigating the solubility of Li^6 and Li^7 in mercury at saturation is now being developed.

(1) P S Baker, F R Duncan, and H B Greene, *Lithium Metal Production*, ORNL CF-53-4-185 (May 1, 1953)

(2) F H. Spedding and A H Daane, *J Am Chem Soc* **74**, 2783 (1952)

In order to obtain metal specimens of sufficient purity for melting-point determinations, an apparatus and procedures for the vacuum distillation of lithium metal were developed and utilized to produce samples with <0.1% total impurities Salient features of the apparatus are its simplicity, efficiency, and ability to prevent loss of valuable, enriched isotopic material. This apparatus has also been used to remove strontium from the barium employed in the thermal reduction of LiCl, in this way, one of the principal contaminants of the lithium so prepared has been eliminated.

In conjunction with the development of the lithium still described above, samples of the normal lithium distillate were taken at varying distances from the heat source and were submitted for isotopic assay. Results of the assays indicate a measurable increase of significant magnitude in the Li^6 concentration as the colder region of the condenser is approached. A preliminary investigation was made of condensers whose lengthwise temperature gradient could be controlled Assays on the samples taken in some of these experiments are, as yet, incomplete.

Thermal diffusion columns charged with aqueous solutions of salts have been investigated to some extent, as have liquid alloys.[3] However, to the best of the authors' knowledge, no such column employing molten lithium metal has been used. For this reason, two such columns have been constructed One has been operated continuously for a number of days with one end at 450°C and the other end at 250°C Isotopic assays of the samples from this column are also incomplete

Another possible separation device, based on surface migration, consisted of small-bore tubing immersed at the lower end in molten lithium Samples obtained from the capillary column are also awaiting assay.

In addition to the projects previously mentioned, this group was concerned with the planning and consulting relative to the relocation of laboratory facilities.

HILSCH TUBE

P. S. Baker W R. Rathkamp

The potentiality of the Ranque-Hilsch (or Vortex) tube as a mass separator has been under investigation for several months. The suggestions that it should work in this way[4,5] have not been entirely clear, therefore additional experiments seemed desirable. Hence, a short-range program was instituted in the Stable Isotope Research and Production Division for the purpose of (1) obtaining data which might justify further development of the tube as a mass separator and/or (2) finding a theory which would permit intelligent interpretation of the results.

It was realized at the start that failure in the first objective would not absolutely rule out the device, since, at best, the significance of only a few of the variables[6] could be determined in the short time available for investigation If it were possible to develop a plausible theory, however, the advisability of further work could be considered on that basis

To date, most of the work by other investigators has been directed toward the use of the Hilsch tube as a refrigeration device, and the theories

(3) K E Grew and T L Ibbs, *Thermal Diffusion in Gases*, chap 8, pp 110 and 114, Cambridge University Press, 1952

(4) W G Stone and T A Love, *An Experimental Study of the Hilsch Tube and Its Possible Application to Isotope Separations*, ORNL-282

(5) K Elser and M Z Hoch, *Z Naturforsch* **6a**, 25 (1951)

(6) Tube geometry (length, diameter, jet orifice, jet angle), tube material, inlet temperature, inlet pressure, properties of gases being used, ratio of volumes of exit streams and their relationship to inlet stream

proposed have, for the most part, been based on superficial measurements of gas flows and temperatures at inlets and outlets and on observation of the "hot-spot."

In 1951, Scheper[7] approached the problem of developing a theory by observing and measuring some of the flow characteristics of the gas within the tube at low pressures. The authors have extended this work to higher pressures and have introduced other measurements and observations.

The first of these experiments employed a tube designed similarly to that suggested by Stone and Love[4] with which they had obtained apparent separation. Air was used as the inlet gas, and numerous samples were taken and were analyzed with a mass spectrometer, with peak-height ratios being used to estimate changes in the composition of the gas. This procedure presumably eliminates errors introduced in other methods of analysis. Some of the typical data are included in Table 5. (It should also be mentioned that recycling the cold-end gas through the tube did not change the ratio, as compared with the inlet gas.)

A mixture of argon and helium was also used, but the separation was no more significant than when air was used, and changes in pressure, tube design, cold-end to hot-end efflux ratio, etc. still gave no better results. In short, no matter what variables were changed, the results were unchanged within the limits of error of the analytical method. Admittedly, the crux of the problem is to be able to predict what change should be brought about by an alteration in a particular variable and then to be able to discern that change. But lack of a good theory and failure to obtain measurable changes made the problem of knowing which way to direct the efforts almost impossible to solve.

Although the absolute values of the ratios as given in Table 5 may vary considerably, it will be noted that each group is consistent within itself and that the values in the last column are indicative of any changes in gas composition for a particular experiment and may be compared with one another.

The differences in ratio values between different experiments are due to long-term variations in mass spectrometer sensitivity. The two or three samples taken during any one experiment were analyzed as rapidly as possible and in random order to minimize any spectrometer errors which might be introduced.

The ratio determinations had average deviations as follows

$$N_2^{28}/O_2^{32} = \pm 0.03 \ (0.6\%)$$

and

$$N_2^{28}/N_2^{29} = \pm 3.0 \ (2\%).$$

An inspection of the last column in Table 5 will show that the most "apparent" enhancements lie within the error of the analytical method and that the direction of enhancement, as indicated by the plus or minus sign, does not seem to follow any consistent pattern. An algebraic summation of the values in the last column for the second group of air samples shows a net positive value for the enhancement of N_2^{28}/O_2^{32} and a net negative value for N_2^{28}/N_2^{29}. These two observations would seem to indicate that there has been no real separation of the nitrogen from the oxygen in air, or of the heavier from the lighter isotope of nitrogen.

