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AN INVESTIGATION OF THE OXYGEN AND CARBON CONTAMINATION OF SOME LANTHANIDE AND ACTINIDE METALS

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Special thesis

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AN INVESTIGATION OF THE OXYGEN AND CARBON CONTAMINATION OF SOME LANTHANIDE AND ACTINIDE METALS

Edward Harris Lowenhaupt

(M. S. Thesis)

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ABSTRACT

An activation analysis technique employing He^3 induced nuclear reactions has been used in a study of the oxygen and carbon contents of some lanthanide and actinide metals. The experimental application of the technique has been refined. Its reliability within the limits of oxygen concentration encountered in this study has been investigated, and an approximation has been eliminated which introduced errors of greater than 50% in some cases in the calculation of results.

The oxygen and carbon content of metals produced by reduction of their respective trifluorides with barium vapor has been studied to determine the ability of some drying techniques to remove these elements from the trifluorides. Metals produced from untreated trifluorides contain about 6000 ppm oxygen. Metals produced from trifluorides treated with anhydrous HF gas were found to contain as little as 300 to 400 ppm oxygen.

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- E. Calculations
- F. Analysis of metals of known oxygen content

III. Metal Production

- A. Trifluoride preparation
- B. Metal production
- C. Results

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I. Introduction

It is known that the crystal structure and lattice constants of metals are often influenced by small amounts of cationic and anionic impurities. High temperature crystalline phases, or structures not observed at all in metals of high purity, are stabilized at room temperature by low contaminations.

Anionic contaminations have not been examined closely, due to analytical difficulties, but appear to be of noticeable effect in several instances.

Calcium metal containing only a few parts per million (ppm) cationic contamination has only two allotropic forms: face centered cubic (fcc) to 464° C., and body centered cubic (bcc) to the melting point. However, when such calcium is deliberatly contaminated by exposure to large amounts of carbon, nitrogen, or hydrogen, an hexagonal closest packed (hcp) and a form of lower symmetry are observed.[1]

If ytterbium metal is air oxidized to form a thin film of oxide to prevent its volatilization during high temperature x-ray studies, the transformation to the high temperature hexagonal form occurs at 710°C., and is not reversed to form the room temperature stable fcc phase until 260°C. In pure ytterbium metal, the hexagonal phase is not observed on heating below 800°C., and after formation reverts to the cubic phase below 600°C.[2]

McWhan[3] has prepared americium metal from AmF_3 and from AmO_2. Metal made from the trifluoride was indexed as double hexagonal closest packed (dhcp), and is taken to be the room temperature stable phase. Metal prepared by volatilization from a mixture of lanthanum metal and americium oxide was collected on tantalum or quartz fibers and was shown

to be face centered cubic in structure. Fcc is probably the high temperature phase of pure americium. These factors seem to indicate that oxygen stabilizes fcc americium. Spedding and Daane[4] have claimed that trace amounts of oxygen, as Y_2O_3, which has a maximum solubility of 2 mole per cent. in YF_3, contributes to oxygen in yttrium metal produced by reduction of the YF_3 with vaporized Ca.

Phase stabilization by impurities is possible to the extent to which it occurs in metals because of the small values for the heats of transition normally observed between two crystal phases. The enthalpy difference between the high and low temperature forms of several metals is given in Table 1.

Table 1

Metal	Transition	ΔH_t, cal/mole
La	dhcp-bcc	760
Yb	fcc-hcp	425
Pr	dhcp-bcc	760
Ca	fcc-bcc	240

Although phase stabilization is the most obvious effect of contamination, significant changes in lattice parameters arise when impurities are present in room temperature stable structures. The effect of varying the oxygen concentration between 100 and 3000 ppm in vanadium metal is shown in Figure 1.[5] The influence of small amounts of gold on the lattice parameter of aluminum is very striking, as indicated in Figure 2.[6]

The following work describes the adaptation of an activation analytical technique for the investigation of anionic contamination in samples of the size encountered in transplutonium research, and studies made of variables in the production of lanthanide and actinide metals.

FIGURE 1

OXYGEN IN VANADIUM METAL

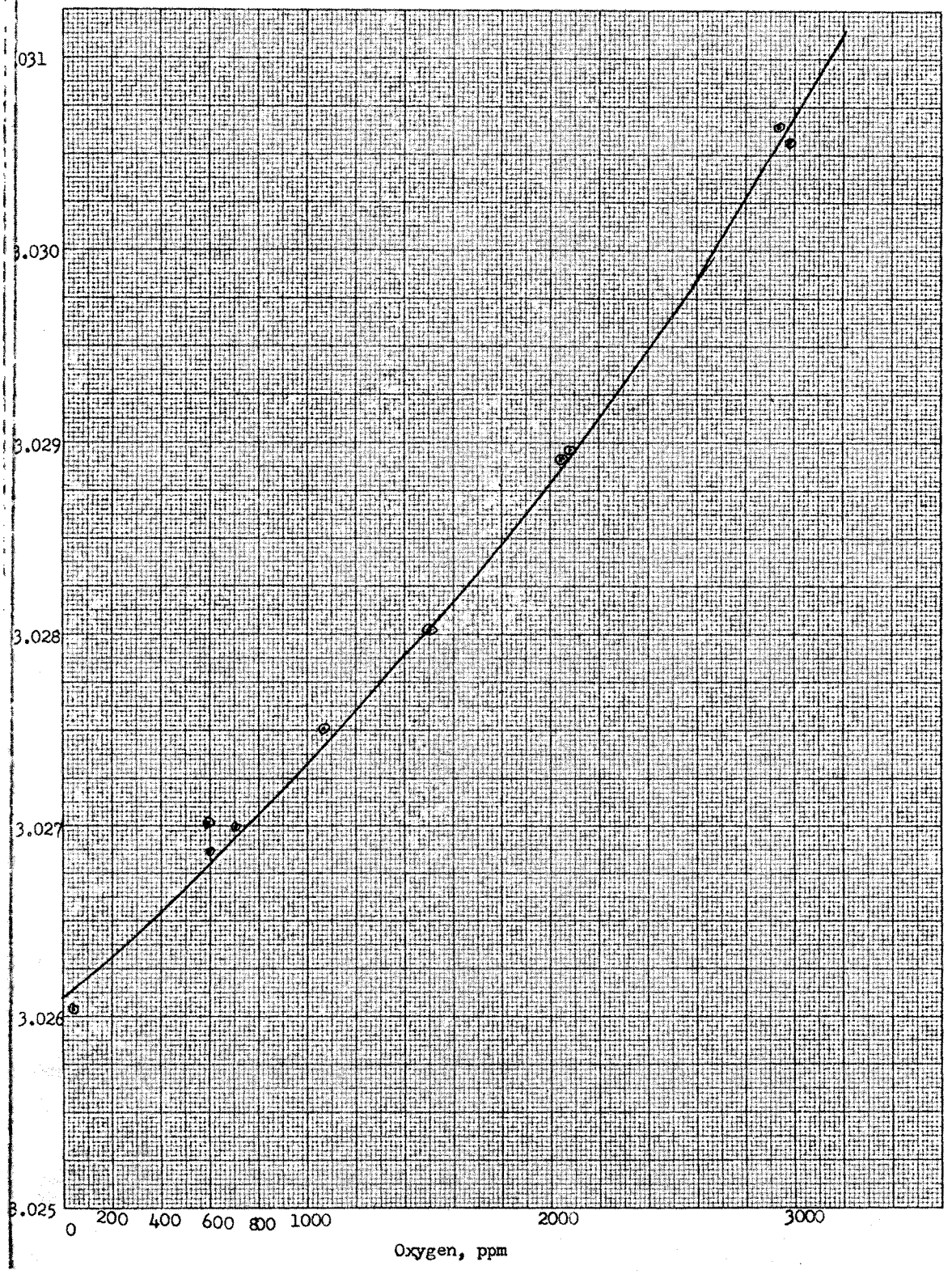

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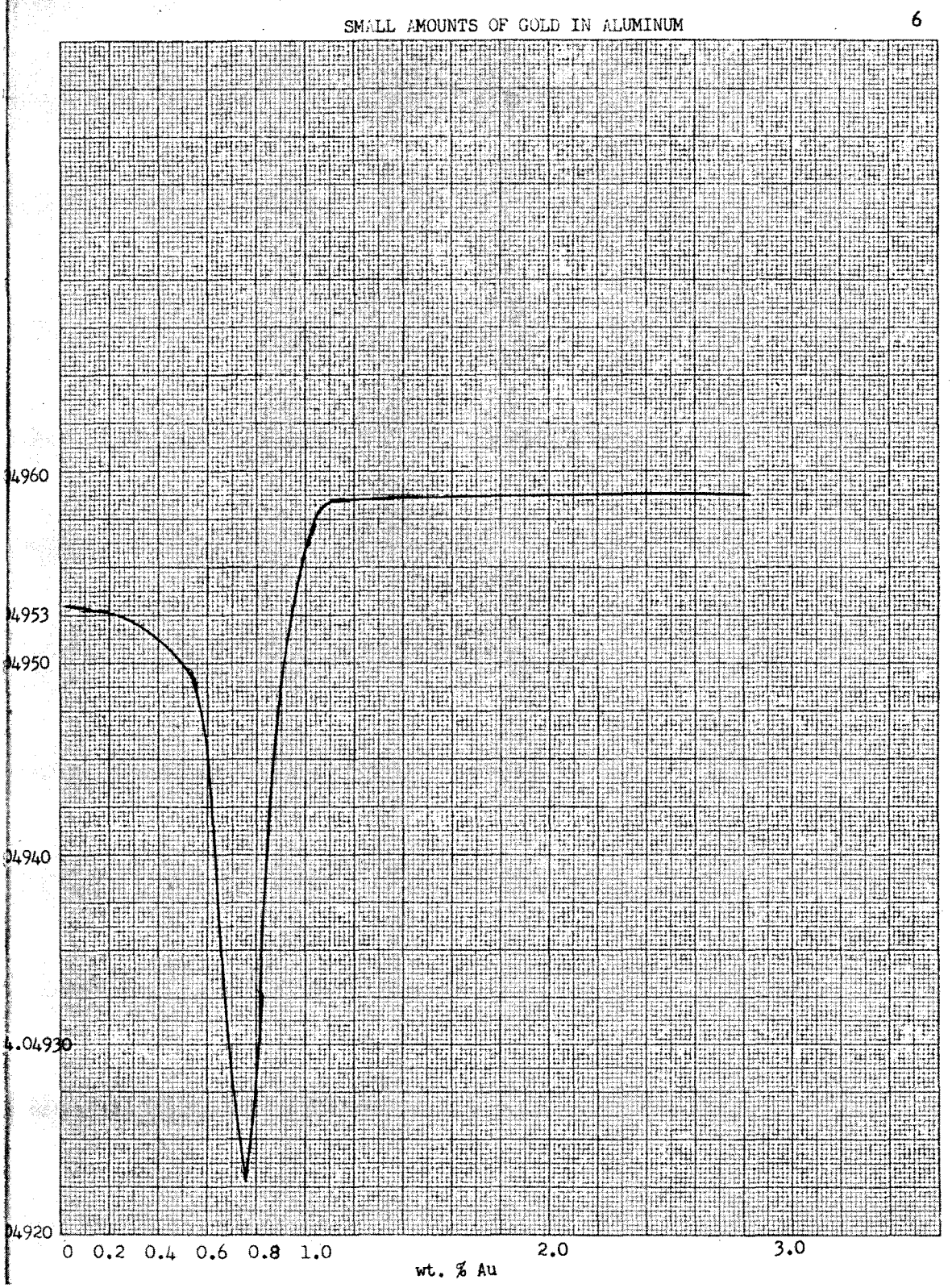
FIGURE 2

SMALL AMOUNTS OF GOLD IN ALUMINUM



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II. The Analytical Technique

A. Detection of impurities in micro samples

Cationic impurities are readily detectable by emmission spectrographic techniques. Sensitivities of 100 ppm are possible for many elements, and may be increased by chemical isolation of a suspected contaminant from the bulk of a sample. The total sample required does not exceed 100 micrograms.

