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1954

QUARTERLY PROGRESS REPORT

STABLE ISOTOPE RESEARCH

AND PRODUCTION DIVISION

JULY 1, 1952 to SEPTEMBER 30, 1952

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Index No. ORNL-1434
This document contains 44 pages.
This is copy 34 of 78, Series A.

Subject Category: Isotope Separation

QUARTERLY PROGRESS REPORT
Stable Isotope Research and Production Division
July 1, 1952 to September 30, 1952

DECLASSIFIED

CLASSIFICATION CHANGED TO
BY AUTHORITY OF AEC Declass List #5
BY: R. Morrison 7/26/57

C. P. Keim, Director

[redacted]

November 7, 1952

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

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Index No. ORNL-1434
Isotope Separation

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Stable Isotope Research and Production Division quarterly progress 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
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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
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STABLE ISOTOPE SEPARATION RESEARCH AND CALUTRON OPERATIONS

C E Normand, Department Head

INTRODUCTION

During the first quarter of fiscal year 1953, isotopes of chlorine, neodymium, germanium, and titanium were collected. A new type of unit suitable for the separation of isotopes of low mass number and incorporating radical changes in both source and receiver design, was built and put into operation in the Alpha channels.[1] In further preparation for the collection of isotopes of the inert gases by the method of Koch[2] an experimental receiver was built, and isotope recovery and purification techniques were developed. Preliminary work was done on a long range project of measuring transference numbers of various isotopes.

COLLECTIONS

Four elements were processed yielding nineteen enriched isotopes These collections, and the special collections now in progress in the Alpha channels 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.

Chlorine, Series FW-XBX

Collection of the isotopes of chlorine (Cl35 and Cl37) in the Beta channels was started July 1 and completed July 25, 1952.

Both chlorine (Cl_2) and boron chloride (BCl_3) were used as externally fed charge. Operation with chlorine was unsatisfactory because of corrosion of the vapor control valve. Boron chloride was satisfactory in this respect, and also gave higher chlorine ion output and process efficiency.

---

1. A project report covering the work being done in the Alpha channels will be issued at a later date
2. Koch, J., Nature 61, 566; April 10, 1948.

The source used was of the low temperature, double gas feed type equipped with a shallow, channelled arc chamber having a floating anode and 3/16-inch ion exit slit. Standard, zero degree electrodes were used.

The isotopes were collected in copper pockets filled with turnings or chips of magnesium or barium metal and placed behind 1/2-inch defining slits. Barium proved to be superior to magnesium as a collecting material in that less loss of metal by sputtering occurred when barium was used and the chlorine retention was increased from about 50% for magnesium to nearly 100% for barium.

A total monitored ion collection of 36,922 man hours during 629 hours of innage yielded the following estimated weights of chlorine isotopes:

Cl35	35.07 gm
37	11.92 gm
Total	46.99 gm

Neodymium, Series FX-XAX

The isotope of neodymium (Nd142, Nd143, Nd144, Nd145, Nd146, Nd148, and Nd150) were collected in the Alpha channels during the period July 2 to July 18, 1952.

Neodymium chloride ($NdCl_3$) charge was processed at 600-700°C in a standard, medium temperature source having a 3/16-inch ion exit slit and standard, zero degree electrodes The isotopes were collected in carbon pockets placed behind 1/8-inch defining slits.

Slow pump down to avoid loss of charge material during evacuation, the incidence of heavy sparking, low production rate, and monitoring uncertainties resulting from samarium contamination of the charge were the principal difficulties encountered in processing this element.

A total monitored collection of 1367 man hours during 147 hours of innage yielded the following estimated weights of neodymium isotopes:

Nd142	2.29 gm
143	1.07 gm
144	1.68 gm
145	0.65 gm
146	1.04 gm
148	0.34 gm
150	0.27 gm
Total	7 34 gm

Germanium, Series FZ-XBX

Collection of the isotopes of germanium (Ge70, Ge72, Ge73, Ge74, and Ge76) was carried out in the XBX channels during the period July 28 to August 28, 1952

Germanium tetrachloride ($GeCl_4$) was fed from an external supply to a standard, low temperature source. Both deep arc chambers with floating anodes and shallow, channeled chambers were used with little difference in output being observed. Ion exit slits varying in width from 3/16 to 5/16-inch were used. Best overall operation was obtained with a 1/4-inch slit and a deep arc chamber having a floating anode.

The isotopes were collected in carbon pockets placed behind 1/8-inch defining slits The appearance of needle-like growths of collected material at the lips of the pockets, Figure 1, leads one to expect low receiver retention for this collection.

A total monitored collection of 45, 181 man hours during 879 hours of innage yielded the following estimated weights of germanium isotopes:

Ge70	25.23 gr
72	34.80 gr
73	8.85 gr
74	44.87 gr
76	8.69 gr
Total	122.44 gr

Titanium, Series GA-XBX

Collection of the isotopes of titanium (Ti46, Ti47, Ti48, Ti49, and Ti50) was started on August 28 in the Beta channels and is still in progress.

Titanium tetrachloride ($TiCl_4$) from an external supply was fed to a standard, low temperature source having a shallow, channeled arc chamber with floating anode and 1/4-inch ion exit slit. Standard, zero degree electrodes and carbon receiver pockets mounted behind 1/8-inch defining slits were used. Operation was quite smooth.

FIGURE I. GERMANIUM GROWTHS ON RECEIVER POCKET

Through September 30, a total monitored collection of 40,075 man hours during 792 hours of innage had yielded the following estimated weights of titanium isotopes:

Ti46	4.82 gr
47	3.51 gr
48	56.13 gr
49	3.62 gr
50	3.37 gr
Total	71.45 gr

DEVELOPMENT

Controlled Collection (P S Baker, G M Banic, W A Bell, H.B Greene, L O Love, and W K Prater)

Production units of the type designed near the end of last quarter[3] have been built and are now being used in sustained production. This production program has utilized all Alpha time since July 18, and represents the major effort of the Separation Research and Calutron Operations Department during the current quarter.

A receiver designed for collecting the isotopes of inert gases has been built and will be used in exploratory collections at an early date. Techniques have been worked out for degasing targets by high frequency heating.

Transference Numbers of Isotopes (P S Baker and W R Rathkamp)

Work was started on a long range project of measuring transference numbers of various isotopes. A cell was constructed, and a constant current supply was developed. The supply consists of a half-wave, voltage-regulated power supply and a modified Micromax (Model C) controlling the grid bias to a pentode tube whose plate current is applied to the cell. Preliminary trials indicate that any value of current between 2 and 10 ma is controlled to within 0.02 per cent for a resistance change as great as 5000 to 55,000 ohms

The next step in the program is the development of a photoelectric device for automatically timing the passage of the moving boundry between two points.

3. Quarterly Progress Report. Stable Isotope Research and Production Division. ORNL-1356.

STABLE ISOTOPE CHEMISTRY, RESEARCH AND PRODUCTION

Boyd Weaver, Department Head

INTRODUCTION

The chief production functions of the Isotope Chemistry Research and Production Department are the supply of suitable charge materials for isotope separation by the calutrons, chemical refinement of enriched isotopes and the preparation of materials for their mass analysis. Chemical services and unusual compounds are also supplied to other departments of the Stable Isotope Research and Production Division.

The department carries on research activities in various fields related to isotope production and use, with current interest centered around the rare earth elements.

All refined isotopes are stored in the chemistry depositories, and the preparation of all samples for shipment is performed by personnel of this department. Unused portions and many processed residues of isotopes are returned by research institutions for restoration in the laboratory's stock of isotopes. Some of these require reprocessing to make them suitable for reuse, others are too small quantities for further handling.

QUARTERLY SAMPLE SUMMARY

Isotope samples on which refinement was completed	6
Samples in process of chemical refinement, September 30	19
Samples awaiting chemical refinement, September 30	19
Samples submitted to Mass Analysis Laboratory	25
Mass analyses reported	26
Samples awaiting mass analysis, September 30	35
Stable Isotope shipments and transfers made	66

SPECIAL PROJECTS

(W C Davis, C W Sheridan, and C F Harrison)

Much of the effort of the department was devoted to special production and research activities which will be reported elsewhere.

CALUTRON SERVICES

(C W Sheridan and C F Harrison)

Preparation of charge materials and other chemical services were supplied for the separation of isotopes of neodymium, chlorine, germanium and titanium.

CHEMICAL REFINEMENT

(R. L Bailey and C F Harrison)

Work was done on the chemical refinement of isotopes of five elements: calcium, tin, boron, barium, and chlorine. In two cases a whole series of isotopes were completed.

Boron was refined by a procedure which included the following steps:

1. Remove boron from copper pockets mechanically and with HNO_3.
2. Dissolve boiling HNO_3 in a flask fitted with a reflux condenser.
3. Remove copper and iron by precipitation with NaOH.
4. Evaporate at a low temperature until solids are dry and add a little CH_3COOH.
5. Transfer to a distilling flask connected to a collection flask fitted with a reflux condenser and half filled with dilute HCl.
6. Add methanol and heat as long as methyl borate distills This occurs at 65°C. Cool, add methanol, and distill repeatedly until all boron is removed With large samples it is necessary to adjust acidity and to reduce the volume by evaporation of water.