The more recent and longer phase of the work has dealt with an attempt to develop a reasonable theory of operation. The most difficult phenomenon to explain is that of the hot-spot. The "explosive diffusion"

(7) G W Scheper, Jr, "Internal Flow Data and a Heat Transfer Theory for the Vortex Refrigerating Tube," *1951 Heat Transfer and Fluid Mechanics Institute*, Preprints of Papers, p 159, Stanford University Press [1952]

TABLE 5. PEAK-HEIGHT RATIOS OBTAINED WITH A HILSCH TUBE

SAMPLE NO	HOT END		INLET		COLD END		HOT RATIO MINUS COLD RATIO	
	N_2^{28} O_2^{32}	N_2^{28} N_2^{29}	N_2^{28} O_2^{32}	N_2^{28} N_2^{29}	N_2^{28} O_2^{32}	N_2^{28} N_2^{29}	N_2^{28} O_2^{32}	N_2^{28} N_2^{29}
Samples Obtained Under Similar Conditions								
7, 8, 9	5 08		5 05		5 05		+0 03	
10, 11, 12	5 33		5 30		5 27		+0 06	
13, 14, 15	4 91		5 01		4 90		+0 01	
16, 17, 18	4 93	134	4 98	137	4 99	135	-0 06	-1 2
24, 29			4 73	136	4 71	132		
Samples Taken at Progressively Larger Hot Flow to Total Flow Ratios								
							COLD RATIO MINUS INLET RATIO	
55, 56			4 66	166	4 63	160	-0 03	-6 5
49, 50			4 69	168	4 68	167	-0 01	-0 3
47, 48			4 67	168	4 73	170	+0 06	+2 3
37, 38			4 52	134*	4 55	134*	+0 03	+0 1
41, 42			4 66	166	4 66	168	0	+1 3
45, 46			4 64	164	4 63	164	-0 01	-0 3

Argon-Helium Mixtures (~ 1 1 Ratio)

	Hot End, A^{40} He^4	Cold End, A^{40} He^4	Hot Ratio Minus Cold Ratio, A^{40} He^4
77, 78, 79	6 57	6 53	+0 04
101, 102	7 19	7 32	-0 13
103, 104	6 39	6 34	+0 05
105, 106	6 25	6 38	-0 13
107, 108	7 05	6 94	+0 11

*Slow-down relay in operation

explanation of Stone and Love does not appear to be entirely conclusive because of the very short mean free path of the molecules and because of the apparent turbulence in the tube. On the other hand, the simple "viscous shear" theory of operation proposed by Ranque,[8] Webster,[9] Fulton,[10] and others does not satisfactorily explain the hot-spot.

By using glass tubes to observe the flow of solids and liquids introduced into the air stream and by using Lucite tubes with numerous probe stations for measuring pressures along the walls, it has been possible to determine that conditions in the tube tend to be nonuniform and unsteady. Under some conditions where there is a hot-spot, there seems to be an almost complete reversal of flow of the gas near the hot-spot, but on the side

(8) G J Ranque, *J phys radium*, series VII, vol 4, part I, Supplement, p 112 S (June 2, 1933)

(9) D S Webster, *Refrig Eng* 59, 163 (1950)

(10) C D Fulton, *Refrig Eng* 59, 473 (1950)

away from the jet. Beyond this, there is very little gas flow or turbulence of any kind. Under slightly different conditions, the position of the reversal point becomes extremely erratic and oscillates up and down the tube - sometimes through a distance of 18 in. and almost instantaneously (faster than can be observed with the eye). A rapid change in the sound of the tube accompanies these oscillations.

Cork balls introduced into the tube have shown angular velocities in excess of 18,000 rpm when the inlet pressure was 25 psig. Beyond that speed, the values became so erratic that measurements with the Strobotac were meaningless.

On the basis of the explosive diffusion theory, maximum enhancement should occur at the hot-spot By means of a hypodermic needle inserted through the wall of a Lucite tube, gas samples were removed in the region of the hot-spot at the periphery and at the axis, the data are shown in Table 6.

An interpretation of these results is rather difficult. It appears that light nitrogen is being concentrated at the hot-spot wall and at the hot end with respect to heavy nitrogen, but it also appears that argon is being concentrated at the hot-spot wall and at the hot end with respect to nitrogen. Also, light nitrogen is being concentrated at the axis with respect to the heavy nitrogen and this is contrary to the theory. In other words, under fixed conditions of operation for a particular tube, it would not be expected that some heavy atoms or molecules would be separated in one direction and that other heavy atoms or molecules be separated in another direction

The significance of the N_2^{29}/A^{40} ratio, if any, is not known at present, but since the values were available, they were included as a matter of interest.