In the purification of source materials for metal preparation, a high degree of purification from cationic impurities can be achieved by ion exchange chromatography. In the case of the actinides, radiochemical assays can show the degree of contamination from other members of the series.

Due to the radioactivity and lack of availiablilty of the transplutonium elements, their metals are produced in such small quantities that common anionic analytical methods can not be employed even when an entire metal preparation is used in one analysis.

Methods usually employed for analysis of carbon, oxygen, nitrogen, and hydrogen involve the fusion of the sample with carbon (in the case of O, N, and H), or oxygen (for C, N, and H analysis). The products of fusion may be swept onto a molecular sieve column in a gas chromatographic analysis, or excited by a DC discharge and detected through their emission spectra. These methods as they exist require nearly milligram amounts of fusion products, whereas an entire metal reduction may weigh less than a milligram, in the case of americium or curium metal. These methods are necessarily destructive of the sample.

For the past few years, activation analyses have been used in many forms for many elements, both metallic and non metallic. These methods need not destroy the sample if the activity of the species of interest can be singled out from other activities. Sample size is not an important

consideration if the activity produced has a convieniently long half life and the cross section for its production is reasonably large.

The most familiar form of activation analysis is neutron activation. However, more than fifty elements undergo the characteristic (n, γ) reaction. The products of (n, γ) reactions are almost all β^- or γ-ray emitters, so if more than one or two species with high (n, γ) cross sections are present in a sample, chemical isolation of the active species is required. Besides destroying the sample, this takes time, with consequent reduction of sensitivity in the case of short lived isotopes.

B. He^3 Activation Analysis

In 1962, Markowitz and Mahony[7] advanced an activation analysis technique for oxygen and a number of other elements through He^3-induced nuclear reactions. The advantage of this method is its specificity for the anions of special interest in actinide metals. All of the principal reactions for oxygen, carbon, and nitrogen activation are exoergic. Hence, He^3 particles accelerated to energies only slightly higher than the couloumb barriers of the nuclei to be activated will suffice. The couloumb barrier of oxygen is about four Mev; in practice, an incident energy of around ten Mev is used. Since the metals to be analyzed have couloumb barriers of greater than 15 Mev for He^3 penetration, no extraneous activity arises from activation of the matrix in which suspected contaminants are present.

Table 2 shows the reactions of interest and half lives of the products of activation.

All three products are positron (β^+) emitters. The half lives of

F^{18}, C^{11}, and N^{13} are convenient, because they are long enough to be detected several minutes after irradiation, but not so long that they need to be watched for several days for identification.

Table 2

Contaminant	Nuclear Reaction	Product half life
O^{16}	$O^{16}(He^3, p)F^{18}$	110 min.
C^{12}	$C^{12}(He^3, \alpha)C^{11}$	20.5 min.
N^{14}	$N^{14}(He^3, \alpha)N^{13}$	10.1 min.

The major advantage of this activation, however, is that the three product isotopes may be distinguished from all extraneous radiation produced in a bombardment, without decomposition of the sample. This is made possible by coincidence counting of the 0.511 Mev gamma radiations produced by the annihilation of a positron and electron. If the decay of the positron emitters as observed by coincidence counting follows the respective half lives of the product isotopes, it may be assumed that other activities are not appreciably influencing the analysis. This method of counting was proposed by Dr. V.A. Ryan.[8]

When the method was advanced by Markowitz and Mahony, the claim was made for an ultimate sensitivity of a fraction of a part ber billion (ppb). It must be emphasized that this is a calculated limit based only on the flux of incident He^3 particles which will not thermally degrade a metal sample. Markowitz and Mahony did not attempt to verify this sensitivity experimentally, and did not obtain good agreement with known samples in the higher 1000 ppm levels.

Nevertheless, the method offers a means of analysis of the small quantities of actinide metals produced in this laboratory. It was ad-

apted to a micro scale by Demildt[9], who with Jere Green[10] performed many of the early analyses.

C. Equipment

1. The rotating target

Because of large fluctuations in the beam intensity of an accellerator, it is desirable to bombard a sample of known oxygen, carbon, or nitrogen concentration along with an unknown sample. The integrated beam flux may then be calculated from the activity of the standard; or more simply, the activity of the unknown may compared with that of the standard. Since the beam is generally inhomogeneous, Demildt sought to insure equal exposure of the samples and standards by placing them in a suitable holder and rotating the holder continuously in the beam, so that each sample is exposed frequently to the entire beam for equal periods of time during an irradiation.

The target holder is made of copper, and must be water cooled, since thermal degradation of the samples would occurr in the absence of cooling. Currently, the maximum beam which can be delivered to the target by the 88-inch cyclotron or the Heavy Ion Linear Accelerator (HILAC) at the University of California Lawrence Radiation Laboratory, Berkeley, is about 1 micro ampere (μa). At ten Mev, this beam deposits 10,000 watts of power.

The rotating target assembly is shown in Figure 3. As designed and constructed by the HILAC Accelerator Technicians, the target was intended to be cooled by the 90 psig water availiable at the HILAC. After some use, the seals began to leak. At about the same time, the author became interested in keeping the assembly under vacuum during bombardment, which would add 14 pounds more differential across the seals. Dr. Cunningham suggested that the coolant be sucked through the system,

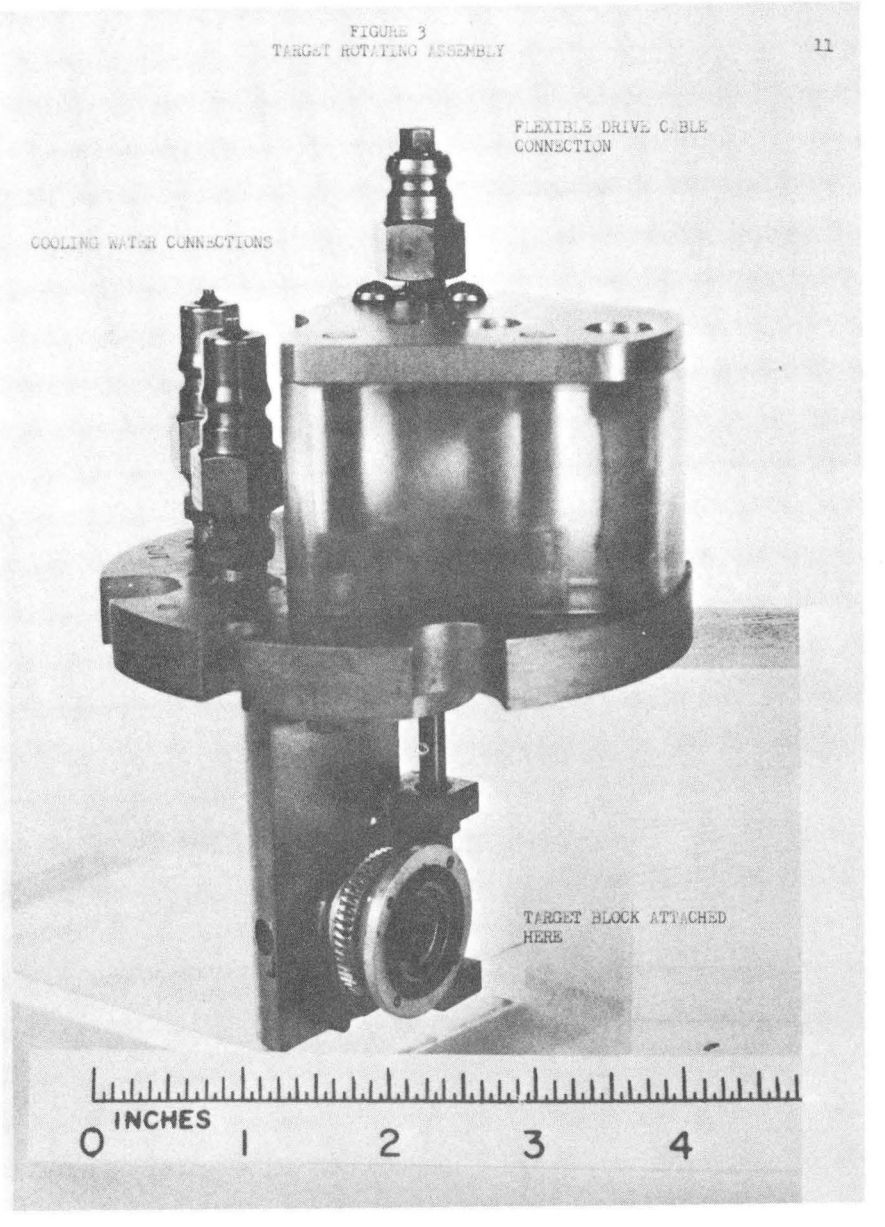


FIGURE 3
TARGET ROTATING ASSEMBLY
11
FLEXIBLE DRIVE CABLE CONNECTION
COOLING WATER CONNECTIONS
TARGET BLOCK ATTACHED HERE
INCHES
0
1
2
3
4

ZN-5752

Fig. 3

rather than forced. This lowers the differential to atmospheric pressure when the system is operated in a vacuum, and serves to stop leakage. The cooling system and its heat exchanger appear in Figure 4.

2. Encapsulation equipment.

Because of the reactivity of metals, particularly lanthanide and actinide metals, with respect to components of the atmosphere, it is necessary to isolate them after preparation and during bombardment. A technique for packaging samples in metal foil was developed. Demildt used tantalum and later platinum foil for packaging; the author has used gold foil in most of this work because it is lower in oxygen content and forms a capsule that is much easier to open after a bombardment, when time is precious if the activity is low. The packaging equipment appears in Figure 6, page 18. Its use is described on page 23.

