27
6/21/77
25-7115

IS-4125

The Ultra - Purification of Metals by Electrotransport Under Outer Space Environmental Conditions

April 1, 1974 to Sept. 30, 1976

FINAL REPORT

Materials Science Program
Ames Laboratory, USERDA
Iowa State University
Ames, Iowa 50011

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THE ULTRA PURIFICATION OF METALS BY ELECTROTRANSPORT
UNDER OUTER SPACE ENVIRONMENTAL CONDITIONS

by

F. A. Schmidt
B. K. Lunde
D. E. Williams

Materials Science Program
Ames Laboratory, ERDA
Iowa State University
Ames, Iowa 50011

Order No. L-1320A
Statement of Work No. 63.120.234

Project Officers

Dr. R. A. Outlaw
Dr. L. T. Melfi, Jr.

Advanced Application Flight Experiment Program
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23365

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *fy*

CONTENTS

	<u>PAGE</u>
ABSTRACT	iii
LIST OF FIGURES	iv
LIST OF TABLES	vi
ACKNOWLEDGEMENT	viii
INTRODUCTION	1
CONCEPTUAL APPROACH	5
EXPERIMENTAL PROCEDURE AND RESULTS	11
1. Phase I (April 1, 1974 to April 30, 1975)	11
A. Preparation and Purity of Materials Used	11
B. Determination of Ideal Sample Size	13
C. Fabrication of Space Simulation Chamber	15
(a). Cryogenic Panel	18
(b). Calibrated Ionization Gauges	19
(c). Residual Gas Analyzers	19
(d). Pre-bakeout Chamber	20
D. Development of Electrotransport Apparatus	20
(a). Radiation Shield and Rack Support	21
(b). Sample Assembly and Electrodes	24
(c). Temperature Monitoring Device and Mirror Assembly	29
(d). Electronic Control Equipment	31
(1). Programmer	31
(2). Power Supply	37
(3). Data Acquisition System	38
E. General Experimental Procedure	39
F. Initial Electrotransport Experiment in Space Simulation Chamber (NASA-1-151)	45
G. Effect of Solar Radiation on the Experiment (NASA-1A-11)	48
H. Simulation of Near-Zero Gravity	54
I. Probability of Meteor Damage to Sample	58
J. Operating Environment for Preparation, Launch, Space Operation and Recovery of the Experiment (SP1-66006)	58

	<u>PAGE</u>
2. Phase II (May 1, 1975 to April 30, 1976)	59
A. Effect of Coldness and Darkness on the Experiment (NASA-1A-85)	59
B. Use of High Purity Cathode Extension (NASA-1A-115)	63
C. Partial Pressure Measurement of Residual Gases in Vicinity of Sample (NASA-1A-149)	64
D. Demonstration of Automatic Control Circuit and Effect of Prolonged Bakeout (NASA-2A-13)	69
E. Preparation of High Purity Single Crystals of Thorium (NASA-2A-44)	72
F. Electrotransport Purification of Once Refined Thorium (NASA-2A-79)	75
G. Electrical Resistance of Sample Assembly	84
3. Phase III (May 1, 1976 to September 30, 1976)	88
A. Effect of High Partial Pressure of Nitrogen on Quality of Thorium Purified (NASA-2A-105 and NASA-2A-138)	88
B. Test Specification for the VAMPS Experiment (SP2-66006)	95
SUMMARY OF RESULTS	96
RECOMMENDATIONS	99
LIST OF INVENTIONS	102
LIST OF PRESENTATIONS	103
LIST OF PUBLICATIONS	104
BIBLIOGRAPHY	105
APPENDICES	
APPENDIX A - Drawings of Electrotransport Apparatus	108
APPENDIX B - Equipment Specification for High Current Power Supply	128
APPENDIX C - Procedure Used for Determination of Gas Content of Chamber	134
APPENDIX D - Reprints of Articles Published to Date	147
APPENDIX E - Ames Laboratory Personnel Directly Associated with Project	150

ABSTRACT

A space simulation chamber capable of achieving pressures of 2×10^{-12} torr (N_2) was designed, fabricated, and used to develop a pre-prototype electrotransport experiment. It was demonstrated that the electrotransport purification of refractory metals could be successfully performed in the non-contaminating environment of an orbiting low density materials laboratory such as the Molecular Shield Device. The zero-gravity of outer space will also be advantageous since "grain-sliding" will be eliminated. As a result of the various experiments, small quantities of the world's purest thorium metal were prepared and evaluated. The electrotransport sample assembly was tested in several environments including near zero-gravity, simulated solar radiation, coldness and darkness, and under various pressures of a representative reactive gas. Ultra-pure single crystals of α thorium were prepared and are presently being characterized. Laboratory electronics for the experiment were also developed and a totally automatic control system was used to heat the specimen. Complete assembly and line drawings of the components of the experiment and specifications for a high current power supply are contained in the Appendices.

FIGURES

	<u>PAGE</u>
Figure 1. Concentration vs distance plot of an electrotransport sample at the steady state.	6
Figure 2. Schematic of space simulation chamber used for electrotransport experiments.	17
Figure 3. Photograph of the electrotransport apparatus showing radiation shield, rack assembly, electrodes, temperature monitoring device and sample assembly.	22
Figure 4. Schematic showing location of electrotransport apparatus and cryogenic panel inside the space simulation chamber.	23
Figure 5. Photograph of the sample assembly including thorium rod and cathode and anode adapters.	25
Figure 6. Flexible mechanical devices that were unsuitable as expansion adapters for thorium rod. (a) "Japanese lantern", (b) "maze" (c) "strap" designs.	28
Figure 7. Electrotransport control circuit with current selection.	32
Figure 8. Detail "A" of control circuit with current selection.	33
Figure 9. Electrotransport control circuit with voltage selection.	36
Figure 10. Photomicrograph of thorium rod prior to loading in electrotransport apparatus. As heated to 750°C for one hour in vacuum. 250X.	40
Figure 11. Schematic of radiation shield showing temperature probe locations.	50
Figure 12. Schematic of force due to magnetic field and current through sample.	55
Figure 13. Thorium rod samples heated for 150 hours at 1600°C. Top photograph (a) shows sample heated under ordinary gravitational forces, (b) sample heated under near zero-gravity conditions.	57

Figure 14.	Space simulation chamber and the related equipment used in the cold-black-body simulation experiment.	61
Figure 15.	Peak heights of residual gases after thorium sample was heated to 1600°C for 120 hours.	66
Figure 16.	Partial pressure of residual gases, as a function of time, present in vicinity of sample during electrotransport experiment. Cryogenic panel not used.	68
Figure 17.	Partial pressure of residual gases, as a function of time, in vicinity of sample when cryogenic pumping was used.	71
Figure 18.	Partial pressure of residual gases, as a function of time, during electrotransport purification and single crystal preparation.	74
Figure 19.	A plot of the resistance ratio ($R_{300K}/R_{4.2K}$) of thorium vs pressure inside the vacuum chamber during electrotransport purification.	76
Figure 20.	Partial pressure of residual gases, as a function of time, during electrotransport purification of once refined thorium.	79
Figure 21.	Plot of resistance of sample assembly vs square root of current for run NASA-1A-149.	86
Figure 22.	Partial pressure of residual gases, as a function of time, during experiment NASA-2A-105.	89
Figure 23.	Partial pressure of residual gases, as a function of time, during experiment NASA-2A-138.	94

TABLES

<u>NUMBER</u>		<u>PAGE</u>
I.	Chemical Analysis of Thorium Metal Used in Electrotransport Experiments.	12
II.	Electrotransport Parameters for Thorium at 1500°C.	14
III.	Time to Steady State of Solutes in Thorium at 1500°C.	15
IV.	Heating Rate of Thorium Sample from Room Temperature to 1600°C.	43
V.	Resistance Ratio ($R_{300K}/R_{4.2K}$) of Thorium Rod from Initial Experiment.	47
VI.	Temperature Profile of Radiation Shield and Rack Assembly During Solar Simulation.	52
VII.	Resistance Ratio ($R_{300K}/R_{4.2K}$) of Thorium Rod from Solar Simulation Experiment.	53
VIII.	Temperature Profile of Radiation Shield and Rack Assembly With and Without Cold-Black-Body Simulation.	60
IX.	Percentages of Residual Gases Present in Space Simulation Chamber During Cold-Black-Body Simulation.	62
X.	Resistance Ratio of Thorium Rod Purified in Experiment NASA-1A-149.	67
XI.	Resistance Ratio of Thorium Rod Purified at 1600°C Using Cryogenic Pumping.	70
XII.	Resistance Ratio of Once and Twice Purified Thorium Segments.	80
XIII.	Chemical Analysis of Once and Twice Electrotransport Purified Thorium.	81
XIV.	Resistance of Sample Assembly During Electrotransport Purification Experiments.	85
XV.	Gauge Constants and Modulation Factors.	137
XVI.	Relative Ionization Gauge Sensitivities for Residual Gases in Space Simulation Chamber.	142

NUMBERPAGE

XVII. Cracking Pattern of Residual Gases in Space
Simulation Chamber.

143

XVIII. Ionization Constants for Residual Gases in
Space Simulation Chamber.

144

ACKNOWLEDGEMENT

The authors and administrators of the Ames Laboratory, and in particular those of the Materials Science Program, wish to gratefully acknowledge Dr. J. H. Bretz of the National Aeronautics and Space Administration for his interest throughout this work. We appreciate the efforts of Dr. L. T. Melfi, Jr., Dr. R. A. Outlaw, Dr. J. E. Hueser, Dr. F. J. Brock, and Mr. J. W. Youngblood of the Langley Research Center for their suggestions, and excellent cooperation during the past two and a half years. Special acknowledgement is made to the Advanced Application Flight Experiment Program of NASA and Mr. R. N. Parker of LRC for supporting this work.

INTRODUCTION

The purification of refractory metals such as thorium, zirconium, niobium, and tungsten are of particular interest since they are or may become important fuel sources, or structural metals in advanced energy systems. The physical and mechanical properties of these metals are notoriously sensitive to the presence of small amounts of impurities such as carbon, nitrogen, and oxygen which enter these metals as interstitial atoms. To properly understand the effects of interstitial impurities on their various properties, it is essential that comparison metal be made available of sufficient purity so that the effects due to contaminants are negligible. Also, once the ultra-pure metal is available, the effect of single or several impurities or alloy additions on the metal's properties can be determined. From these empirical data, our present understanding of the behavior of metals can be substantiated or refuted. Further, segments of the pure samples can be used as analytical standards and in the preparation of small fabricated parts, i.e., filaments or foils for use in sophisticated electronic devices.

One of the most effective methods of purifying refractory metals is by electrotransport at high temperatures. In this process, a direct current is passed through a metal (sample) rod, thereby heating it by internal resistance as well as producing the electrotransport phenomenon. Purification occurs as the charge carriers transport impurities with them, so that the impurities are swept to one of the ends of the rod, thus purifying a major portion of the rod. The earliest electrotransport work was done by Seith and Kubaschewski¹ in 1935 on the movement of carbon in iron. In 1940, DeBoer and Fast² reported

that oxygen moves toward the anode in zirconium and Claissé and Keonig³ observed that oxygen moves in the same direction in titanium. Dayal and Darken⁴ found carbon to migrate toward the cathode in iron and hydrogen was observed to have a similar behavior in palladium⁵. It, therefore, is obvious that certain solute atoms can migrate either with or against the electron flow, depending on the solvent, and that each case must be considered individually. In most of the earlier investigations of the electrotransport phenomena, it was assumed that the electric field exerted the only force on the solute atom, which was thought to be charged. In 1953, Seith and Wever⁶ showed that this interpretation was incomplete and that the interaction between moving electrons and the solute must be considered. Reviews by Heumann⁷, Verhoeven⁸, and Huntington⁹ consider both the electrostatic force and the force resulting from moving electrons being scattered by the solute.

The potential for applying electrotransport for the ultra-purification of metals has been described by Verhoeven¹⁰ and Peterson¹¹. During the past eleven years, this technique has been developed into a refining process at the Ames Laboratory, ERDA, for removing carbon, nitrogen, and oxygen from many of the refractory and rare earth metals.⁽¹²⁻²⁴⁾ However, this process has been limited by the presence of the residual gases of the Earth's atmosphere even under so-called high vacuum laboratory conditions. In Peterson's review¹¹ of the experimental factors affecting the purification of metals by electrotransport, he states that a pressure of 10^{-9} torr(N₂)* is almost a minimum requirement to avoid having contamination seriously limit the purity that is obtained. The inability to reliably obtain metal purities below part-per-million

*torr (N₂) denotes the nitrogen equivalent pressure in the system.

levels has been an insurmountable impediment to many basic research efforts in solid state physics and metallurgy, even though most of the purification experiments have been performed at pressures of 5×10^{-10} to 5×10^{-11} torr (N_2).

In order to overcome this limitation imposed by the terrestrial atmosphere, we propose to perform electrotransport purification in the noncontaminating environment of a molecular shield device that will be deployed from the space shuttle orbiter. Such a device is being studied by the Environmental Science Group at Langley Research Center and would serve as an orbiting low-density materials laboratory. A theoretical analysis of a hemispherical shield has been made by Hueser and Brock²⁵. From this analysis, Melfi et al.²⁶ have shown that the atmospheric component of the gas density within the shield would be very low and non-contaminating to the electrotransport purification process.

Another problem that is often encountered in the electrotransport purification of polycrystalline metals in earth-bound experiments, is that of high-temperature "grain-sliding" which is a displacement of the grains due to plastic deformation caused by the weight of the rod. This sliding becomes apparent after only one to two days of heating, and as a result, a region of high electrical resistance often develops giving rise to localized over-heating and premature termination of the experiment by "melt-off". The micro-gravity present in a space experiment should eliminate this problem, thereby insuring continuation of the electrotransport process until the steady state is achieved and maximum purification attained.

It was therefore the purpose of this study, Project VAMPS*, to perform laboratory experiments to demonstrate the feasibility of employing electrotransport as a method of purification in the non-contaminating and weightless conditions of outer space. The results of these experiments were then applied to the design, construction, operation, and evaluation of a preprototype flight model so that appropriate instrumentation for a flight experiment could be determined.

*VAMPS is an acronym for this experiment which stands for the Vacuum Assisted Metal Purification in Space.

CONCEPTUAL APPROACH

In order to predict the ability to purify a specific metal by electrotransport, the electric mobility, U , of the solutes and their diffusion coefficients, D , must be known at the temperature of purification and under the conditions of an applied electric field, E . In our previous studies, we have determined these parameters for several metals and these data can be used for establishing the ideal conditions for purifying a particular metal of interest. The relation between these parameters, the length of the sample, ℓ , and the concentration C , can be seen in Figure 1 which is a plot of concentration vs distance along a rod of metal at the steady state conditions. Equation 3 in Figure 1 is a simplified version of Equation 1, since $1 - e^{-UE\ell/D}$ in Equation 2 approaches unity when a 0.10 volt/cm electric field is applied to a 10 cm long rod and the ratio of U/D is approximately 10 V^{-1} , which is the case in most of our studies.

We have used electrotransport to reduce the level of carbon, nitrogen, and oxygen in several of the refractory and rare earth metals to 10^{-1} to 10^{-2} of their original concentration. While this has often resulted in metal of the highest purity yet attained on Earth, these values fall far short of the amount of purification that is theoretically possible by the electrotransport process. The major problem in the earth-bound electrotransport experiments concerns the residual gases present in the vicinity of the sample even in the highest vacuum attainable. These gases can serve as contaminants and as a result, the steady state condition is achieved sooner at a higher concentration of impurities than could otherwise be attained. On the assumption that the ends of the rods are sufficiently cool to insure negligible

Figure 1. Concentration vs distance plot of an electrotransport sample at the steady state.

atomic transport, Verhoeven¹⁰ has shown that the ratio of the mean concentration, $\frac{C_m}{C_0}$, for the solutes in the purer half of the rod at any time up to and including the steady state condition* is described by the following equation:

$$\frac{C_m(t)}{C_0} = 2 \left[\frac{1-e^{-S/2}}{1-e^{-S}} - \sum_{n=1}^{\infty} C_n e^{-S/4} \sin\left(\frac{n\pi}{2}\right) e^{-\lambda_n t} \right]$$

$$\text{where } C_n = \frac{32n\pi S [1 - (-1)^n e^{S/2}]}{(S^2 + 4n^2\pi^2)^2} \quad \text{Eq. (4)}$$

$$\lambda_n = \left(n^2\pi^2 + \frac{S^2}{4} \right) \frac{D}{\ell^2}$$

$$S = - \frac{U}{D} E \ell$$

We chose thorium as the host metal for our proposed experiment because (1) it has a low vapor pressure (5×10^{-8} torr at 1500°C), (2) the mechanical and physical properties of thorium are extremely sensitive to carbon, nitrogen, and oxygen which have high mobilities under the influence of an electric field, (3) thorium has been used in most of our previous development work and we are quite familiar with its electrotransport properties, and (4) thorium is a fertile material and can be used as a nuclear fuel, and an understanding of its true intrinsic properties and the effect of impurity solutes on these properties is of practical interest. From previous electrotransport studies of thorium¹³, the values of U and D were determined for carbon,

* The steady state was considered to have been achieved in our work when the value of C_m/C_0 became constant to four significant figures.

nitrogen, and oxygen at several temperatures. By substituting these values in Equation (4) and performing the calculations with the aid of a digital computer, we can determine C_m/C_o for the steady state condition for any length rod at a specific temperature.

The two boundary conditions for Equations (1) and (4) are that no flux enters the rod at its ends and that zero flux of solutes passes through the surface of the rod from the environment. The first of these conditions is controlled by inserting a tantalum adapter between the rod and the electrode at the cathode end. The adapter is made of tantalum since in this metal carbon, nitrogen, and oxygen move against the flow of electrons²⁰, which at the cathode end means away from the rod to be purified. Further, tantalum is compatible with thorium and does not form any low melting alloys or compounds. At the anode end of the rod, a thorium adapter is attached which is thicker in diameter and cooler in temperature than the specimen rod. This adapter acts as a "sink" and tends to retain the migrating solutes, thereby minimizing their back diffusion into the rod due to the concentration gradient that exists.

The secondary boundary condition, zero flux of solutes passing through the surface of the rod, is not easily achieved in practice. In earlier work, we noted an increase in the purification achieved at the steady state condition, with a decrease of the residual gas concentration within the vacuum chamber in which the rod was heated. One of the main objectives of the present work was, therefore, to minimize the residual gas content of the environment in which the thorium rod was heated, thereby indicating the potential for processing in an orbiting low-density materials laboratory such as the molecular shield

proposed by Melfi, et al²⁶. This hemispherical shield would be placed in terrestrial orbit above 200 km and would be extended from the space orbiter by a 100 m boom or be deployed as a "free-flyer". Final degassing of the shield and experiment would be executed in a vacuum enclosure where they are stowed under ultra-high vacuum from ground preparation through orbit trim. If the boom configuration is used, the shield would be deployed several orbiter lengths away from the aft of the orbiter under servo control. In this manner, the probability of atmospheric gas scattering off the Orbiter directly into the Shield is minimized as is the risk of experiment contamination due to sources aboard the Orbiter. According to the analyses by Melfi, et al., the atmospheric component of the gas density within the shield is less than 10^3 cm^{-3} , principally atomic hydrogen*. This environmental condition would be near ideal for an electrotransport experiment since carbon, nitrogen, and oxygen containing gases would not be present and the residual hydrogen would not be harmful since its solubility in thorium at the temperature of transport (1500°C) is extremely low²⁷.