At present, the authors believe that the aerodynamic-thermodynamic explanation,[7,11] seems most plausible, although a complete theory is still lacking. Such an explanation would not support the contention that the Hilsch tube is a good mass separator, except in its capacity as a centrifuge, but neither does the data given here support that contention

[11] J J van Deemter, *Appl Sci Research* **A3**, 174 (1952)

TABLE 6. PEAK-HEIGHT RATIOS OF SAMPLES REMOVED FROM HILSCH TUBE*

PROBE LOCATION	N_2^{28} N_2^{29}	N_2^{28} O_2^{32}	N_2^{28} A^{40}	N_2^{29} A^{40}
Hot end	145	4.88	56.9	0.393
Inlet	140	4.83	65.1	0 466
Cold end	140	4 85	65.3	0.469
At wall	145	4.83	60.2	0.414
1/3 to axis	138	4.79	64.9	0 467
2/3 to axis	139	4.85	59 7	0 430
At axis	141	4.93	64.7	0 459

*As was explained for the data in Table 5, the absolute values here are not important, but the differences are comparable

STABLE ISOTOPE SEPARATION RESEARCH AND CALUTRON OPERATIONS

C. E. Normand, Department Head

INTRODUCTION

Six elements (silicon, boron, lithium, palladium, platinum, and neodymium) that yielded 26 enriched isotopes were processed during the period from January through May 1953. All collections were made by operating personnel under the direction of W. A. Bell, R. L. Caldwell, G. J. Fisher, C. V. Ketron, L. O. Love, and K. A. Spainhour. Equipment maintenance was directed by W. K. Prater.

COLLECTIONS

Silicon, Series GC-XBX. Collection of the isotopes of silicon (Si^{28}, Si^{29}, Si^{30}) was started on December 1, 1952 and completed on January 14, 1953. Equipment and operating procedure remained as reported previously.[1] For this series, 1187 hr of innage[2] was obtained in 1320 operating hours. The highest sustained production rate was 42.9 ma, and the average rate during 29,045 ma·hr of production was 24.5 ma. The following estimated weights, in grams, of silicon isotopes were collected

Si^{28}	28.21
Si^{29}	1.37
Si^{30}	0.86
Total	30.44

Lithium, Series GD-XBX. Collection of lithium isotopes (Li^6, Li^7) was started on January 14, 1953 to produce Li^6 of high isotopic purity, the collection was completed on February 25, 1953.

The charge material was ionized in a medium-temperature Beta-type ion source having a deep arc chamber with reflecting anode, a 1/8-in. ion exit slit, standard zero-degree electrodes, and a 170-mil tantalum filament.

Ions were received in water-cooled copper pockets shielded, as far as possible, from neutral contamination. Ion entry into the Li^7 pocket was through a 1/2-in. defining slot, whereas entry into the Li^6 pocket was through a 1/4-in. slot.

Output during separation was limited to a total of approximately 125 ma of received ion current. In this series, 350 hr of innage was obtained in 458 operating hours. The peak production rate was 140 ma, and the average rate during 31,352 ma·hr of production was 89.6 ma, Li^6 of 99.866% purity was obtained.[3] The following estimated weights, in grams, of lithium isotopes were collected

Li^6	0.82
Li^7	7.23
Total	8.05

Lithium, Series GE-XBX. Collection of the isotopes of lithium (Li^6, Li^7) in Series GE-XBX was started on January 14 and completed on February 25, 1953. The purpose of this collection was to produce lithium of high Li^7 content, and the collecting was accomplished by using a charge of lithium chloride enriched to 99.9% Li^7. The ion source and receiver were the same as those in Series GD-XBX, except that the Li^7-receiver defining slot was reduced to 1/4 in. and the Li^6 slot was increased

(1) *Stable Isotope Research and Production Quar Prog Rep Dec 31, 1952*, ORNL-1483, p 3

(2) Innage is the time during which isotopes are being monitored in the collection.

(3) Reported by Y-12 Spectrometer Laboratory

to 1/2 inch. Also, this collection was made at the same time as that of Series GD-XBX.

During 536 hr of operation, the total production was 30,723 ma·hr in 392 hr of innage, the product purity attained was 99.999% Li^7,[3] and the following estimated weights, in grams, of lithium isotopes were collected

Li^6	0.01
Li^7	8.01
Total	8.02

Boron, Series GF-XAX Collection of the isotopes of boron (B^{10}, B^{11}) was started on January 19 and completed on February 7, 1953. This collection was made in the Alpha channels by using a grid type of ion source with the receiver placed at an 8-in. collection radius. The ions were received in water-cooled copper pockets placed behind 1/4-in. defining slots. Ion beam separation at the receiver was 0.8 inch.

In operation, the boron arc was easily sustained with a BCl_3 charge, and production was better without the nitrogen support. The gradual formation of a deposit on the grid surface facing the arc resulted in a progressive lowering of output. Beam focus was such that approximately 50% of the ions produced entered the receiving pockets. Filament life was approximately 12 hours.

In the series, 256 operating hours resulted in a total production of 18,074 ma·hr during 197 hr of innage. The average production rate was 94 ma, in comparison with an average rate of 25 ma obtained in previous boron collections in which conventional ion sources were used in Beta channels. The following estimated weights, in grams, of boron isotopes were collected

B^{10}	1.58
B^{11}	5.85
Total	7.43

Palladium, Series GG-XBX. The first calutron collection of the isotopes of palladium (Pd^{102}, Pd^{104}, Pd^{105}, Pd^{106}, Pd^{108}, Pd^{110}) was started on February 11 and completed on March 30, 1953. This collection was made by using a metallic palladium charge vaporized at approximately 2100°C in a newly developed, and somewhat novel, ion source. The arc chamber was a 1/2- by 5/8-in. groove machined in a 1- by 1 1/2- by 6-in. graphite block. A trough-like recess along the bottom of the arc cavity held the palladium metal charge. This entire structure was heat shielded by graphite sheets and was heated by electron bombardment from an auxiliary filament. Ion exit slits were either 1/16 or 3/32 in. wide, and standard zero-degree electrodes were used throughout the runs.