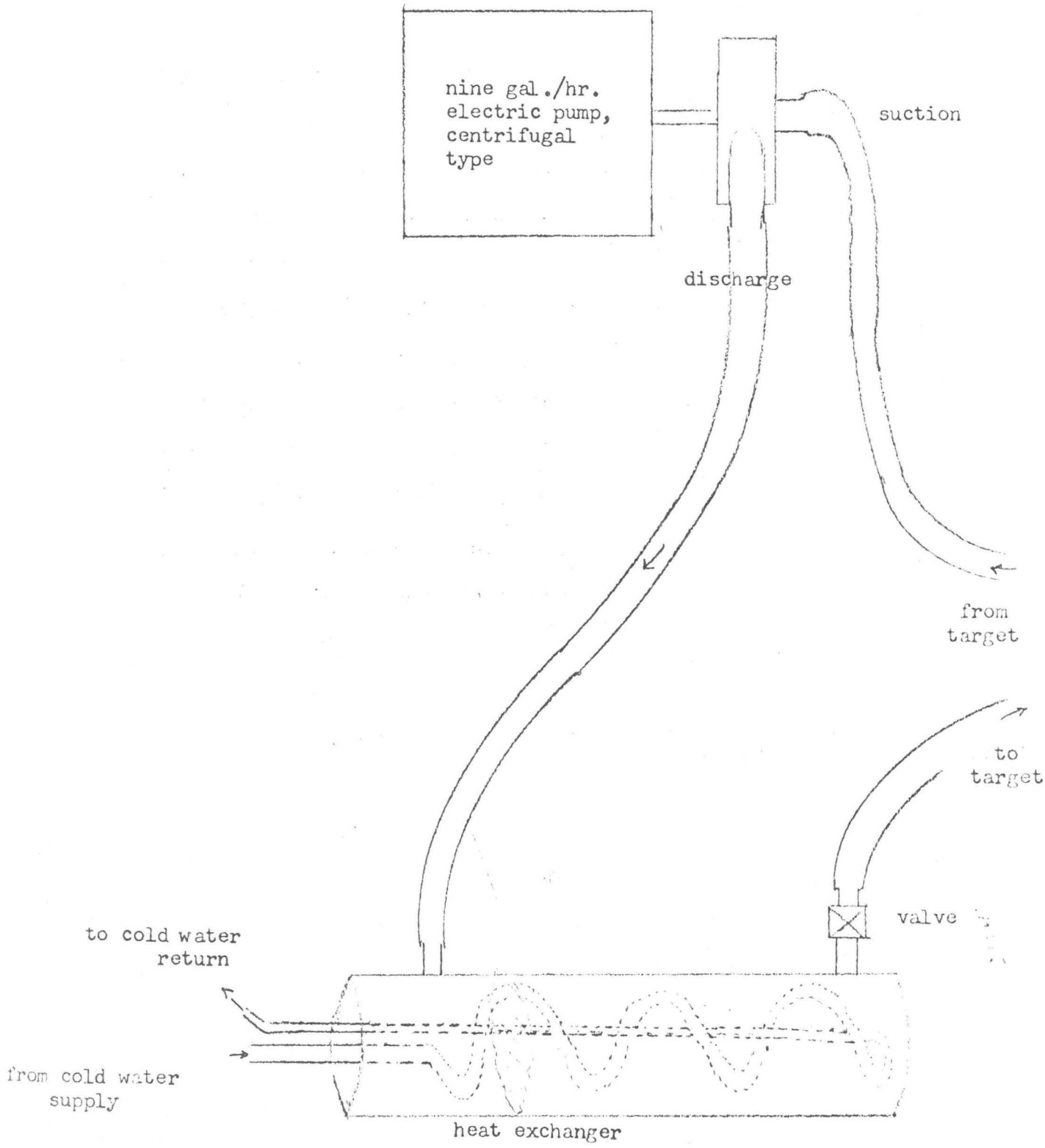
3. Inert atmosphere equipment

Metals prepared by the micro reduction procedure described later are coated with a great deal of slag. Other metal samples are cut from foil and are coated with varying degrees of tarnish. To remove surface contaminations, samples are scraped until clean, and worked to the proper shape for analysis, in inert atmosphere boxes.

A number of such boxes have been constructed in this laboratory. Most of the boxes are of the flush type. Two have recycle systems which purify gas from a box that has been flushed overnight and then isolated. The isolated gas is passed continuously through a coil at liquid nitrogen temperature and then over copper wool heated to

FIGURE 4

LOW PRESSURE TARGET COOLING SYSTEM



Approximately 1/6 actual size

600° C.

An enclosure constructed by the author has been used for more recent work. It is constructed of materials strong enough to withstand total evacuation, and connected to a large Welch Duoseal pump (capacity 1400 l./min.) via a four inch diameter cold baffeled tubing. The system is evacuated to 0.1 micron of Hg, vented to high purity inert gas, evacuated again, etc. After about three such cycles, it is vented to atmospheric pressure with pure gas and used as an ordinary glove box.

A special vacuum tight hydraulic press[11] is mounted in the lucite top of both "recycle" boxes and the evacuable box, for the purpose of packaging samples in gold foil. These boxes are fitted with "Buta-Sol" gloves, which have lower coeficients of diffusion for water vapor than ordinary neoprene gloves. (Availiable from Charleston Rubber Co., Charleston, South Carolina.)

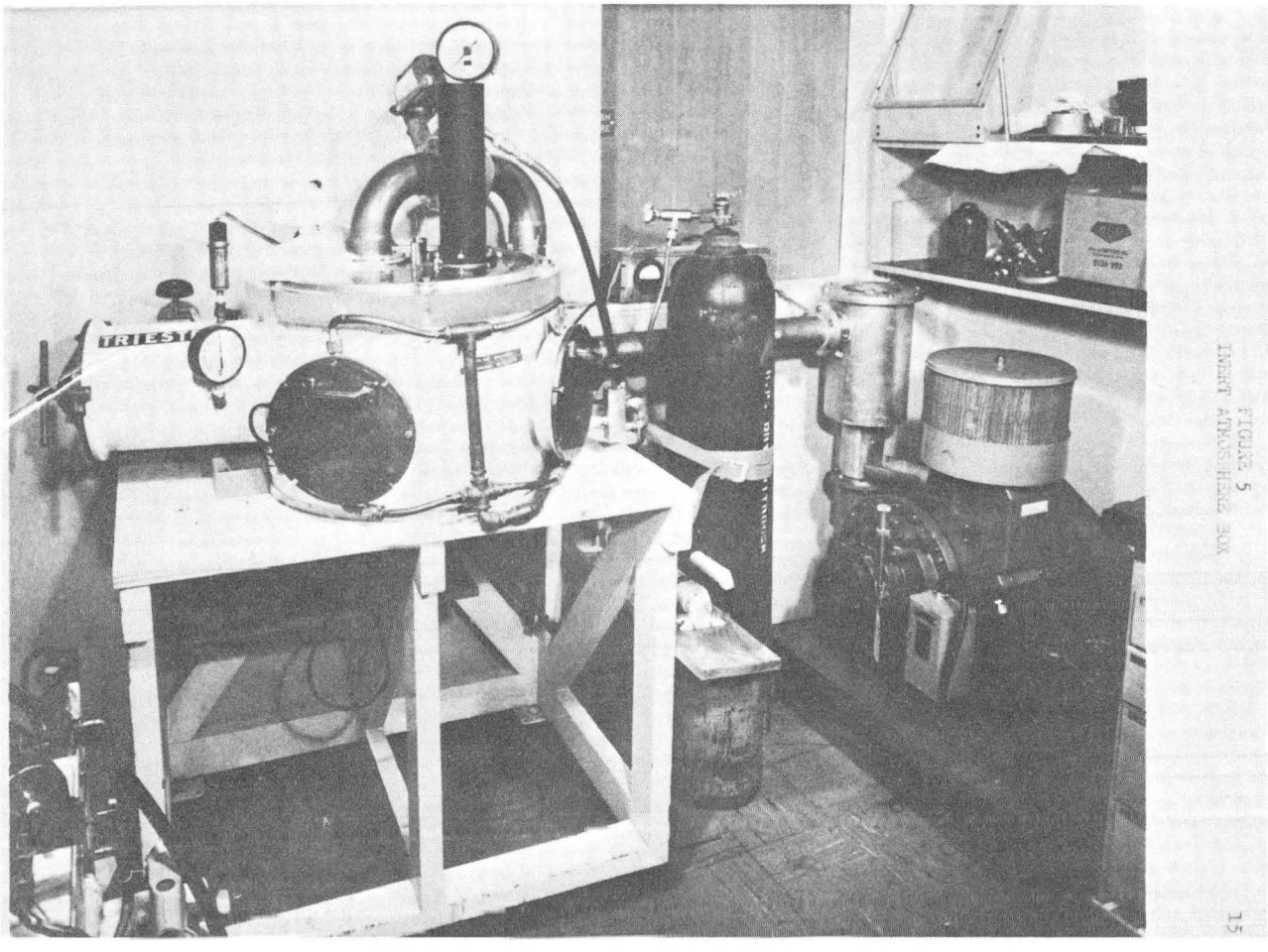
The evacuable box appears in Figure 5.

D. Experimental

1. Preparations

As stated above, all sample preparation is done under vacuum or in inert atmosphere boxes. Although the inert boxes are equipped with evacuable air locks, it is good practice to put all necessary paraphernalia into the working area before creation of a good atmosphere. This avoids the possibility of contamination of the atmosphere after cleaning of a sample has begun.

Prior to placing the tools in the box, gold foil discs must be cut for packaging the samples. Figure 6 shows the cutting tools,



ZN-5753

Fig. 5

as well as the other important sample preparation equipment.

For each sample, a 5/8 inch diameter gold bottom disc is cut with tool G, fig. 6. One mil (0.001 inch thick) gold foil is placed in the slot near the base of the large portion of the cutter. The 5/8 inch steel dowel is placed keen end down in the hole in the cutter body in gentle contact with the gold foil. The dull end of the dowel is struck lightly with a small hammer to cut the disc.

A similar number of 5/32 inch diameter gold "hats" are cut from 1 mil gold using the large cutting tip (B) attached to cutter (A). Note that it is necessary to weigh accurately (nearest 0.1 mg.) about ten square centimeters of the same foil from which the hats were cut. This is done to figure accurately the beam stopping power for the foil used for hats. The cutter (A) must be fitted with a 5/8 inch diameter copper disc under a 5/8 inch diameter paper disc to avoid dulling the cutting tips. These discs are placed in the recessed hole directly below the tip.

After the packaging foils are cut, they must be fired to remove grease, dust, etc. This is done by placing each disc separately on a platinum counting plate of the type used for radiochemical assays. The plate is then lowered with a pair of forceps into the working coil of a 300 watt induction heater, which has been set to produce a dark cherry red glow in the platinum plate. A few seconds at this temperature is sufficient. No advantage has been observed when using foils fired under high vacuum.

After firing, each foil should be kept in a clean, individual

glass vial. Two pieces of gold cleaned by firing tend to adhere tenaciously to each other if they are allowed to come into contact.

When the foils have been prepared, they should be placed in an inert atmosphere box along with the following equipment: cutter (A), equipped with the small tip as in fig. 6; the sealing die, consisting of the base (C), washer (D), cover (E), and plunger with O-ring (F); also a lab jack, petri dishes and slotted covers (I), two or three fine tipped forceps, a Bard-Parker knife handle with several extra blades, a finely ruled reticule from a microscope eyepiece, and some bottles to receive the prepared samples. All bottles should have their caps removed prior to placing them in the box, as the caps retain air.

If only foil samples are to be analyzed, they may be cut before hand with the small cutter (J). Lump metal samples should be placed in a sealed evacuated glass capillary. The samples should be introduced into the box along with the tools. If samples not in foil form are to be prepared, the equipment for cold-working them into shape (K) should be included.

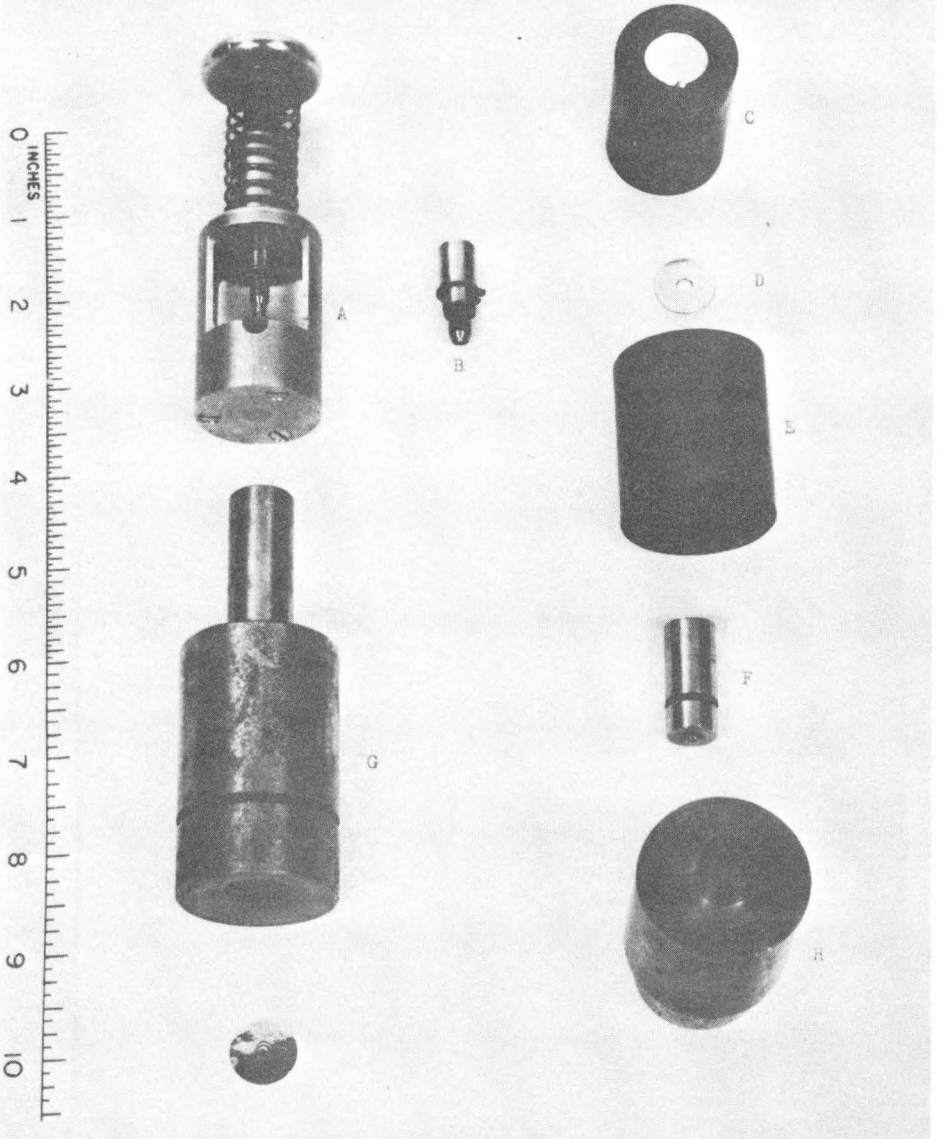
This equipment consists of a small machinist's vice, two pieces of tool steel, and small shims of 6 mil tantalum which have been drilled with various sized holes.