Our approach to demonstrating that the ultra-purification of metals by electrotransport can effectively be performed in the environment of the Molecular Shield was divided into three phases. In Phase I, a high integrity space simulation chamber capable of achieving pressures of 5×10^{-11} torr (N_2) or lower was developed. A laboratory electrotransport apparatus was then fabricated and operated from which the basic design parameters for an in-flight experiment could be deduced. Prior to each experiment, the apparatus was subjected to a high temp-

*An equilibrium gas density of 10^3 cm^{-3} corresponds to a pressure of 3×10^{-14} torr at 300K.

erature bakeout under low pressure similar to a pre-flight degassing step. The determination of the ideal sample dimensions, power requirements, and the optimum power control were part of Phase I. The effect of simulated solar irradiation on the experiment was also determined. In a separate experiment, a thorium rod was heated in a near zero-gravity condition and the results were evaluated. A definition of the operating environment for the experiment was also developed.

During Phase II, the partial pressures of 13 residual gases inside the space chamber and in the vicinity of the thorium sample were accurately measured and their effect upon the quality of the purified metal determined. The conditions of coldness and darkness of space were simulated and their effect upon the experiment were determined. Also during this period, high purity single crystals of α thorium were prepared. The results of the laboratory experiments were used to establish the final design and operating procedure for a preprototype flight model; the appropriate instrumentation for a "one-button-start" was also developed during this phase.

The effect of various concentrations of nitrogen gas on the purity of the thorium sample was determined during Phase III. The test specifications for the electrotransport experiment, as developed during Phase I and Phase II, were also written.

EXPERIMENTAL PROCEDURE AND RESULTS

The purpose of the various experiments was to study the feasibility of using electrotransport as a method of purification in the non-contaminating and weightless condition of outer space. As the results of these experiments were obtained, they were applied to the design, construction, operation, and evaluation of a preprototype flight model from which a flight experiment could be prepared. This portion of the report is divided into three sections namely, Phase I, Phase II, and Phase III, which correspond to the subdivisions of the Statement of Work No. 63.120.234. All of the work was performed at the Ames Laboratory, ERDA, Ames, Iowa.

1. PHASE I: (April 1, 1974 to April 30, 1975)

During this period, a high integrity space simulation chamber was constructed and an electrotransport apparatus developed. Two electrotransport experiments were made and the quality of the purified metal determined. A definition of the operating environment for the experiment was also developed.

A. Preparation and Purity of Materials Used. The thorium metal used in this study was prepared in our Laboratory by a magnesium intermediate alloy process developed in 1964 by Peterson et al.²⁸ All samples were prepared from a single ingot (BEB-1-341) that was homogenized and purified by triple electron beam melting under a pressure of 2×10^{-7} torr (N_2). This ingot weighed 1 kg (2.2 lbs) and the rod samples used in the various electrotransport experiments were fabricated by rolling and swaging at ambient temperature. An analysis of this material is shown in Table I. The carbon content was determined by combustion chromatographic analysis and the hydrogen, nitrogen, and oxygen

Table I. Chemical Analysis of Thorium Metal Used in Electrotransport Experiments.

<u>Element</u>	<u>Concentration, ppmw</u>
C	50
H	<1
N	50
O	30
Al	<0.02
Cl	0.75
Co	<0.01
Cr	0.20
Cu	<0.05
Fe	0.30
Mg	0.60
Mo	2.5
Ni	0.20
Re	6.5
Si	2
Sn	<0.02
Ta	7.5
Ti	0.40
W	3
Zr	0.40

concentration were measured by vacuum fusion analysis. The other elements listed in Table I were determined by spark source mass spectrometry. The concentration of all other elements, not shown in the Table, was less than 3 ppmw.

The tantalum metal used as adapters for the thorium sample was obtained from the Norton Co., Newton, Massachusetts and was of 99.95 w/o purity. It was double electron beam melted in our Laboratory for further purification before it was fabricated into the desired parts.

The nickel and titanium used for the fabrication of the flexible "bow" adapters were also of 99.95 w/o purity and were obtained commercially. The nickel was supplied by the Belmont Co., Long Island, New York and the titanium by the Titanium Metals Corporation of Henderson, Nevada. Both of these materials were further purified by electron beam melting before they were arc melted to form the NiTi "memory alloy".

The type 304 or 316 stainless steel was obtained from various commercial suppliers and was used to construct all other parts of the electrotransport apparatus except the electrodes which were made of copper.

B. Determination of Ideal Sample Size. In order to determine the ideal sample size for our experiment, it was necessary to consider several parameters. First, the assumption was made that the duration of the electrotransport experiment would be six days which coincides with the projected experimental time available on early space orbital missions. In our previous electrotransport studies, we purified thorium in various shapes including tubes, ribbon, wire, rod, and bar at 1500°C. It was found that the highest current densities can be achieved with fine wire or foils since the thermal dissipation is the greatest and, conversely, the

lowest current density is achieved with large diameter rods. When fine wire or thin foil is used, the amount of material that is purified is small and the contamination from the residual gases in the vicinity of the sample is relatively large. Also with such thin samples, characterization is more difficult and the preparation of single crystals of significant size is extremely difficult. For these reasons, a rod sample having a diameter of 0.25 cm (0.10 inch) was found to afford an acceptable "trade-off" between the current density required and the amount of sample to be purified.

The most suitable length of sample for our experiment was determined using Equation 4. The electrotransport parameters¹³ for carbon, nitrogen, and oxygen in thorium at 1500°C are shown in Table II. These values are for a rod 0.25 cm (0.10 inch) in diameter and heated with a current density of $\sim 1700 \text{ A/cm}^2$. The values shown in the Table for the electric mobility, U , the diffusivity, D , and the electric field, E , were used and the length of sample, ℓ , was varied from 16.5 cm (6.5 inch) to 35 cm (13.8 inch). With the aid of a digital computer, the ratio of the mean concentration C_m , of the solutes in the purest half of the rod, to the original concentration, C_0 , was determined. The values for this ratio and the times required to achieve the steady state condition for different length samples are shown in Table III.

Table II. Electrotransport Parameters for Thorium at 1500°C.

	v , cm/hr	E , V/cm	U , ($10^{-4}\text{cm}^2/\text{V-s}$)	D , ($10^{-5}\text{cm}^2/\text{s}$)	$\frac{U}{D}$
Carbon	0.08	0.154	1.38	1.09	13
Nitrogen	0.44	0.151	8.05	2.89	28
Oxygen	0.90	0.156	16.05	5.49	29

TABLE III. Times to Steady State of Solutes in Thorium at 1500°C.

Sample Length, cm	<u>Carbon</u>		<u>Nitrogen</u>		<u>Oxygen</u>	
	Time to S. State, days	C_m/C_o Final	Time to S. State, days	C_m/C_o Final	Time to S. State, days	C_m/C_o Final
16.5	30.5	0.20×10^{-6}	4.5	0.19×10^{-14}	2.0	0.1×10^{-15}
20	37	0.68×10^{-8}	5.5	0.12×10^{-17}	2.5	0.36×10^{-19}
25	45	0.52×10^{-10}	7	0.35×10^{-22}	3.5	0.42×10^{-24}
30	52	0.39×10^{-12}	8.5	0.98×10^{-27}	4	0.48×10^{-29}
35	59.5	0.30×10^{-14}	10	0.27×10^{-31}	4.5	0.56×10^{-34}

It can be seen from these data that the steady state condition for nitrogen and oxygen would be achieved after six days for a sample of either 16.5 cm (6.5 inch) or 20 cm (7.9 inch) in length. The steady state condition for carbon would not be achieved for 30.5 or 37 days due to the low electric mobility of carbon. A thorium rod length of 16.5 cm was therefore chosen for all our developmental experiments since the carbon concentration would be the lowest in the purer half of the shorter rod after a six day period. If longer times in space are available, such as on a "free-flyer", rods of greater length could be used and better purification achieved in the purer half of the rod. Also with longer flights, lower current densities could be used which would enable larger diameter rods to be processed and consequently larger quantities of material to be purified.

C. Fabrication of Space Simulation Chamber. A space simulation chamber measuring 46 cm (18 inch) in diameter and 91 cm (36 inch) long was designed and constructed from 304 stainless steel. This unit served

as a high integrity vacuum chamber for the electrotransport experiment. A "mock-up" of the unit was first prepared from thin aluminum sheet, wood, cardboard, and tape which was then used by our metals fabrication shop to construct the steel chamber and to bore the holes for the pipe extensions and flanges. The holes were bored using water as the coolant instead of oil, in an effort to minimize hydrocarbon contamination. The flanges were tungsten inert gas (TIG) welded to the pipe extension inside a glove box containing argon gas. These assemblies were then inside-welded to the chamber using the Heli-arc process. During this operation, a flow of argon gas was maintained around the outside of the weld area using a perforated plate from which the inert gas was emitted.

The chamber was equipped with three Ultek Model 236-1500 sorption pumps and one Ultek 214-0400 titanium sublimation pump. The titanium sublimation pump was fitted with a shield so that the titanium sublimate condensed only on the inside surface of the 46 cm (18 inch) end cover. An Ultek 206-1520 differential ion pump equipped with an internal titanium sublimation pump and a cryogenic shroud was used to pump the gas loads during bakeout. An Ultek Model 206-1500 differential ion pump was used during the electrotransport experiments. The 15.2 cm (6 inch) all-metal main valve, and the smaller valves used in conjunction with the sorption pumps were obtained from the Huntington Mechanical Laboratories, Inc., Mountain View, California. Figure 2 is a schematic of the space chamber and shows the location of the vacuum pumps, viewports, power feedthroughs, mechanical feedthrough, residual gas analyzer head assembly, nude-type Bayard-Alpert gauge, rupture disc and liquid nitrogen inlet and outlet tubes.

The entire chamber was wrapped with 14 gauge Kanthal A-1 furnace

Figure 2. Schematic of space simulation chamber used for the electrotransport experiments.

wire which was electrically insulated from the chamber wall by beads of high fired aluminum oxide (Al_2O_3). The Model 206-1500 ionization pump, residual gas analyzer, and end cover were also wrapped with furnace wire. Individual power supplies were used to heat these wires so that the temperature of each unit could be controlled separately from ambient temperature to 400°C . The power supplies were equipped with ground-fault-interrupter controls so that if the aluminum oxide insulation failed at any point, electrical arcing to the chamber wall and a possible burn-through would be prevented. Prior to baking the chamber at elevated temperature, the chamber was double wrapped with 2.54 cm (1 inch) thick fiber glass insulation which was secured with 0.50 cm (0.190 inch) diameter asbestos rope.

(a) Cryogenic Panel. A cryogenic panel was fabricated from 0.31 cm (0.125 inch) thick 304 stainless steel plate. This unit was designed so that it could be placed inside the space simulation chamber directly opposite the electrotransport experiment in order to simulate the coldness and darkness of space. The panel had a curved cross-section with a radius of curvature that matched that of the space chamber wall. The front of the panel, which measured 41 cm (16 inch) wide and 56 cm (22 inch) long was purchased from Tri-Industries, Inc., Terra Haute, Indiana. It was also 0.31 cm (0.125 inch) thick stainless steel and contained a 0.80 cm (0.31 inch) thick layer of stainless steel honeycomb. The honeycomb was made of steel ribbon 0.007 cm (0.003 inch) thick and the hexagonal cells measured 0.08 cm (0.031 inch) across. It was attached to the panel by vacuum brazing.

The cryogenic panel, which had a liquid nitrogen capacity of four liters, was used in most of the electrotransport experiments as a high

capacity cryogenic pump. The nitrogen was delivered to the panel from a 400 liter liquid nitrogen storage tank. The panel was kept full during the experiment by means of an automatic temperature sensing device and a solenoid valve located on the storage tank.

(b). Calibrated Ionization Gauges. Two Bayard-Alpert ionization gauges, Model 971-5008, were obtained from the Varian Corporation, Palo Alto, California. These gauges were sent to Dr. R. A. Outlaw at the Langley Research Center (LRC) where one of them was converted to a modulated gauge as described by Redhead²⁹. Both of these gauges were calibrated at LRC by determining their gauge constants for helium, argon, and nitrogen. The modulation factor for the converted gauge was also determined. Both gauges were then returned to us and mounted on the space chamber. The procedure used to determine the nitrogen equivalent pressure in the space chamber is given in Appendix C. The unmodulated gauge was used in conjunction with a Ultek Digital Vacuum Gauge, Model 605-0013, or a Kiethley Model 417 picoammeter, to determine pressures of 1×10^{-4} to 1×10^{-10} torr. Pressures less than 1×10^{-10} torr were determined using the modulated gauge which was not affected by x-ray emission at pressures below $\sim 5 \times 10^{-11}$ torr. The ion current from the modulated gauge was measured using the picoammeter.

(c). Residual Gas Analyzers. In our early experiments, a Quad 150 residual gas analyzer obtained from Electronic Associates Inc., was used to identify the remaining gases present inside the space chamber prior to and during an electrotransport experiment. This unit was subsequently replaced by a UTI Model 100C gas analyzer supplied by Uthe Technology International, Sunnyvale, California. The sensitivity of this unit to helium, argon and nitrogen was determined and it was used to measure the

partial pressures of the residual gases present during several electrotransport experiments. The procedure used for these determinations is also described in Appendix C.

(d). Pre-bakeout Chamber. A stainless steel vacuum chamber was designed and constructed for use as a pre-bakeout tank for the various component parts of the experiment prior to placing them in the space simulation chamber. This tank measured 46 cm (18 inches) inside diameter and 91 cm (36 inches) deep, which were the same dimensions as the space chamber. It was designed so that it could be attached to one of our high capacity vacuum units; pressures of 2×10^{-7} torr (N_2) were routinely obtained. The tank was surrounded with an insulated electric furnace that was capable of heating the unit to $500^\circ C$. The power supply for this furnace is the same one used to heat the Kanthal A-1 wire surrounding the space chamber. The inside and outside temperatures of the pre-bakeout chamber were measured with chromel-alumel thermocouples. All components of the experiment, except the sample assembly, residual gas analyzer heads and pressure gauges, were degassed in this unit prior to being loaded in the space chamber.

D. Development of Electrotransport Apparatus. The development of the electrotransport apparatus proceeded simultaneously with the design and construction of the space simulation chamber. It became apparent early in Phase I that several components of the initial apparatus would be quite satisfactory for use in the preprototype model. Consequently, the design of the preprototype model proceeded much faster than anticipated and, in fact, was near completion at the end of Phase I. In the following subsections, the various components and features of the preprototype apparatus are described. Detailed assembly drawings and

line drawings of each component can be found in Appendix A of this report. A photograph of the completed electrotransport apparatus is shown in Figure 3. The unit is designed so that a thorium metal sample 16.5 cm (6.5 inch) long and 0.25 cm (0.10 inch) in diameter can be purified using the electrotransport process. The approximate volume of the apparatus (as determined by the smallest box that would hold it) is 35 liters (1.24 cu ft) including a 10% contingency. The weight of the unit is 7.95 kg (17.5 lbs). In Figure 4, the location of the electrotransport apparatus and the cryogenic panel inside the space simulation chamber is shown.

(a). Radiation Shield and Support Rack. In our experiment, the inside surface of the space simulation chamber was considered to be similar to the curved surface of a molecular shield device. The radiation shield and support rack are designed so they could be mounted horizontally or vertically onto this surface. The radiation shield was a concave reflector with an elliptical cross section having a semi-major axis of 19.00 cm (7.50 inch) and a semi-minor axis of 16.85 cm (6.63 inch). The longitudinal axis of the sample assembly was located 9.5 cm (3.75 inch) from the back of the reflector. The reflector was made from 304 stainless steel sheet 0.16 cm (0.062 inch) thick and had an opening that measured 28 cm (11 inches) by 33.70 cm (13.25 inches). The end pieces were joined by TIG welding in a glove box. The inside of the shield was mechanically polished using an electric powered buffing wheel and jewelers rouge until a highly reflective surface was achieved.

A slot measuring 1.27 cm (0.50 inch) by 20.0 cm (7.87 inch) was machined in the bottom of the shield so that the sample could be observed through a sight glass mounted on the chamber wall (item B, Figure 2).

During the developmental work, three support racks were made of the

Figure 3. Photograph of the electrotransport apparatus showing radiation shield, rack assembly, electrodes, temperature monitoring device and sample assembly.

Figure 4. Schematic showing location of electrotransport apparatus and cryogenic panel inside the space simulation chamber.

basic design shown in the Appendix A. Type 304 stainless steel was used for each unit, however, different thicknesses of material were used in an effort to determine the most sturdy design. The support rack fabricated from 0.64 cm (0.25 inch) thick material was found to be quite satisfactory and showed no tendency to flex when the radiation shield and electrode were attached. The support rack was attached to the inside surface of the space chamber by two 1.27 cm (0.5 inch) diameter steel bolts so that the radiation shield and sample assembly were in the vertical position.

(b). Sample Assembly and Electrodes. A photograph of the sample assembly developed for our experiment is shown in Figure 5. Detailed assembly and line drawings of this unit are also shown in Appendix A. A thorium sample 16.5 cm (6.5 inch) long and 0.25 cm (0.10 inch) in diameter was threaded into a tantalum cathode adapter and a thorium anode adapter. Tantalum was used at the cathode end since interstitial solutes migrate against the flow of electrons in this metal and as a result carbon, nitrogen, and oxygen do not migrate into the thorium sample. This adapter was reduced in cross section at its end where the sample was attached in order to decrease the thermal gradient along the thorium rod. As a result of other electrotransport studies made in our Laboratory, it has been learned that tantalum migrates with the flow of electrons in thorium. However, its velocity is quite low at the temperature of our experiment and as a result, the portion of the thorium rod which was contaminated by tantalum was limited to less than 0.2 cm (0.08 inch) as determined by spark source mass spectrographic analysis.

The thorium anode adapter was larger than the sample and during an electrotransport experiment its temperature was lower than the sample. It, therefore, served as a sink for the migrating solutes. This adapter was

Figure 5. Photograph of the sample assembly including thorium rod and cathode and anode adapters.

threaded into a tantalum coupling which was connected to the anode electrode with a copper bolt. The entire assembly was so designed that the externally threaded members have larger thermal expansion coefficients than do the internally threaded members, so that as the sample temperature is increased to the operating level ($\sim 1500^{\circ}\text{C}$), all joints become more electrically conductive and mechanically sound. These qualities were further insured by slightly crimping the threaded joints prior to initiating the experiments.

One of the major problems encountered during Phase I concerned the development of an expansion adapter for the sample assembly. This feature was needed to compensate for the 0.36 cm (0.140 inch) increase in length of the thorium rod due to thermal expansion. It was desirable for the sample to remain straight during heating to minimize the formation of areas that would have high electrical resistance. The expansion adapter was also necessary to minimize the stress placed on the sample during cooling and thereby prevent mechanical working of the purified metal. An additional benefit of a straight sample was the increased simplicity of automatic optical temperature measurement.

The design problem associated with the expansion adapter was made difficult because thorium has extremely low mechanical strength above 900°C ³⁰. Since Joule heating was used to maintain the sample temperature, the adapter not only had to accommodate a soft expanding rod but it also had to carry ~ 86 amps of current. Further, since it was in the immediate vicinity of the sample, it could not emit gases that might serve as contaminants. A total of twenty different designs were fabricated and evaluated in a separate electrotransport system by attaching them to a 16.5 cm (6.5 inch) thorium rod and heating it to temperature. Most of the

designs included shapes that relied on mechanical flexing to compensate for the rod's expansion. A detailed description of the failures encountered would not be of interest, however, three of the adapters which seemed most promising are shown in Figure 6. These include (a) a flexible "Japanese Lantern" design, made from copper braid, (b) a "maze" design made from thin silver or copper and (c) a thin "strap" design. However when these adapters were evaluated, each was found to allow the thorium rod to bend slightly during heating, especially in the temperature range of 1000 to 1500°C. Consequently, they were unsatisfactory for our application. In a further effort to solve this problem, a "plunger" type adapter was made of tantalum and contained liquid tin to insure good electrical contact. This unit allowed for the expansion of the rod but small amounts of tin were emitted into the vicinity of the sample.