Singly charged palladium ions were received in graphite pockets placed behind 1/8-in. defining slots. Space limitation between ion beams prohibited collection of all isotopes in a single receiver, hence in some collections, the pocket for Pd^{105} was omitted, whereas in the others, the Pd^{104} and Pd^{106} pockets were omitted. Operation was quite normal, except that the length of the run was limited by electron-bombardment erosion of the graphite block and the heat control was critical.

In the complete series, 1375 tank hours were utilized in obtaining 439 hr of innage and 4188 ma·hr of production. The average production rate was 9.5 ma, with a peak rate of 37.2 ma. The following estimated weights, in grams, of palladium isotopes were collected

Pd^{102}	0.43
Pd^{104}	2.26
Pd^{105}	1.70
Pd^{106}	4.28
Pd^{108}	5.71
Pd^{110}	2.29
Total	16.67

Platinum, Series GH-XBX The first calutron collection of platinum isotopes (Pt^{190}, Pt^{192}, Pt^{194}, Pt^{195}, Pt^{196}, Pt^{198}) was started on March 24, 1953 and is still in progress.

As in the processing of palladium, electron-bombardment heating is used to vaporize the platinum metal charge. Because of the higher temperature required (about 2300°C) and the condensation of platinum on conventional ion exit slits, the cross section of the arc chamber was changed from rectangular to circular, and the ion exit slit was made an integral part of the heated carbon block. Operation is quiet except for sparking in the region of the auxiliary filament in the early stages of a run. Temperature control is critical.

The highest sustained production rate was 8.8 ma, with the average being 2.7 ma. The length of the run initially was 2 to 3 hr, at present, this has increased to approximately 10 hr, and the production rate is averaging close to 4 ma. The following estimated weights, in grams, of platinum isotopes were collected by May 18, 1953

Pt^{190}	0.03
Pt^{192}	0.30
Pt^{194}	1.11
Pt^{195}	4.30
Pt^{196}	1.00
Pt^{198}	0.73
Pt^{200}(4)	0.03
Total	7.50

Neodymium, Series GI-XAX Collection of neodymium isotopes (Nd^{142}, Nd^{143}, Nd^{144}, Nd^{145}, Nd^{146}, Nd^{148}, Nd^{150}) was started on April 16, 1953 and is still in progress.

Charge material of fused neodymium chloride is being used in a medium-high-temperature ion source operating at approximately 800°C with nitrogen support. A standard arc chamber, a 3/16-in. ion exit slit, standard zero-degree electrodes, and a 170-mil tantalum filament have been used in all runs.

The ions are received in graphite pockets placed behind 1/8-in. defining slots. Operation is accompanied by considerable sparking, the flurries being sensitive to slight variations in temperature. The peak production rate has reached 22.8 ma, and the average rate thus far has been 12 ma. The following estimated weights, in grams, of neodymium isotopes were collected in runs terminating prior to May 18, 1953

Nd^{142}	10.98
Nd^{143}	5.54
Nd^{144}	8.89
Nd^{145}	3.69
Nd^{146}	5.08
Nd^{148}	1.48
Nd^{150}	1.06
Total	36.72

DEVELOPMENT

Developmental work on Alpha equipment has been limited to exploratory runs with grid sources in which carbon dioxide and metallic zinc charges were used. In the first instance, carbon collection was at a short radius, focus was acceptable, but output was below the expected value. In the second case, zinc was collected at standard Alpha radius and with shims present in the tank, focus was extremely poor.

In the Beta equipment, developmental work has been primarily that of designing, fabricating, and testing the ion source used in the processing of palladium and platinum. Limited time has been devoted to diode type of filament operation by O. C. Yonts of the Isotope Analysis Methods Laboratory.

(4) Pocket placed in this position but isotope not known to exist.

STABLE ISOTOPE CHEMISTRY, RESEARCH, AND PRODUCTION

Boyd Weaver, Department Head

INTRODUCTION

The Stable Isotope Chemistry, Research, and Production Department continued its normal functions of supplying charge materials to the calutrons, chemically refining the separated isotopes, and preparing portions of the isotopes for distribution to research institutions. Current activities in the separation of isotopes of the rarer and more expensive elements have necessitated an increased effort in the separation of the rare earths and the recovery of these elements and those of the platinum groups from the calutrons. An extensive chemical program in connection with a special project has been nearly completed.

LOT SUMMARY

Isotope lots on which refinement was completed	20
Lots in process of refinement, May 20	20
Lots awaiting chemical refinement, May 20	15
Samples submitted to mass analysis laboratories	22
Mass analyses reported	20
Lots awaiting mass analysis, May 20	28
Stable isotope shipments and transfers made	115

SPECIAL PROJECTS

W. C. Davis C. F. Harrison
C W. Sheridan R. L. Bailey

Chemical contributions to special research and production projects are described in reports of limited distribution.

CALUTRON SERVICES

W. C. Davis C. W. Sheridan
C. F. Harrison

Preparation of charge materials and other chemical services were supplied for the separation of isotopes of lithium, boron, palladium, platinum, and neodymium.

Palladium was charged into the calutron as the metal and required no preparation. However, palladium is sufficiently expensive that it was desirable to recover as much of it as possible. This involved its separation from large quantities of graphite, copper, and the constituents of stainless steel. A total of 433 g of metal was used as charge material.