After all necessary equipment has been assembled, an inert atmosphere may be created in the enclosure.

2. Cleaning and photographing

It can not be stressed too strongly that great patience is

FIGURE 6
SAMPLE PACKAGING TOOLS



A, cutter with small tip attached; B, large tip; C, die base; D, positioning washer; E, die cover; F, plunger with o-ring; G, large foil cutter; H, assembled die

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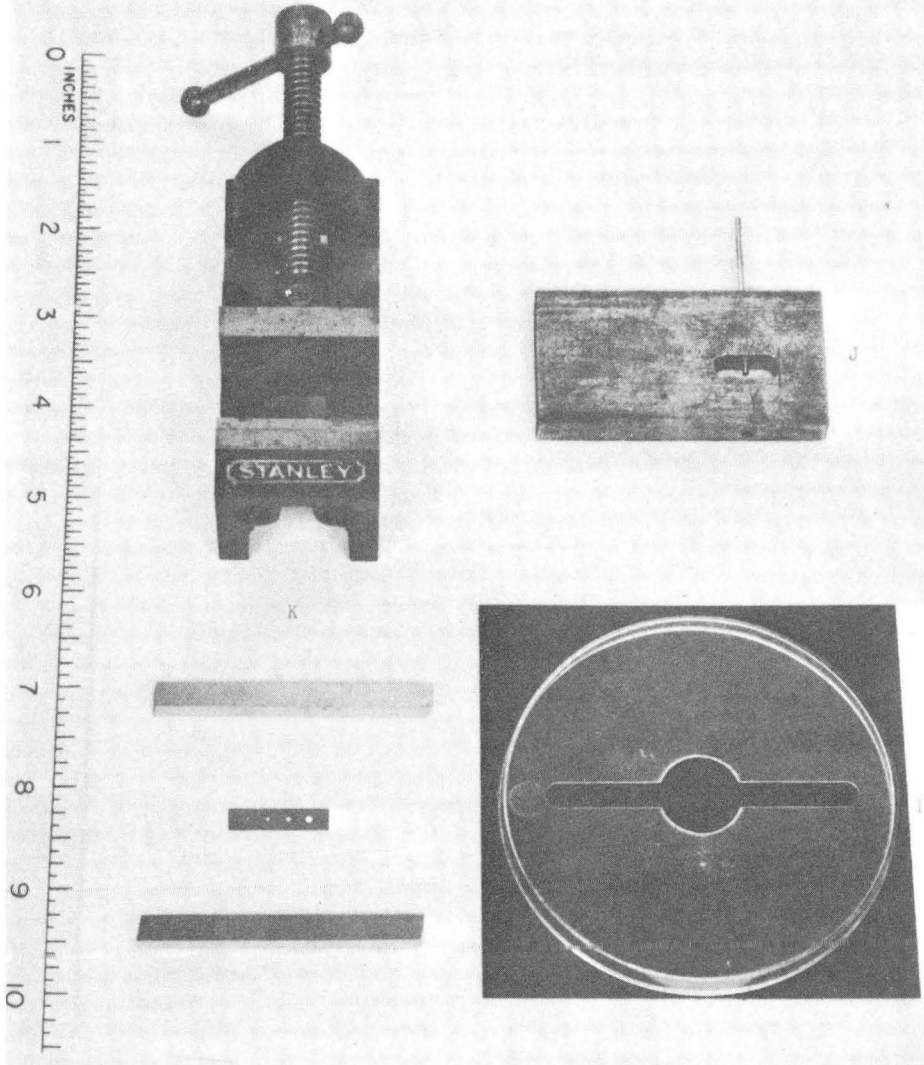
FIGURE 6, cont.
SAMPLE SHIPPING TOOLS



I, slotted plastic cover; J, small cutter for foil samples; K, cold working equipment for metal "coupons"--small vice, tool steels, and tantalum shim

ZN-5754

required to obtain reliable and reproducible results. The area in which the sample is worked must be kept clean, as must the tools with which the smaple is handeled and worked. Thoroughness in carrying out all steps is essential. To recognize the attention to detail that is required in cleaning metals and protecting them from recontamination, note that in a one milligram sample, one microgram (μg) of contamination corresponds to 1000 ppm.

If a sample of actinide or lanthanide metal prepared by the micro reduction process described in Part III of this work is to be analyzed, the following steps must be taken:

a. The metal will be in the form of a bead of about a millimeter in diameter. It will be attached to a piece of 3 mil tungsten wire, and will be surrounded by a coating of barium difluoride slag. It is often convenient to remove this slag prior to the time of preparation for analysis in order to deep the area free from BaF_2 dust. Using the wire as a "handle" to be grasped by forceps, scrape the bead of metal with the knife until all slag and tarnish are removed from the bead and its entire surface is bright and shiny. This work is done under a binocular microscope, as are all of the cleaning processes. The bead should be held in a clean petri dish. The possibility of loss of the bead from the dish is reduced if a slotted plastic cover (I), Figure 6, is placed over the bead while scraping is in process.

b. After this initial cleaning, change the petri dish and knife blade. Now remove the wire to which the bead is attached, and clean the groove which it occupied in the metal by scraping with the tip of the knife. Scrape the entire bead surface once more.

c. Examine the bead at this time to see if it is large enough to be split into duplicate samples. As described in step (d) below, the sample will be worked into proper shape for analysis by pressing it into a hole in a 6 mil tantalum shim (see K, Figure 6). If the bead is large enough to be divided, each half should be large enough to completely fill one of the two largest holes in the shim. If one of the smaller holes must be used after division of the bead, it is too small to be split.

d. Place a piece of tool steel on the lower jaw of the small machinist's vice. Put a 6 mil tantalum shim on the tool steel. Insert a metal bead, or half a bead if duplicate samples are to be prepared, in an appropriately sized hole in the shim, and place the other piece of tool steel over the tantalum. Lower the upper jaw of the vice, making sure that the tantalum remains sandwiched evenly between the tool steels. Apply the pressure required to flatten the sample and force it evenly around the curcumference of the hole in the shim.

e. Remove the shim from the vice and place it in a clean petri dish. Scrape both sides of the metal sample

while it is held in the shim. Each face should be cleaned by scraping the entire surface four times, or more if necessary to remove tarnish or other contamination. The metal should be rotated about sixty degrees between scrapings to assure that all portions of the faces are cleaned to the same degree. At no time should the point of the knife or forceps indent the surface, as this would drive contamination deep within the region penetrated by the He^3 beam. Scraping is a gentle process, removing only a few microns of metal at a time.

If the metal samples have been cut from a piece of foil, rather than prepared in the form of a bead, they will already be of the proper dimensions for analysis, and a final cleaning is all that is necessary. The following steps apply either to foil samples, or metal as treated in steps (a) through (e) above.

f. Remove the sample from the shim by pressing gently with the tip of the knife at the point where the tantalum and metal sample meet, while slightly bending the shim. Holding the faces of the little disc of metal gently with the forceps, scrape around the circumference. If the metal has come from the shim, there may be some flashings around the edge, and these must be removed at this time.

g. Scrape the faces three times again. Select the face which will be exposed to the beam. Invert a petri dish on the lab jack, place the sample on the dish with the selected face up, and place the small reticule over the sample. Make sure that the ruled side of the reticule is the side

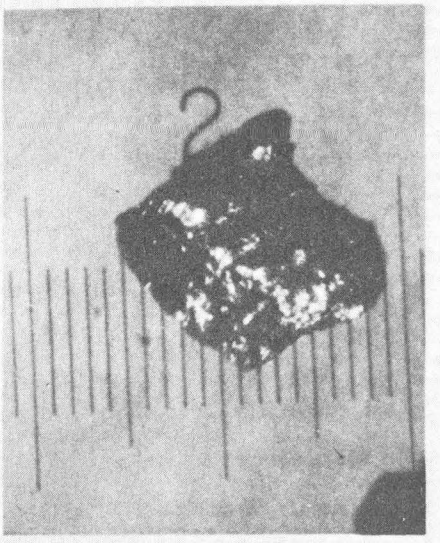
in contact with the sample, and that the rulings are directly over the metal. Raise the lab jack until the sample can be brought into focus in a monocular microscope placed on the lucite top of the glove box.

h. Center the sample in the microscope. Connect a photomicroscopy unit equipped with a Polaroid camera to the microscope, and photograph the magnification of the sample and ocular scale. (If no photographic equipment is availiable, a camera lucida may be used to sketch the perimeter of the sample, as was done in previous work. The author has used the photographic method in most of this work.) The purpose of the above step is to obtain the area of the targets, which is required in calculating the results. Some pictures of samples may be seen in figure 7.

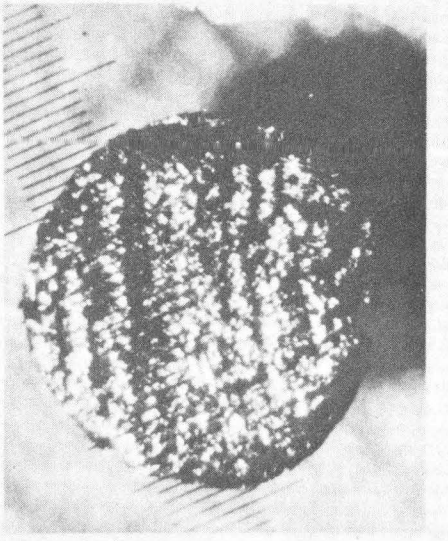
i. Scrape the face of the sample which will be exposed to the beam once more. Be cautious not to alter the area, which has already been recorded.

j. Put a 5/8 inch diameter gold foil disc in the recessed portion of the sealing die base (C), fig. 6. Press the washer (D) over the gold. Center the metal sample in the center of the hole in the washer, being certain that the face which has been photographed is up. Put a gold foil hat over the sample. The hat should exactly fill the hole in the washer. Insert the plunger (F) in the die cover(E) from the flat side of the die cover. The end of the plunger