As a result of this experimentation and one of our concurrent research projects which involved the NiTi "memory" alloy³¹, a "bow" type adapter of this alloy was designed, fabricated, and successfully used to compensate for the expansion of the thorium rod. The NiTi adapter was made of two strips of the alloy 1.27 cm (0.50 inch) wide and 0.0152 cm (0.006 inch) thick. These strips were placed at right angles to each other in a "bow" design as shown in Figure 5. Prior to use in an experiment, the "bow" was pre-set by mounting it in a holder and deflecting it the 0.26 cm (0.140 inch) necessary to compensate for the thermal expansion of the thorium rod. The holder and adapter were then heated to 480°C in vacuum to set the "memory" of the alloy and then cooled to room temperature. The bow was removed from the holder, expanded and connected to the tantalum adapter. When the thorium rod was first heated, and the NiTi bow reached a temperature of approximately 45°C, thus causing it to assume

Figure 6. Flexible mechanical adapters that were unsuitable as expansion adapters for thorium rod. (a) "Japanese lantern", (b) "maze", and (c) "strap" designs.

its preset memory state which allowed the thorium, as it was resistively heated, to expand into a relaxed condition. The thorium rod was therefore kept straight during heating and was constrained with a minimum amount of force. In test experiments, an adapter of this design was successfully used to support a rod that was heated 87 times from room temperature to 1500°C. The NiTi adapter was used in all but our first electrotransport purification experiments.

The copper electrodes used at each end of the sample support assembly were obtained from the Ultek Co. They were Model 281-1000 500 amp feed-throughs and were modified for our experiment as shown in Appendix A. These electrodes were insulated from their mounting flanges which helped to insure the electrical integrity of the system.

(c) Temperature Monitoring Device and Mirror Assembly. A temperature monitoring device (TMD) was developed that could continually observe the heated sample yet be out of its optical path. This was accomplished by mounting the TMD onto the support rack assembly so that it would be directed to a metal mirror which reflected the sample image. This arrangement can be seen in Figure 3. Since the TMD was located inside the chamber, it had to withstand the six-day, 380°C vacuum bakeout of the space chamber required to minimize the residual gases present. A solar cell manufactured by Optical Coating Laboratories, Inc., Pasadena, California, was used as the temperature indicator in the TMD. It is a 2 cm (0.8 inch) by 4 cm (1.6 inch) chemically polished, N on P cell having a base resistivity of 2 ± 1 ohm-cm, a junction depth of 0.3 cm and a SiO anti-reflective coating. The cell has titanium and silver contact materials with a silver thickness of 3 to 8 μ m. The contacts were silver plated molybdenum tabs parallel-gap welded to the cell. A 140 mw/cm² solar simulator caused an output of 245 ma at 470 mV.

A picture-frame type holder for the rectangular solar cell was fabricated from aluminum and lined with strips of hard fired aluminum oxide. The aluminum oxide strips were grooved to accommodate the edge of the solar cell. In this manner the cell was held in the proper position and was electrically insulated from its metal mounting. The leads were made accessible through high density aluminum oxide tubes which insulated the leads from the aluminum mounting.

A 304 stainless steel extension tube was attached to the front of the cell holder and served as a shade against extraneous light. The TMD was used during the electrotransport experiments to monitor the average temperature of the sample by viewing its light as reflected by a commercial quality chromium plated 304 stainless steel mirror, Grade A, from the Reliance Art Metal Co., Cincinnati, Ohio. It also serves as a back-up system for keeping the temperature constant in case of a failure in the amperage or voltage monitoring equipment. There was an optical path length of 34 cm (13.4 inch) from the cell to the sample with one reflection of the light by the chromium mirror. A typical output of this cell was 190 mV with 1.9 μ a. This operating point was used to maximize the voltage so that the output could be precisely determined. In actual practice, an operating point at higher current would be desirable. A technical letter describing the TMD has recently been published³². An assembly drawing and line drawings of this unit and the mirror and bracket assembly are shown in Appendix A.

Prior to the development of the TMD described above, two other efforts were made to attach a silicon solar cell to a bakcable support. In one approach, the cell was attached to a Kovar substrate by fluxless inert gas silver soldering. After soldering, the output efficiency of the cell

was substantially decreased due to the excessive heat required for soldering. In the second study, a satisfactory support for the cell was fabricated from two pieces of anodized aluminum; however, their insulating oxide coat was thin and thought to be insufficient for a preprototype device.

(d) Electronic Control Equipment. The electronic control equipment used in this experiment consisted of a power supply, programmer, and a data acquisition system. During Phase I and Phase II, these units were integrated into an automatic control system. This system was demonstrated to completely control the heating of the samples during a six-day experiment after a single on-switch was activated. The control system was also adapted and used to cycle the temperature of the thorium rod through its polymorphic transformation temperature at 1340°C, subsequent to electrotransport purification at 1600°C, in order to prepare large single crystals of α thorium.

(1). Programmer. An electro-mechanical processor was constructed to demonstrate automatic operation in the laboratory. The final operating version used an analog to digital converter (A/D) and a digital to analog converter (D/A). In this system, the A/D converter is triggered to sample the voltage after the sample is heated with a current of 86.5 amps. The output of this converter is used by the D/A converter to drive the programmed power supply to furnish the voltage. In this manner, the voltage was controlled during the six-day electrotransport experiment and any increase in the resistance of the sample assembly would result in a power decrease and, consequently, a slight cooling of the sample. The circuit for the entire controller is shown in Figure 7 and 8 and has recently been published in the literature.³³

The programmer allowed the current to start at 15 amps for the first

Figure 7. Electrotransport control circuit with current selection.

REVISED 11-26-75	ELECTROTRANSPORT CONTROL CIRCUIT	DATE 9-29-75
REVISED 3-19-76		DESIGNED BY R. H. H. H.
		CHECKED BY
		APPROVED BY
		DATE
		FILE NO.

Figure 8. Detail "A" of control circuit with current selection.

minute and then increase at a rate shown in Table IV until it reached 86.5 amps. It then measured the voltage across the sample and held this voltage for six days. If cycling was desired for single crystal growth, the voltage was lowered and raised so that the temperature of the thorium rod fluctuated through its polymorphic transformation at 1340°C. If single crystal growth was not to be a part of the experiment, the voltage was simply turned off after six days.

A Leeds and Northrup Trendtrak Programmer, Model 220-202-105-0240-6-048 was used to ensure the prescribed turn-on sequence. The desired program for current increase was entered into the programmer by drawing an approximate profile on a circular graph of current vs time. Switches in the Trendtrak were used to activate previously set resistors when the current was near 86.5 amps to achieve that set-point precisely.

The A/D and D/A converters were obtained from Data Systems, Inc., Canton, Massachusetts. The A/D converter was a Model DAC-169-16B and the D/A was a Model ADC-149-14B. Power supplies Model BPM-15/100 (15 volt) and Model UPM-5/250 (5 volt) were used with the digital circuitry.

The Multi-pulse Timer, Model MP-5A6-15-MP5-40, was obtained from the Eagle Signal Co., Davenport, Iowa. It was used to trigger the A/D converter a few minutes after the 86.5 amps was supplied and then apply the measured voltage after the D/A converter had completed its function. The voltage was not measured for a few minutes after applying the 86.5 amps current to allow any initial "burn-in" of the circuit to occur. In this manner, an equilibrium value of the voltage was used for control. During some experiments, the voltage dropped slightly for one half hour or more; therefore, in a flight experiment, it would be necessary to allow for this "burn-in" period.

A CHC skipper clock was used to count the six day period of the experiment. It was also used to determine when temperature cycling should begin when single crystals of α thorium were prepared.

The predetermined counter, Model 41156-400 was obtained from Durant Digital Instruments, Watertown, Wisconsin. It was used to count the temperature cycles needed for single crystal preparation.

The control circuit with voltage selection operated successfully, but it was found undesirable to combine digital circuitry with micro-switches, relays, and motors. The latter generate pulses which trigger the digital circuitry, unless shielding is provided. It was also found that it is important, during development, to use packaged circuits so they are easily accessible.

The entire programmer depended on a programmable power supply for its operation. During the period of controlled current, the programmer presented a control voltage, proportional to the desired current, to the current control terminals of the power supply. The maximum voltage the power supply would offer to the sample was determined by a control voltage supplied to the voltage control circuit of the power supply.

When a constant voltage was required, the desired voltage was also commanded by a control voltage. At this time, the maximum current was set by a resistance presented to the current control circuit of the power supply. The details of the control scheme would depend on the precise power supply that is used.

During Phase I of the project, an electrotransport control circuit with voltage selection was developed. This circuit is shown in Figure 9 and would be used if voltage control were used for the six-day period. This is a simpler circuit than the control circuit with current selection and was implemented in early experiments.

Figure 9. Electrotransport control circuit with voltage selection.

Both of the circuits developed during this work were not optimum, but merely built and used in our Laboratory to demonstrate the automatic operation of the electrotransport purification experiment. In a flight experiment, a solid state programmer, probably using a microprocessor, would be used to accomplish this function. The IBM Space Division of Huntsville, Alabama, has an experiment controller that would probably be adaptable to our experiment. Some work was initiated on developing a microprocessor in our Laboratory near the end of Phase III. Sufficient time was not available to develop this unit, however, project notes may be consulted on the progress that was made.

(2). Power Supply. A laboratory type programmable D.C. power supply, Model SCR-10-500, was obtained from Electronic Measurements, Inc., Neptune, New Jersey and used in the laboratory demonstrations of purification. This unit weighed 106 kg (233 lbs) and was 65% efficient. It was modified so that a smooth transition could be made between the voltage and current control modes. It was also modified to allow the current to be programmed by a control voltage. This supply was found to be quite satisfactory and only a slight problem of instability resulted during a few of the experiments. We believe this was due to the carbon control potentiometers in the supply.

For space processing, a programmable power supply suitable for the environment should be mounted near the sample because of the large currents involved. A feasible location appears to be just outside the wall of the Molecular Shield. A switching supply should be especially developed for this application. It should be smaller and more efficient than our laboratory model. It was not within the scope of this project to develop such a power supply, however, a purchase specification for such

a unit was written and is included as Appendix B.

(3). Data Acquisition System. During our experimental work, it was necessary to record the temperature of the sample, its mounting, the radiation shield, current through the sample, and the voltage drop across the sample and the main current leads. In a flight experiment such monitoring would be integrated with other telemetry data returning from the spacecraft. In our laboratory experiments, these data were recorded on a Leeds & Northrup Numatron Data Acquisition System. This system used a four digit voltmeter to scan across fifteen inputs and print their values, taking as little as 0.1 second per input. The unit scanned the data points and printed the time, input number, datum, and units on paper tape. Precision shunts were used to measure current, voltage dividers for voltages over 1.100 volts and chromel-alumel thermocouples for temperatures under 1000°C.

The temperature of the sample was recorded using this unit and a Leeds & Northrup Spectray Model 8886-1-12. This recording pyrometer was less successful than the simple temperature monitoring device (TMD) since the field of view of the Spectray was quite small. A slight change in position of the sample greatly affected the amount of radiation the sample contributed to the pyrometer and, as a result, large temperature variations were indicated. This did not happen when the TMD was used to monitor the temperature. However, temperature readings with the TMD were affected by slight changes in reflectivity of the radiation shield.

The Numatron Data Acquisition System was reasonably successful and was far superior to manual methods of data recording since it could read more frequently to an accuracy of more significant figures, and

record the time and datum precisely. An improved system would be computer compatible to facilitate data analysis although it should also have output readable by humans and should record more frequently. The vacuum gauging should also be modified to be recorded on the same system.

A Hewlett Packard Model HP 970 A and a Simpson Model 460 digital voltmeters were used to read voltage directly across the sample. The current was measured from the voltage drop across a precision shunt using a Keithly Digital Voltmeter Model 168.

E. General Experimental Procedure. A total of ten electrotransport purification experiments were made during this study and although the purpose of each experiment was different, a general experimental procedure was followed. This was necessary in order for the results of the experiments to be compared and to insure the integrity of the apparatus after repeated heating.

The threaded thorium rod sample measuring 16.5 cm (6.5 inch) long and 0.25 cm (0.10 inch) in diameter was first electropolished in a chilled methanol-perchloric acid bath as described by Hopkins et al.³⁴ It was then wrapped in a degassed tantalum sheet and heated to 750°C under a pressure of 5×10^{-8} torr (N_2) in a small annealing furnace to degas the sample and to remove any trace of thorium chloride from the surface. The "bow" expansion adapter, the tantalum anode adapter, the thorium and cathode adapter and the copper bolts of the assembly were also degassed under these same conditions. A photomicrograph of the thorium after heating to 750°C in a vacuum is shown in Figure 10.

The radiation shield, rack assembly, electrodes, mirror and brackets and the temperature monitoring device, minus the solar cell, were

Figure 10. Photomicrograph of thorium rod prior to loading in electrotransport apparatus. As heated to 750°C for one hour in vacuum. 250X.

vacuum degassed by heating to 400°C under a pressure of 2×10^{-7} torr (N_2) for 72 hours in the prebakeout chamber. The cryogenic panel was also degassed prior to its use in the space simulation chamber.

The thorium sample was then loaded into the radiation shield and rack assembly, under clean laboratory conditions, after which the unit was bolted to the inner wall of the space chamber so that the sample was in a vertical position. The chamber was then sealed and the three sorption pumps used to evacuate it to $\sim 1 \times 10^{-2}$ torr (N_2) prior to starting the ionization pump K in Figure 2. The magnets were removed from the differential ion pump, L, and its housing wrapped with insulated Kanthal A-1 wire. The 46 cm (18 inch) diameter main flange was also wrapped with Kanthal A-1 wire and the entire chamber covered with a double layer of 2.5 cm (1 inch) thick fiberglass insulation that was secured with asbestos rope. The temperature of the chamber was gradually increased so that the pressure inside the chamber was held near 5×10^{-6} torr (N_2), at which pressure the ionization pump has the fastest pumping speed. Heating of the chamber was continued until the surface reached 380°C as measured in several locations using chromel-alumel thermocouples. The chamber and its components were heated at this temperature for six days after which time the pressure inside the chamber was 1 to 5×10^{-8} torr (N_2). At this time, all of the titanium filaments associated with the titanium sublimation pumps were degassed by heating with their separate control units. The chamber was then cooled to 250°C and the titanium filaments again degassed. When the chamber wall reached 100°C, the filaments were degassed once more and the insulation and heating wires removed from the clean ion pump (item L, Figure 2). This pump was cooled to room temperature while

the chamber was still at 100°C and its magnets attached. It was then energized for five minutes to allow its elements to degas after which it was turned off and the chamber cooled to ambient temperature. The pressure inside the chamber at this point was 1 to 2×10^{-10} torr (N_2). The fiberglass insulation was then removed from the chamber and the power supply and related electronic control equipment placed around the chamber. The 15.2 cm (6 inch) right angle valve (item J in Figure 2) was closed and the differential ion pump, L, started. Each joint of the system was leak tested with nitrogen and helium gases using the residual gas analyzer to measure any response. Final leak testing was done by placing a plastic cover over the system and flooding the space between it and the chamber with helium. The titanium sublimation pump (item D, Figure 2) was then started. The elements of the pump were surrounded by a stainless steel deflector so that the sublimed titanium condensed on the inner surface of the 46 cm (18 inch) cover flange and none came in contact with the ion pump or the sample. If the cryogenic panel was to be used during the experiment, it was cooled by filling with liquid nitrogen from the 400 liter storage vessel.

Upon lowering the temperature of the cryogenic panel to 77K, the peak heights of the residual gases were determined using either the Quad 150 EAI or the UTI-100C residual gas analyzer. The UTI-100C analyzer was used during Phase II to continually monitor the partial pressure of thirteen residual gases present during the experiments. The pressure inside the chamber before the electrotransport sample was heated, was 2 to 4×10^{-11} torr (N_2). The calibrated ionization gauge received from Langley Research Center was used to measure these nitrogen equivalent pressures.

The thorium sample was resistively heated to temperature using the

direct current applied by the Model SCR-10-500 power supply. In early experiments, the heating was manually controlled; however this operation became automated with the development of the electronic control circuit. In each experiment the temperature of the sample was slowly but steadily increased to 1600°C. The manually controlled heating program shown in Table IV, was a stepwise process. This rate was translated to a linear function which was used in the control system for automatic heating of the sample. The voltage shown in Table IV was measured across the electrodes extending from the space chamber and the current was measured using the calibrated shunt.

Table IV. Heating Rate of Thorium Sample from Room Temperature to 1600°C

<u>Time,</u> <u>(minutes after start)</u>	<u>Amps</u>	<u>Volts</u>	<u>Sample Temperature</u> <u>°C</u>
Start	15.0	0.50	--
1.0	24.5	0.85	--
1.5	34.0	1.15	--
2.0	44.0	1.50	--
2.5	56.0	1.95	--
3.0	65.0	2.33	1110
3.5	71.5	2.63	1340
4.0	80.0	3.05	1450
4.5	85.0	3.20	1530
5.0	86.0	3.25	1580
5.5	86.4	3.30	1600

The current to the sample was increased to a level of 86.4 amps after which the power supply was placed in the current control mode. This amperage was sufficient to heat the sample to 1600°C which was the temperature used in most of the experiments. After the sample was at temperature for two minutes, the control was switched to the voltage mode for the duration of the experiment. The voltage control

mode was used since any increase in resistance of the sample due to "grain-sliding", or loosening of the assembly, would result in a decrease in the power supplied to the sample and a consequent lowering of the sample temperature. If a high resistance point developed in the assembly using the current control, the voltage would be increased and consequently the power would also increase, which could result in the sample melting.

The thorium samples were heated to either 1550 or to 1600°C in the actual experimentation. These temperatures are higher than that used for the steady state calculations (1500°C) but they were selected to confirm that the design of the sample assembly was mechanically and electrically stable elevated temperatures.

The temperature of the sample was measured with a calibrated optical pyrometer and the observed temperature was corrected for the emissivity of the sample and for absorption by the viewing window. The temperature was constant during the six day runs to within $\pm 5^\circ$. The surface of the midpoint of the rod was about 75°C hotter than the ends at a point 1 cm (0.4 inch) from the adapters because the adapters were somewhat cooler than the specimen. Consideration was given to the uniformity of the sample temperature from its center to its outer surface. An equation by Kutateladze³⁵ states,

$$t_{R=R_2} = t_{R=0} - \frac{qvR_2^2}{4\lambda} \quad (\text{Eq. 5})$$

for a rod in which heat is being generated at a rate qv Kcal/m³·hr with a thermal conductivity λ Kcal/m·hr·°C. Using this equation for our experiment in which ~270 watts are dissipated in a 16.5 cm (6.5 inch) long rod having a 0.13 cm (0.05 inch) radius, and using the 20°C thermal conductivity value of 0.090 cal/cm sec °C for thorium, the temperature

difference between the center and the outside of the rod was determined to be only 3.4°C.

After the thorium rod was purified by electrotransport for six days, the power was shut off and the sample was allowed to cool quickly to ambient temperature. The next day the pressure inside the space simulation chamber was increased to atmospheric by adding dry nitrogen gas. The end flange of the chamber was then removed and the radiation shield and rack assembly containing the sample were unloaded.