7 Complete the hydrolysis of the collected methyl borate by addition of water Transfer to a boron free (preferably fluorothene) beaker and evaporate liquids at a low temperature This requires several days

8 Repeat the process if analysis shows it to be necessary In the present instance this was necessary for only the B 11 sample Production data for the pair of isotopes are tabulated below·

Isotope	10		11	
Weight of H_3BO_3	12.5754 g		11.5194 g	
	Impurities found (per cent)			
	Mg	<0.04	<Cu	0.04
	Si	<0.08	Na	0.01

The yield of B 10 was 73% of the estimated production, while the yield of B 11 was only 14%.

Chlorine isotopes were collected in copper pockets containing barium metal in some cases and magnesium metal in others. Observation of the calutron operation indicated that retention on the magnesium was very poor

The procedure for refinement of the barium collection was as follows·

1. The barium metal and $BaCl_2$ were dissolved in water and the solution was filtered and heated until it was reduced to half volume.

2. $Ba(OH)_2$ crystallized out on cooling and was filtered and washed until free of chloride. The quantity was large.

3 The filtrate was reduced to half volume and another crop of $Ba(OH)_2$ crystals were removed. These required redissolving and recrystallization to obtain all of the chloride.

4. Na_2CO_3 was added to the combined filtrates to remove barium.

5. The filtrate, containing Na_2CO_3 and the chlorine as NaCl, was evaporated to near dryness and transferred to a distilling flask fitted with a thistle tube and a source of air.

6. Sulfuric acid was added and the HCl was distilled and collected in a flask of water.

7. The HCl was exactly neutralized with NaOH, evaporated to dryness and melted in a platinum dish.

8. The cooled solid was dissolved in water, filtered and evaporated to dryness.

The procedure for refinement of the magnesium collection was as follows:

1. The magnesium chunks, turnings and powder were allowed to react with water until most of the magnesium had been converted to $Mg(OH)_2$.

2. The solids were filtered and washed with H_2O until free of chloride. The quantity was large.

3. The filtrate was made slightly alkaline with Na_2CO_3, evaporated to a low volume and filtered.

4. This filtrate was evaporated to near dryness, transferred to a distilling flask and treated as in the case of chlorine collected on barium.

Results of the two kinds of collection were as follows:--

Collection on barium:

Isotope	35	37
Weight of NaCl (g)	14.5870	7.9138
Percentage of estimated production	101.7	167 1

Impurities found (per cent)

B	0.01	Fe	0.04
Ca	<0.08	K	0.04
K	0.06	Li	<0.01
Li	<0.01		
Si	0.2		

Collection on magnesium

Isotope	35	37
Weight of NaCl (g)	29.0588	9.3892
Percentage of estimated production	63.4	59.8

Impurities found (per cent)

Al	<0.04	K	0.04
B	0.008		
Cu	0.02		
K	0.02		
Mn	0.01		
Ni	0.04		
Si	0.15		

The quality of isotopic separation has not been determined yet, but the high yields on barium bring those collections under suspicion. On the other hand, there was considerable loss from the magnesium. This was observed as sputtering during the collection. Cross contamination could have occurred There is still need for a more satisfactory method of collecting chlorine isotopes.

ACTIVITIES ASSOCIATED WITH MASS ANALYSIS

(F M Scheitlin)

Samples of isotopes of the five elements calcium, lithium, tin, boron and barium were prepared in suitable form for mass analysis.

SEPARATION OF RARE EARTHS

(F A Kappelmann, F B Thomas, F M Scheitlin, and A C Topp*)

The separation of rare earths by liquid-liquid extraction was continued and more effort was applied to the investigation of fundamentals.

All recent production scale separations have been made with a York-Scheibel Laboratory column with 11 mechanical stages and a diameter of

* Research Participant, Georgia Institute of Technology

one inch. With total throughputs of about 1500 ml per hour and maximum agitation, about 4 actual stages are achieved. The agitation system of this type of column is its weakest point.

The rare earth feed has been supplied to this column as nitrates in 13N HNO_3. The aqueous stripping solvent was 10N HNO_3. These two solvents were used in the ratio necessary to give a mixture approximately 12N in HNO_3. The organic solvent was a 60:40 mixture of tributyl phosphate and varsol equilibrated with 12N nitric acid. Thus the sections above and below the feed entry differed with respect to both the acidity and the rates of flow of the aqueous phases. By adjustment of the rates of flow of the phases it was possible to divide between any two adjacent rare earths and to make this division point the same in both sections.

The rare earth material used had already been greatly enriched in gadolinium by means of a batch extraction system. It was passed through the column to obtain separation first on the samarium side and then on the terbium side of gadolinium. In general separation factors between adjacent elements appear to be about 1.5 between tributyl phosphate and 12N HNO_3 and a little less for 10N HNO_3.

As a result of the operation of batch and continuous extraction systems there is now on hand more than a kilogram of material with a gadolinium oxide content about 95%. The contaminants are terbium, which is not particularly objectionable in the separation of gadolinium isotopes, and samarium, which can be removed in any of several ways. There is also material which will be a very rich source of the yttrium earths. The following tables give average production data from some typical production experiments. The analyses are averages of spectrographic analyses of several samples taken throughout the experiments.

Experiment A

Flow Rates (ml/hr)		
Feed	550,	11.5 g oxide
Organic	390	
Aqueous	380	

Analyses

	Feed	Organic	Aqueous
Total Oxide (g)	1423	530	893
	Rare Earth Distribution (per cent)		
Sm_2O_3	2	<1	3
Gd_2O_3	66	34	85
Tb_4O_7	7	12	4
Dy_2O_3	17	32	7
$(YE)_2O_3$*	8	22	1

* The symbol YE is used for yttrium and elements above dysprosium

Experiment B

Flow Rates (ml hr)

Feed	700, 11 5 g oxide
Organic	390
Aqueous	340

Analyses

	Feed	Organic	Aqueous
Total Oxide (g)	863	317	546
	Rare Earth Distribution (per cent)		
Sm_2O_3	3	<1	5
Gd_2O_3	84	71	93
Tb_4O_7	7	13	2
Dy_2O_3	5	14	-
$(YE)_2O_3$	1	2	-

Experiment B

Flow Rates (ml/hr)

Feed	550, 11 5 g oxide
Organic	780
Aqueous	380

Analyses

	Feed	Organic	Aqueous
Total oxide (g)	475	432	43
	Rare Earth Distribution (per cent)		
Sm_2O_3	8	4	45
Gd_2O_3	90	93	55
Tb_4O_7	2	2	-
Dy_2O_3	0 5	0 5	-
$(YE)_2O_3$	-	-	-

The original starting material contained about 30% Gd_2O_3. Previous fractionation by crystallization and the operation of a batch extraction system had segregated most of the gadolinium into several fractions with Gd_2O_3 contents above 50%. From information gained in these experiments it would be possible to set up a much better batch arrangement than was used here.

Since these separations were made, 275 pounds of oxide has been obtained containing 25% Gd_2O_3. Since it also contains 1.5% Eu_2O_3, separations are planned so as to obtain nearly all of this along with the Gd_2O_3 Several successful experiments have been performed in which division was made between samarium and europium. Feed rates have been increased to 50 grams of oxide per hour without greatly decreasing the separation factor. The large scale separation will be transferred to a pulse column when one is available.

Recently an increased amount of research has been done on the determination of distribution coefficients and the effect of various conditions on these values. Most of this work has been done with neodymium and samarium. Results may be summarized as follows:

1. In the system (60% TBP - 12N HNO_3) there is a separation factor of 2.8 between Sm_2O_3 and Nd_2O_3 over a wide range of concentration and temperature.

2. Distribution coefficients decrease in value as temperature increases.

3. Distribution coefficients increase slightly in value as salt concentration increases - provided the organic solvent is freshly prepared.

4. Solvent which has been used in the column gives distribution coefficients approximately 2 5 times as high as those obtained with freshly prepared solvent.

5. The increase in distribution coefficients is not due to formation of butyl phosphoric acids by hydrolysis, since the effect is not lost by washing with alkalies.

6. With "used" solvent distribution coefficients decrease as concentration of salts increases.

7. Attempts to synthesize the "used" solvent by treatment of new solvent with water or acid or by aging have caused no apparent alteration in the extracting ability of the solvent.

8 While the "used" 60% solvent gives distribution coefficients approximating those of new 95% TBP, there is no other evidence that Varsol is removed from the mixture to this extent.

A discussion of production results was given as a paper at the 122nd National Meeting of the American Chemical society at Atlantic City, N. J., on September 16, 1952. This has been rewritten for circulation as a project report[4] and for submission for publication in the Journal of the American Chemical Society. Topp[5] has also written a summary of his research during the summer.

---

4. Weaver, Boyd, F. A. Kappelmann, and A. C. Topp, ORNL-1408, "Quantity Separation of Rare Earths by Liquid-Liquid Extraction."
5 Topp, A. C., ORNL-1409, "Liquid-Liquid Extraction of Neodymium and Samarium Nitrates."

ISOTOPE SHIPMENTS AND REQUESTS

Preparation for Shipment

Sixty-six individual samples were prepared for shipment to laboratories within and outside of the Atomic Energy Commission. Details of shipments during the quarter and the present status of requests for isotopes are given in Table I.