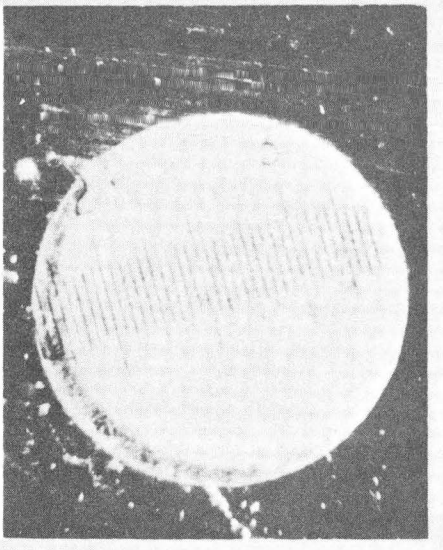
FIGURE 7
PHOTOMICROGRAPHS OF TARGETS



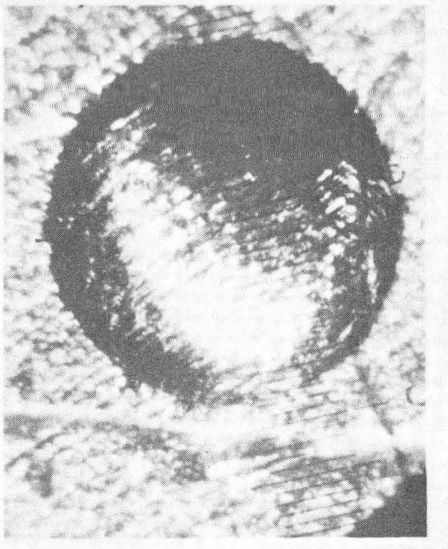
AMERICIUM METAL



TERBIUM METAL



QUARTZ



THORIUM METAL

with the small raised ring should be towards the hollow part of the die cover. Do not insert the plunger so far that it protrudes into the hollow portion.

k. Gently place the die cover with plunger over the die base. The small hole in the cover should be opposite the "channel" in the top of the die base to facilitate pumping out the sample area. Now press the plunger gently but firmly down on the gold hat. Being careful not to tilt or knock the die assembly so as to displace the sample, place it in the recessed portion of the base of the press mounted in the top of the glove box.

l. Evacuate the box to a pressure of one micron or less for twenty minutes. Then put about 1200 pounds pressure (six small scale divisions)on the die. This serves to cold weld the gold foils together around the sample. Release the pressure and vent the tank to atmospheric pressure with a pure inert gas.

m. Dissassemble the die and remove the target. Put it hat side up in the 5/8 inch recession in the cutting tool (A), which should be fitted with the small cutting tip. The target fits in the recession so that the portion containing the sample is exactly under the cutting edge. With the palm depress the plunger until the sample package is cut from the main portion of the gold bottom foil.

n. Inspect the package to acertain that the seal has

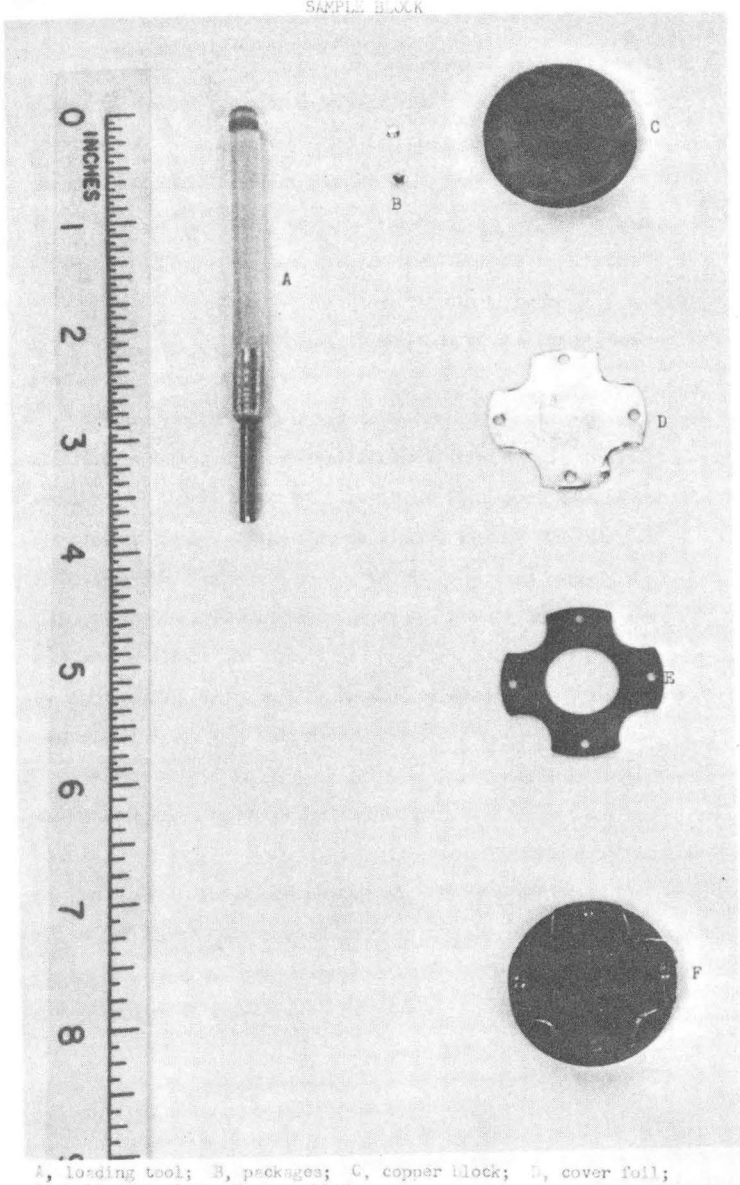
not been cut and that the package will be air tight. The standards which are run along with the samples do not require cleaning. For oxygen standards, quartz discs of 1/16 inch diameter are used. Small pieces of corborundum are used for carbon standards. Neither material tarnishes, so they may be used without preparation. Since the standards should be bombarded at the same energy as the samples, they are packaged in the same way as the samples using the same gold for hats that covers the samples.

3. Activation and counting.

The copper block in which the targets are mounted is drilled with six 1/8 inch diameter recessions on a 5/8 inch diameter circle. The packages are a snug fit in the recessions, and a special tool is used to press them into position. It is desirable to place the quartz standards 180° apart, so that as many metal samples as possible can be placed adjacent to them. One corborundum standard is usually included in an analysis. Care must be taken to assure that the "hat side" of the targets faces away from the copper block.

After the samples and standards have been placed in the block, an aluminum foil of the desired thickness, which has been weighed to determine its stopping power per unit area, is cut to fit the block. It must be shaped so as to expose the holes through which the block is bolted to the rotating assembly. A hold-down ring is then bolted over the foil. The block, loading tool, a gold package, aluminum foil and the hold-down ring are shown in figure 8.

FIGURE 8
SAMPLE BLOCK



A, loading tool; B, packages; C, copper block; D, cover foil; E, hold-down ring; F, assembled

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The target block is bolted to the rotating assembly, and it is placed in the beam tube of an accelarator in a mounting which will position one portion of the 5/8 inch circumference on which the targets are mounted directly behind a 1/8 inch collimator..

The collimator is grounded to the mounting, so that a beam current reading may be taken from it, and from the target itself, which is insulated from the mounting. An electrometer lead to the control room of the accelerator is attached to the target, and another to the mounting.

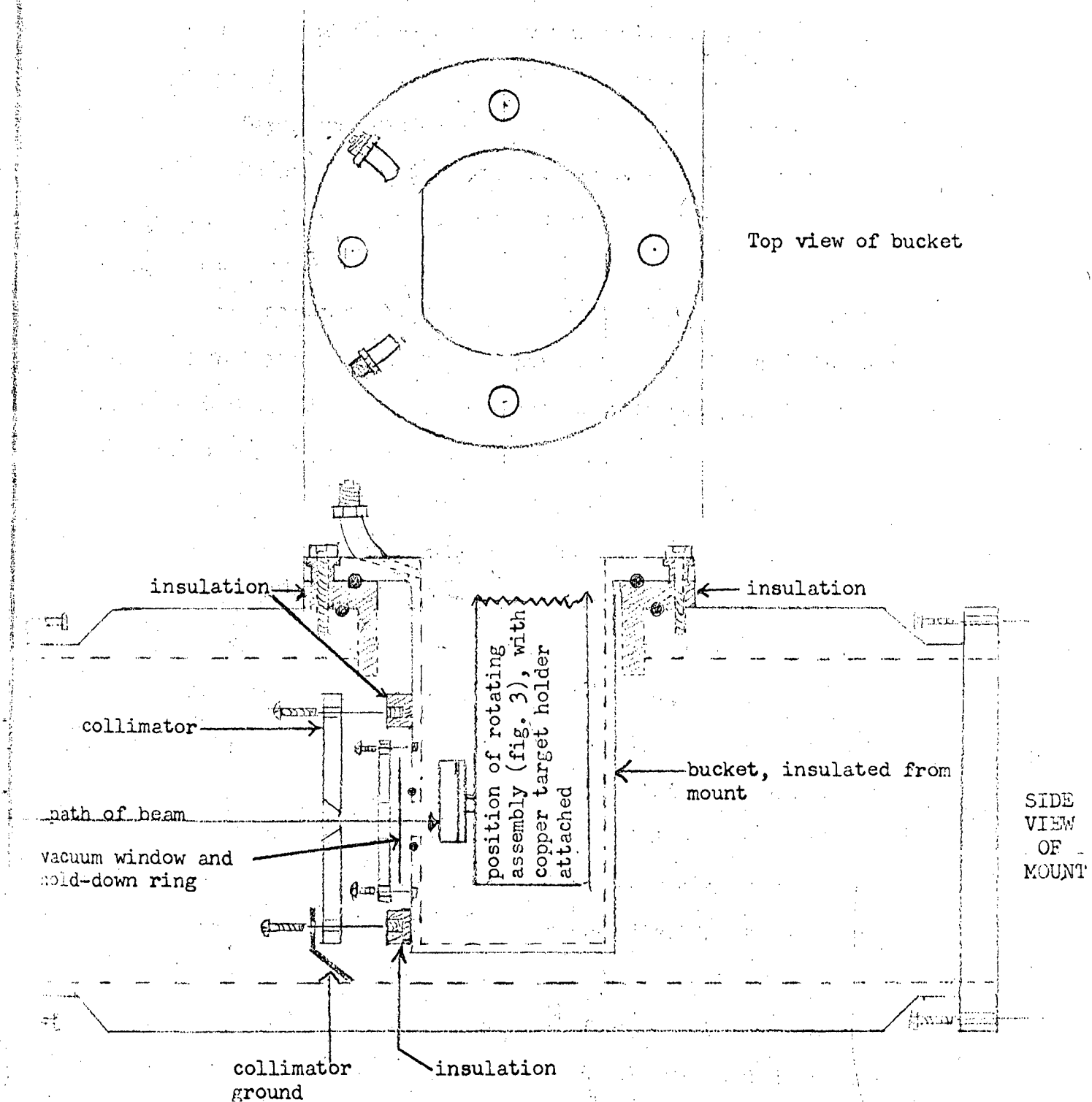
If the rotating targets are to be bombarded in a vacuum, a small manifold is attached to two small tubes leading to the "bucket" which receives the target assembly. See figure 9 for a diagram of the mounting apparatus. Vacuum may be applied through this manifold, or alternately, the vacuum window (20 mil aluminum) between the "bucket" and beam tube can be removed so that the vacuum of the accelarator itself is used. When operating under vacuum, all seals in the rotating target must be previously checked for leaks with a mass spectrometer type helium leak detector.

Shortly before bombardment is to start, the cooling water leads and motor drive flex cable are connected to the target, and the water pump is started. Bombardment at a beam current of about 500millimicro amperes of He^{3++} ions should be carried out for a period of time dependent on the oxygen contamination expected in the purest metal sample in the target. For a sample containing about 100 ppm oxygen, a total integrated beam of at least 800 to 1000 millimicro ampere hours must be

FIGURE 9

BEAM TUBE MOUNT FOR ROTATING TARGET ASSEMBLY

APPROXIMATELY ONE HALF ACTUAL SIZE



accumulated to produce a useable amount of F^{18} activity. A sample containing about 1000ppm oxygen will be sufficiently activated by around 500 millimicro ampere hours.

If the 20.5 minute C^{11} activity is to be measured for carbon analyses, the copper block containing the targets must be brought to the counting area as quickly after bombardment as possible. Unpackaging equipment consisting of a small screwdriver, forceps, and sharp tipped Bard-Parker knife should be previously laid out in a ventilated hood next to a binocular microscope and aluminum counting holders. If radioactive materials are being analyzed, unpackaging should be done in a glove box.