After each experiment the purified thorium rods were sectioned into four equal lengths and their quality determined by measuring their resistance ratio ($R_{300K}/R_{4.2K}$). This parameter is easily obtained and while it reflects the total amount of solutes and impurities in solution it does not identify which impurities are present. The higher the ratio, the lower the impurity level of the metal. Prior to the present work, the highest purity thorium prepared had a $R_{300K}/R_{4.2K}$ of 1200. This material had been purified under a pressure of $\sim 1 \times 10^{-10}$ torr (N_2).

Sections of some of the purified rods were chemically analyzed for impurity content. The carbon content was determined by combustion chromatographic analysis and the hydrogen, nitrogen, and oxygen concentrations were measured by vacuum fusion analyses. All other elements were determined by spark source mass spectrometry.

F. Initial Electrotransport Experiment in Space Simulation Chamber. Our initial electrotransport experiment was performed on January 23, 1975. The purpose of this run, NASA-1-151, was to test the sample support assembly, power supply, and related measuring equipment. The cryogenic panel was not used. The sample was heated slowly to 1500°C and held for six days (144 hours). A three strand

copper "bow" adapter was used to compensate for the sample expansion since the adapter prepared from Ni-45 w/o Ti "memory" alloy had not yet developed. The copper adapter was made from three strips 0.008 cm (0.003 inch) thick, 1.27 cm (0.50 inch) wide and 15.25 cm (6.0 inch) long. This adapter flexed enough to accommodate the increase in length of the thorium due to expansion during heating and as a result the sample remained straight during this part of the experiment. The surface temperature of the thorium was measured to be 1450°C using a calibrated optical pyrometer. With application of the proper corrections for the emissivity of the sample and the absorption of the sight glass, the actual temperature of the specimen was 1600°C. During the heating of the specimen, the pressure inside the chamber increased to a maximum of 1.1×10^{-8} torr (N_2) when the sample temperature reached 1250°C. The pressure gradually decreased as the specimen was heated to 1600°C at which time it was measured as 8.3×10^{-10} torr (N_2). After 24 hours at 1600°C, the pressure had decreased to 6.6×10^{-11} torr (N_2). Some sagging of the copper adapter due to creep was noted and after 75 hours the adapter "bottomed out" due to this process as was expected from previous experimentation. The thorium sample remained straight until significant bending occurred due to the creep process after 72 hours. This bending continued until the run was shut off, at which time the rod was severely distorted near the cathode end (bottom). After the sample was removed from the chamber, it was found to be 17.14 cm (6.75 inch) long which corresponds to a 0.61 cm (0.25 inch) increase in length. The creep process will not occur in a near zero-gravity environment and the rod and adapter would remain straight for the duration of the experiment. This assumption was substantiated in a subsequent experiment described in sub-

section H of this section of the report.

A very light film was noted on the surface of the radiation shield after the run. Swipes of this minute residue were analyzed by emission spectrometry and were found to contain calcium, chromium, manganese, and tin, all of which were probably volatilized from the thorium during the six-day heating period. The specular reflectivity of the radiation shield before and after the run was measured to be the same within $6.7\% \pm 2.5\%$. Measurements of specific areas repeated to within $\pm 0.2\%$. The reflection was determined by measuring the apparent temperature of the reflection of a standard wide filament tungsten lamp with a Leeds and Northrup optical pyrometer.

The thorium rod was sectioned into four equal lengths and the impurity profile of the rod measured by determining their resistance ratio ($R_{300K}/R_{4.2K}$). This profile, from the cathode to the anode end of the rod, is shown in Table V. The original material, as annealed, had a resistance ratio of 35.

Table V. Resistance Ratio ($\frac{R_{300K}}{R_{4.2K}}$) of Thorium Rod from Initial Experiment.

Run No.	(-) Cathode		Anode (+)	
	(1)	(2)	(3)	(4)
NASA-1-151	135;830	1080;1380	1000;820	510;30.5

The quality of the thorium produced in our first experiment was the best we had made to date in a single experiment. The cathode end of the rod, Section 1, did not have the highest ratio since the end of the rod was slightly cooler due to the thickness of the tantalum adapter. In subsequent experiments, the diameter of the tantalum cathode adapter was decreased to minimize the temperature gradient between it and the sample.

The purest section, Section 2, was analyzed and found to contain 6 ppmw carbon, 2 ppmw nitrogen and 1 ppmw oxygen. The original materials contained 52 ppmw carbon, 45 ppmw nitrogen and 25 ppmw oxygen (Table I). The tantalum content of the cathode end of Section I was traced by spark source mass spectrometry. It was found to contain 4 ppmw tantalum immediately adjacent to the tantalum adapter and 2 ppmw at a distance 0.9 cm (0.35 inch) from the end. Since the original thorium contained 7.5 ppmw of tantalum (Table I) it appears that this solute moved with the flow of electrons to the anode end of the specimen. Further, the tantalum from the cathode adapter did not seem to migrate into thorium since it was at a slightly cooler temperature. This analysis is in good agreement with the other electric mobility and diffusivity parameters of tantalum in thorium which have been measured.

G. Effect of Solar Radiation on the Experiment. The purpose of this experiment, NASA-1A-11, was to determine the effect of solar radiation on the experiment by measuring any increase in temperature of the sample and its surroundings. In this run the Ni-Ti "bow" type expansion adapter was successfully used for the first time. The calibrated modulated and unmodulated ionization gauges received from LRC were installed on the space simulation chamber and used to measure the nitrogen equivalent pressure during the experiment.

The temperature profile of the electrotransport apparatus was measured using eight chromel-alumel thermocouples attached to the surface of the radiation shield and rack assembly as shown in Figure 11. The thermocouples were contained in small stainless steel tubes resistance welded to the surfaces. The other ends of the couples were passed through the chamber wall using a 26 pin high vacuum feedthrough.

The initiation of this experiment was delayed about four weeks because of leaks that developed in the 15.25 cm (6.0 inch) diameter sight glass and in the flange assembly of the large right angle valve after the system had been baked at 400°C. Following the resolution of these problems, the chamber was baked at 380°C for six days and cooled to ambient temperature. The pressure inside the system after bakeout was 6.6×10^{-12} torr (N_2) as measured using the new vacuum gauging.

A type 64002-2 carbon arc lamp manufactured by the Strong Jet-Arc Co., of Toledo, Ohio was used as a solar simulator for this experiment. A high intensity carbon electrode, type L, 1240 obtained from the Union Carbide Co., New York was used as the negative electrode. The positive electrode was an "Ulrex" type L 0203 electrode obtained from the same company. The reliability of the 15.25 cm (6.0 inch) diameter sight glass against the heat generated by the solar simulator was first tested with the thorium sample at ambient temperature. The high intensity carbon arc lamp was positioned so that a 15.25 cm (6 inch) diameter beam of collimated light, having a unit solar intensity, was projected onto the thorium sample and radiation shield assembly for 32 minutes. A temperature of 74°C was obtained in the center of the radiation shield, position #5, which was the highest observed. The pressure in the system under these conditions was 2×10^{-11} torr (N_2) as measured by

Figure 11. Schematic of radiation shield showing temperature probe locations.

the calibrated ionization gauge. A Fresnel lens was then placed on the 15.25 cm (6.0 inch) diameter sight glass and the arc lamp moved closer so that a circular area around the sample, having a diameter of 30 cm (12 inch), was subjected to one solar constant. The radiation shield and sample were heated in this manner for 30 minutes and a maximum temperature of 109°C was observed at position #5. The pressure of the system during this test was 3 to 8×10^{-11} torr (N_2).

The thorium rod was then heated to 1600°C and both of the above solar simulation procedures repeated. Using the slide port in the back of the radiation shield, the temperature of the sample could be monitored with an optical pyrometer during the solar simulations. It was found that when the collimated beam was used, a 12°C rise in the sample temperature occurred and a 14°C rise was observed when the dispersed beam was used. An increase in temperature of this magnitude was expected since the radiation shield was a concave reflector having an elliptical configuration and the sample was located at a focal point. With this design, only the radiant energy striking the sample directly and that passing through the other focal point of the ellipse would affect the temperature of the specimen.

The temperature profile of the radiation shield and rack assembly during solar simulation with the dispersed beam is shown in Table VI. Also included in Table VI are the temperatures of the surfaces at the various points when solar simulation was not applied and the sample is at 1600°C.

Table VI. Temperature Profile of Radiation Shield and Rack Assembly During Solar Simulation.

Position (See Figure 11)	<u>Temperature, °C</u>		
	Solar Simulation (Dispersed Beam)	Without Solar Simulation	
	<u>Sample at Ambient Temp.</u>	<u>Sample at 1600°C</u>	<u>Sample at 1600°C</u>
#1	52	134	128
#2	65	137	123
#3	75	140	121
#4	81	139	120
#5	109	185	142
#6	39	129	125
#7	34	99	90
#8	27	75	72

After about 30 minutes of solar simulation, the temperature at the various positions was nearly constant except at positions #7 and #8. The temperature at these locations was slowly but steadily increasing. The pressure in the system increased to 1×10^{-10} torr (N_2) during the collimated light experiment and to 3×10^{-10} torr (N_2) when the dispersed light was applied. This increase in pressure was due to additional degassing of the electrotransport apparatus which could not be rapidly removed from the vicinity of the sample by the limited capacity of the ionization pump. The high pumping capacity of the Molecular Shield Device would minimize this increase in residual gas content near the sample during actual solar radiation.

After the solar simulation tests were completed, heating of the

thorium sample was continued for four and one half days. The Ni-45% Ti "bow" adapter worked very well despite the two separate bakeouts at 400 and 380°C. Its "memory" was not changed by these heats, and it kept the sample straight during the initial heating and expansion. The current flow to the sample was interrupted twice during the run because of severe electrical storms in our area. After the first power outage, the sample was successfully reheated to 1600°C by applying the same current as that used before the outage. This test indicated that no significant change in the sample assembly took place during heating and cooling. When the temperature of the sample as measured with the optical pyrometer was 1600°C, a power reading of 296 watts was observed which held nearly constant during the experiment.

The nitrogen equivalent pressure in the system during this experiment was 3.4×10^{-11} torr as measured with the calibrated modulated ionization gauge. A resistance ratio ($R_{300K}/R_{4.2K}$) profile of the purified thorium rod is shown in Table VII. The highest ratio obtained was 1440 which compares favorably to the 1380 value obtained from our initial experiment in which the sample was heated for six days at a pressure of 7×10^{-11} torr (N_2).

Table VII. Resistance Ratio ($R_{300K}/R_{4.2K}$) of the Thorium Rod from Solar Simulation Experiment.

Run No.	(-) Cathode			Anode (+)
	Section			
	(1)	(2)	(3)	(4)
NASA-1A-11	280;1180	1440;1250	1150;810	335;9

(The thorium rod had a resistance ratio of 35 before purification).

H. Simulation of Near-Zero Gravity. A problem that is often encountered in the electrotransport purification of polycrystalline metals in earth bound experiments is high temperature grain boundary "sliding". This phenomenon is caused by a displacement of the grains due to plastic deformation caused by the weight of the rod. It has been our experience that the problem is prevalent in the more dense refractory metals. This "sliding" becomes apparent after only one or two days of heating, and as a result, a region of the high electrical resistance often develops giving rise to localized excessive heating and premature termination of the experiment by melt-off. This condition also occurs, but to a lesser extent, in a sample which is heated in a vertical condition, especially between grains whose boundary is not exactly perpendicular to the longitudinal axis of the specimen.

In an effort to show that this phenomenon should not occur in the weightlessness of a space experiment, an electrotransport experiment was performed under a near-zero gravity environment. This was accomplished by applying an external magnetic field to the thorium sample so as to interact with the field associated with the current used to heat the specimen to generate an upward force as shown in Figure 12. In this manner, the Earth's gravitational force acting upon the specimen was opposed and a near-zero gravity environment achieved. This effect was demonstrated by heating an electrotransport sample in a horizontal position inside a specially adapted vacuum chamber. This chamber was part of a separate electrotransport apparatus and was made of non-magnetic stainless steel. Two sets of coils were wound around the chamber. One set was placed so that when current was applied to the coil a magnetic field would be created perpendicular to the sample, thereby placing a vertical

force upon it. A second set of coils was wound on the chamber to create

Figure 12. Schematic of force due to magnetic field and current through sample.

a field in a perpendicular direction which could be used to adjust for errors due to imperfect mounting of the first set of coils. With an 86 amp current passing through the thorium sample, a 16.5 amp current to the coil provided a 62 gauss field which just balanced the force of gravity on the sample.

The equation for the forces on the sample is, $F = F_m - F_g$ where F is the net force on the sample, F_m is the magnetic force and F_g is

the gravitational force. This equation can also be written,

$$F = KI_p \cdot I_m \ell \sin Q - mg \quad (\text{Eq. 6})$$

where K is a constant, I_p is the current through the sample, I_m is the current in the magnetic coil, Q is the angle between the direction of current in the coil and the magnetic field, m is the mass of the sample, ℓ is its length and g is the acceleration due to gravity. It was found that to avoid deformation of the wire, the current in the magnet had to be as high as possible at the start of the run to provide maximum support to the sample when the sample current was low. As the sample current was raised during warm-up, above the amount which provides a magnetic force component equal to the gravitational force, the current through the magnet was lowered. During the run, at constant high sample current, the magnet current was adjusted manually so the sample would exhibit no deflection by the net gravitational and magnetic forces. At the end of a run, the magnetic current would be raised, as the sample current was lowered to maintain a zero net force over a time of approximately two minutes, which was long enough for the sample to cool and regain its strength. When the magnetic current had reached its maximum level of 46.1 amps, the sample current was shut off.

Figure 13(a) is a photograph of a thorium rod that was heated in a horizontal position with a dc current for 150 hours under normal gravitational force and shows the result of "grain-sliding". Figure 13(b) shows the effect of a near-zero gravity environment upon a similarly heated sample. In this case, the grain-sliding was greatly reduced and estimated to be less than 10% of the sliding in the sample heated with no opposing magnetic field. The results of this experiment clearly indicate that

(a)

(b)

Figure 13. Thorium rod sample heated for 150 hours at 1600°C. Top photograph (a) sample heated under ordinary gravitational forces, (b) sample heated under near zero gravity conditions.

"grain-sliding" will not be a problem in a flight experiment and that the micro-gravity of space should prevent high resistance areas from developing in the specimen as a result of "grain-sliding".

I. Probability of Meteor Damage to Sample. A review of the meteorite data shows that the probability of a particle, with a mass of 10^{-6} grams or greater, hitting an area the size of our 10 gram thorium sample over a five-day period is one in 30,000. If such a particle were incorporated within the sample, it would cause a 0.1 ppmw contamination.

J. Operating Environment for Preparation, Launch, Space Operation and Recovery of the Experiment. A separate report, SPI-66006, covering this subject was prepared in our Laboratory and completed in April, 1975. Copies of this report are available from the authors upon request.

2. PHASE II (May 1, 1975 to April 30, 1976)

During this phase of the project, the design of the electrotransport apparatus was finalized and it was operated under various environmental conditions. Particular attention was directed toward improving the environment of the experiment so that metal of high purity could be prepared. The partial pressures of 13 residual gases in the vicinity of the sample were determined during several of the experiments. The appropriate instrumentation for a "one-button-start" was incorporated and the preparation of several high-purity single crystals of α thorium was demonstrated.

A. Effect of Coldness and Darkness on the Experiment. The purpose of this experiment was to simulate the coldness and darkness of outer space inside the chamber and to determine what effect these conditions have on the parameters of the experiment. The electrotransport apparatus containing the thorium sample was loaded inside the space chamber in the usual manner. The threaded connections of the sample assembly were crimped so that they could not loosen during heating. The radiation shield was again equipped with eight thermocouples (Figure 11) as was done in the experiment in which the thorium sample was subjected to solar simulation (NASA-1A-11). In order to simulate the coldness and darkness of space, the cryogenic panel was placed inside the chamber directly opposite the sample and radiation shield. The face of this panel was covered with stainless steel honeycomb having a 6 to 1 ratio of hole-depth to hole-diameter to assure a good black body condition. The system was baked out, and after cooling to ambient temperature, the pressure in the system was 1.7×10^{-11} torr (N_2) as determined using the calibrated modulated ionization gauge. The thorium sample was heated

to 1600°C for 24 hours after which liquid nitrogen was slowly added to the cryogenic panel. After 50 minutes, the panel was full and the automatic fill control system attached. The pressure in the system dropped very quickly to 7×10^{-12} torr (N_2) as the panel was cooled and continued to drop during the six-day experiment until a minimum pressure of 4×10^{-12} torr (N_2) was obtained. The space simulation chamber and the related equipment used in this experiment are shown in Figure 14.

The effect of the cryogenic cooling on the temperature of the radiation shield and rack assembly was determined by monitoring the temperature of the eight thermocouples throughout the run. Table VIII shows the temperature at these points with and without cold-black-body simulation while the thorium sample was at 1600°C.

Table VIII. Temperature Profile of Radiation Shield and Rack Assembly With and Without Cold-Black-Body Simulation.

Position (See Figure 11)	Temperature, °C (Sample at 1600°C)	
	<u>Cold-Black-Body Simulation</u>	<u>Without Cold-Black- Body Simulation</u>
#1	96	128
#2	89	123
#3	91	121
#4	94	120
#5	108	142
#6	100	125
#7	70	90
#8	46	72

The hottest area during this experiment was position #5 of the radiation shield which reached 108°C. During the solar simulation experiment (subsection G, Phase I) this same area increased to 185°C.

Figure 14. Space simulation chamber and the related equipment used in the cold-black-body simulation experiment.

These data show that a maximum fluxuation of 77°C could be expected as the experiment passes from sunlight to the darkness of space. No change in the sample temperature was observed while the cryogenic panel was chilled to -195°C.

The thorium metal purified in this experiment had a resistance ratio ($R_{300K}/R_{4.2K}$) of 2035. The percent of the total pressure of each of the residual gases in the system after the rod had been heated for 100 hours is shown in Table IX. These data were determined with the aid of a computer program obtained from the Oak Ridge National Laboratory.³⁶ The input to the program included the sensitivity of our EAI Quad 150 residual gas analyzer to the 13 gases shown in Table IX, their ionization constants as listed by Summers³⁷, their cracking patterns, and the peak heights expressed in true amps at each m/e ratio. The sensitivity of our instrument to the various gases was calculated from its sensitivity to nitrogen as determined after a previous electro-transport purification experiment.

Table IX. Percentages of Residual Gases Present in Space Simulation Chamber During Cold-Black-Body Simulation

<u>Gas</u>	<u>Percent of Total Pressure</u>
H ₂	55.33
He	26.08
Ne	8.54
CO	4.85
N ₂	1.74
H ₂ O	1.47
CH ₄	0.66
CO ₂	0.48
O ₂	0.31

Table IX. (Continued)

<u>Gas</u>	<u>Percent of Total Pressure</u>
Ar	0.25
C ₂ H ₄	0.23
C ₂ H ₆	0.04
C ₃ H ₈	<0.01
	<hr/> 99.99%

From this experiment, it is concluded that the coldness and darkness of space will not be detrimental to the electrotransport experiment and it appears that the void of space should aid in decreasing the partial pressure of the reactive gases present in the vicinity of the sample assembly. This should decrease the flux of contaminants into the surface of the sample and purification should be enhanced.

B. Use of High Purity Cathode Extension. A major problem that persists in the purification of metals by electrotransport is the migration of impurity solutes from the electrodes used to support the sample and to carry the current. The proper selection of material for the cathode is particularly important since the electrons first flow through the cathode prior to entering the sample and can transport impurities into the rod. The rate of movement of these solutes is usually slow since the cathode supporting piece, more commonly called the cathode adapter, is at a temperature somewhat lower than that of the sample. In designing the sample assembly for our experiment, we have minimized this effect by using tantalum as the cathode adapter. Interstitial solutes migrate against the flow of electrons in tantalum and therefore should not enter the thorium rod. However, it has been found that the first centimeter

length of the cathode end of the thorium rod can also serve as a source of impurities. This segment is 75°C cooler than the remaining portion of the rod and the interstitial solutes do not migrate at a sufficient velocity to be substantially removed during a six-day experiment. As a result, they serve as contaminants to that portion of the rod from which solutes have already been electrotransported.