All calutron parts containing palladium were washed with nitric acid, and the palladium metal was then dissolved by boiling the acid. Graphite parts were ignited, and the ash was leached with nitric acid. Nitrate ion was removed from the filtered solutions by repeated treatment with hydrochloric acid, and complete oxidation of palladium was ensured by treatment with chlorine. Addition of ammonium chloride gave quantitative precipitation of the palladium as $(NH_4)_2PdCl_6$, as shown by testing with dimethylglyoxime, and palladium metal was obtained by ignition of the salt. Appearance of the metal sponge indicated that still further purification is desirable, the total recovery is not known yet.

Platinum is now being recovered in a similar manner, except that aqua regia is required to dissolve the metal and $(NH_4)_2PtCl_6$ is precipitated from a nitrate solution.

Neodymium is being recovered from the calutron and re-used in order to conserve material and to obtain experience in the recycle of much more expensive rare earths. Purified neodymium oxide is converted to anhydrous chloride and fused to reduce its volume before introduction into charge bottles.

CHEMICAL REFINEMENT

R. L. Bailey W C. Davis

Work was done on the chemical refinement of isotopes of lithium, tin, neodymium, silicon, palladium, and sulfur. Only in the case of tin was a new series completed. After repeated experiences with the difficult separation of this element from the impurities encountered, such satisfactory results have been obtained that a standard refinement procedure has been established

Tin isotopes may be refined by a procedure which includes the following steps

1 The carbon pockets are burned in an oxygen atmosphere at 800°C

2 Tin oxide in the ash is reduced to metal by hydrogen at 550°C.

3. The tin metal is chlorinated, and the $SnCl_4$ is collected in a dilute solution of HCl and H_2SO_4

4 Metastannic acid is precipitated by the addition of NH_4OH in the presence of H_2O_2, centrifuged, and washed with NH_4NO_3 solution

5 The precipitate is dissolved in HCl, complexed by the addition of tartaric acid, and freed of some insoluble hydroxides by their precipitation with NH_4OH. Addition of H_2S, followed by boiling and filtering, completes the purification.

6. Acidification of the filtrate with HCl precipitates the tin as SnS_2 which is filtered hot and washed with NH_4NO_3 solution.

7. Ignition of SnS_2 at 900°C gives SnO_2.

The yields and spectrographic analyses of the latest series are given in Table 7.

SEPARATION OF RARE EARTHS

F. A. Kappelmann F. B. Thomas
F. M. Scheitlin R. J. McAlister

The separation of rare earths by extraction between tributyl phosphate and nitric acid was continued with some increase in effort. Both a 2-in. pulse column with 140 steel plates and a 1-in. Scheibel column with 11 mechanical stages were operated, also, a pseudo countercurrent batch system was started recently.

The pulse column was used to divide 43 kg of samarium-gadolinium concentrate into two fractions. The organic extract containing the greater part of all the rare earths of atomic number above that of europium was further divided into several fractions, some of which were rich in gadolinium while others contained more than 50% dysprosium When the quantities of these fractions became inconveniently small for this equipment, they were set aside, and the first division of the remaining 82 kg of concentrate was begun. An attempt is being made to retain nearly all the europium in the organic extract, the throughput is about 500 g/hr.

Maximum over-all separation factors between dysprosium and gadolinium were about 60. Table 8 gives operating conditions and analytical results for one run. Separations attained were considerably less than those anticipated from this equipment. Increasing the acidity to 12 *N* in the aqueous stream and to 15 *N* in the feed did not give any noticeable improvement in separation.

The Scheibel column was operated to perform the final extractions in the preparation of single kilogram quantities of neodymium, samarium, and gadolinium oxides of about 99% purity It was also hoped that optimum

TABLE 7. PRODUCTION DATA ON TIN ISOTOPES

LOT NO	ISOTOPE	WEIGHT OF SnO_2 (g)	IMPURITIES FOUND (%)										
			Al	Co	Cu	Fe	K	Li	Mg	Na	Ni	Pt	Si
FS 710(a)	112	0 2702			0 04	<0 04	0 01	0 01	<0 04	0 01			0 04
FS 711(a)	114	0 1407			0 04	0 04			<0 04		0 08		<0 04
FS 712(a)	115	0 1139			0 04	0 04			<0 04	0 01			0 04
FS 712(b)	115	0 1361			<0 02						0 08		<0 08
FS 713(a)	116	5 6535			<0 04	0 04			<0 04				0 04
FS 713(b)	116	3 7282			<0 04								
FS 714(a)	117	3 3495			<0 04	<0 04			<0 04				
FS 714(b)	117*	1 8798											
FS 715(a)	118	15 0345	<0 04		<0 04	0 08			<0 04				
FS 715(b)	118*	6 3412											
FS 716(a)	119	5 6257			<0 04				<0 04				
FS 716(b)	119	2 2265			0 04							<0 08	<0 08
FS 717(a)	120	21 1039			<0 04				<0 04				
FS 717(b)	120	7 8745			<0 04								
FS 718(a)	122	0 6684		<0 04						<0 01			0 04
FS 718(b)	122	1 2444			0 08								
FS 719(a)	124	0 7036			0 10	<0 04				0 04			0 08
FS 719(b)	124	1 1673			<0 02								<0 08