Stable Isotope Sales (Fees)

On the basis of the nominal charge of $50 made to non-commission users of stable isotopes for individual shipments, the following summary has been compiled·

	April 1 to June 30, 1952	July 1 to September 30, 1952
Transfers within AEC	$1600.00	$2100.00
Cash Sales (Fees)	2150.00	1200 00
Total Sales (Fees) and Transfers to Date	$77,750.00	$81,050 00

TABLE I

SHIPMENTS OF STABLE ISOTOPES DURING JULY, AUGUST, AND SEPTEMBER, 1952

Request Serial No	Requestor	Isotope	Series No	Sample No	Quantity Shipped (mg)	Date Shipped
B-2765	University of Michigan	V 50	FM	683(b)	50.5	7-7-52
B-2779	University of Pennsylvania	Pb 207	BO	259(a)	300 7	7-7-52
B-2780	University of Pennsylvania	Pb 208	BO	260(a)	252 5	7-7-52
B-2820S	Oak Ridge National Laboratory	Sn 124	EC	536(as)	49 2	7-8-52
B-2823S	Oak Ridge National Laboratory	Sn 114	EC	528(a)	11.2	7-11-52
B-2832S	Oak Ridge National Laboratory	Sn 114	EC	528(s)	10.3	7-15-52
B-2833S	Oak Ridge National Laboratory	Sn 112	EC	527(au)	22 1	7-15-52
B-2812S	Knolls Atomic Power Laboratory	Ti 50	EN	580(a)	15.1	7-15-52
B-2813S	Knolls Atomic Power Laboratory	Cr 54	EU	612(a)	17.4	7-15-52
B-2814S	Knolls Atomic Power Laboratory	Zr 92	EE	541(a)	15.8	7-15-52
B-2815S	Knolls Atomic Power Laboratory	Fe 57	IM	459(a)	18 2	7-15-52
B-2816S	Knolls Atomic Power Laboratory	Fe 58	FN	688(i)	17 6	7-15-52
B-2786	University of Michigan	Cl 37	DH	438(a)	150 5	7-17-52
B-2787	University of Michigan	Ni 62	FJ	672(a)	100 7	7-17-52
B-2788	University of Michigan	Ni 64	FJ	674(a)	100 7	7-17-52

Request Serial No	Requestor	Isotope	Series No	Sample No	Quantity Shipped (mg)	Date Shipped
B-2789	University of Michigan	Zn 64	EK	556(a)	200 8	7-17-52
B-2842S	Oak Ridge National Laboratory	Tl 203	BX	284(a)	2,903 6	7-21-52
B-2843S	Oak Ridge National Laboratory	Tl 203	CH	326(a)	1,587 1	7-21-52
B-2844S	Oak Ridge National Laboratory	Tl 205	BU-3	277(a)	4,245 7	7-21-52
B-2845S	Oak Ridge National Laboratory	Tl 205	BY-3	287(a)	2,705 5	7-21-52
B-2825S	Brookhaven National Laboratory	Ni 61	DF	424(a)	40 0	7-23-52
B-2808	Washington University	Zr 96	EE	543(a)	91 4	7-28-52
B-1709S	Argonne National Laboratory	Ni 64	FJ	674(a)	175.2	8-5-52
B-2847	Georgia Institute of Technology	Br 79	EJ	552(a)	50 6	8-5-52
B-2848	Georgia Institute of Technology	Br 81	EJ	553(a)	50.6	8-5-52
B-2799	Mass Institute of Technology	Zr 92	CV	383(a)	1,003.1	8-7-52
B-2800	Mass Institute of Technology	Se 77	CY	399(a)	300 5	8-7-52
B-2801	Mass Institute of Technology	Zn 67	EK	558(a)	301 5	8-7-52
B-2802	Mass Institute of Technology	Ti 50	EN	580(a)	150.7	8-7-52
B-2836	Mass. Institute of Technology	Se 80	FG	658(a)	50 5	8-8-52
B-2837	Mass Institute of Technology	Sn 120	EC	534(a)	50 8	8-8-52
B-2838	Mass Institute of Technology	Cd 114	CE	320(a)	50.2	8-8-52
B-2839	Mass Institute of Technology	Sm 154	EM	574(a)	50 9	8-8-52
B-2867S	Oak Ridge National Laboratory,	Li 6	ED	537(a)	50.3	8-8-52
B-2868S	Oak Ridge National Laboratory	Li 7	EZ	628(e)	2,000 6	8-8-52
B-2866S	Los Alamos Scientific Laboratory	Zn 68	EK	559(a)	40 9	8-12-52
B-2758S	Ames Laboratory	Pb 204	EO	581(a)	500 3	8-15-52
B-2857	University of Southern California	Si 29	AI-AJ	104-107(a)	10.6	8-15-52
B-2883S	Ames Laboratory	Mg 24	DZ	519(a)	2,000 3	8-27-52
B-2879S	Brookhaven National Laboratory	Cr 50	EU	609(a)	100 8	8-28-52
B-2880S	Brookhaven National Laboratory	Cr 52	CD	310(a)	100 6	8-28-52
B-2881S	Brookhaven National Laboratory	Cr 53	CD	311(a)	100 6	8-28-52
B-2882S	Brookhaven National Laboratory	Cr 54	EU	612(a)	50 6	8-28-52
B-2912S	Oak Ridge National Laboratory	Ge 70	BD-BE	205-210(a)	100.2	9-3-52
B-2913S	Oak Ridge National Laboratory	Ge 72	BD-BE	206-211(a)	100.6	9-3-52
B-2914S	Oak Ridge National Laboratory	Ge 73	BD-BE	207-212(ar)	100 4	9-3-52
B-2915S	Oak Ridge National Laboratory	Ge 74	BD-BE	208-213(a)	100 5	9-3-52
B-2917S	Oak Ridge National Laboratory	Zr 90	EE	539(a)	100 4	9-3-52
B-2918S	Oak Ridge National Laboratory	Zr 91	CK	335(ar)	100 7	9-3-52
B-2919S	Oak Ridge National Laboratory	Zr 92	EE	541(a)	100 3	9-3-52
B-2920S	Oak Ridge National Laboratory	Zr 94	EE	542(a)	100 6	9-3-52
B-2921S	Oak Ridge National Laboratory	Zr 96	CK	338(ar)	20 7	9-3-52
B-2925S	Oak Ridge National Laboratory	Zr 96	AA	84(a)	22.1	9-3-52
B-2933S	Oak Ridge National Laboratory	Li 6	FI	667(d)	202 0	9-4-52
B-2930S	Oak Ridge National Laboratory	Hg 202	DR	490(e)	50.5	9-5-52
B-2931S	Oak Ridge National Laboratory	Cr 54	EU	612(a)	40 1	9-5-52
B-2896	Mass Institute of Technology	Cu 63	DV	497(a)	2,002 7	9-9-52
B-2897	Mass Institute of Technology	Cu 65	DV	498(a)	2,001.0	9-9-52
B-2873	Naval Research Laboratory	Ni 62	FJ	672(a)	400 8	9-9-52
B-2934S	Oak Ridge National Laboratory	Sr 84	FL	679(a)	50 5	9-11-52
B-2928S	Brookhaven National Laboratory	Re 185	CP	356(a)	20.5	9-19-52
B-2929S	Brookhaven National Laboratory	Re 187	CP	357(a)	20.5	9-19-52
B-2942	Washington University	Ti 48	EN	578(a)	3,000 6	9-23-52
B-2960	University of Michigan	W 186	EL	565(a)	100 2	9-24-52
B-2976S	Oak Ridge National Laboratory	Cu 63	DU	497(a)	2,000 8	9-29-52
B-2978S	Radiation Lab , Univ. of California	Zn 67	EK	588(a)	25 6	9-30-52

UNFILLED REQUESTS ON HAND SEPTEMBER 30, 1952

Requests for isotopes which have not been separated

Request Number	Date	Requestor	Isotope	Quantity Desired (mg)
S-148	10-21-47	Argonne National Laboratory	Ir 191	20-30
S-148	10-21-47	Argonne National Laboratory	Ir 193	20-30
S-297	10-2-49	Argonne National Laboratory	Pd 102, 104, 105, 106, 108, 110	200 ea.
S-342	3-3-49	Oak Ridge National Laboratory	Gd 158, 160	10 ea
S-343	3-3-49	Oak Ridge National Laboratory	Dy 158, 160	10 ea

Requests awaiting replenishment of inventory (quantity insufficient)

S-324	3-2-49	Oak Ridge National Laboratory	Cl 37	3,000
S-328	3-2-49	Oak Ridge National Laboratory	B 11	10,000

Requests awaiting Purchase Orders

B-2688	5-8-52	Columbia University	Cr 50	100
B-2840S	7-22-52	Argonne National Laboratory	Hf 180	50
B-2841S	7-22-52	Argonne National Laboratory	Ti 50	10
B-2872S	8-15-52	Argonne National Laboratory	Mo 100	200
B-2586S	8-18-52	Argonne National Laboratory	Mo 100	200
B-397	9-16-52	University of Wisconsin	Ca 46	12
B-736	9-16-52	University of Chicago	Ca 46	28
B-2944S	9-19-52	Argonne National Laboratory	Sb 123	1,000
B-2945S	9-19-52	Argonne National Laboratory	Hg 198	700
B-2946S	9-19-52	Argonne National Laboratory	Hg 199	340
B-2947S	9-19-52	Argonne National Laboratory	Hg 200	1,000
B-2948S	9-19-52	Argonne National Laboratory	Hg 202	1,000
B-2949S	9-19-52	Argonne National Laboratory	Hg 204	1,000
B-2950S	9-19-52	Argonne National Laboratory	Hg 204	10
B-2956	9-19-52	Vanderbilt University	Hf 174	20
B-2966	9-30-52	University of California	Cr 53	440
B-2967	9-30-52	University of California	Ca 43	85