An effort was made to overcome this problem by purifying a thorium sample with a high purity segment welded to its cathode end. The welding step was done by resistance welding in vacuum. The composite sample was loaded, the system baked out and cooled to room temperature. The cryogenic panel was cooled to -195°C after which the thorium rod was heated for six days at 1575°C. The pressure in the system after the fourth day at temperature was 4×10^{-12} torr (N_2) as measured using the calibrated modulated ionization gauge. A slight leak was found in the head assembly of the EAI Quad 150 residual gas analyzer and as a result the nitrogen and oxygen concentrations were somewhat higher during this experiment than in previous runs. Consequently, the resistance ratio ($R_{300K}/R_{4.2K}$) of the high purity cathode section was decreased from ~1500 before the experiment, to a value of only 800 after the run, thus confirming that some sample contamination took place during processing. The highest resistance ratio obtained in the purest section of the rod was 1690 which is considerably lower than expected. Due to the leak in the system, the objective of this experiment was not completely met. However, if the purified cathode extension had not been used, metal of even considerably poorer quality would have resulted.

C. Partial Pressure Measurements of Residual Gases in Vicinity of Sample. In this experiment, NASA-1A-149, the UTI Model 100C residual

gas analyzer was mounted directly opposite the thorium rod and the partial pressures of 13 residual gases inside the space chamber and in the vicinity of the sample were determined. The tip of the ionizer assembly was located approximately 12.5 cm (5.0 inch) from the thorium sample. The cryogenic panel was not used in this run so that higher concentrations of residual gases could be achieved and their effect on the quality of the purified metal determined.

After the bakeout procedure was completed, the control system was used to heat the sample slowly to 1600°C. The peak heights of the 13 gases present in the chamber were measured every 24 hours during the experiment. The gases measured were: H_2 , He, CH_4 , H_2O , Ne, N_2 , CO, C_2H_4 , C_2H_6 , O_2 , Ar, CO_2 and C_3H_8 . A trace of their peak heights after the sample was heated for 120 hours is shown in Figure 15. After the thorium rod was cooled to room temperature, the chamber was back-filled with pure nitrogen gas to various pressures between 1×10^{-9} and 8×10^{-7} torr and accurate pressure readings were made using the calibrated unmodulated ionization gauge from LRC. The corresponding nitrogen peak heights, in amps, were also determined in addition to the gain of the electron multiplier. From these data, the sensitivity of the gas analyzer to nitrogen, independent of the gain, was determined to be 3.85×10^{-4} amps/torr.

Using this value for the nitrogen sensitivity, and the values of the relative ionization gauge sensitivities for the 13 gases from Summers³⁷, the sensitivity of the UTI to each gas was determined as described in Appendix C. With the aid of the adapted computer program received from the Oak Ridge National Laboratory³⁶, these sensitivities and the values of the peak heights were used to calculate the partial pressures of the

Figure 15. Peak heights of residual gases after thorium sample was heated to 1600°C for 120 hours.

gases. Plots of the partial pressures as a function of time were then made and are shown in Figure 16. From these graphs, it was observed that as the sample was heated to 1600°C, an increase in pressure of all the gases was noted, except for oxygen, which decreased, indicating that it was being picked up by the thorium rod. The pressure of all the gases then gradually decreased with time and most of them were present at a constant partial pressure after 72 hours. The pressure of hydrogen continued to decrease with time until the run was terminated. After cooling to room temperature, the pressure of all the gases, except nitrogen and carbon monoxide was found to decrease. The pressure of these two gases actually increased indicating they were being removed by "gettering" of the hot thorium rod. The partial pressure of oxygen, after the sample was cooled, was 7×10^{-14} torr.

The nitrogen equivalent pressure during the run as measured using the calibrated modulated ionization gauge was 2.2×10^{-11} torr (N₂). The resistance ratio ($R_{300K}/R_{4.2K}$) profile of the purified thorium is shown in Table X.

Table X. Resistance Ratio of Thorium Rod Purified in Experiment NASA-1A-149.

	(-) Cathode End		Anode End (+)	
Section	(1)	(2)	(3)	(4)
	330;800	1540;1475	1255;1060	410;15

Since the thorium rod processed in this experiment had a resistance ratio of only 1540 as compared to a ratio of 2035 when the cryogenic panel was used (Subsection A, Phase II) it is concluded that this unit is quite effective in reducing the reactive gas concentration in the

Figure 16. Partial pressure of residual gases, as a function of time, present in vicinity of sample during electrotransport experiment. Cryogenic panel not used.

vicinity of the sample, thereby enhancing the purification process. The effect of the cryogenic panel upon the partial pressure of the residual gases is quantitatively described in subsequent experiments.

D. Demonstration of Automatic Control Circuit and Effect of Prolonged Bakeout. The primary purpose of this experiment, NASA-2A-13, was to demonstrate the automatic control system which had been developed during Phase I of the project. The effect of an extended bakeout period (20 days) was also evaluated by the quality of the thorium prepared during subsequent electrotransport processing.

The cryogenic panel was installed inside the space simulation chamber and was used as a high capacity pump during this experiment. The chamber was baked for 20 days at 380°C after which the unit was cooled to room temperature and the cryogenic panel filled with liquid nitrogen. When the surface of the panel reached -195°C, a single button was pushed and the automatic control system regulated the heating of the sample to 1600°C, maintained this temperature for six days, and then shut off.

Six weeks previous to this run, the programmer had been tested and used to control the heating of a thorium sample contained in a separate electrotransport chamber. A few days before it was used in this experiment, the controller was again tested using a platinum rod that, because of its oxidation resistance, could be heated in air. The diameter of the platinum was such that it had the same resistance as the thorium contained in the sample assembly at 1550°C. The settings of the programmer were left unchanged and the thorium rod was successfully heated to temperature with 86.5 amps as programmed. This pretesting of the automatic control system, by heating a platinum rod of the same resistance as the electro-

transport sample, worked so well that it is recommended as a check out procedure for a flight experiment. The nitrogen equivalent pressure, after the rod was heated for five days, was 2×10^{-12} torr as measured using the calibrated modulated ionization gauge from Langley Research Center. After the rod was cooled to room temperature and the cryogenic panel warmed to ambient temperature, the simulation chamber was back-filled with pure N_2 and the sensitivity and gain of the UTI Model 100C residual gas analyzer determined. Using the procedure described in Appendix C, the partial pressures of each of the 13 gases was calculated with the aid of a computer. In Figure 17, the partial pressures of the various gases are plotted as a function of time. A summation of these partial pressures, after the thorium rod was heated for five days, showed the true total pressure in the chamber to be 2.5×10^{-11} torr.

After the thorium sample was removed from the chamber, it was sectioned into four equal lengths 4.1 cm (1.6 inch) long. Two resistance ratio ($R_{300K}/R_{4.2K}$) measurements on each section were made and the results are shown in Table XI.

Table XI. Resistance Ratio of Thorium Rod Purified at 1600°C Using Cryogenic Pumping.

Run No.	(-) Cathode End		Anode End (+)	
	(1)	(2)	(3)	(4)
NASA-2A-13	565;1130	2000;2080	1760;1475	665;16

The thorium metal before purification had a resistance ratio of 35.

It is concluded from this experiment that a 20 day vacuum bakeout at 380°C of the experiment does not appreciably increase the quality of the thorium metal purified. Metal of the same quality, resistance

Figure 17. Partial pressure of the residual gases, as a function of time, in the vicinity of the sample when cryogenic pumping was used.

ratio of 2035, was prepared in experiment NASA-1A-85 which employed only a six-day bakeout period. The automatic control system worked very well during this experiment and a control system with these features should be used in a flight experiment.

E. Preparation of High Purity Single Crystals of Thorium. In previous studies in our Laboratory, we have prepared thorium single crystals by first purifying a rod of the metal by electrotransport and then heating it several times through its polymorphic transformation³⁸. In this work, after the electrotransport purification process was completed, the temperature of the rod was decreased to 1300°C which was slightly below its transformation at 1340°C. This temperature was held for 20 minutes and the rod heated to 1500°C for 20 minutes. This temperature cycle was repeated three times, after which the rod was held at 1310 to 1320°C for 24 hours. At 1310°C, the electric mobility of carbon, nitrogen, and oxygen in thorium is very slow not only because of the low temperature but also because of the crystal structure of thorium. At this temperature, thorium has a face-centered-cubic structure (α thorium) which is not as conducive to high solute mobility as is the body-centered-cubic structure (β thorium). Efforts to prepare high purity single crystals in other chambers, with high residual gas contents, have always resulted in contamination of the crystals. Consequently, the resistance ratio ($R_{300K}/R_{4.2K}$) of the highest purity thorium single crystals prepared prior to this experiment was 500.

It was the purpose of experiment NASA-2A-44 to prepare ultra-high purity single crystals of thorium in the low pressure environment of the space simulation chamber equipped with the cryogenic panel. With this unit, it should be possible to convert several of the crystals of β

thorium into crystals of α thorium without severely contaminating the specimens. The polycrystalline thorium rod was loaded into the space chamber as usual and the unit baked at 380°C for six days. The automatic control system was adapted for this experiment so that the programmer, as modified to work with voltage control, was used to (1) heat the sample to 1600°C for six days, (2) cycle the temperature between 1300°C and 1500°C three times with 20 minute holds at each temperature, (3) hold the sample temperature at 1310°C for 24 hours and (4) terminate the run. This desired program was followed in a "hands off" operation. The only operator assistance necessary was a re-start when the timing clock turned off unexpectedly early in the run due to a bent mechanical contact.

The anode currents for the peaks of the residual gases H_2 , He, Ne, N_2 , CH_4 , CO, C_2H_4 , C_2H_6 , C_3H_8 , H_2O , CO_2 , Ar and O_2 were measured before and during the six-day-purification run. Measurements were also made during the 24 hour "soak" period at 1310°C and after the experiment was terminated. In Figure 18, the partial pressure of these gases are plotted as a function of time for run NASA-2A-44. The nitrogen equivalent pressure after the fifth day of heating was 3.7×10^{-12} torr. A summation of the partial pressures of the gases revealed the total pressure in the chamber to be 1.6×10^{-11} torr.

After the sample had been carefully removed from the chamber, it was macro-etched by electrically anodizing in a 50% ortho phosphoric acid-50% glacial acetic acid solution. A 6 V potential was applied for several short periods (5-10 seconds) until the individual grains could be easily distinguished. Two single crystals, 11 mm in length, were observed, one near the cathode end of the rod and the other near the

Figure 18. Partial pressure of residual gases, as a function of time, during electrotransport purification and single crystal preparation.

center of the rod. These single crystals were spark cut from the rod and their single crystallinity confirmed by back-reflection Laue X-ray patterns. The remaining pieces of rod were sectioned and the polycrystalline specimens submitted for resistance ratio ($R_{300K}/R_{4.2K}$) measurements. The ratios of the single crystals were not measured in an effort to preserve their perfection since a small amount of mechanical stress can be introduced during the measurement. The quality of the prepared crystals was estimated from the ratio of their adjacent polycrystalline segments. The estimated ratio of one crystal, (Section 2), was 1840 and was sent to Dr. R. A. Outlaw at Langley Research Center. The second crystal, Section 4, had an estimated ratio of 1700 and was sent to Dr. J. Schirber at the Sandia Laboratory for studies concerning the pressure dependence of the De Hass-van Alphen effect in thorium.

These crystals are the purest single crystals of thorium ever prepared which illustrates the importance of the low residual gas content in the vicinity of the sample. These crystals will be used to further determine the intrinsic properties of thorium. Since these properties have been found to change as the thorium becomes more refined³⁹⁻⁴¹, the crystals prepared in a flight experiment would be of special interest.

F. Electrotransport Purification of Once Refined Thorium. The resistance ratio ($R_{300K}/R_{4.2K}$) of the highest purity section of several electrotransport purified rods were plotted as a function of the nitrogen equivalent pressure inside the vacuum chamber during processing. These data are plotted in Figure 19 and show a good fit to the curve except at 2×10^{-12} torr which is the lowest pressure achieved in this study. An increase in the resistance ratio was noted in all other experiments

Figure 19. A plot of the resistance ratio ($R_{300\text{K}}/R_{4.2\text{K}}$) of thorium versus pressure inside the vacuum chamber during electrotransport purification.

as the nitrogen equivalent pressure was diminished by more efficient bakeout and pumping techniques. At 2×10^{-12} torr (N_2) it appears that the impurities migrating slowly into the thorium rod from the cooler cathode end are limiting the purification more than the reactive gases present in the chamber. If the movement of these solutes could be stopped, the residual gas concentration should again become the limiting factor of purification. An extrapolation of the data from Figure 19, indicates that the resistance ratio of thorium purified in a single step electro-transport process should be ~ 6000 when done under a nitrogen equivalent pressure of 1×10^{-14} torr. An even higher resistance ratio would be obtained if once refined thorium were again processed in the environment of the Molecular Shield Device.

There are two techniques that can be used to greatly reduce the movement of these solutes into the thorium rod. The first involves thinning the tantalum cathode adapter so it is heated near 1600°C ensuring that the entire thorium rod is at the same temperature. This would result in excessive alloying between the thorium and the tantalum and termination of the run because of the eutectic reaction at 1565°C between these metals. Further, from recent work in our Laboratory, it has been found that tantalum moves with the flow of electrons in thorium and could serve as a major contaminant if the tantalum-thorium interface were to reach 1450°C .

The second method of reducing the movement of solutes into the thorium rod, and thereby enhancing the purification, is to attach a high purity thorium extension piece at the cathode end. This was done in experiment NASA-1A-115, however, a slight leak developed during that experiment and the results were inconclusive. In an effort to duplicate

this experiment and to determine what quality of thorium could be prepared under a nitrogen equivalent pressure of less than 5×10^{-12} torr, a composite sample was prepared consisting of four sections of once refined thorium metal. In this experiment, NASA-2A-79, the tantalum-thorium interface, at the cathode end, would be kept below 1450°C thereby stopping the tantalum movement. Since the interstitial content of this composite rod were low at the start, no significant contamination from the ends should be observed.

The four sections of once purified thorium were vacuum resistance welded in tandem. Each of these sections were 0.23 cm (0.90 inch) in diameter and approximately 3.8 cm (1.5 inch) long and had resistance ratios of 2040, 1990, 1915 and 1440. This rod was loaded into the electrotransport apparatus and the system evacuated and baked for six days. From diffusion data⁴², contamination of the composite rod was not expected to be excessive during the six-day bakeout at 380°C even though pressure during this step reached 5×10^{-7} to 5×10^{-8} torr (N_2). After bakeout, the system was cooled to ambient temperature and liquid nitrogen was added to the cryogenic panel. The sample was then heated for six days at 1615°C and the anode currents for the peaks of the residual gases measured at 24 hour intervals. In Figure 20, the partial pressure of these gases are plotted as a function of time. The nitrogen equivalent pressure after the fifth day of heating was 4.1×10^{-12} torr as determined from the calibrated modulated ionization gauge. A summation of the partial pressures yielded the total pressure in the chamber to be 1.3×10^{-11} torr.

After the run was completed, the rod was carefully removed from the chamber and sectioned into its original components and the resistance

Figure 20. Partial pressure of residual gases, as a function of time, during electrotransport purification of once refined thorium.

ratios of each measured. These data along with the original resistance ratios of the segments are shown in Table XII.

Table XII. Resistance Ratio of Once and Twice Purified Thorium Segments

	(-) Cathode End			Anode End (+)
Section	(1)	(2)	(3)	(4)
Once Purified	2000;2080	1940;2035	1930;1900	1190;1690
Twice Purified	2800;4000	4100;3400	4200;3500	2500;325

A considerable increase in purity of each segment of the composite rod was achieved as indicated by the increase in the resistance ratios. The ratio of the anode half of Section (4) decreased due to the migration of impurities which "pile-up" in this point. The metal contained in Sections (2) and (3) and having ratios of 4100 and 4200 respectively is the purest thorium ever prepared.

A small portion of Section (3), along with a sample of the original rod, and a section of a once refined rod having a resistance ratio of 2200, were characterized by analysis; the data obtained are shown in Table XIII. The carbon content was measured by combustion chromatographic analysis and the oxygen, nitrogen, and hydrogen by vacuum fusion analysis. All other elements were determined by spark source mass spectrometry. Several elements other than carbon, nitrogen, and oxygen were found to decrease in concentration during electrotransport processing. These elements are indicated in Table XIII. Some of these

Table XIII. Chemical Analysis of Once and Twice Electrotransport Purified Thorium.

Element	<u>Concentration, ppmw</u>			<u>Decrease in Concentration Noted</u>
	BEB-1-341 ($\frac{R_{300}}{R_{4.2}} = 30$) <u>Original</u>	NASA-2A-105(2) ($\frac{R_{300}}{R_{4.2}} = 2200$) <u>Once Purified</u>	NASA-2A-79(2) ($\frac{R_{300}}{R_{4.2}} = 4200$) <u>Twice Purified</u>	
C	50	<10	<10	✓
N	50	<1	<1	✓
O*	30	13	21	✓
H	<1	<1	<1	
Al	<0.02	<0.01	0.008	✓
Ag	<0.03	<0.003	<0.01	✓
As	0.02	<0.01	<0.01	✓
Au	<0.08	<0.08	<0.07	✓
B	0.003	0.005	0.002	✓
Ba	<0.06	<0.06	<0.06	
Be	<0.0003	<0.0001	<0.0008	
Bi	<0.05	<0.05	<0.05	
Br	<0.02	<0.01	<0.01	
Ca	0.12	0.05	0.12	✓
Cd	<0.20	<0.015	<0.015	✓
Ce	<1.2	<0.10	<0.10	✓
Cl*	0.75	0.15	0.15	✓
Co	<0.01	<0.01	<0.01	
Cr	0.20	0.10	0.02	✓
Cs	<0.01	<0.003	<0.003	✓
Cu	<0.05	<0.01	<0.01	✓
Dy	<0.40	<0.35	<0.35	

face contamination due to electropolishing.

Element	BEB-1-341	NASA-2A-105(2)	NASA-2A-79(2)	Decrease in Concentration Noted
Er	<0.45	<0.45	<0.45	
Eu	<0.15	<0.15	<0.15	
Fe	0.30	0.25	0.15	✓
Ga	<0.05	<0.01	<0.01	✓
Gd	<0.40	<0.40	<0.40	
Ge	<0.01	<0.02	<0.02	
Hf	<0.60	<0.70	<0.55	
Hg	<0.09	<0.09	<0.08	
Ho	<0.15	<0.15	<0.15	
I	<0.02	<0.03	<0.03	
In	<0.15	<0.20	<0.15	
Ir	<0.25	<0.25	<0.25	
K	<0.03	<0.08	<0.03	
La	<0.20	<0.10	<0.10	✓
Li	<0.003	<0.0001	<0.0003	✓
Lu	<0.25	<0.25	<0.25	
Mg	0.60	<0.02	0.05	✓
Mn	<0.02	<0.005	<0.005	✓
Mo	2.5	<0.30	<0.25	✓
Na [†]	0.09	0.20	<0.40	
Nb	<40	<8.0	<2.00	✓
Nd	<0.30	<0.30	<0.30	
Ni	0.20	<0.05	<0.05	✓
Os	<0.50	<0.40	<0.55	
P	0.08	<0.005	<0.004	✓
Pb	<0.30	<0.30	<0.20	
Pd	<0.20	<0.05	<0.04	✓
Pr	<0.20	<0.20	<0.20	
Pt	<0.25	<0.40	<0.35	
Rb	<0.02	<0.003	<0.003	✓
Re	6.5	<0.40	<0.40	✓
Rh	0.25	<0.03	<0.03	✓
	<0.25	<0.15	<0.15	✓

[†]Susceptible to surface contamination during analysis.