*No impurities detected

TABLE 8 FRACTIONATION OF RARE EARTHS

AQUEOUS PHASE		FEED		ORGANIC PHASE	
Conditions					
Throughput 2 2 gal/hr (10 4 *N* HNO_3)		Throughput 2 5 gal/hr containing 20 g/liter in 13 7 *N* HNO_3		Throughput 1 0 gal/hr TBP (3 9 *N* in HNO_3)	
Weight of oxide 1 3 kg		Weight of oxide 2 0 kg		Weight of oxide 0 7 kg	
Analyses					
Oxide	Per Cent	Oxide	Per Cent	Oxide	Per Cent
Sm_2O_3	14	Sm_2O_3	9	Gd_2O_3	8 8
Eu_2O_3	1 6	Eu_2O_3	1 0	Tb_4O_7	8 5
Gd_2O_3	70	Gd_2O_3	48	Dy_2O_3	57
Tb_4O_7	7	Tb_4O_7	8	Y_2O_3	19
Dy_2O_3	7 6	Dy_2O_3	28	Ho_2O_3	3 4
Y_2O_3	0 5	Y_2O_3	7	Er_2O_3	1 5
		Ho_2O_3	1		
		Er_2O_3	1		
		Separation factor	Dy/Gd = 60		

operating conditions could be determined quickly with this column and translated to the pulse column. Operation at high acidities gave separation factors as high as 60 between dysprosium and gadolinium on this short column. Throughput was usually about 20 g/hr. Identical acidities, salt concentrations, and relative flow rates did not result in separations at the same point in the rare-earth series when applied to the two columns.

PUBLICATIONS

Paper accepted for publication

Boyd Weaver, F. A. Kappelmann, and A. C. Topp, "Quantity Separation of Rare Earths by Liquid-Liquid Extraction. I - The First Kilogram of Gadolinium Oxide," to be published in the *Journal of the American Chemical Society*, July or August, 1953.

Papers presented at the 123rd National Meeting of the American Chemical Society, March 16-19, 1953

1. Boyd Weaver, F. A. Kappelmann, F. M. Scheitlin, F. B. Thomas, and A. C. Topp, "Quantity Separation of Rare Earths by Liquid-Liquid Extraction. II - Investigation of the Applicability of the Tributyl Phosphate-Nitric Acid System."
2. Boyd Weaver, "The Separation Factor - A Criterion for Evaluation of Fractional Separation Processes," submitted for publication in *Analytical Chemistry*.
3. Boyd Weaver, "Fractional Separation of Rare Earths by Precipitation with Mandelic Acid,"

submitted for publication in *Analytical Chemistry*.

ISOTOPE SHIPMENTS AND REQUESTS

Preparation for Shipment. One hundred eighteen individual samples were prepared for shipment to laboratories within and outside the jurisdiction of the AEC. Details of the shipments made and the present status of requests for isotopes are given in Table 9.

TABLE 9. SUMMARY OF ISOTOPE SHIPMENTS AND REQUESTS, JANUARY 1 TO MAY 20, 1953

REQUEST NO	REQUESTER	ISOTOPE	LOT NO	QUANTITY (mg)
	Shipments Made			
B-3150S	Oak Ridge National Laboratory	Ge^{73}	FZ 749(a)	30.1
B-3151S	Oak Ridge National Laboratory	Ge^{76}	FZ 751(a)	30 1
B-3152S	Oak Ridge National Laboratory	Ti^{49}	BF 218(ar)	10.4
B-3072	University of Wisconsin	Ce^{138}	FR 707(a)	30 1
B-3115	University of Wisconsin	Ca^{48}	FO 694(a)	20 1
B-3084	Purdue University	Li^{6}	ED 537(a)	10 3
B-3085	Purdue University	Mg^{25}	DZ 520(a)	20.3
B-3086	Purdue University	Mg^{26}	DZ 521(a)	20.4
B-3139	Massachusetts Institute of Technology	Pb^{204}	EO 581(a)	400.1
B-3126S	Brookhaven National Laboratory	Ga^{69}	EI 554(a)	20.3
B-3127S	Brookhaven National Laboratory	Ga^{71}	EI 555(a)	20.1
B-3144S	Argonne National Laboratory	Li^{6}	FI 667(d)	381 2
B-3163	Washington University	S^{33}	CX 392(a)	40.1
B-3195S	Los Alamos Scientific Laboratory	Ti^{47}	EN 577(a)	500.3
B-3119	Purdue University	In^{113}	ER 594(a)	10 3
B-3202S	Oak Ridge National Laboratory	Re^{187}	CP 357(a)	150 0
B-3203S	Oak Ridge National Laboratory	Re^{185}	CP 356(a)	250 3
B-3171	University of California	K^{41}	EY 626(er)	950 2
B-3191S	Ames Laboratory	Nd^{148}	EQ 592(ar)	120.4
B-3197	Massachusetts Institute of Technology	Se^{80}	FG 658(a)	1,001 3
B-3201	University of Michigan	Rb^{87}	EW 620(a)	1,000 5
B-3166	Bartol Research Foundation	Zr^{96}	CK 338(a)	27 2
B-3198	Massachusetts Institute of Technology	Zr^{92}	CK 336(a)	100.3
B-3199	Massachusetts Institute of Technology	Rb^{87}	EW 620(a)	100.4
B-3236S	Oak Ridge National Laboratory	Li^{6}	ED 537(a)	20 3
B-3248S	Oak Ridge National Laboratory	Cd^{108}	CE 315(a)	16.4
B-3221	Massachusetts Institute of Technology	Zr^{94}	EE 542(a)	100.2
B-3274S	Oak Ridge National Laboratory	Li^{7}	GE 767(j)	678.7
B-3266	Carnegie Institute of Washington	Rb^{87}	EW 620(a)	30 6
B-3243	California Institute of Technology	Fe^{54}	FC 634(a)	200 5
B-3244	California Institute of Technology	Fe^{57}	FC 636(a)	200.5
B-3292S	Oak Ridge National Laboratory	Si^{30}	EW 282(a)	100.3
B-3200	Massachusetts Institute of Technology	Sr^{84}	FL 679(a)	75 1
B-3268	University of California at Los Angeles	Mg^{25}	DZ 520(a)	200 7