Request with Purchase Order awaiting replenishment of inventory

B-269	3-17-48	Princeton University	B 11	.500

Requests held by AEC Isotopes Division

S-361		Argonne National Laboratory	Os 192	10
S-483		Brookhaven National Laboratory	Ba 132	100
S-581		Brookhaven National Laboratory	K 40	10
B-875		University of Illinois	Ba 132	10
B-1062		Kansas State College	K 40	1,000
B-1161		Princeton University	K 40	150
B-1606		Naval Medical Research Laboratory	Zn 66	3,000

Request Number	Date	Requestor	Isotope	Quantity Desired (mg)
B-1819		University of Illinois	Ce 136	10
B-2007S		Brookhaven National Laboratory	Ba 132	10
B-2333		Princeton University	Cd 152	50
B-2392		Ohio State University	Ba 130	100
B-2396		Argonne National Laboratory	Ge 76	50
B-2401		Argonne National Laboratory	Nd 150	20
B-2577S		University of California	Gd 152	10
B-2581S		Argonne National Laboratory	Mo 94	600
B-2900S		Knolls Atomic Power Laboratory	Li 7	50,000
B-2916S		Oak Ridge National Laboratory	Ge 76	100

ISOTOPE ANALYSIS METHODS LABORATORY

J R McNally, Jr , Department Head

Nuclear Resonance (H E Walchli and H W Morgan)

Numerous nuclear resonance measurements have been made on Se77 in various compounds Magnetic shielding effects in H_2SeO_3 versus H_2Se contribute a 0. 1504% shift of the resonance. Results are

$$\nu\, Se^{77}/\nu_D 2 = \begin{cases} 1.2421 \pm 0\ 0001 & \text{in } H_2Se \\ 1.0015 \pm 0.00005 & \text{in } H_2SeO_3 \end{cases}$$

$$\nu\, Se^{77} \text{ in } H_2SeO_3/\nu Se^{77} \text{ in } H_2Se = 1.001504.$$

Search for the resonance of U235 in liquid UF_6 was postponed when the quartz sample tube ruptured at 43°C during a pre-run heat trial. Adequate precautions had been taken to prevent loss of the enhanced material.

A compilation of nuclear magnetic dipole moments was initiated during this quarter. Much new unpublished data in this field is being included The preliminary draft is expected to be completed shortly and will include resonance frequency ratios, stated tolerances, compounds investigated, and method of detection. The contribution of chemical and temperature shifts and nuclear shielding effects will be discussed.

No additional investigations have been made of "double-quantization" of nuclei in applied external magnetic fields and directed internal electric fields.[6] Volkoff et al.,[7] have recently studied this effect in single crystals as a function of angle about the crystal symmetry axis.

Microwave Spectroscopy (H W Morgan and J H. Goldstein*)

The pure rotational spectrum of vinylacetylene has been investigated in a Stark effect microwave absorption spectrograph. Five weak lines,

6. Walchli, H. E. and H. W. Morgan, see Quarterly Report ORNL-1356, August 5, 1952.
7. Volkoff, Petch and Smellie, Can J. Res. 30, 270 (1952).

* Consultant, Emory University , Atlanta, Georgia

comprising the J=2 to J=3 group, were found and identified on the basis of estimated rotational constants and qualitative Stark effects Table II lists the observed spectrum. Frequency measurements are good to 0.05 megacycles.

TABLE II

MICROWAVE ROTATIONAL SPECTRUM OF J=2 TO J=3 TRANSITIONS IN VINYLACETYLENE

Transition	Frequency
$2_{02} \rightarrow 3_{03}$	27212 71
$2_{11} \rightarrow 3_{12}$	27845 35
$2_{12} \rightarrow 3_{13}$	26600.00
$2_{20} \rightarrow 3_{21}$	27237 09
$2_{21} \rightarrow 3_{22}$	27226 03

The data reveals an appreciable centrifugal distortion in the vinylacetylene molecule. Rotational constants have been calculated to minimize errors from this perturbation. The value of (b - c) was determined from $\nu_2 - \nu_3$, δ from $\nu_4 - \nu_5$, and (b + c) from $\nu_1 + \nu_4 - \nu_5$. The final results are

$$(b + c) = 9074.59 \quad \text{Mc}$$

$$(b - c) = 415.12 \quad \text{Mc}$$

$$\delta = 0.008842.$$

The J=3 to J=4 transitions have been observed also. Preliminary calculations indicate that either this group cannot be satisfied by the simple distortion theory or a measurement error has been made The 3 to 4 frequencies are being remeasured. Work on the centrifugal distortion and on the Stark effects in the 2 to 3 group is continuing.

Spectro-Isotopic Analysis (D D. Smith, G K Werner, O. B. Rudolph, and Z. Combs)

A constant current power supply for excitation of the hollow cathode source has been applied to the lithium problem. It is planned to integrate this into the spectro-isotopic analysis technique by conversion from constant current operation to constant lithium intensity operation.

Results on a recent group of samples submitted for both mass spectrometric analysis and spectro-isotopic analysis are as given in Table III. The standard deviation, σ, between methods is ± 0.25% and the 95 per cent confidence level is ± 0.53%. The bias is 0 07%.

TABLE III

COMPARISON OF MASS SPECTROMETRIC AND OPTICAL SPECTRO-ISOTOPIC ASSAY OF LITHIUM

Sample	Mass Spectrometer Abundance, Li 7	Optical Spectro-Isotopic Abundance, Li 7	Difference
10-34L	92.00 %	92 10 %	0.10
10-36L	91 80	91 60	0 21
10-37L	93 51	93.70	0 19
10-38L	91 79	91.95	0 16
10-39L	93 50	93 90	0 40
10-40L	92 17	92.40	0.23
10-41L	93 24	93 60	0.36
10-42L	92.00	92 30	0 30
9-52L	91 63	91.55	0 08
9-53L	93 67	93.45	0.22
9-54L	91 83	91 65	0.18
9-55L	93.82	93.90	0.08
9-56L	91.58	91.40	0 18
9-57L	93.78	94 30	0 52
9-58L	91 52	91.65	0.13
9-59L	93.95	93 85	0 10
9-60L	91 60	91.50	0.10

Optical Spectroscopy (P M Griffin, G L Stukenbroeker and O C Yonts)

Difficulties experienced earlier in Zeeman studies have been traced to an induced distortion of the spectrograph due to the magnetic materials used in construction. Equilibrium is attained in approximately 3 hours after the magnetic field has been turned on, during which time spectra have shifted approximately 0.1 mm or 0.05 A. This effect is illustrated in a line of neon in Figure 2. Such drifts limit the spectrographic resolution to less than 100,000 for long exposure.

The magnetic field determination is based on the resonance doublet of potassium at 7665 A and 7699 A. These lines, separated by 57.7 cm^{-1}, introduce negligible Paschen-Back effect at the field strengths used. In addition, the K lines are intrinsically more sharply defined than the Na principal series doublet formerly used for field calibration.[8] Resulting field determinations are given in Table IV. The anomalous g factor correction permits the evaluation of true g values which are related to the Landé g factors by the expression $g' = g_L + 0.00229\,(g_L - 1)$.

TABLE IV

FIELD DETERMINATIONS BY ZEEMAN EFFECT OF POTASSIUM DOUBLET

Transition	Uncorrected Field	Field Corrected for Anomalous g Factor
$^2S_{\frac{1}{2}} - {}^2P^o_{\frac{1}{2}}$	25050 oersteds	25021 oersteds
$^2S_{\frac{1}{2}} - {}^2P^o_{1\frac{1}{2}}$	25010	24991
	weighted average	25001 ± 50 oersteds

Preliminary measurements of these and other lines indicate that g values may be measured to ± 0.004 units. Zeeman studies of uranium give about fifteen lines, not previously classified,[9] in the wavelength range 7000 to 8700 A

Tests on the feasibility of using an echelle spectrograph for isotopic analysis of uranium show that all isotopic components of a sample containing 8.39% U238, 0.84% U236, 89.34% U235, and 1.43% U234 were