<u>EI</u>	<u>it</u>	<u>BEB-1-341</u>	<u>NASA-2A-105(2)</u>	<u>NASA-2A-79(2)</u>	<u>Decrease in Concentration Noted</u>
S		0.40	0.10	<0.01	✓
Sb		<0.03	<0.03	<0.03	
Sc		<0.09	<0.08	<0.08	
Se		<0.002	<0.002	<0.002	
Si [†]		2.0	0.25	1.5	
Sm		<0.25	<0.25	<0.25	
Sn		<0.02	<0.02	<0.02	
Sr		<0.007	<0.007	<0.007	
Ta		7.5	6.0	2.5	✓
Tb		<0.15	<0.15	<0.15	
Tc		<0.01	<0.01	<0.01	
Ti		0.40	<0.01	<0.001	✓
Tl		<0.06	<0.06	<0.06	
Tm		<0.07	<0.07	<0.07	
U		0.40	0.40	<0.30	✓
V		<0.01	<0.004	<0.004	✓
W		3	<1.5	<0.80	✓
Y		<0.03	<0.04	<0.03	
Yb		<0.20	<0.20	<0.20	
Zn		<0.01	<0.01	<0.01	
Zr		0.40	0.40	0.35	
Diamond Pyramid Hardness					
		37.6	39.4	37.3	

† Suceptible to surface contamination during analysis.

elements are volatilized from the thorium by the heating in the vacuum environment. However, a decrease in concentration of the several metallic solutes, having very low vapor pressures, was also observed indicating their movement under the influence of the electric field. These metallic solutes are copper, iron, lanthanum, molybdenum, niobium, nickel, palladium, rhenium, rhodium, ruthenium, tantalum, titanium, uranium, vanadium and tungsten. The decrease in their concentration during electrotransport processing is quite significant since many of them cannot be removed from thorium by other refining techniques. The determination of the electric mobility and diffusivity of these solutes in thorium are presently being pursued in separate studies in our Laboratory.

G. Electrical Resistance of Sample Assembly. The electrical resistance of the sample assembly was determined during several of the experiments. These data are summarized in Table XIV and include only those experiments in which the threaded connections were crimped to assure good electrical contact. The resistance values were calculated by dividing the value for voltage by the simultaneous value of current as displayed on the read-out of the Numatron Data Acquisition System.

Table XIV. Resistance of Sample Assembly During Electrotransport Purification Experiments.

Run Number	Initial		Final		Temp. °C
	Resistance, ohms	Current, amps	Resistance, ohms	Current, amps	
NASA-1A-85	0.0354	89.8	0.0383	83.5	1600
NASA-1A-115	0.0361	82.4	0.0378	78.9	1575
NASA-1A-149	0.0358	86.2	0.0370	83.8	1600
NASA-2A-13	0.369	87.2	0.0387	84.3	1600
NASA-2A-44	0.0366	86.3	0.0379	84.2	1600

As can be seen from these data, the resistance of the sample assembly always increases during the experiment. This increase is approximately linear with time and is believed due to the phenomenon of grain-sliding. This phenomenon should not be observed when a rod is heated in a microgravity environment.

Figure 21 is a plot of the resistance of the sample assembly vs the square root of the current for experiment NASA-1A-149 which is typical of those listed in Table XIV. The square root of the current was used because it should be proportional to temperature, at high temperature, by the equation,

$$E = I^2 R = \epsilon \delta T^4 A \quad (\text{Eq. 7})$$

where, ϵ is the emissivity, δ is a constant equal to 5.6699×10^{-5} in cgs units, T is temperature K and A is the surface area of the sample. As can be seen from the plot, the resistance is nearly linearly dependent on temperature indicating these laws are obeyed. The resistance of the

Figure 21. Plot of resistance of sample assembly vs square root of current for run NASA-1A-149.

assembly at room temperature was $0.014\ \Omega$. The room temperature resistance of the thorium rod, 0.25 cm (0.1 inch) in diameter and 16.0 cm (6.5 inch) long, was calculated to be $0.0042\ \Omega$ using $13\ \mu\Omega\text{-cm}$ as the resistivity for thorium. This indicates $0.010\ \Omega$ resistance in the connections of the sample assembly.

3. PHASE III. (May 1, 1976 to September 30, 1976)

During PHASE III of the project, two electrotransport purification experiments were made in an effort to determine the effect of a reactive gas, such as nitrogen, on the quality of thorium refined. Also during this period, the document concerning the test specifications for the experiment was finalized.

A. Effect of High Partial Pressure of Nitrogen on Quality of Thorium Purified. Two separate electrotransport purification experiments were made in which the sample was heated under a high partial pressure of nitrogen gas. In the first experiment, NASA-2A-105, a thorium sample was loaded into the electrotransport apparatus and baked out in the usual manner. The liquid nitrogen cryogenic panel was not used during these experiments. After bakeout, the pressure inside the chamber was 2.0×10^{-11} torr (N_2). The thorium rod was then heated to 1600°C and after 22 hours, high purity nitrogen gas was admitted into the chamber through a variable leak valve until a pressure of 4×10^{-10} torr (N_2) was achieved. The UTI Model 100C residual gas analyzer was used to determine the anode current for the N_2 peak to be 1×10^{-7} amp which was maintained for the remaining five days of the experiment. The peak heights of the other residual gases were determined at 24 hour intervals and their partial pressures measured. These data are shown in Figure 22. After the sample was removed from the chamber, a resistance ratio ($R_{300K}/R_{4.2K}$) profile of the rod was made. The purest section, Section 2, had a resistance ratio of 2200, which was equivalent to metal prepared when the cryogenic panel was used and the pressure in the vicinity of the sample was 4×10^{-12} torr (N_2).

In an effort to better understand this result, a calculated re-

Figure 22. Partial pressure of residual gases, as a function of time, during experiment NASA-2A-105.

sistance ratio for the purified rod was determined from the partial pressure of nitrogen that could be compared with the measured ratio. Three assumptions were made in order to make this calculation, (1) all the nitrogen molecules that hit the hot surface of the thorium sample stuck and dissociated into monatomic nitrogen which has a sticking coefficient of one, (2) the accumulation of impurities at the anode end of the rod due to electrotransport was confined to a section no longer than three centimeters and had no effect on the center of the sample and (3) the reservoir of impurity atoms at the cathode end due to the cooler end effect was confined to a section no longer than three centimeters. Any flux of impurity atoms from this reservoir was much smaller than the flux contributed by the pickup of impurities from the gas around the sample. This reservoir may then be ignored except that it contributes a constant residual impurity concentration throughout the sample.

43

Langmuir's equation was used to calculate the mass in grams of nitrogen incident on a square centimeter of sample surface per second.

$$G = (0.05833)P(M/T)^{1/2} \quad (\text{Eq. 8})$$

where,

P = partial pressure of nitrogen

M = molecular weight of nitrogen

T = temperature of gas (398K)

After a sufficient period of time, the nitrogen contribution from the environment will have caused the concentration profile of nitrogen to become linear over most of the sample with the exception of the anode end. Ignoring back diffusion down this linear concentration gradient, an approximate value of the concentration at any point along the sample may be found, according to:

$$C = 2GL/EUR, \quad (\text{Eq. 9})$$

where,

G = incident mass of nitrogen

L = distance from anode to point under investigation

E = electric field

U = mobility of nitrogen in thorium

R = radius of sample

Since the concentration gradient is linear, its value may be found by dividing the concentration at a point by the distance to the point, or

$$dC/dx = C/L \quad (\text{Eq. 10})$$

The concentration profile at any point L along the rod may now be calculated using,

$$C = \frac{2GL}{EUR} + \frac{D \left(\frac{dC}{dx} \right)}{EU} \quad (\text{Eq. 11})$$

where, D = diffusion coefficient of nitrogen in thorium.

The value for L was set equal to 8.75 centimeters which corresponds to Section 3 of the thorium rod from experiment NASA-2A-105. The concentration, C, at this point was calculated and converted to ppmw by weight. Peterson and McLachlan⁴⁴ have reported that the contribution of nitrogen interstitials to the resistivity of thorium is $3.5 \times 10^{-3} \mu\Omega\text{-cm/ppmw}$ nitrogen at 4.2 K. Using this value and the nitrogen concentration in ppmw calculated for Section (3) (Eq. 11), the resistivity due to nitrogen contamination from the environment was found to be $8.05 \times 10^{-4} \mu\Omega\text{-cm}$. The residual resistivity due to a constant flux of impurity atoms from the cold end reservoir at the cathode was taken to be $7.62 \times 10^{-3} \mu\Omega\text{-cm}$. This value was obtained from Section 2, experiment

NASA-2A-13, which had a resistance ratio of 2080 and was the best thorium that had been prepared to date by similar processing. These two values were then added to obtain a total resistivity, ρ_T of $8.43 \times 10^{-3} \mu\Omega\text{-cm}$.

Peterson et al.³⁹ have shown that the resistivity of pure thorium at 300K is $15.78 \mu\Omega\text{-cm}$. Dividing this value by the total resistivity ρ_T , at 4.2K, a calculated resistivity ratio of 1870 was obtained. This resistivity ratio is equal to the resistance ratio if we assume negligible contraction of the sample upon cooling to 4.2K. This value is in good agreement with the measured resistance ratio of Section (3) which was 1800. The contribution of the residual gases containing carbon and oxygen were not included in the calculation since their contribution would be less than 10%.

A second thorium rod was loaded in the electrotransport apparatus and heated under a higher partial pressure of nitrogen. The chamber was first baked out at 380°C and after cooling to room temperature, the thorium sample was heated to 1600°C . The variable leak valve controlling the nitrogen flow was adjusted so that the nitrogen equivalent pressure in the chamber was 5×10^{-9} torr. The 28 m/e peak was maintained at 1×10^{-11} amps throughout the 144 hour experiment. This current was measured directly at the Faraday cup to eliminate the electron multiplier from the system. This could be done in this experiment because the partial pressure of nitrogen was sufficiently high.

After the electrotransport processing was completed, it was found that the electron multiplier failed due to an open resistor in the circuit. As a result, the gain of the electron multiplier and the sensitivity of the residual gas analyzer to nitrogen could not be determined. The current measurements associated with the peak heights of the other

residual gases present in the system were made at the anode of the electron multiplier during the experiment since their concentration was quite low. In order to determine their partial pressures, the average sensitivity from the four most recent experiments and the gain of the electron multiplier from the most recent experiment were used as input to the computer program. The partial pressures of the residual gases plotted as a function of time for this experiment, NASA-2A-138, are shown in Figure 23. The partial pressure of nitrogen in the system was 1.7×10^{-8} torr which was higher than the nitrogen equivalent pressure. The reason for this was the large increase in the helium content throughout the experiment. Helium was a contaminant in the nitrogen gas and was not pumped by the system. After 125 hours, helium constituted 63% and nitrogen only 23% of the residual gases present. Since the nitrogen equivalent pressure is calculated assuming the entire gas atmosphere to be nitrogen, and in this experiment 63% of the residual gas was helium, the value for the nitrogen equivalent pressure has little significance under these conditions.

A calculated resistance ratio for this sample was determined as described for experiment NASA-2A-105. The calculated ratio for Section 3, was 200 compared to a measured resistance ratio of 1330. This discrepancy may have been due to an inaccuracy in the average sensitivity value used for this experiment and consequent incorrect partial pressure values for nitrogen, and/or to the possibility that the assumed value of one for the sticking coefficient of thorium is not correct.

It is concluded from these two experiments that a high partial pressure of a reactive gas such as nitrogen in the vicinity of the thorium sample can be detrimental to the purification process. There

Figure 23. Partial pressure of residual gases, as a function of time, during experiment NASA-2A-138.

also appears to be a threshold value of $\sim 2 \times 10^{-10}$ torr for the partial pressure of nitrogen, below which other sources of contamination such as impurities migrating from the ends of the sample, are dominant. When the partial pressure of nitrogen was maintained at $\sim 2 \times 10^{-8}$ torr, the quality of the thorium decreased as indicated by a drop in the resistance ratio to 1330.

It should be noted that the resistance ratio measurement is believed to be quite sensitive to the interstitial solute concentration in thorium and as a result the good agreement between a calculated resistance ratio and a measured value may be fortuitous.

B. Test Specifications for the Electrotransport Experiment. The test specifications for the electrotransport experiment were written as a separate report in March 1976. Copies of this report, SP2-66006, are available from the authors upon request.

SUMMARY OF RESULTS

1. A preprototype electrotransport experiment for the purification of refractory metals, such as thorium, under outer space environmental condition was developed. This experiment could be performed in an orbiting low density materials laboratory such as the Molecular Shield Device.
2. A space simulation chamber was fabricated that could be evacuated to a nitrogen equivalent pressure of 2×10^{-12} torr. In this unit, ten electrotransport evaluation experiments were performed and the results discussed.
3. Detailed assembly drawings and line drawings of the preprototype electrotransport apparatus are given in Appendix A.
4. Simulated solar radiation had little effect on the experiment.
5. The coldness and darkness of space were also simulated. The coldness of space could aid in the purification process by suppressing the vapor pressure of reactive gases in the vicinity of the sample as demonstrated in our experiments by use of a cryogenic panel.
6. A method was devised and demonstrated to counter the force of gravity on the electrotransport sample. In this demonstration, the phenomenon of "grain-sliding" was reduced by 90%. The microgravity of space processing should eliminate the "grain-sliding."
7. The probability of a meteorite particle hitting our sample during a flight experiment over a five day period was determined to be one in 30,000.

8. The concentration of impurities contained in the cathode end of the rod should be minimized to ensure maximum purification.
9. The world's highest purity polycrystalline thorium was prepared during this work and it had a resistance ratio ($R_{300K}/R_{4.2K}$) of 4200. This material was prepared by refining once purified material.
10. Two single crystals of thorium having resistance ratios of ~ 1800 were prepared. These crystals are the world's purest and are presently being characterized.
11. The metallic solutes copper, iron, lanthanum, molybdenum, niobium, palladium, rhenium, rhodium, ruthenium, tantalum, titanium, uranium, vanadium and tungsten were found to migrate with the flow of electrons in thorium. Many of these solutes cannot be removed by any other refining technique.
12. Reactive gases in the vicinity of the sample do affect the purity of the metal and should be minimized during processing.
13. The control electronics, power supply, and test measuring system pose no insurmountable problems for a space experiment. These components were implemented in the laboratory; the sample was automatically controlled, adequate power was supplied, and valuable data were acquired and recorded.
14. The specifications for a high current power supply for a flight experiment are given in Appendix B.
15. The electrical resistance of the sample increases slightly during

the first several hours of the experiment. After this "burn-in" period, the power to the sample remained constant for the duration of the purification process.

16. An expansion compensating device was developed which kept the sample straight during repeated heating to 1600°C.
17. A temperature monitoring device (TMD) was developed which can withstand low pressure bakeout procedures at 380°C and can still be used to monitor the temperature of the sample during purification.
18. A document entitled "Operating Environment for Preparation, Launch, Space Operation and Recovery of the Experiment" was prepared.
19. A document entitled "Test Specification for the VAMPS Experiment" was prepared.
20. Several presentations concerning this work have been made.
21. Technical articles concerning the control circuit and the temperature monitoring device have been published. Reprints are given in Appendix D.
22. The publication of two additional articles concerning this project are anticipated.

RECOMMENDATIONS

The development of an orbiting low density materials laboratory, such as the Molecular Shield Device, is essential to the development of an electrotransport purification flight experiment. Our recommendations concerning this flight experiment are as follow:

1. Since the electric mobility, U , and the diffusivity, D , for the interstitial solutes in thorium are well known, the ideal sample size for any specific flight experiment can be determined. The maximum sample length and thickness would be calculated based upon the available power for the experiment and the available time for purification. These calculations would be made using our computer programs.
2. A flight experiment should include the preparation of single crystals by cycling the temperature of the sample, after purification, several times through its polymorphic transformation. This technique has been demonstrated in our Laboratory and the resulting crystals would be quite valuable in characterization studies.
3. The thorium sample used in a flight experiment should be once refined by electrotransport processing in a terrestrial laboratory. This will minimize the contamination due to the end effects and should maximize purification in space.
4. A five day low pressure bakeout at 380°C should be used prior to loading the experiment aboard the Orbiter. The unit should be kept very clean and protected from reactive gases until it is deployed in space.

5. The control method of preselected constant power (voltage times current) should be used in an operation system.
6. If a reflective mirror is used in conjunction with the temperature monitoring device (TMD) a small change in sensor output may be noted due to changes in the angle of the mirror with changes in temperature. This was not found to be objectionable in our experiments since the TMD was used as a monitor and not a temperature regulating device. This problem could be eliminated by removing the mirror and viewing the sample directly with the TMD.
7. The residual gas content in the vicinity of the sample should be monitored before, during, and after the experiment.
8. The vacuum gauging should be part of any control system. This was not done in our experiment and no major problem is anticipated from the incorporation of this feature.
9. A microprocessor controller should be developed for a specific flight experiment. International Business Machine (IBM), Space Systems Division, Huntsville, Alabama could be a possible source for this unit.
10. A programmable power supply suitable for the environment should be mounted near the sample because of the current involved. A feasible location appears to be just outside the wall of the Molecular Shield. A switching supply should be specially developed for this purpose.
11. A platinum rod having the same resistance as the thorium sample

should be used to test the automatic control system. The platinum specimen can be heated in air without oxidizing, thereby facilitating the test procedure.

12. Vibration tests of the assembled preprototype electrotransport apparatus should be made prior to a flight experiment. Although such tests were not made during this project, no vibration induced instability is expected.
13. Other refractory metals could be purified by electrotransport processing during a flight experiment. From previous studies in our Laboratory, the electrotransport parameters of most of these metals are known, and the precise conditions necessary for maximum purification could be readily calculated.

LIST OF INVENTIONS

1. Analog-to-Digital and Digital-to Analog Circuit. This circuit was developed to sample the voltage of the thorium rod and maintain it for a week or more with at least 99.9% precision. A publication describing the circuit is included in Appendix D.
2. Temperature Monitoring Device. This device was developed to withstand the prolonged high temperature bakeout under vacuum necessary to degas the chamber prior to an electrotransport experiment. It was used to monitor the sample temperature during the run. A pre-print of an article describing this unit is included in Appendix D. Detailed drawings are included in Appendix A, Drawing No. 4.
3. Ni-Ti Expansion Device. The expansion compensating device fabricated from strips of Ni-Ti "memory" alloy was quite successful in allowing for the thermal expansion of the thorium rod as it was heated to 1600°C. It was also mechanically flexible, easily outgassed, had excellent creep resistance and was capable of carrying the 86 amps necessary to heat the sample.
4. Micro-Gravity Method. This method was developed to provide a simulation of the near-zero gravity conditions of space. It was used to demonstrate that under this condition there is almost no "grain-sliding" in the sample. "Grain-sliding" has been a continuing concern with laboratory experiments but the employment of this method has demonstrated that in space there will be no problem.