Using the screwdriver, the hold down ring and aluminum foil are removed from the copper block. The purest sample will have the lowest activity, and should be unpackaged first so that counting can begin on it immediately. Unpackaging is performed as follows:

a. Remove a gold package from the copper block with the forceps, and place it under the binocular microscope.

b. Press down on the outer edge of the package with the forceps tips, holding them slightly separated so that each tip contacts the edge of the package 180° apart.

c. With the package held in place by the forceps tips, slice gently with the sharp point of the knife through the top of the package (the hat). Cut through the hat outside of the portion of the package occupied by the sample to avoid removing activity from the surface of the sample itself. Cut the hat as much as is necessary to peel it back, revealing the sample.

d. Remove the sample with the forceps and place it in a counting card. Tape a cover over the card and take it to the

counter.

Unpackaging is a simple process, but care should be taken not to scratch the surface of the sample, thus removing activity. The forceps should not be closed while being used to hold the package during the cutting process. This will crimp the gold, making it more difficult to extract the sample, and can break a fragile target such as a quartz standard. Unpackaging does not need to be carried out in an inert atmosphere, since atmospheric contamination after activation is of no consequence as far as the analysis is concerned.

All samples should be counted through at least three half lives of the longest lived activity (110 min. F^{18}). The standards contain about two orders of magnitude more oxygen or carbon than the samples, and consequently will "saturate"the counter when they have just come from bombardment. Hence, they may be unpackaged at leisure, since they will have to "cool off"before they can be counted. The corborundum standards for carbon analysis may be counted after about thirty minutes; the quartz standards after three of four hours.

E. Calulations.

Preparation of a thin foil target of uniform surface density (weight per unit area) from the quantities of metal prepared in this laboratory would be nearly impossible. In addition, a thin target would be undesirable because the effects of surface contamination would be approximately doubled if the He^3 beam could pass through both surfaces of a target. Effectively infinitely thick samples only have been used in this work.

The problem of defining the portion of a target surface exposed to the beam is eliminated if the target is smaller than the beam. All targets used were 1/16 inch in diameter or smaller, so were easily cov-

ered by the 1/8 inch collimated beam.

The activity of a product isotope of half life ($t_{\frac{1}{2}}$) at any time (t) after the end of activation (t_o) is given by the expression:

$$-\left(\frac{dN}{dt}\right) = N\sigma\Phi\left[1-e^{-\frac{0.693t}{t_{1/2}}}\right]$$

in which N = the number of atoms of the species to be activated which are seen by the beam,

Φ = the intensity of the He^3 beam in He^3/cm^2-sec.

σ = the cross section for activation in barns (10^{-24} cm.^{2})

For the case of a thick target which is smaller than the beam,

$$N = RSx\delta$$

where R = the range of the beam in the target substance, in mg./cm.^{2}

S = the surface area of the sample in cm.^{2}

x = the weight fraction of the species (for example, O^{16}) in the sample

δ = a constant for the species in units of atoms/mg.

this gives:

$$-\left(\frac{dN}{dt}\right) = \delta\sigma RSx\Phi\left[1-e^{-\frac{0.693t}{t_{1/2}}}\right]$$

Since the cross section (σ) is dependent on the energy of the activating He^3 particle, sigma will not be constant if the target is thick enough to signifigantly degrade the beam energy, as is the case in all targets used in this work.

Sigma is dependent on the energy, and the range of He^3 particles in a given target is also dependent on the energy. Knowing the relation of sigma to energy (the excitation function), and the relation of range to energy, a function relating sigma to the range may be obtained. This funtion may then be integrated between the range corresponding to the

maximum energy of the He^3 particles incident on the target surface, and zero range--corresponding to zero energy or stoppage of the particle in the thick target. This integration in practice is carried out graphically. Expressed mathmatically it is:

$$\int_0^{R_{max}} \sigma(R)\, dR$$

Hence we have the activity of a target at any time (t) after t_0 as:

$$-\left(\frac{dA}{dt}\right) = \delta S \Phi \chi \int_0^{R_{max}} \sigma(R)\, dR \left[1 - e^{-\frac{0.693t}{t_{1/2}}}\right]$$

However, we are comparing the activities of samples <u>relative</u> to standards, since the intensity of the beam (Φ) is difficult to regulate exactly. Relating the activities of a target (1) and a target (2) at the same time (t), we have, for $t=t_0$:

$$\frac{A_{0_1}}{A_{0_2}} = \frac{S_1 \chi_1 \int_0^{R_{1max}} \sigma(R_1)\, dR_1}{S_2 \chi_2 \int_0^{R_{2max}} \sigma(R_2)\, dR_2} \left(\frac{1 - e^{-\frac{0.693 t_0}{t_{1/2}}}}{1 - e^{-\frac{0.693 t_0}{t_{1/2}}}}\right)\left(\frac{\delta \Phi}{\delta \Phi}\right)$$

which after cancellation of the constant terms gives:

$$\frac{A_{0_1}}{A_{0_2}} = \frac{S_1 \chi_1 \int_0^{R_{1max}} \sigma(R_1)\, dR_1}{S_2 \chi_2 \int_0^{R_{2max}} \sigma(R_2)\, dR_2}$$

Rearranging to obtain the weight fraction of the species of interest in target (1), we get:

$$\chi_1 = \left(\frac{A_{0_1}}{S_1}\right)\left(\frac{S_2}{A_{0_2}}\right)\left[\frac{\int_0^{R_{2max}} \sigma(R_2)\, dR_2}{\int_0^{R_{1max}} \sigma(R_1)\, dR_1}\right] \chi_2$$

Since wt. fraction X 10^6 equals ppm,

$$ppm_1 = \left(\frac{A_{0_1}}{S_1}\right)\left(\frac{S_2}{A_{0_2}}\right)\left[\frac{\int_0^{R_{2max}} \sigma(R_2)\, dR_2}{\int_0^{R_{1max}} \sigma(R_1)\, dR_1}\right] \chi_2 \cdot 10^6$$

The surface area of the samples (S) is obtained from the photomicrographs taken of each target before encapsulation is gold. Figure 7 is a full size reproduction of photographs taken of three metal samples and a quartz standard. In order to obtain maximum sensitivity, the microscope objective is varied in power so as to maximize the image of each sample on the film area availiable.

Note that the space between the reticule rulings superimposed over the picture of americium in fig. 7 is much larger than in the picture of the quartz standard, although the same reticule was used for both targets. The americium was a much smaller target than the quartz, so was photographed through a stronger objective lens. Differences in focal length due to varying extensions of the lab jack on which the samples are photographed give rise to differences in magnification even when the same lens is used on all targets.

Hence, the reticule rulings are used to normalize the areas of all samples and standards to a common unit of area, the square reticule division. The area of the sample in the photomicrograph is first obtained with a planimeter. An accurate centimeter rule is then laid perpendicular to the reticule markings to obtain the average number of reticule divisions per centimeter. Then simply, the area on the photograph, times (the number of divisions per cm.)^2 gives the normalized area in div.^{2} If the exact sample area in cm.^{2} is required, the value in div.^{2} must be multiplied by the factors (cm.^{2}/planimeter unit) and (cm./div.)^{2}obtained from measuring the reticule itself. These two factors are the same for all photographs if the same reticule and planimeter are used, and need not be introduced when comparing one sample relative to another.

Earlier workers[7,9] did not take into account the dependence of cross section on range. The assumption that sigma and range are independent was made, which allows a very slight simplification of the calculations through cancellation of (σ) in the numerator and denominator of the expression derived above. The author has found that use of this assumption gives results in excess of 60% too low in the case of the actinide metals. The error decreases in magnitude with decreasing atomic number of the target material, and would vanish in the case of an unknown possessing the same range-energy relationship as the standard.

This is the trend which one would expect from consideration of the dependence of the efficiency of activation (as expressed by the exitation function) on the energy of the activating particle. A He^3 particle entering a dense metal such as an actinide would be degraded in energy much more rapidly than a particle of the same energy incident on a quartz target. The particle entering the quartz would travel for a longer distance before stopping, and would activate the oxygen atoms it encountered at a high efficiency because it would retain an energy corresponding to a high cross section for a great percentage of its penetration. In an actinide metal, the particle would loose its energy early in flight, so in addition to traveling for a shorter distance than the particle in quartz, it would not activate oxygen imbedded in the metal as well. A greater percentage of its travel would be spent at low cross section.

A simple ratio of the respective ranges, used when the approximation that the sigmas will cancel is made, expresses only the difference in the

depths of penetration of He^3 particles of like energy. Use of the ratio:

$$\frac{\int_0^{R_{2max}} \sigma(R_2)\, dR_2}{\int_0^{R_{1max}} \sigma(R_1)\, dR_1}$$

takes into account the differences in efficiency of activation in targets of different atomic number. It expresses the different dependencies of cross section on range.

The only activation for which a reasonably accurate excitation function is currently availiable is that for $O^{16}(He^3,p)\,F^{18}$.[12] It is anticipated that excitation functions for $C^{12}(He^3,\alpha)\,C^{11}$ and $N^{14}(He^3,\alpha)N^{13}$ will be availiable shortly.[13] All analyses made for carbon have been calculated by the assumption of constant cross sections. No nitrogen analyses have ever been made in this laboratory by He^3 activation analysis, as the N^{13} half life activity has never been observed in a metal sample.

Range-energy data used in this work was taken from the tables compiled by Williamson and Boujot.[14] These range-energy functions are calculated semi-empirically for He^3 and other particles for a number of elements throughout the periodic table. When data has not been calculated for a specific atomic number, that of the closest element to the missing one may be used. The error introduced by such an approximation is not great, and may be reduced by graphical interpolation between atomic numbers adjacent to the element of interest. At a given energy, the range of a particle in a chemical compound may be calculated by the following formula,[15] in which quartz (SiO_2) is used as an example:

$$\frac{1}{\text{Range in } SiO_2} = \frac{\text{wt. fraction Si in } SiO_2}{\text{Range in Si}} + \frac{\text{wt. fraction O in } SiO_2}{\text{Range in O}}$$

Figure 10 represents the dependence of the cross section for the nuclear reaction $O^{16}(He^3, p)F^{18}$ on the energy of the incident He^3 particle. Figure 11 demonstrates the dependence of the range of He^3 in quartz on particle energy. Figure 12 shows the cross section $\sigma(R)$ as a function of range in quartz and other targets, as derived from the energy dependent functions of Figs. 10 and 11. From a plot such as Fig. 12, the integration $\int_0^{R_{max}} \sigma(R) dR$ may be performed graphically.

F. Analysis of metals of known oxygen content.

It was necessary to study the degree of reliability of the individual analyses and to determine whether a lower limit to the oxygen content was set by oxygen contamination during the analytical procedure or during reduction.

To answer the first question, a number of milligram samples of metallic thorium were analyzed for oxygen by the activation method. These samples were all taken from the same large piece of 5 mil thorium foil, and a sufficient amount of this foil was submitted for analysis for oxygen by the vacuum fusion technique. Oxygen analysis results of 1160, 1170, 1240, and 1700 ppm were reported on four separate samples, for an average of 1320 ppm with an average deviation of 192 ppm. The results of the activation analysis of this thorium foil are shown in Table 3.

In order to investigate contamination during sample preparation and encapsualtion immediately prior to analysis arising from sources other than the atmosphere, milligram samples of pure gold were substituted for the active metals. Demildt[20] analyzed four portions of

gold foil by activation analysis. He found oxygen contents of 16, 98, 199, and 34 ppm O, assuming in his calculations that the cross section for the $O^{16}(He^3,p)F^{18}$ neclear reaction is a constant. The author has corrected these results using the method of calculation described above. Correct calculation gives 22, 137, 279, and 48 ppm O, respectively, for the gold analyzed by Demildt.