8. See Quarterly Report, ORNL-1356, August 5, 1952.
9. See The Chemistry of Uranium, NNES-VIII-5 (1951).

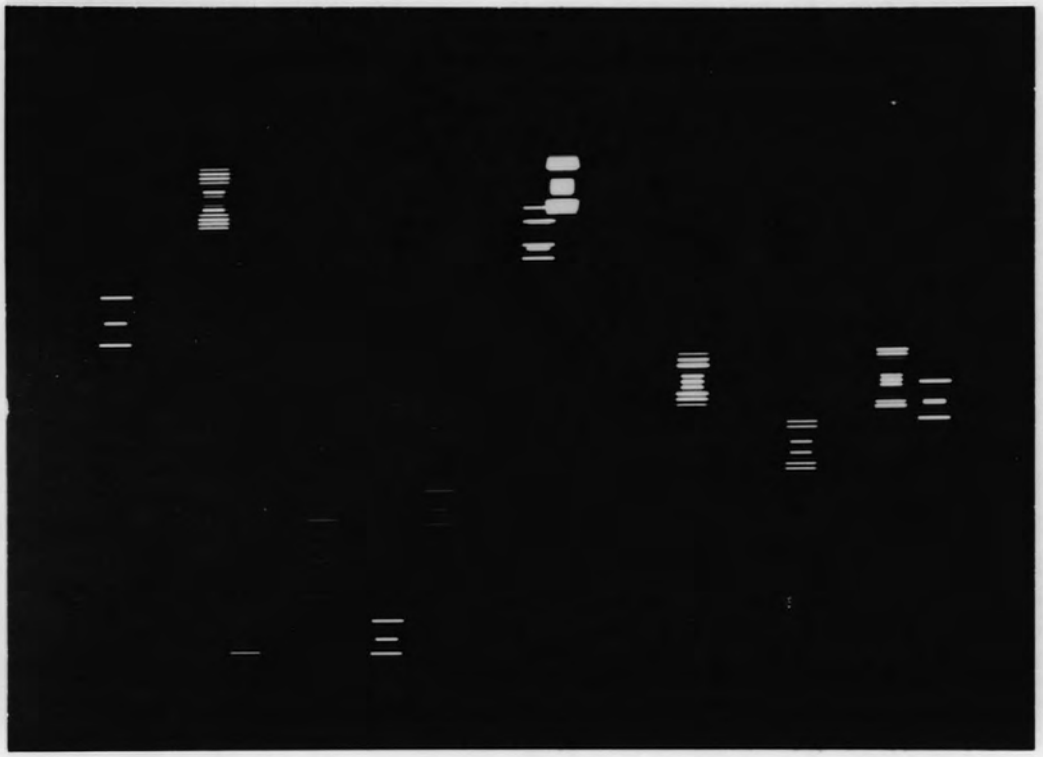

FIGURE 2.

DISPLACEMENT OF ZEEMAN COMPONENTS DUE TO MAGNETIC DISTORTION OF THE ECHELLE SPECTROGRAPH

THE π COMPONENTS (SHORT LINES) WERE PHOTOGRAPHED 15 MINUTES AFTER THE START OF THE EXPOSURE FOR THE σ COMPONENTS (LONG LINES)

readily detected in the 4244 A line group. Hyperfine resolution of U235 lines using the echelle spectrograph is limited to four components or less. Presumably, the lower resolution (300, 000 vs 600, 000 for the Fabry-Perot) plus the considerable quadrupole perturbation from the U235 nucleus contribute to this limitation.

Isotopic spectrum shifts in thorium (Th230 and Th232) electron configurations are shown in Figure 3. The level shifts have been correlated to zero for the smallest level displacement, i. e., in Th II (Group A) to level $fd^2\ {}^4G_{3\frac{1}{2}}$, in Th II (Group B) to level $16l_{2\frac{1}{2}}$. Datum for this latter level appears to be lower than other data by about 0. 05 cm^{-1} and hence comparison of shifts in Group A with those in Group B may contain an error of this magnitude. Consideration of intensities, g values and level splittings point to strong configuration interactions between certain of these levels, especially $ds^2\ (a^2D_{1\frac{1}{2}})$ and $d^2s\ (a^4F_{1\frac{1}{2}})$ which also show almost identical isotope shifts.

Zeeman data[10] show a large mutual sharing of g factors (-0. 161 and + 0. 186 Landé g units, respectively). Intermediate coupling calculations including configuration interaction in the group by Eisenberg[11] indicate that the $d^2s\ (a^2D_{1\frac{1}{2}})$ level contains 46. 3% of the $d^2s\ (a^4F_{1\frac{1}{2}})$ eigenfunction and only 26. 9% of the $ds^2\ (a^2D_{1\frac{1}{2}})$ eigenfunction. Such mixing of configurations makes it difficult to interpret isotope shift data and also accounts for the difficulty in assigning meaningful LS quantum character and configuration character to energy levels in the heavy atoms.

Spectrochemistry (J A. Norris, M R Skidmore, C E Pepper and Z Combs)

Development work on the analysis of Sr in Ba metal, Hf in ZrO_2, U in ore concentrates and fuel mixtures, impurities in ionium (Th230), and specification analysis of stainless steels has been carried out Rare earth studies have been extended to include erbium, terbium and holmium in the range 1 to 20%. The limit of error of these latter analyses appears to be ± 10%. Sampling rates for complete rare earth analyses, including yttrium and lanthanum, of neodymium, samarium and gadolinium base materials have been reduced to about three man hours on single samples and less than one man hour per sample on groups of five or more.

A total of 7603 individual element determinations were made during this quarter or 3. 5 determinations per man hour.

10. McNally, J. R., Jr., J. Opt. Soc. Am. 35, 390 (1945).
11. Eisenberg, Y., Physica 18, 177 (1952).

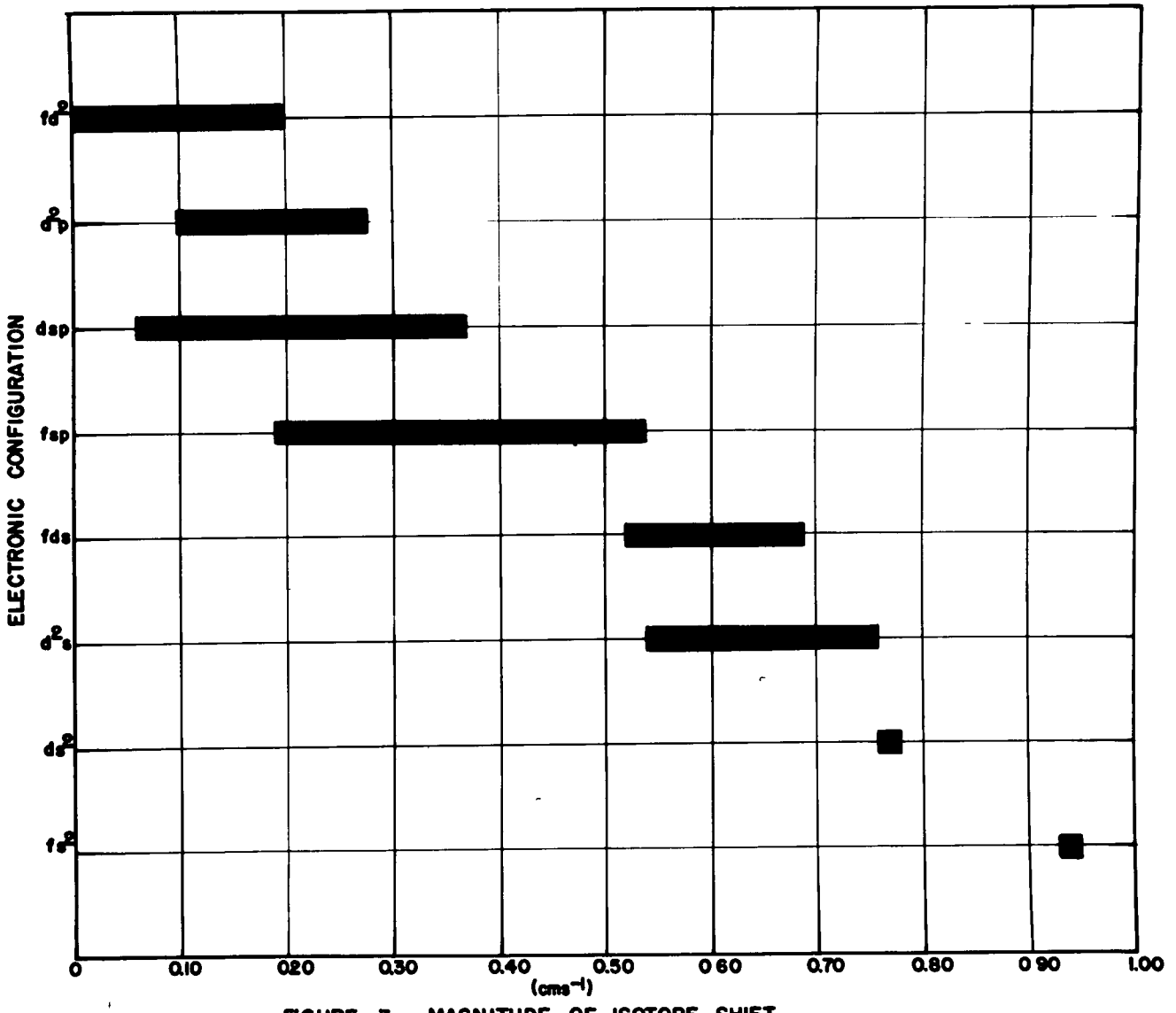

FIGURE 3 MAGNITUDE OF ISOTOPE SHIFT

X-Ray Spectroscopy (W F. Peed, H W Dunn and W B. Wright, Jr *)

An X-ray fluorescence method for analysis of zirconium in U_3O_8 has been developed The range of standards is 1% Zr to 5% Zr. Measurement of intensity ratio of Zr K_{α_1, α_2} with respect to UL_{β_2} is made There is a slight contribution of UL_{β_6} to the zirconium intensity (see Figure 4).

The limit of error for a single determination is ± 4% of the amount present; analysis time is twenty minutes. In general, the presence of impurities in concentrations up to 40% have no influence on the analysis when proper background correction is made (see Figure 5). Table V compares X-ray analyses versus independent colorimetric analyses.