LIST OF PRESENTATIONS

1. F. A. Schmidt, "Project VAMPS-A Progress Report", Seminar, Materials Science Program, March 20, 1975, Iowa State University, Ames, Iowa.
2. B. K. Lunde, and F. A. Schmidt, "Purification of Thorium by Electrotransport on the Space Shuttle", Iowa Academy of Science, April 19, 1975, Iowa State University, Ames, Iowa.
3. F. A. Schmidt, "The Ultra Purification of Metals by Electrotransport Under Outer Space Environmental Conditions", Program Review, November 13, 1975, Langley Research Center, Hampton, Virginia.
4. D. K. Rehbein and F. A. Schmidt, "Electrotransport Purification of Thorium Metal", Iowa Academy of Science, April 10, 1976, Clarke College, Dubuque, Iowa.
5. F. A. Schmidt, "Electrotransport in Space", (short contribution) Fall Meeting TMS-AIME, September 22, 1976, Niagara Falls, New York.
6. O. N. Carlson, "Electrotransport: Principles and Applications".
This presentation included Project VAMPS and was given at the following:
 - Max-Planck-Institute for Metals
Research, Stuttgart, Germany,
November, 1974.
 - Nuclear Research Center, Julich,
Germany, February, 1975.

Institute for Metals Research,
University of Münster, Germany,
March, 1975.

Euratom Laboratory, Petten,
Holland, March, 1975.

Center for Nuclear Study, Mol,
Belguim, May, 1975.

Center for Materials Science,
University of Birmingham, England,
June, 1975.

LIST OF PUBLICATIONS TO DATE

1. B. K. Lunde and F. A. Schmidt, "Precision Sample and Hold Stores Voltage for a Week", Electronics, 49, No. 15 (1976) p. 120.
2. B. K. Lunde and F. A. Schmidt, "Light Sensor for Ultra High Vacuum Systems Utilizing a Silicon Photovoltaic Cell", Applied Optics, 15 (1976).

BIBLIOGRAPHY

1. W. Seith and O. Kubaschewski, *Z. Electrochem.*, 41 (1935), 551.
2. J. H. DeBoer and J. D. Fast, *Rec. Trav. Chim.*, 59 (1940), 161.
3. F. Claisse and H. P. Koenig, *Acta Met.*, 4 (1956), 650.
4. O. Dayal and L. S. Darken, *Trans. AIME*, 188 (1950), 1156.
5. C. Wagner and G. Heller, *Z. Phys. Chem.*, (B), 46 (1940), 242.
6. W. Seith and H. Weber, *Z. Electro-chem.*, 57 (1953), 891.
7. Th. Heumann: *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds*, vol. 1, Paper 2C, Her Majesty's Stationery Office, London, 1959.
8. J. D. Verhoeven, *Met. Rev.*, 8 (1963), 311.
9. H. B. Huntington in A. S. Nowick and J. J. Burton (eds.) Diffusion in Solids, Academic Press, New York, 1975, p. 303.
10. J. D. Verhoeven, *J. Metals*, 18 (1966), 26.
11. D. T. Peterson in A. Lodding and T. Tagerwall (eds.) Atomic Transport in Solids and Liquids, Verlag der Zeitschrift für Naturforschung, Tübingen, Germany, 1971, p. 104.
12. O. N. Carlson, F. A. Schmidt, and D. T. Peterson, *J. Less-Common Metals*, 10 (1966) 1.
13. D. T. Peterson, F. A. Schmidt, and J. D. Verhoeven, *Trans. AIME*, 236 (1966) 1311.
14. D. T. Peterson and F. A. Schmidt, *J. Less-Common Metals*, 24 (1971) 223.
15. F. A. Schmidt and J. C. Warner, *J. Less-Common Metals*, 13 (1967) 493.
16. O. N. Carlson, F. A. Schmidt, and D. G. Alexander, *Met. Trans.*, 3 (1972) 1249.
17. F. A. Schmidt, O. N. Carlson, and C. E. Swanson, Jr., *Met. Trans.*, 1 (1970) 1371.
18. O. N. Carlson, F. A. Schmidt, and J. C. Sever, *Met. Trans.*, 4 (1973) 2407.
19. O. N. Carlson, F. A. Schmidt, and R. R. Lichtenberg, *Met. Trans.*, 6A (1975) 725.

20. F. A. Schmidt and O. N. Carlson, J. Less-Common Metals, 26 (1972) 247.
21. F. A. Schmidt and O. N. Carlson, Met. Trans., 7A (1976) 127.
22. F. A. Schmidt and O. N. Carlson, J. Less-Common Metals, 50 (1976) 237.
23. D. T. Peterson and F. A. Schmidt, J. Less-Common Metals, 18 (1969) 111.
24. D. T. Peterson and F. A. Schmidt, J. Less-Common Metals, 29 (1972) 321.
25. J. E. Hueser and F. J. Brock, J. Vac. Sci. Technol., 13 (1976) 702.
26. L. T. Melfi, Jr., R. A. Outlaw, J. E. Hueser and F. J. Brock, J. Vac. Sci. Technol., 13 (1976), 698.
27. M. W. Mallett and I. E. Campbell, J. Am. Chem. Soc., 73 (1951) 4850.
28. D. T. Peterson, W. E. Krupp, and F. A. Schmidt, J. Less-Common Metals, 7 (1964) 288.
29. P. A. Redhead, Rev. Sci. Instr., 31 (1960) 343.
30. J. F. Smith, O. N. Carlson, D. T. Peterson and T. E. Scott, Thorium: Preparation and Properties, Iowa State University Press, Ames, Iowa 1975, p. 102.
31. C. M. Jackson, H. J. Wagner, and R. J. Wasilewski, NASA Report No. SP-5110, Washington, D.C. 1972.
32. B. K. Lunde and F. A. Schmidt, Applied Optics, 15 (1976).
33. B. K. Lunde and F. A. Schmidt, Electronics, 49, No. 15, (1976) 120.
34. E. N. Hopkins, D. T. Peterson and H. H. Baker, Oak Ridge National Laboratory Report ORNL-TM-1161, (1976).
35. S. S. Kutateladze, Fundamentals of Heat Transfer, Academic Press, 1963, p. 83.
36. D. S. Easton, C. A. Giles, S. H. Merriman, and R. E. Clausing, Report No. ORNL-TM-3455, Oak Ridge National Laboratory, Oak Ridge, Tennessee, September, 1971.
37. R. L. Summers, Report No. NASA-TN-D-5285, Lewis Research Center, Cleveland, Ohio, June, 1969.

38. D. T. Peterson and F. A. Schmidt, *J. Less-Common Metals*, 24 (1971) 223.
39. D. T. Peterson, D. F. Page, R. B. Rump, and D. K. Finnemore, *Phys. Rev.* 153, (1967) 701.
40. D. T. Peterson and R. L. Skaggs, *Trans. TMS*, 242 (1968) 922.
41. H. G. Schittler, J. J. Martin, F. A. Schmidt and G. C. Danielson, *Phys. Rev.*, 187 (1969) 801.
42. J. F. Smith, O. N. Carlson, D. T. Peterson, and T. E. Scott, Thorium: Preparation and Properties, Iowa State University Press, Ames, Iowa 1975, p. 175.
43. S. Dushman and J. M. Lafferty (Ed.), Scientific Foundations of Vacuum Techniques, J. Wiley and Sons, Inc., New York, 1962, p. 14.
44. D. T. Peterson and D. R. McLachlan, *Met. Trans.*, 6A, (1975) 1359.

This Appendix contains the assembly drawings and line drawings of the various components of the preprototype electrotransport apparatus developed during this work. A photograph of the assembled unit is shown in Figure 3 of the text.

Drawing Number	Title	Page
1	Radiation Shield and Mirror Bracket Assembly	110
	1-A Radiation Shield (Weldment)	111
	1-B Mirror Brackets	112
	1-C Mirror	113
2	Support Rack and Slide Port Assembly	114
	2-A Rack	115
	2-B Slide Port	116
3	Sample Assembly and Electrodes	117
	3-A Bottom Electrode	118
	3-B Top Electrode	119
	3-C Expansion Compensating Bow and Sample Mounting Stud	120
	3-D Studs for Sample Assembly	121
4	Temperature Monitoring Device Assembly	122
	4-A Solar Cell Frame	123
	4-B Solar Cell Base	124
	4-C Mounting Bracket	125
	4-D Extension Tube	126
	4-E Insulators and Connectors	127

Drawing 1. Radiation Shield and Mirror Bracket Assembly.

1	RADIATION SHIELD (welded ass'y)	ST. S.	1
PART No	DESCRIPTION	MAT'L	REQ'D

Drawing 1-A. Radiation Shield (Weldment).

6	BOTTOM MIRROR BRACKET (.. ..)	ST. S	1
5	TOP MIRROR BRACKET (welded ass'y)	ST. S	1
PART No.	DESCRIPTION	MAT'L	REQ'D

Drawing 1-B. Mirror Brackets

4b	ALIGNMENT PIN	ST. S	1
4a	RETAINING NUT	ST. S	2
4	MIRROR, (Reliance Art Metal Co.)	—	1
PART No	DESCRIPTION	MAT'L	REQ'D

Drawing 1-C. Mirror

Drawing 2. Support Rack and Slide Port Assembly.

Drawing 3. Sample Assembly and Electrodes.

7a	HEX NUT	Cu	1
7	BOTTOM ELECTRODE (Utek Vacuum Equip.)	—	1
PART No	DESCRIPTION	MAT'L	REQ'D

Drawing 3-A. Bottom Electrode

8	TOP ELECTRODE (Utek Vacuum Equipment)	—	1
PARTY No	DESCRIPTION	MAT'L	REQ'D

Drawing 3-B. Top Electrode

(10)

(11)

11	SAMPLE MOUNTING STUD	To	1
10	EXPANSION COMPENSATING BOW	Ni-Ti	2
PART No.	DESCRIPTION	MAT'L	REQ'D

Drawing 3-C. Expansion Compensating Bow and Sample Mounting Stud.

(11a)

(12)

(13)

13	STUD	Th	1
12	COUPLING	To	1
11a	HEX NUT	To	1
PART No	DESCRIPTION	MAT'L	REQ'D

Drawing 3-D. Studs for Sample Assembly

Drawing 4. Temperature Monitoring Device Assembly

16

16a

16b

16b	MOUNTING SCREW	ST. S	1
16a	ALIGNMENT SCREW	ST. S	1
16	SOLAR CELL FRAME	AL.	1
PART No	DESCRIPTION	MAT'L	REQ'D

Drawing 4-A. Solar Cell Frame

15	SOLAR CELL BASE	ST. S.	1
PART No	DESCRIPTION	MAT'L	REQ'D

Drawing 4-B. Solar Cell Base

14	MOUNTING BRACKET	ST. S	1
PART NR	DESCRIPTION	MAT'L	REQ'D

Drawing 4-C. Mounting Bracket

NOTE: .18 TAB IS LOCATED ON OPPOSITE SIDE
2. SPOT WELD ASS'Y

17	EXTENSION TUBE (welded ass'y)	ST. S.	1
PART No	DESCRIPTION	MAT'L	REQ'D

Drawing 4-D. Extension Tube

NO	DIMN. 'A'	REQ'D
18a	.860	1
18b	1.560	2

NO	DIMN. A	REQ'D
18c	.406	1
18d	.625	2

(18e)

(18f)

(18g)

18g	HOLD DOWN INSULATOR	..	2
18f	SPACER ..	..	1
18e	LEAD ..	..	2
18d		..	2
18c	MOUNT INSULATOR	..	1
18b		..	2
18a	STRIP INSULATOR	Al ₂ O ₃	1
PART No	DESCRIPTION	MAT'L	REQ'D

Drawing 4-E. Insulators and Connectors

APPENDIX B

EQUIPMENT SPECIFICATION FOR HIGH CURRENT POWER SUPPLY

1.0 SCOPE

This specification covers the high current power supply (HCPS) for the electrotransport purification experiment. The power supply shall provide an output current of 0 to 100 amps DC at a voltage of 0 to 5 volts DC externally adjustable by a two-wire control input using a voltage at low current for control of the voltage applied to the load. The input voltage will be equal to the voltage applied to the load and the input impedance will be 10,000 ohms.

2.0 DOCUMENTS

2.1 Referenced Specifications

The following documents form a part of this specification:

- SP 1-66006 Operation Environment for Preparation, Launch, Space Operation, and Recovery of the Vacuum Assisted Metal Purification Experiment.
- JSC 07700 Volume XIV Revision C change of January 7, 1975, Space Shuttle Program, Space Shuttle System Payload Accommodations, Level II, Program Definition and Requirements.
- SL-E-0002 Specification of Electromagnetic Interference Characteristics, Requirements for Equipment for the Space Shuttle Program, June 4, 1973.

3.0 GENERAL REQUIREMENTS

The design of the high current power supply (HCPS) shall be suitable for use as the power supply for a metals purification experiment to be used with the Molecular Shield on the Space-

Shuttle. The design, selection of specifications and standards and selection of parts and materials shall be in accordance with SP 1-66006. The HCPS shall meet or exceed all performance requirements individually or in combination.

3.1 PERFORMANCE REQUIREMENTS

- 3.1.1 Input voltage - The power supply shall be designed to operate from the spacecraft mid payload bay 27.0 to 32.0 V DC supply as described in JSC 07700, Vol. XIV. Peak-to-peak ripple will be 0.9 volts or less at any single frequency and 1.6 volts or less over a broad range of frequencies. It shall comply with all provisions of SL-E-0002.
- 3.1.2 Input power - The input power from the 27 to 32 volt line to the HCPS shall be minimized but sufficient for the normal operating conditions for the experiment of 90 amps at 3.2 volts.
- 3.1.3 General noise current - The HCPS shall comply with document SL-E-0002.
- 3.1.4 Output load current - The HCPS shall be capable of providing an output current of from 0 to 100 amps over the range of operating voltage 2.0 to 5.0 volts. The output current shall be limited to 100 amps under any load conditions.
- 3.1.5 Output load voltage - The voltage supplied to the load shall be adjustable by the input voltage from 0.0 to 5.0 V DC and shall equal the input voltage.
 - (a) Ripple - The ripple of the load voltage shall not exceed 0.25 volts at frequencies above 1Hz.

- (b) Output load regulation - The voltage supplied to the load shall go up by less than 0.1% or down by less than 5% in response to a 5% increase in the current over the range of currents from 70 amps to 100 amps. It shall go up by less than 5% or down by less than 1% for a 5% decrease in the current over the ranges of currents from 70 amps to 100 amps.
- (c) Output line regulation - The load voltage shall not vary more than $\pm 0.1\%$ in response to supply voltage changes over the entire range of supply voltages.
- (d) Temperature regulation - The load voltage shall not change more than 0.1% for cold plate temperatures in the range 0 to 71°C.
- (e) Stabilizing time - The load voltage shall come to within 0.1% of its final value within 40 seconds following power turn-on or change in programming control. The HCPS shall meet all performance requirements within 60 seconds of turn-on or change in programming control. Overshoot voltage shall be such that its integral with time shall not exceed 4% of the nominal operating voltage-seconds.
- (f) Control - The load voltage shall be controllable by means of a two-line voltage input.
- (g) Remote sensing - The load voltage shall be sensed by two wires connected directly to the load. The load will be between one foot and ten feet from the supply. A specification of the type of leads that are necessary for remote sensing of the sample voltage shall be supplied

by the vendor.

- (h) Longterm voltage drift - The load voltage shall not vary more than 0.1% in one year of intermittent or continuous operation. (Note: Satisfaction of this requirement shall be by analysis in lieu of testing).

3.1.6 Short circuit protection - The HCPS shall not be damaged or degraded by operation under any load, including arc or corona condition, at any ambient pressure between one atmosphere and hard vacuum.

3.1.7 Environments

- (a) Operating environment - The HCPS shall operate in a hard vacuum on a cold plate of 0 to 71°C with the thermal and nuclear solar radiation and meteroid environment specified in 3.3.2 of SP 1-66006 and in normal laboratory environments for testing on the ground. It shall be possible to monitor its condition under all the environmental conditions specified in SP 1-66006.
- (b) Storage environment (non-operating) - The HCPS shall operate without degradation after storage in packaging to be specified by the vendor under any combination of the environmental conditions stated in paragraph 3.4.1.b (2) of SP 1-66006 for a period of three years.
- (c) Transportation environment (non-operating)- The HCPS shall operate without degradation after transportation in packaging to be specified by the vendor under any combination of the environmental conditions specified in paragraph 3.4.1.a of SP 1-66006, and the HCPS shall

operate without degradation after transportation under any combination of the environmental conditions specified in 3.3.2 of SP 1-66006.

- 3.1.8 Design qualification tests - The unit must be able to function without degradation after subjugation to design qualification tests. Generally, test exposure levels are computed by multiplying expected levels by 1.5 or increasing the expected temperature range by $\pm 10^{\circ}\text{C}$.
- 3.1.9 Grounding - The HCPS shall provide isolation between case, power return, and output power return.
- 3.1.10 Size, mounting and connections - The size of the HCPS shall be minimized. A drawing of the supply with suitable mounting provisions and connection provision for the supply power, input signal, remote sensing loads, test leads and output shall be furnished.
- 3.1.11 Test points - Test points shall be provided in parallel with the output connections so the output voltage can be monitored. Test points shall be provided to monitor the current output and the voltage applied to the load of the HCPS to an accuracy of 0.1%. Means should be provided to determine the operability of the HCPS and the resistance of the load while applying less than 1 amp or 40 coulombs per 40 seconds to the load.

APPENDIX C

This Appendix describes the procedures used in determining the nitrogen equivalent pressure and the partial pressures of the residual gases contained in the space simulation chamber.

NITROGEN EQUIVALENT PRESSURE DETERMINATION

Two dual-filament Bayard-Alpert Nude Ionization Gauges, Model 971-5008, were obtained from the Varian Corp. and were sent to Langley Research Center for modification and calibration. One was left in the original configuration and is referred to as an unmodulated gauge. The other gauge was modified in the manner described by Redhead²⁹ and is called a modulated gauge. Both gauges were calibrated for He, N₂ and Ar.

A. Unmodulated Gauge

1. Uncalibrated Filament

One of the dual filaments of this gauge was left uncalibrated for use as a constant monitor of the pressure during the initial pumpdown for each run and during the run itself. This was done in order to prolong the lifetime of the two calibrated gauges and to safeguard them against possible contamination. The gauge was used in conjunction with an Ultek Digital Gauge Control, Model 605-0013.

2. Calibrated Filament

The other filament of this gauge was calibrated to determine the gauge constants for He, N₂ and Ar. The pressure determination equation for this filament is:

$$\text{pressure (N}_2\text{)} = i^+ / i^- K(\text{N}_2) \quad (\text{Eq. 12})$$

where, i^+ = collector current (measured using Keithley Model 417 picoammeter)

i^- = filament emission current (set at 4×10^{-3} amp)

$K(N_2)$ = gauge constant for nitrogen (given in Table XV)

This gauge was used when an accurate pressure measurement was needed for pressures greater than 1×10^{-10} torr.

B. Modulated Gauge

Conversion of this gauge to the modulated form was accomplished by removing one of the filaments and replacing it with a modulator electrode. The difference in the collector currents as measured by the Keithley picoammeter when this modulator is shorted to the collector, and when it is shorted to ground, is then free of any residual current caused by soft X-rays.

When the modulator and grid are shorted, the collector current (I_1) is:

$$I_1 = i^+ + i_r \quad (\text{Eq. 13})$$

where, i^+ = collector current from ion impact

i_r = collector current due to soft X-rays.

When the modulator is shorted to ground, the collector current (I_2) is:

$$I_2 = i^+ \alpha(N_2) + i_r \quad (\text{eq. 14})$$

where, $\alpha(N_2)$ = modulation factor for nitrogen.