Three other portions of the same gold were submitted for vacuum fusion analysis. The results were 21,12, and 78 ppm O. J.W. Frazer and co-workers of the Lawrence Radiation Laboratory, Livermore, kindly performed the vacuum fusion analyses.

In addition, the author analyzed two samples of gold, and a sample of silver, by activation analysis. The gold samples were found to contain 53 and 122 pp, O, and the silver gave a result of 145 ppm O. This gold was not analyzed by other methods. The silver was reported to contain less than 5 ppm O, based on vacuum fusion results. No further investigation of the reason for the large spread in values was made, since all were substantially less than the lowest values found for the lanthanide and actinide metal preparations.

3. Analysis of Lanthanum metal

In order to investigate the importance of oxygen contamination during reduction of lanthanide and actinide trifluorides, the oxygen content of lanthanum metal before and after remelting in a standard reduction apparatus was investigated.[10] Three samples of commercial lanthanum (Research Chemicals Corp.) were analyzed by activation analysis and found to have an average oxygen content of 970 ppm with an average deviation of 215 ppm. Two samples of the same material were subjected to the usual reduction (exposure to Ba vapor in a vacuum) and remelted at 1150° C. The remelted metal had an

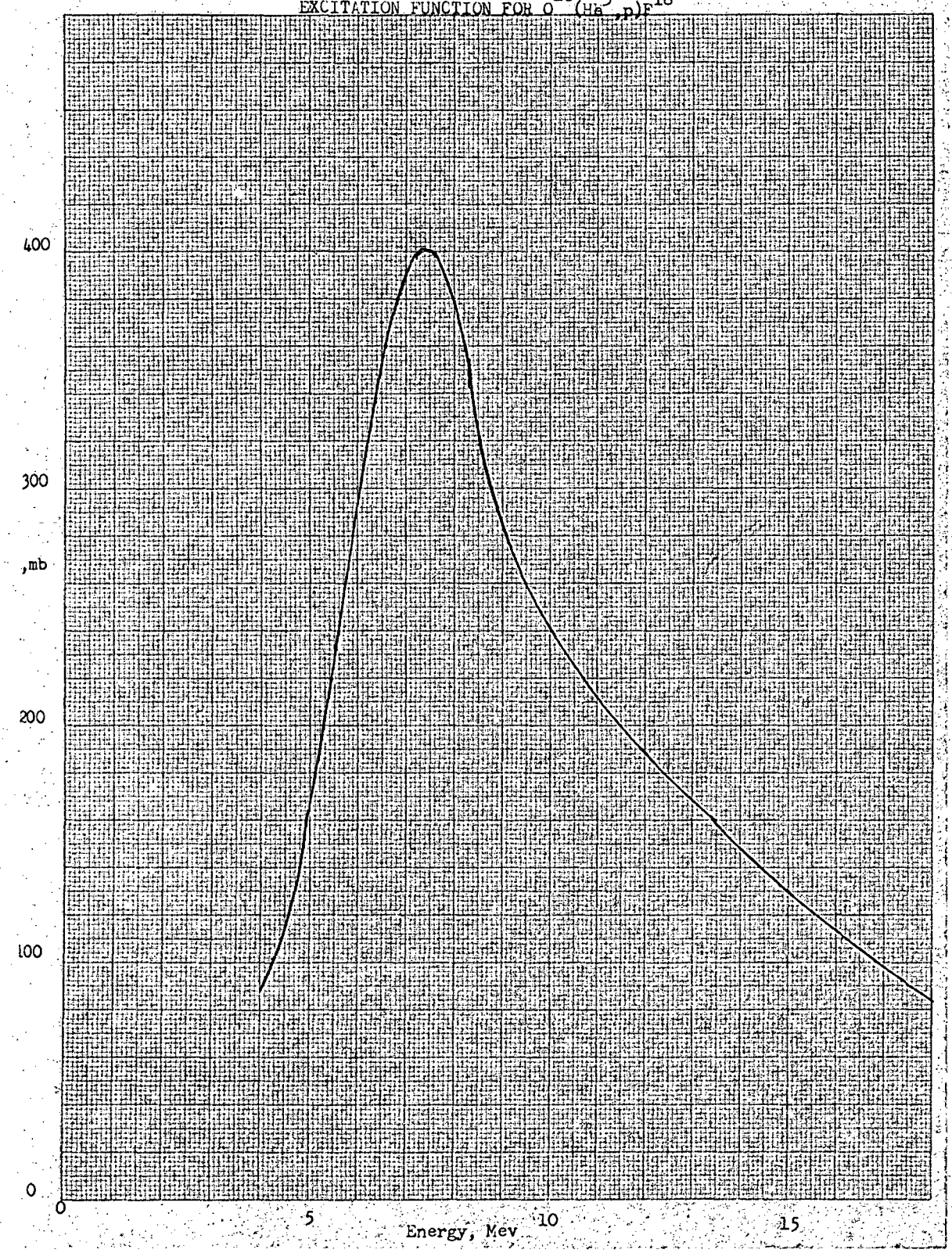
average oxygen content of 1000 ppm with an average deviation of 40 ppm. These results indicate that there was no significant oxygen contamination due to the preparative technique in the 1000 ppm range.

Table 3
Activation Analysis of Th Foil

Analysis	Results
1	1280
2	1100
3	1330
4	1460
5	1500
6	1460
7	1370
8	1390
9	1660
Average	1394
Average deviation	112

FIGURE 10

EXCITATION FUNCTION FOR $O^{16}(He^{3},p)F^{18}$



MUB-12960

FIGURE 11

RANGE OF HE^3 IONS IN QUARTZ

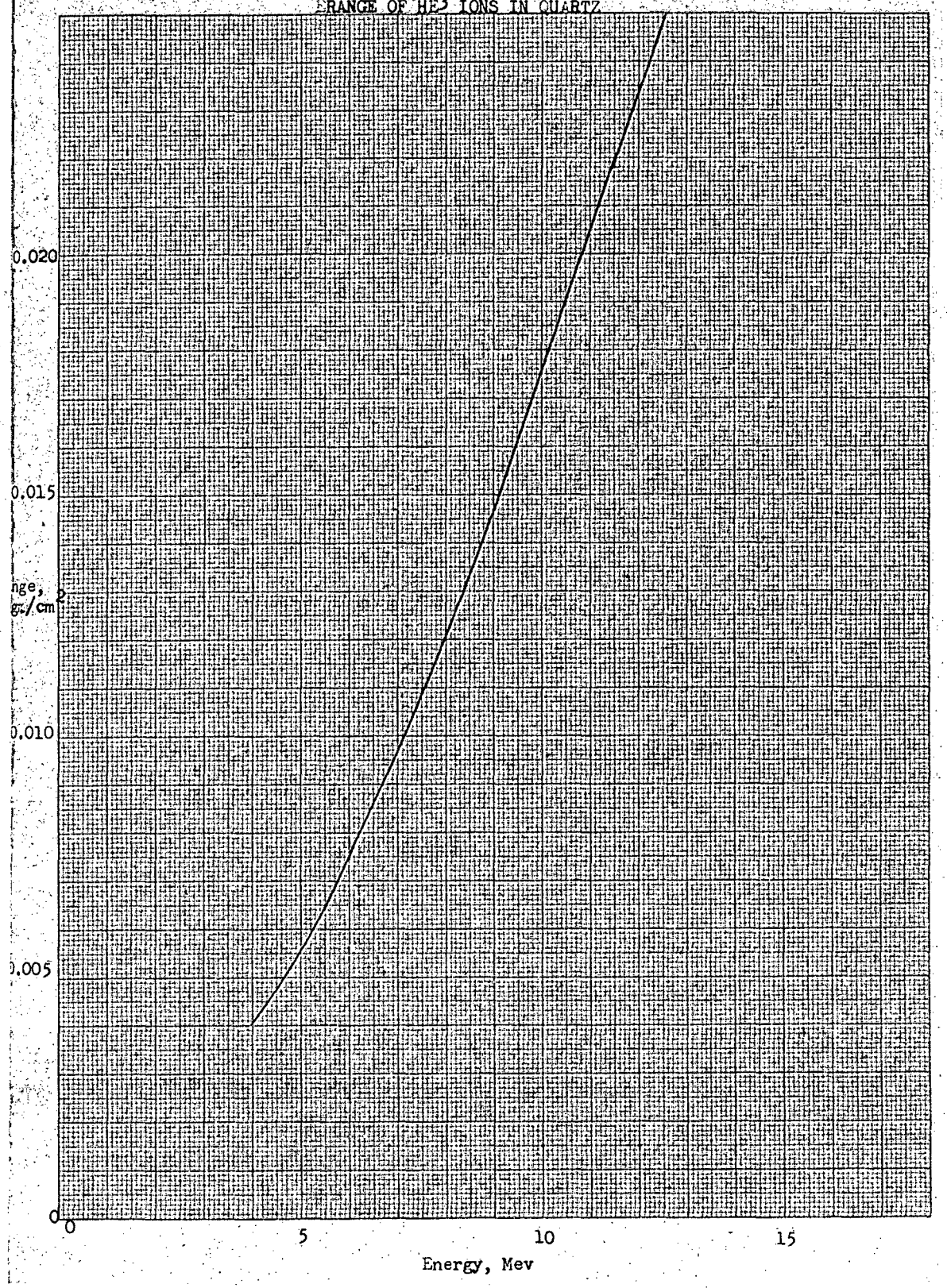


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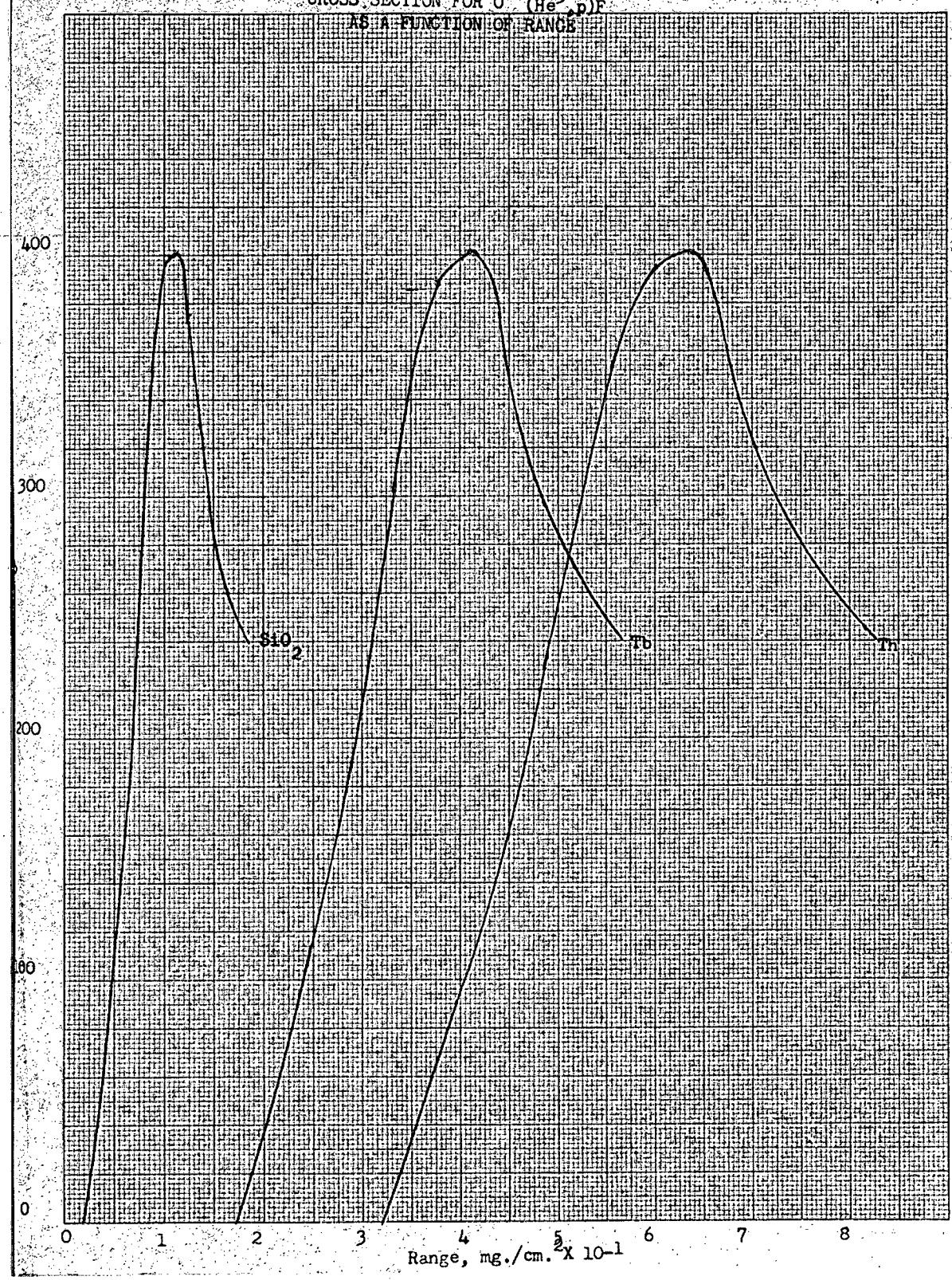
FIGURE 12

CROSS SECTION FOR $O^{16}(He^3,p)F^{18}$ AS A FUNCTION OF RANGE



MUB-12956

III. Metal Production

A. Trifluoride Preparation

The production of small samples of actinide and lanthanide metals by reduction of the trifluorides with barium vapor at elevated temperatures has been described in detail.[16, 17] All lanthanide and actinide metals made in this work were prepared by methods similar to those used by McWhan, Cunningham, and Wallman.[17] The experimental procedures are summarized below.