TABLE V

COMPARISON OF X-RAY FLUORESCENCE AND COLORIMETRIC ANALYSIS METHODS FOR ZIRCONIUM IN URANIUM OXIDE

Sample	X-Ray	Colorimetric**	% Deviation
1	2 39 %	2.36 %	1.3 %
2	2.42	2.42	0 0
3	2.45	2.41	1.6
4	1.97	2.00	1 5
5	3 00	2.90	3.4
6	2.18	2 17	0.5
7	2 93	2.94	0.3
8	2.79	2 76	1.1
9	2 25	2 27	0 9
			s = ± 1.6 %

** Work done by H. G. King, Y-12 Analytical Laboratory.

More than 300 samples were investigated by X-ray crystal structure methods. These included uranium-beryllium fluoride phases and lithium-sodium-potassium fluochromate phases as well as fuel and corrosion product identifications.

* On loan from Y-12 Analytical Laboratory

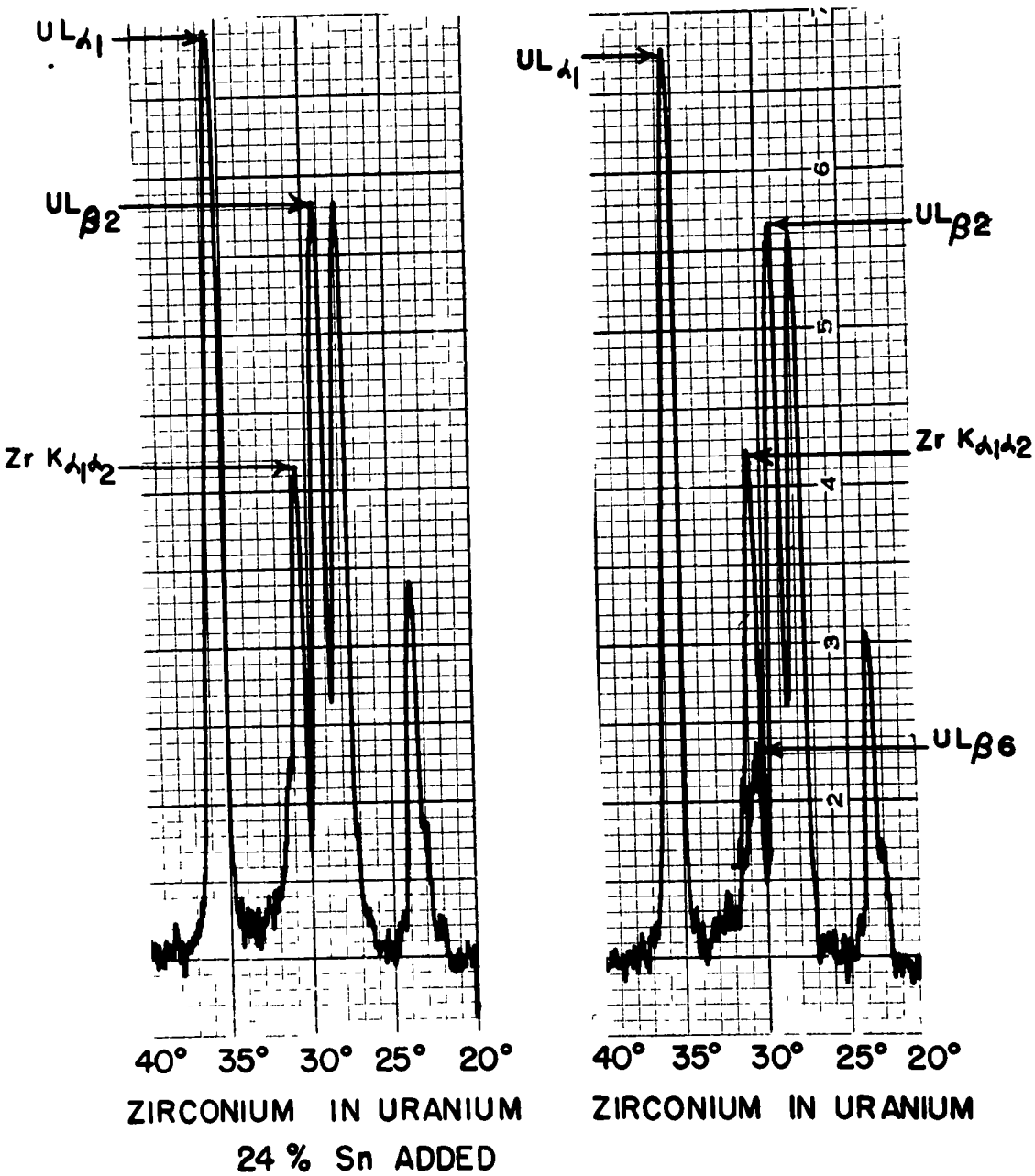
UL$_{\alpha 1}$
UL$_{\beta 2}$
Zr K$_{\alpha 1 \alpha 2}$
40° 35° 30° 25° 20°
ZIRCONIUM IN URANIUM
24 % Sn ADDED
UL$_{\alpha 1}$
UL$_{\beta 2}$
Zr K$_{\alpha 1 \alpha 2}$
UL$_{\beta 6}$
6
5
4
3
2
40° 35° 30° 25° 20°
ZIRCONIUM IN URANIUM

FIGURE 4.

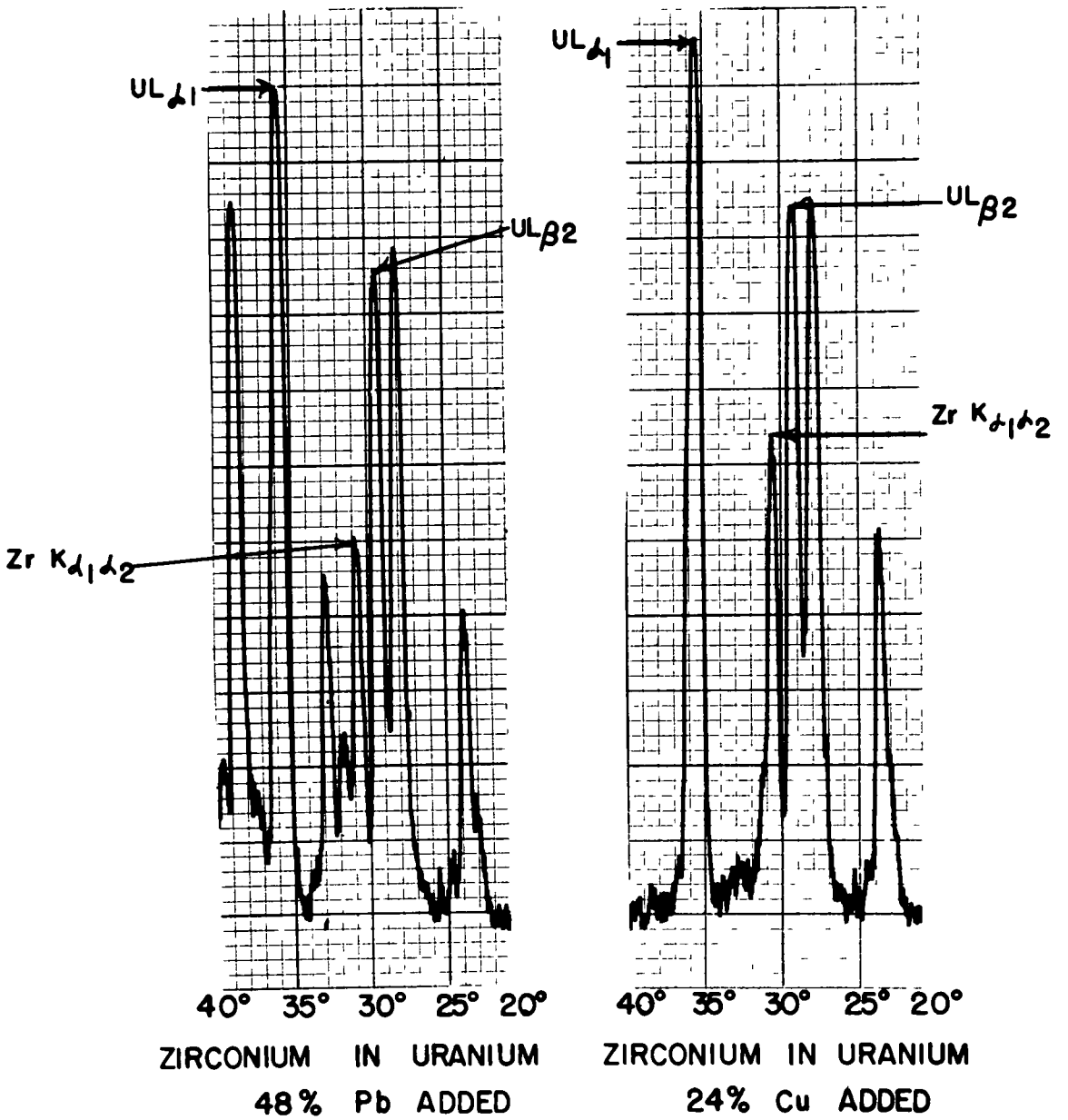
ULα_1
ULβ_2
Zr K$\alpha_1\alpha_2$
40° 35° 30° 25° 20°
ZIRCONIUM IN URANIUM
48% Pb ADDED
ULα_1
ULβ_2
Zr K$\alpha_1\alpha_2$
40° 35° 30° 25° 20°
ZIRCONIUM IN URANIUM
24% Cu ADDED

FIGURE 5.