Subtracting (Eq. 14) from (Eq. 13) gives:

$$I_1 - I_2 = i^+ - i^+ \alpha(N_2)$$

or

$$i^+ = (I_1 - I_2) / [1 - \alpha(N_2)] \quad (\text{Eq. 15})$$

Substituting this into (Eq. 12) gives the pressure determination formula for the modulated gauge.

$$\text{pressure } (N_2) = (I_1 - I_2) / [1 - \alpha(N_2)] i^- K(N_2) \quad (\text{Eq. 16})$$

This gauge was used when an accurate pressure measurement was needed for pressures less than 1×10^{-10} torr.

The values of α and K for He, N_2 , and Ar as determined at LRC are given in Table XV.

Table XV. Gauge Constants and Modulation Factors

Gas	Unmodulated Gauge	Modulated Gauge	
	$K \text{ (torr}^{-1}\text{)}$	α	$K \text{ (torr}^{-1}\text{)}$
He	4.06	0.712	2.31
N_2	24.77	0.6985	14.06
Ar	31.83	0.718	18.90

The nitrogen equivalent pressure determined from Eq. (12) or (16) may be converted to a He and Ar equivalent pressure by substituting the appropriate values for α and K from Table XV.

PROCEDURE FOR GAS ANALYSIS

A model 100C Precision Mass Analyzer was purchased from Uthe

Technology International of Sunnyvale, California for determination of accurate partial pressure measurements of the residual gases in the vicinity of the sample. This residual gas analyzer (RGA) is a quadrupole type using a DC voltage superimposed on a 2400 volt 2MHz radio frequency signal for ion discrimination. Ion detection is accomplished using a 16-stage electron multiplier with Cu-Be oxygen activated dynodes. The output of the multiplier is amplified for read-out by an eight decade picoammeter. The analyzer was used in conjunction with a Hewlett-Packard model 130C oscilloscope for observation and identification of the ion currents detected and a Hewlett-Packard model 680 Stripchart Recorder to obtain a permanent record of the peaks. A sample of the trace from the stripchart is shown in Figure 15.

The partial pressures of 13 gases were measured for each experiment. These gases were : H_2 , He, CH_4 , H_2O , Ne, N_2 , CO, C_2H_4 , C_2H_6 , O_2 , Ar, CO_2 , and C_3H_8 . The partial pressures were calculated from the data with the aid of a digital computer using a computer program obtained from Oak Ridge National Laboratory³⁶ and adapted for our computer system. Input to the computer program consists of four numbers or sets of numbers for each gas. They are:

1. Sensitivity of the RGA to the gas
2. Cracking pattern of the gas
3. Ionization constant of the gas
4. Ion current of each ion contributing to the partial pressure of the gas.

The four input parameters for each gas were obtained in the following manner.

1. Sensitivity of the RGA to the Gas

The sensitivity of the RGA to nitrogen, $S(N_2)$, was determined experimentally after each electrotransport experiment. The sensitivity of the RGA to He and Ar after each electrotransport experiment were then obtained using the equation:

$$S(X) = \left[\frac{S(X)}{S(N_2)} \right] \cdot S(N_2) \quad (\text{Eq. 17})$$

where, $\frac{S(X)}{S(N_2)} = \text{RIGS}^* \text{ of gas X to } N_2$

$S(N_2) = \text{sensitivity of RGA to nitrogen}$

The RIGS values of He and Ar were determined experimentally since the calibrated gauges from LRC were available to obtain the accurate pressure measurements needed. At the same time, the electron multiplier gain of He, N_2 , and Ar were measured so that the gain ratios of He and Ar to N_2 could be calculated.

Calculation of the RIGS and gain ratio for He and Ar to N_2 was accomplished by determining the sensitivity and electron multiplier gain of the RGA to He and Ar and then comparing them to the corresponding numbers for N_2 . Since neither He nor Ar could be pumped efficiently in the space simulation chamber, the sensitivity and gain values were determined successively for N_2 and He and then the process repeated for N_2 and Ar.

The space simulation chamber was pumped to $<1 \times 10^{-10}$ torr before each sensitivity and gain measurement to minimize any effects of the residual gases in the system. The system was then backfilled with the

*Relative Ionization Gauge Sensitivity

gas under investigation through 10^{-7} torr using a controlled leak valve. The gases used were of research purity and were obtained from the Matheson Gas Products Co.

At three points in each of the 10^{-9} , 10^{-8} , and 10^{-7} torr ranges, the pressure in the system was allowed to equilibrate and a pressure measurement was made using Eq. (12). At the same time, the current at the anode of the electron multiplier from the major peak of the gas under investigation, m/e 4 for He, m/e 28 for N_2 , and m/e 40 for Ar, was recorded. For the three points in the 10^{-7} torr range, the Faraday cup current for the major peak was also recorded. The average electron multiplier gain was calculated from these three current readings according to the relation:

$$\text{E.M. Gain} = I_A / I_{F.C.} \quad (\text{Eq. 18})$$

where, I_A = current at anode of electron multiplier
 $I_{F.C.}$ = Faraday cup current

To calculate the sensitivity of the gas under investigation, the values of the anode current obtained were divided by this average gain to obtain a value for the current in true amps for each pressure. The slope of a straightline drawn through a log-log plot of the current in true amps (ordinate) and pressure (abscissa), is the sensitivity of the RGA to the gas used, independent of the electron multiplier gain of that gas.

By comparing the values of the sensitivity of the RGA to He and Ar to the value with respect to N_2 , the following RIGS values were obtained.

He to N ₂	-----	0.149 : 1
Ar to N ₂	-----	2.548 : 1

Comparison of the average electron multiplier gains found gave the following gain ratios:

N ₂ to He	-----	1 : 2.37
N ₂ to Ar	-----	1 : 0.59

The sensitivity of each of the other residual gases was calculated after each electrotransport experiment by the equation:

$$S(X) = [S(X)/S(N_2)] \left[\frac{\text{Mol. wt. of } N_2}{\text{Mol. wt. of Gas } X} \right]^{1/2} S(N_2) \quad (\text{Eq. 19})$$

where, $\frac{S(X)}{S(N_2)} = \text{RIGS}$

$S(N_2)$ = Sensitivity of RGA to nitrogen

The RIGS values for these ten gases were taken from Summers³⁷ and are given in Table XVI. The term involving the molecular weight ratio was included to compensate for the mass dependence of the electron multiplier gain.

The sensitivity and electron multiplier gain of the RGA to N₂ were determined after each run so that any sensitivity or gain changes in the apparatus between experiments would be known. This was done in the same way as for the calculation of the RIGS values for He and Ar except that only N₂ was used. From this value, and the RIGS values in Table XVI, the sensitivity of the RGA to the other 12 residual gases was calculated using Eq. (17) for He and Ar, and Eq. (19) for the other ten gases.

Table XVI. Relative Ionization Gauge Sensitivities for Residual Gases in Space Simulation Chamber

Gas	$S(X)/S(N_2)$
H ₂	0.430
He	0.149
CH ₄	1.500
H ₂ O	0.968
Ne	0.306
N ₂	1.000
CO	1.070
O ₂	0.975
Ar	2.548
CO ₂	1.440
C ₂ H ₄	2.299
C ₂ H ₆	2.634
C ₃ H ₈	3.838

2. Cracking Pattern of the Gas

At the same time as the RIGS values for He and Ar were determined, the cracking pattern of He, N₂, and Ar was also determined. The cracking pattern of a gas is the amount of gas that appears at each m/e ratio when the gas is ionized. Nitrogen was found to produce peaks at m/e ratios of 14, 28 and 29, He at m/e 4 only and Ar at m/e 20 and 40. The actual values found are given in Table XVII. The cracking pattern for the other ten gases were obtained from the technical library at Uthe Technology International. It is a compilation of experimental data from various sources for the UTI Model 100C. These data are also shown in Table XVII.

Table XVII. Cracking Pattern of Residual Gases in Space Simulation Chamber.
m/e

Gas	2	4	12	13	14	15	16	17	18	20	22	26	27	28	29	30	32	40	44
H ₂	1.00																		
He		1.00																	
CH ₄			0.016	0.057	0.13	0.83	1.00	0.012											
H ₂ O							0.021	0.243	1.00										
Ne										1.00	0.099								
N ₂					0.055									1.00	0.008				
CO			0.035					0.011						1.00	0.012	0.002			
O ₂								0.211									1.00		
Ar										0.021								1.00	
CO ₂			0.047					0.123			0.005			0.38	0.004				1.00
C ₂ H ₄			0.021	0.035	0.063							0.623	0.648	1.00	0.022				
C ₂ H ₆			0.003	0.007	0.023	0.039	0.001					0.226	0.32	1.00	0.197	0.256			
C ₃ H ₈			0.004	0.005	0.020	0.066	0.007			0.007		0.092	0.425	0.635	1.00	0.028		0.026	0.268

3. Ionization Constant of the Gas

The ionization constant for a gas represents the efficiency of ionization of a molecule of the gas normalized to nitrogen. The ionization constants were taken from the values of peak total ionization cross section as listed in Summers³⁷. The peak total ionization cross section is the maximum ionization cross section that occurs as the energy of the ionizing electrons is increased. The values of the ionization constants used are shown in Table XVIII.

Table XVIII. Ionization Constants for Residual Gases in Space Simulation Chamber.

<u>Gas</u>	<u>Ionization Constant (normalized to N₂)</u>
H ₂	0.384
He	0.148
CH ₄	1.463
H ₂ O	0.990
Ne	0.310
N ₂	1.000
CO	1.050
O ₂	1.072
Ar	1.130
CO ₂	1.406
C ₂ H ₄	2.305
C ₂ H ₆	2.800
C ₃ H ₈	3.720

4. Ion Current of Each Ion Contributing to the Partial Pressure of the Gas.

At 24-hour intervals throughout each electrotransport experiment, the anode current of the electron multiplier was recorded for each of the m/e ratios in Table XVII. After the experiment was terminated at 144 hours and the sensitivity and gain of the RGA to N₂ measured the ion current of the m/e ratios at each of the recording times was measured. This was done for each m/e ratio except m/e 4 and m/e 40 by the equation:

$$\text{ion current} = I_A / \text{Gain (N}_2\text{)} \quad (\text{Eq. 20})$$

where, I_A = current at anode of electron multiplier

gain (N₂) = electron multiplier gain for N₂.

The ion currents for m/e 4 and m/e 40 were calculated from the following equations:

$$\text{ion current of m/e 4} = [I_A^{(4)} / \text{Gain (N}_2\text{)}] \cdot G(\text{N}_2) / G(\text{He}) \quad (\text{Eq. 21})$$

where, $I_A^{(4)}$ = current at electron multiplier anode for m/e 4

$G(\text{N}_2) / G(\text{He})$ - gain ratio of N₂ to He (1:2.37)

$$\text{and ion current of m/e 40} = [I_A^{(40)} / \text{Gain (N}_2\text{)}] \cdot G(\text{N}_2) / G(\text{Ar}) \quad (\text{Eq. 22})$$

where, $I_A^{(40)}$ = current at electron multiplier anode for m/e 40

$G(\text{N}_2) / G(\text{Ar})$ = gain ratio of N₂ to Ar (1:0.59)

The computer program was used to compute a partial pressure for each of the 13 residual gases at each of the recording times. From the

cracking pattern and ion currents of the m/e ratios, the program determines how much of the current at each m/e ratio is contributed by each gas. The total ion current of each gas is found and is converted to a partial pressure after correcting for the ionization constant. The conversion to partial pressure is accomplished by dividing the total ion current of a gas by the sensitivity of the RGA to that gas.

APPENDIX D

Precision sample-and-hold stores voltage for a week

by B. K. Lunde and F. A. Schmidt
Iowa State University Ames, Iowa

A voltage can be sampled and held for a week or more with at least 99.9% precision by an analog-to-digital converter followed by a digital-to-analog converter. The a-d converter is triggered when the voltage is to be sampled, and its output is used by a d-a converter to set a programmable power supply. The supply then continues to furnish that voltage for as long as desired.

This circuit is useful in automating the electrotransport process for purifying metals. In this process, a direct current passes through a metal rod, heating it by internal resistance and producing charge carriers that sweep impurities along with them to one end of the rod. The current necessary to reach a specific temperature is known at the beginning of the run, and the voltage necessary to provide this current should be held for the remainder of the run.

The circuit to do this is shown in the figure. The timer, a spring-driven or motor-driven clock mechanism to control some switches, first connects the current control of the power supply to R_1 , which holds the current at the desired level of 86.5 amperes. An override constant-voltage control is also used to put an upper limit on the output voltage of the supply during this time.

After three minutes, when the sample has reached a stable condition at about 1,600 C, the a-d converter is triggered to read the voltage across the rod. This voltage

is about 3.1 volts for a rod resistance of 0.037 ohm. The signals from the a-d converter are fed into a d-a converter, and, after the conversion is complete, the timer applies the output of the d-a converter to the power supply. This commands the supply to furnish the same voltage it was applying at the time of the trigger. The inverting amplifier is necessary in the system to correct the polarity, because a control voltage of about -2 v is applied to the supply to provide a +3.1-v output. For safety of the sample rod, the timer switches the current control resistor to R_2 , somewhat larger than R_1 , which puts an upper limit on the current supplied.

This program of applying a chosen current and then continuing to furnish the voltage which that current requires is necessary because purification is optimum at a particular temperature. The most accurate automatic way of attaining this temperature is to apply a specified current. The diameter, resistivity, and emissivity of separate samples of metal vary less from one to another than the resistance of the assembly, which includes adaptors and vacuum feed-throughs. It is therefore necessary to specify the current, rather than the voltage, at the start of the purification experiment. However, it is desirable to keep the voltage, rather than the current, constant for the remainder of the run, because, as purification continues, the sample deforms and the resistance rises. If constant current were applied, the increased resistance would cause enough of an increase in power and temperature to melt the metal and end the run prematurely.

The circuit shown holds the voltage across the metal rod constant and equal to that required for a specified current at the beginning of the experiment. This voltage is held for the remainder of the run, about a week, by the digital number stored in the d-a converter. □

Holds the voltage. A-d and d-a converters sample and hold a voltage for a week at a time. Timer triggers a d converter to measure voltage, and d-a converts it back to analog signal that controls output voltage of power supply. This control signal can be held indefinitely, stored as a precise digital number. Entire process of purifying metal rod is started by timer.

Light sensor for ultrahigh vacuum systems utilizing a silicon photovoltaic cell

B. K. Lunde and F. A. Schmidt

Ames Laboratory ERDA, Iowa State University, Ames,
Iowa 50011.

Received 19 July 1976.

A light sensor suitable for use as a pyrometer is described for application in an ultrahigh vacuum system which must be baked for six days at 375°C to attain pressures of 2×10^{-12} Torr. The sensor is a silicon photovoltaic cell with welded leads which has withstood such a bakeout cycle three times with no damage. The sensor can be used inside vacuum systems on earth or in extremely low pressure environments in space and thus can avoid viewing through sight glasses.

The cell used is manufactured by Optical Coating Laboratory, Inc. It is a 2 cm $\times$ 4 cm chemically polished *N* on *P* cell with base resistivity of $2 \pm 1 \Omega/\text{cm}$, junction depth of 0.3 μm , with SiO antireflection coating. It has titanium and silver contact materials with a silver thickness of 3–8 μm . The contacts are silver-plated molybdenum tabs parallel-gap welded to the cell. A 140 mW/cm² solar simulator caused an output of 245 mA at 470 mV.

The cell is mounted in a grooved high density aluminum oxide inner frame in an aluminum mounting on a stainless steel shadow box 3.2 cm $\times$ 5.1 cm and 12.7 cm long. The shadow box limits the field of view so the cell sees principally a 1600° sample, which it monitors. The leads are made accessible through high density aluminum oxide tubes which insulate them from the aluminum mounting.

The cell was used as an optical pyrometer in three metal purification experiments. In each experiment the vacuum chamber containing the sample and cell was baked out for six days at 375°C under a pressure of 6×10^{-9} Torr. After cooling to ambient temperature, the sample was resistively heated to 1600°C for six days under a pressure of 2×10^{-12} Torr. The cell was used during this period to monitor the average temperature of the sample by viewing its light reflected by a commercial quality chromium plated steel mirror from the Reliance Art Metal Co., Cincinnati, Ohio. There is an optical pathlength of 34 cm from the cell to the sample with one reflection of the light by the chromium mirror. The typical output of the cell is 190 mV with 1.9 μA . This operating point was used to maximize the voltage so the output could be precisely determined. In actual practice, an operating point at higher current would be desirable.

At the end of each run, the chamber was returned to one atmospheric pressure, the sample removed, and a new one loaded. The sensor and mirror were simply returned to the chamber. The output of the cell for the second run was the same as the first run within an uncertainty of 1%. The output of the cell during the third run was the same as the other two within an uncertainty of 20%. This uncertainty is due to the fact that a cryogenic panel was used in the first two runs, but not in the third. Since the cell and equipment were at different temperatures, it is difficult to compare the data.

A sensor has been developed which is useful in an ultrahigh vacuum environment and can withstand the high bakeout temperature necessary to attain a very low pressure condition.

Ames Laboratory Personnel Directly Associated with Project

Frederick A. Schmidt, Metallurgist, Project Manager, and Principal Investigator.

Dr. Barbara K. Lunde, Associate Engineer, Co-Investigator and Head of Engineering Development and Support Section.

Daniel E. Williams, Associate Metallurgist, and Administration Coordinator.

Dr. O. Norman Carlson, Senior Metallurgist, Advisor, Metallurgy.

Dr. David T. Peterson, Senior Metallurgist, Advisor, Metallurgy.

Dr. Robert F. Brodsky, Head Aerospace Engineering ISU, Advisor, Aerospace Engineering.

Dr. Leverne K. Seversike, Aerospace Engineer. Dr. Seversike was co-author of the document concerning the Operating Environment for the Preparation, Launch, Space Operation, and Recovery of the Experiment. He also assisted in the preparation of the Test Specification for the experiments.

Marvin E. Thompson, Senior Research Technician. Mr. Thompson was in charge of the sample preparation, loading, integrity of the space simulation chamber and maintenance of all vacuum equipment and gauging.

Jerome E. Ostenson, Assistant Physicist. Mr. Ostenson was in charge of all cryogenics associated with the project. He also performed the resistance ratio measurements and aided in the design of the radiation shield and the expansion adapters.

Marvin S. Anderson, Assistant Physicist. Mr. Anderson assisted with the cryogenics in Mr. Ostenson's absence.

David K. Rehbein, Research Assistant. Mr. Rehbein assisted in setting up and running the various experiments. He was in charge of identifying the residual gases in the space simulation chamber and in determining their partial pressures. He also helped construct some of the control electronics.

Gregor A. Junk, Associate Chemist. Mr. Junk assisted in the identification of the residual gases present in the space chamber and in adapting a computer program for determining their partial pressure.

David H. Birlingmair, Head Experimental Engineering. Mr. Birlingmair and the various shop personnel under his supervision, were responsible for the fabrication of the space simulation chamber and several of the component parts used in the electrotransport apparatus.

Lanny P. Lincoln, Laboratory Technician II. Mr. Lincoln assisted in the assembly of the experiments and in the collection of the data.

Gaylord L. Stowe, Senior Research Technician. Mr. Stowe also assisted in the assembly of the experiments and in the collection of the data.

Cynthia A. Ustrud, Laboratory Technician I. Miss Ustrud assisted in the experimental work and in the calculations for determining the diffusion coefficients and electric mobilities of solutes in thorium.

Larry J. Barr, Graphic Specialist II. Mr. Barr assisted in the preparation of the assembly and line drawings listed in Appendix A. He was also responsible for the cover design of this report.

Joyce E. Cook, Secretary, Phase I.

Chrisanne Yuva, Secretary, Phase II.

Jean L. Royster, Secretary, Phase III.

The authors wish to make a special acknowledgement to the various service groups within the Ames Laboratory and in particular those in the Materials Science Program and the Building and Engineering Services Group, without whose splendid support this work could not have been completed.