TABLE 9. (continued)

REQUEST NO.	REQUESTER	ISOTOPE	LOT NO	QUANTITY (mg)
	Shipments Made			
B-3270	University of California at Los Angeles	Mg^{26}	DZ 521(a)	200.2
B-3148S	Ames Laboratory	Li^{7}	EZ 628(e)	300.3
B-3272	Stanford University	Cu^{63}	DU 497(a)	600.7
B-3293	University of Michigan	Ca^{46}	FO 693(a)	10.1
B-3321	Massachusetts Institute of Technology	Ca^{48}	FO 694(a)	15.1
B-3322	Massachusetts Institute of Technology	Rb^{87}	EW 620(a)	100.2
B-3323	Massachusetts Institute of Technology	Sr^{84}	FL 679(a)	40 2
B-3294	University of Chicago	Li^{7}	EZ 628(e)	200.4
B-3330S	Oak Ridge National Laboratory	Li^{7}	EZ-FI 628(f) and 668(g)	28.35 g
B-3306S	Argonne National Laboratory	Zn^{64}	EK 556(a)	2,001.1
B-3307S	Argonne National Laboratory	Zn^{66}	EK 557(a)	2,000.3
B-3308S	Argonne National Laboratory	Zn^{67}	EK 558(a)	800.2
B-3309S	Argonne National Laboratory	Zn^{68}	EK 559(a)	2,000.4
B-3279	Illinois Institute of Technology	Hg^{202}	DR 540(a)	10.8
B-3327S	Ames Laboratory	Nd^{146}	EQ 591(a)	40.4
B-3336S	Argonne National Laboratory	Ga^{71}	EI 555(a)	1,201.4
B-3361S	Westinghouse Electric Corp.	Hf^{174}	ET 602(a)	10.3
B-3349S	University of California	K^{41}	DT 496(a)	351.3
B-3350S	University of California	Sn^{124}	EC 536(as)	500.6
B-3352	Duke University	Cu^{63}	DU 497(a)	7,403.6
B-3353	Duke University	Cu^{65}	DU 498(a)	7,406.4
B-3351	Duke University	Ga^{69}	EI 554(a)	7,402.0
B-3343	Duke University	Pb^{204}	CN 349(ar)	852.2
B-3346	Duke University	Pb^{208}	EO 584(a)	19,046.5
B-3396S	Oak Ridge National Laboratory	Ga^{71}	EI 555(a)	30.7
B-3220	Bartol Research Foundation	Ti^{48}	EN 578(a)	50.1
B-3392	University of Illinois	Zn^{68}	EK 559(a)	500.3
B-3143S	Ames Laboratory	Li^{6}	FY 745(x)	322.2
B-3401	Massachusetts Institute of Technology	Mo^{100}	FP 701(a)	100.1
B-3365	Columbia University	In^{113}	ER 594(a)	400.4
B-3366	Columbia University	In^{115}	ER 595(a)	1,000.2
B-3379S	Brookhaven National Laboratory	Cd^{110}	CE 316(a)	50.3
B-3380S	Brookhaven National Laboratory	Ba^{135}	DG 432(a)	401.0
B-3381S	Brookhaven National Laboratory	Ba^{136}	DG 433(a)	180.3

TABLE 9. (continued)

REQUEST NO.	REQUESTER	ISOTOPE	LOT NO.	QUANTITY (mg)
	Shipments Made			
B-3382S	Brookhaven National Laboratory	Ba^{137}	FU 732(a)	1,000.5
B-3383S	Brookhaven National Laboratory	Ba^{138}	DG 435(a)	1,000.9
B-3407	Indiana University	Te^{130}	CA 299(a)	300 2
B-3408	Indiana University	Rb^{85}	EW 619(a)	300 9
B-3399	Duke University	Cl^{37}	FW 737(a)	5,000.3
	Argonne National Laboratory	Terbium oxide		25.3
B-3431S	Radiation Laboratory, University of California	Nd^{150}	EQ 593(ar)	15.4
B-3418	Massachusetts Institute of Technology	Ca^{48}	FO 694(a)	27.5
B-3369S	Knolls Atomic Power Laboratory	Li^{6}	ED 537(a)	25.1
B-3374S	Knolls Atomic Power Laboratory	Li^{6}	FY 745(x)	25.2
B-3446S	Brookhaven National Laboratory	Hf^{177}	ET 604(a)	788.0
B-3447S	Brookhaven National Laboratory	Hf^{178}	ET 605(a)	1,443.0
B-3448S	Brookhaven National Laboratory	Hf^{179}	ET 606(a)	558.7
B-3449S	Brookhaven National Laboratory	Hf^{180}	ET 607(a)	1,328.4
B-3450S	Brookhaven National Laboratory	Ag^{107}	EA 522(a)	600.0
B-3451S	Brookhaven National Laboratory	Ag^{109}	EA 523(a)	601.3
B-3424	Duke University	Tl^{203}	BY 203(a)	4,518.1
B-3425	Duke University	Rb^{85}	EW 619(a)	2,500.7
B-3478S	Brookhaven National Laboratory	Rb^{87}	EW 620(a)	30.6
B-3432S	Argonne National Laboratory	Br^{79}	EJ 552(a)	50.6
B-3429	Michigan State College	Cu^{63}	AV 161(cu)	100.1
B-3453	University of Michigan	Sb^{121}	AE 93(ar)	201.0
B-3454	University of Michigan	Sb^{123}	AE 94(ar)	200.2
B-3474	Massachusetts Institute of Technology	K^{41}	EY 626(e)	100.4
B-3475	Massachusetts Institute of Technology	Ca^{42}	FF 649(a)	100.3
B-3476	Massachusetts Institute of Technology	Ca^{44}	FF 651(a)	100.4
B-3461	Florida State University	Mo^{92}	AW 163(ar)	201.0
B-3482S	Oak Ridge National Laboratory	Si^{30}	BW 282(a)	100.2
B-3485S	Oak Ridge National Laboratory	Mo^{96}	FP 698(a)	150.6
B-3412	Harvard University	Ga^{69}	EI 554(a)	503.2
B-3413	Harvard University	Zn^{64}	EK 556(a)	1.4
B-3414	Harvard University	Zn^{66}	EK 557(a)	501.0
B-3394	Ohio State University	Ca^{48}	FF 653(a)	50.0