Reports and Papers in Preparation

1. Morgan, H. W., and J. H Goldstein, "Chemical Aspects of Microwave Spectroscopy."

2. Morgan, H. W., and J. H. Goldstein, "Microwave Spectrum of Vinylacetylene."

3. Stukenbroeker, G. L., and J. R. McNally, Jr., "Isotope Shifts in Thorium - Th230 and Th232."

4. McNally, J. R., Jr., G. K. Werner, and D. D. Smith, "Further Investigations of Spectro-Isotopic Analysis of Lithium."

5. Griffin, P M., R A. Loring, and J. R. McNally, Jr., "The Use of an Echelle Spectrograph in the Investigation of Zeeman Spectra."

6. Smith, D. D., "Isotope Spectrum Shift Data on Uranium Spectrum Lines."

7. Peed, W. F., L. E. Burkhart, R. A. Staniforth, and L. G. Fauble, Joint ORNL-Mound Laboratory report, "The X-Ray Spectra of Polonium-Atomic Number 84."

Reports Submitted for Publication

1. Spitzer, E. J., and D. D. Smith, "Spectrochemical Analysis of Zirconium Oxide," to be published in Applied Spectroscopy.

2. Werner, G. K., "Semi-Automatic Recording of Wavelength Data," to be published in Review of Scientific Instruments.

Reports Published and Papers Presented

1. Norris, J. A., and C. E. Pepper, "Quantitative Spectrochemical Analysis of Rare Earth Mixtures," Analytical Chemistry 24, 1399-1403 (1952).

2. Walchli, H. E., and H. W. Morgan, "Magnetic Shielding Effects in Compounds of Vanadium," Phys. Rev. 87, 541 (1952).

MASS SPECTROMETER LABORATORY

Russell Baldock, Department Head

INTRODUCTION

A new high temperature ion source oven has been developed for use in mass spectrometry, thus enabling the investigation of refractory materials such as the oxides of uranium. A quantitative method of analysis for uranium pentafluoride in uranium tetrafluoride has been perfected. Techniques have also been developed for studying the mechanism of corrosion of stainless steel. The new laboratory has been completed and the General Electric analytical mass spectrometer is operating satisfactorily

HIGH TEMPERATURE ION PRODUCTION

Ion Source Oven (Joe R. Walton and Russell Baldock)

Most of the research undertaken this quarter was made possible by the development of an extremely high temperature ion source oven. A direct heating type oven, Figure 6 was constructed from tantalum metal and this makes it possible to heat materials to a temperature that approaches the melting point of tantalum (2850°C). The oven is small, contains no thermal insulating material and thereby is free of troublesome outgassing. The heater is mounted on a subassembly which is readily attached to and removed from the ion source, thus providing easy change of samples. Due to the favorable sample location, the ion generating efficiency has shown considerable improvement over previous equipment. Power for heating is readily supplied by a single six volt storage battery. A detailed report is being prepared on this development.

Ionization Chamber (George Wells)

A complete redesign of the ionization case subassembly of the ion source unit has been completed and the new components are in operation. The major aims in the redesign were to simplify the assembly procedure, to provide for various types of sample systems, and to maintain the present accurate jig alignment of the subassembly with the other components of the source. Provisions were made for introducing the sample via the standard rear entrance tube for gas samples and a high temperature oven or a filamentary resistance heated oven for solid samples It is now possible to remove any of these sample holding systems and introduce fresh

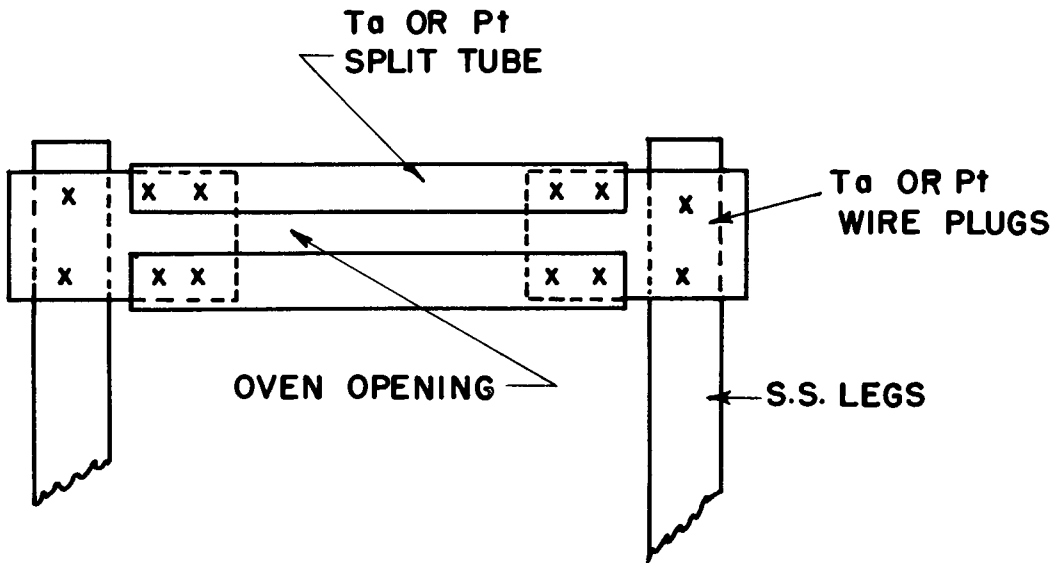

FIGURE 6. MASS SPECTROMETER OVEN

samples without disturbing the pre-jigged alignment of the rest of the ion source unit. A report on this development is in progress

Temperature Measurement (L. O Gilpatrick)

The ion source end plate of the mass spectrometer vacuum system was modified to allow the incorporation of a viewing window. This window now allows the direct measurement of source temperatures with an optical pyrometer during operation. This procedure of concurrent temperature measurement has greatly increased the value of the data obtained at elevated temperatures

Twenty-four investigations have been made in the mass spectrometer with the above described high temperature equipment The ion source efficiency is greatly improved as illustrated by the fact that less than one and one-half milligrams of uranium tetrafluoride (UF_4) was operated at 800°C for 30 hours without sample exhaustion.

REACTOR ASSOCIATED STUDIES

Analysis for Uranium Pentafluoride (L O Gilpatrick, H. E. Carr*, Russell Baldock)

The previous quarterly report recorded the discovery by this laboratory of the contamination of uranium tetrafluoride (UF_4) with small amounts of uranium pentafluoride (UF_5). The UF_5 originates as a product of the reaction of UF_4 with UO_2F_2. A time integral method of analysis has now been developed for quantitatively measuring the contamination and a separate report on this analytical method is in preparation

Other Uranium Compounds (J. R Sites)

The methodical investigation of the more refractory compounds of uranium has continued. When uranium dioxide (UO_2) was examined in a tantalum oven of the type previously described in this report, detectable uranium ion currents were found at 1300°C. Ions of tantalum oxide (TaO_2) and UO_2 became prominent at 1500°C. The presence of tantalum oxide while unexpected, was not surprising since tantalum is a well known getter for oxygen The thermally produced positive ions were examined with the surprising result that the only ions present were those of UO^+ and UO_2^+ while there was a complete absence of U^+ ions.

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* Consultant, Alabama Polytechnic Institute, Auburn, Alabama

When U_3O_8 was examined, a rise and fall of O^+ and O_2^+ ion peaks at 750°C indicated thermal decomposition of the U_3O_8. At 850°C, UO_3^+ ions and its dissociation products were recorded. Above 1200°C, the UO_3^+ ions disappeared leaving UO_2^+ ions and its dissociation products as were previously found for UO_2 Thermal ions due to UO^+ and UO_2^+ were also found. When uranyl fluoride (UO_2F_2) was examined, ions of UF_4 appeared at 600°C At approximately 800°C, various oxides and oxyfluorides of tantalum appeared. Previous work in this laboratory[12] has shown that heating UO_2F_2 gives rise to UF_5. Apparently, any oxygen or fluorine freed from either of these compounds by thermal decomposition or by ionization, readily reacts with the tantalum oven. It was noted that at higher temperatures with very intense thermal ions of UO^+ and UO_2^+, we observed for the first time a very small amount of U^+ ions

A sample of standard commercial UF_4 material, not pretreated to remove UO_2F_2 was investigated in a tantalum oven. As was observed with UO_2F_2, there was heavy interference from the oxides and oxyfluorides of tantalum. An oven constructed of platinum gave typical UF_4 dissociation with no interference. The future examination of uranium fluorides will be restricted to platinum ovens.

When a sample of very pure uranium trifluoride (UF_3) was examined, a nearly pure UF_4 dissociation pattern was obtained at 800°C. There was indication that there was a slight excess of UF_2^+ ions from the UF_3, but further data is needed to establish this point.

Uranyl sulphate (UO_2SO_4) has also been investigated At 800-900°C, SO_2 and SO_3 ion currents are observed. Around 1500-1600°C ions originating from both UO_2 and UO_3 are observed At 1800°C, a very clean UO_2 dissociation pattern is observed and the thermal ion emission is quite abundant

Nickel Fluoride (J R. Sites)

In an effort to find the reason for some non-stoichiometric compounds of nickel and fluorine prepared in the Materials Chemistry Division, several tests were made on their NiF_2 material. The prepared NiF_2 was carried to charge exhaustion in an older model source oven which went only to 750°C. The residue of this test was subsequently examined at 1100°C in the new type oven heater and proved to be nickel oxide (NiO). Evidence from this and subsequent tests proved that above 1100°C, the NiO dissociates by thermal decomposition to nickel and oxygen. It was also noted that the oxygen comes off as O_2.

12. Gilpatrick, L. O., Russell Baldock, and J. R. Sites, "Mass Spectrometer Investigations of UF_3 " ORNL-1376.

Stainless Steel (R. E Rummel*, H E Carr**, Russell Baldock)

A number of investigations have been made on type 347 stainless steel. The specimens were small rectangular slivers spotwelded to electrical leads and were heated by power supplied by a six volt storage battery. When a sample which had had no special treatment, that is, it was used as received, was heated to 1100°C, chromium ions appeared In order to get peaks of appropriate size, the temperature was advanced to approximately 1200°C. Both chromium and iron peaks were present at this temperature They both increased in size with time, but the iron increased at a greater rate than the chromium. The iron peak at first was smaller than the chromium peak, but it ultimately overtook the chromium peak. This is a non-reversible process.

A sample of 347 stainless steel which had been treated to remove as much of the oxide coating as possible was examined in a manner similar to that above. In this case, both the chromium and iron peaks appeared at approximately 1100°C. The iron peak at the beginning was larger than the chromium and remained that way throughout the experiment.

A sample of 347 stainless steel which had been treated to remove as much as possible of the oxide from the surface was subsequently corroded in water at 250°C. This sample behaved similarly to the untreated sample first mentioned above.

Data was also taken over a period of 22 hours on an untreated sample of 347 stainless steel. During the initial part of the test, the chromium peak height decreased while the iron peak height increased. Subsequently, the iron peak height stayed essentially constant while the chromium peak height continued to decrease. Finally both the iron and chromium peak heights increased but the iron peak height increased at a greater rate than at any previous time.

From the above information, it appears that the following takes place. The surface of the stainless steel has an oxide coating which is predominately Cr_2O_3. The formation of the Cr_2O_3 layer causes a certain depletion of the chromium in the metal layer next to the oxide coating. When this material is heated, the chromium in the oxide will migrate to the surface of the oxide and escape Positive thermal chromium ions were detected while neither iron nor nickel thermal ions were noted Also, while the chromium is migrating through the lattice of the Cr_2O_3, iron from the iron

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* Consultant, Vanderbilt University, Nashville, Tennessee

** Consultant, Alabama Polytechnic Institute, Auburn, Alabama

rich metal adjacent to the oxide will tend to migrate through the oxide layer At first, the amount of chromium escaping will be larger than the amount of iron escaping. At a temperature around 1000°C, the vapor pressure of iron is much greater than that of chromium, therefore, iron would tend to escape into the oxide at a greater rate than the chromium. It will be recalled that in the 22 hour run, the chromium peak height decreased during at least the first half of the run (chromium poor metal layer behind oxide, therefore replacement of chromium in oxide was small). In the same run (temperature supposedly constant), the tendency for chromium to decrease was reversed and both chromium and iron increased in amounts to the end of the run The iron increased at a greater rate than the chromium. The increase in the amount of chromium being due to the layer of metal next to the oxide becoming richer in chromium because the iron content was decreasing at an appreciable rate.

Full interpretation of this data is limited by the fact that the temperature of the test specimen gradually increased during the test. However, a method has already been developed to remove this limitation.

FISSION PRODUCTS

Samarium (J R Sites and Russell Baldock)

A preliminary check has been made on the operating characteristics of samarium oxide (Sm_2O_3) and the precision with which isotopic abundances could be measured using thermal ion emission The abundances found were well within the probable error reported by Inghram [13] This work was done in preparation for examining some irradiated samarium 144.

NEW FACILITIES

A General Electric analytical mass spectrometer has been received and placed in satisfactory operation (see Figure 7 and Figure 8). Installation of the chemical laboratory facilities has also been completed (see Figure 9 and Figure 10). The two hydrogen-deuterium machines have been redesigned and the construction is more than fifty per cent complete. A gas handling system has been built for deuterium studies and a technique was developed for making extremely small holes in tantalum discs to be used as gas leaks. A report is being prepared on this work. An air drying chamber was added to the automatic liquid nitrogen dispenser to prevent the formation of ice in the dispensing tube. This has eliminated the only source of trouble experienced in over a year's operation. A report is in preparation of this equipment.

13. Inghram, M. G., D. C. Hess, Jr., and R J. Hayden, Phys. Rev. 73, 180 L (1948).

FIGURE 7. MASS SPECTROMETER CONTROL PANEL

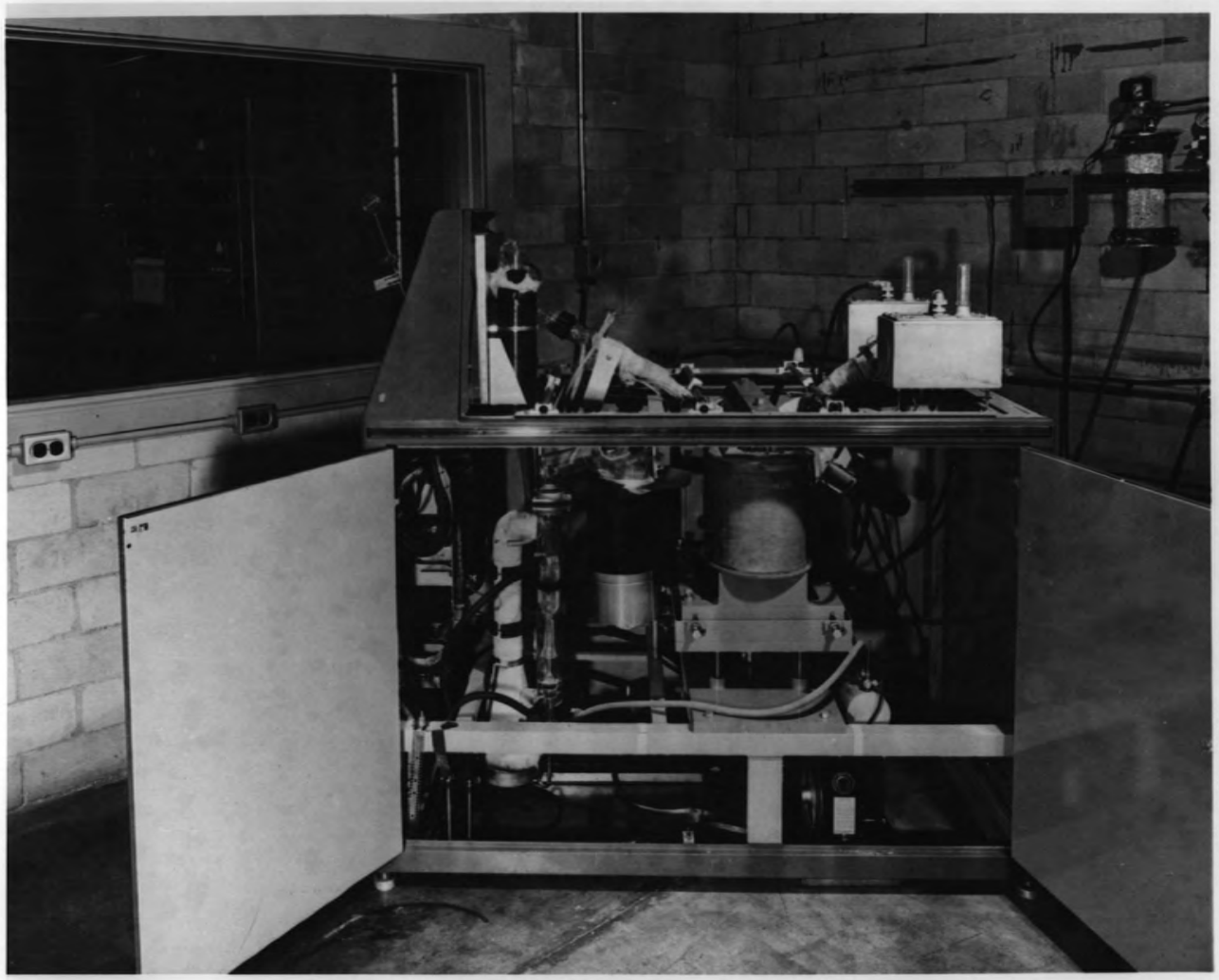

FIGURE 8. MASS SPECTROMETER TUBE RACK

FIGURE 9. SAMPLE PREPARATION AREA

FIGURE 10. DISTILLATION AND SUBLIMATION EQUIPMENT

Reports Published and Papers Presented

1. Sites, John R., Russell Baldock, and L. O. Gilpatrick, "Mass Spectrometer Study of Technetium," ORNL-1327.

2. Gilpatrick, L. O., Russell Baldock, and John R. Sites, "Mass Spectrometer Investigation of UF_3," ORNL-1376.

3. Sites, John R., and Russell Baldock, "Mass Spectrometer Studies of High Vacuum Materials," ORNL-1405

4. Rummell, Robert E., John R. Sites, and Russell Baldock, "Mass Spectrometer Study of Silicon Tetrafluoride," ORNL-1406.