TABLE 9. (continued)

REQUEST NO.	REQUESTER	ISOTOPE	LOT NO.	QUANTITY (mg)
Shipments Made				
B-3395	Ohio State University	Ba^{130}	FT 720(a)	35.8
B-3456	Yale University	Hf^{176}	ET 603(a)	30.8
B-3457	Yale University	Hf^{174}	ET 602(a)	30.5
B-3310S	Argonne National Laboratory	Hg^{201}	DR 489(c)	211.2
B-3442S	Argonne National Laboratory	Hg^{201}	DR 489(d)	184.3
B-3443S	Argonne National Laboratory	Hg^{201}	DR 489(e)	121.4
B-3438	University of Wisconsin	Ca^{42}	EV 614(a)	76.9
B-3439	University of Wisconsin	B^{11}	FV 735(a)	100.0
B-397	University of Wisconsin	Ca^{46}	FO 693(a)	12.1
B-3510	Indiana University	Ge^{70}	FZ 747(a)	503.8
B-3499	Columbia University	Li^{6}	ED 537(a)	174.1
B-3458	Yale University	K^{39}	DA 407(a)	200.7
B-3459	Yale University	K^{41}	DT 496(a)	150.6
B-3483	Massachusetts Institute of Technology	Ca^{44}	EV 616(a)	250 5

Requests on Hand or Held by AEC as of May 20, 1953

REQUEST NO.	REQUESTER	ISOTOPE	QUANTITY DESIRED (mg)
Awaiting purchase order			
B-3146S	Ames Laboratory	Li^{6}	400
B-3147S	Ames Laboratory	Li^{6}	200
B-3217	National Institute of Health	K^{41}	100
B-3431	University of California	Nd^{150}	15
B-3440	Massachusetts Institute of Technology	B^{10}	2,000
B-3462	Florida State University	Mo^{95}	182
B-3463	Florida State University	Mo^{100}	203
B-3470	Bell Telephone Laboratories	Li^{6}	1
B-3471	Bell Telephone Laboratories	Cu^{65}	3
B-3472	Bell Telephone Laboratories	Ni^{61}	1
B-3489	University of Michigan	Te^{130}	200
B-3490	University of Michigan	Te^{128}	200
Inventory insufficient as to quantity or quality			
S-3281	Oak Ridge National Laboratory	B^{11}	10,000
B-269	Princeton University	B^{11}	500
S-581	Brookhaven National Laboratory	K^{40}	10

TABLE 9. (continued)

Requests on Hand or Held by AEC as of May 20, 1953			
REQUEST NO	REQUESTER	ISOTOPE	QUANTITY DESIRED (mg)
B-1062	Kansas State College	K^{40}	1000
B-1161	Princeton University	K^{40}	150
B-1819	University of Illinois	Ce^{136}	10
B-2392	Ohio State University	Ba^{130}	100
B-2581S	Argonne National Laboratory	Mo^{94}	600
B-3062	University of Illinois	Si^{29}	100
B-3249	Brookhaven National Laboratory	Ni^{64}	50
B-3267	University of California	Si^{29}	200
B-3269	University of California	S^{33}	200
B-3310	Wright Air Development Center	Hg^{201}	1000
B-3333	Columbia University	Ni^{64}	100
B-3372	Princeton University	Li^{6}	150
B-3394	Ohio State University	Ca^{48}	50
B-3398	Duke University	K^{41}	3000
Requests for isotopes which have not been separated			
S-148	Argonne National Laboratory	$Ir^{191,193}$	20 to 30 each
S-297	Argonne National Laboratory	$Pd^{102,104}$ $Pd^{105,106}$ $Pd^{108,110}$	200 each
S-342	Oak Ridge National Laboratory	$Gd^{158,160}$	10 each
S-343	Oak Ridge National Laboratory	$Dy^{158,160}$	10 each
S-361	Argonne National Laboratory	Os^{192}	10
B-2333	Princeton University	Gd^{152}	50
B-2577S	University of California	Gd^{152}	10
B-3069	University of Michigan	Gd^{158}	100
B-3290	Yale University	Gd^{152}	100
B-3291	Yale University	Gd^{154}	100