Metal trifluoride is precipitated from high purity chloride stock solutions, using reagents purified as described by McWhan, et al. The trifluoride precipitate is centrifuged, and the supernatant discarded. Two washings are performed by slurrying the precipitate with about ten times its volume of pure water. After the first wash, the slurry is centrifuged and the wash discarded. The second slurry is transferred to small leached quartz cones for centrifuging. After removal of the second wash supernatant, the precipitate is centrifuged for several hours in the small cones to compact it to an easily handeled "chunk". These chunks are stored over anhydrous magnesium perchlorate in a dessicator until further treatment is initiated.

Ryan, Green, and Lowenhaupt[10] have investigated the effects of prolonged vacuum dessication, and anhydrous HF or BrF_3 at elevated temperatures, on the oxygen and carbon content of metals prepared from trifluorides obtained as described above. Such "wet precipitated" trifluoride is known to contain about ½ molecule of water per molecule of trifluoride[18], but weight changes on further drying suggest

that this water may be eliminated.

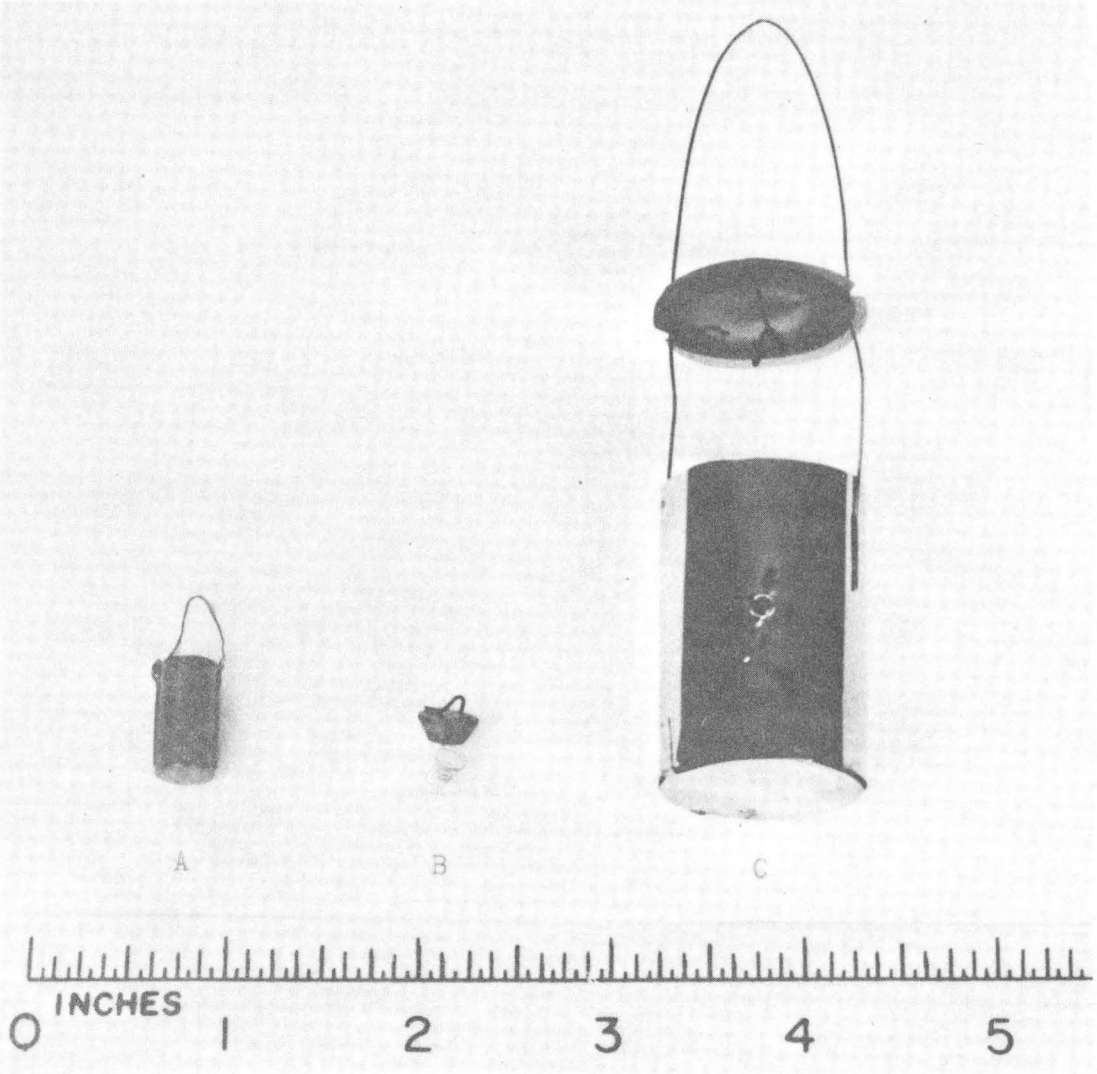
Trifluoride chunks to be treated with anhydrous HF or BrF_3 are placed in a monel alloy boat in a monel tubing which may be evacuated to about 10^{-6} mm Hg. After evacuation, anhydrous HF is passed through the tube at about 400 to 700 mm Hg at a rate of about 15 l./hr. for varying lengths of time, while the sample is heated to as high as 800° C. by a resistance furnace. After treatment, the trifluoride is removed from the system and stored over dessicant until it is to be reduced.

B. Metal Production

A photograph of the reduction system is shown in figure 13, and a diagram given in Fig. 13 b. It consists of a tantalum crucible suspended within a cylindrical tantalum induction shield of 2 or 4 mil thickness. To the crucible cap is attached a small conical spiral of 3 mil tungsten wire which receives the trifluoride chunk. Use of the spiral instead of the tantalum basket employed by McWhan and coworkers was suggested by Weigel.[19] It is a decided improvement over the basket, since much less wire is exposed for the product metal to wet. The crucible cap is pierced with a small hole of about 0.5 mm diameter through which the barium reductant and BaF_2 effuse. An arm of a high vacuum line is surrounded with an induction coil, in the center of which are suspended the crucible and shield.

Temperatures of between 800° and 1400° C. are used in most reductions. Since the power required to bring the crucible to a certain temperature varies with the orientation of crucible, shield, and induction coil, an empirical relationship must be established between the power

FIGURE 13



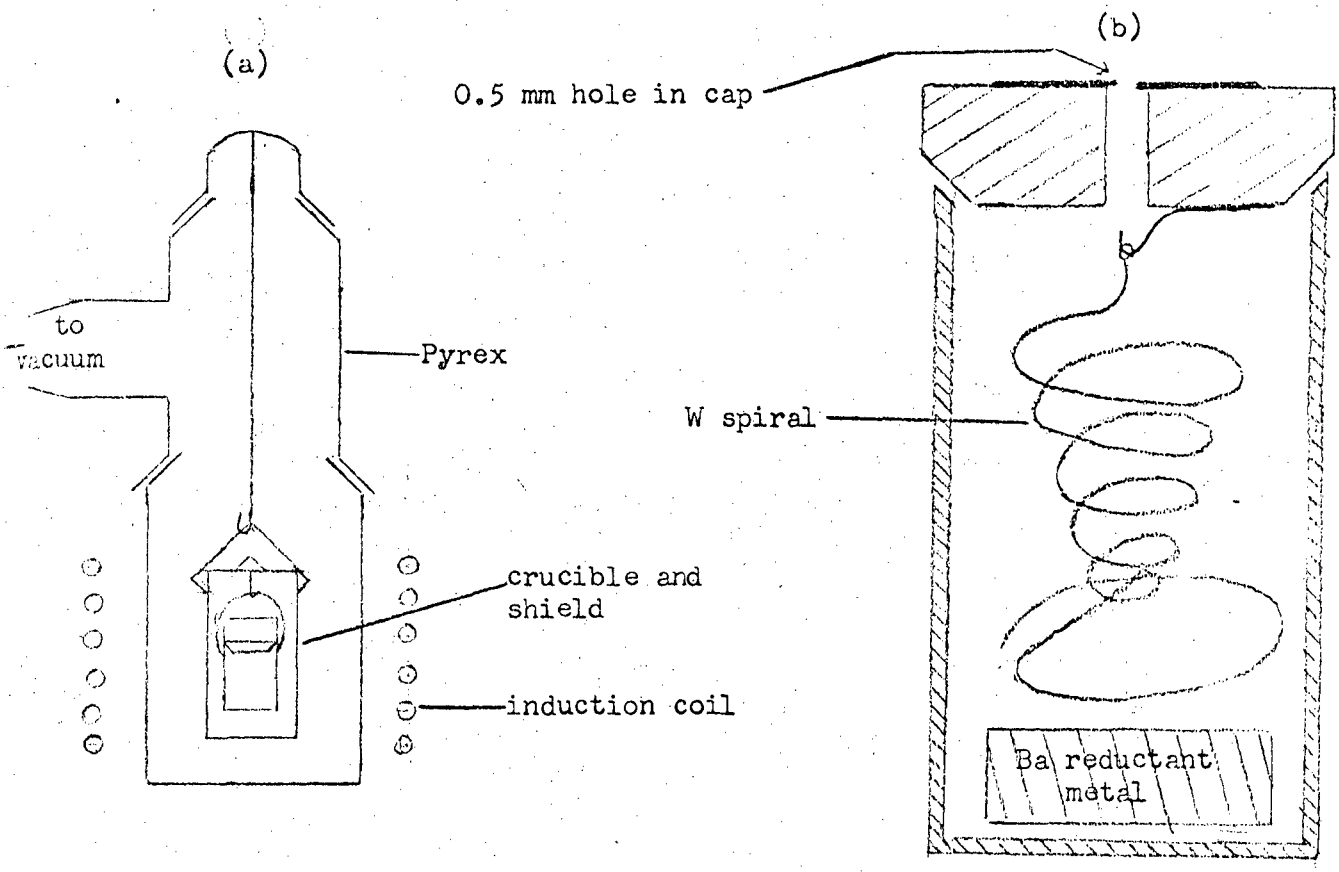
Tantalum reduction system:

A: crucible

B: crucible cap with tungsten spiral

C: induction shield and cap

FIGURE 13b



Reduction system:

(a) Ta crucible and induction shield suspended in high vacuum line

(b) Ta crucible and cap, containing W spiral and Ba metal

output of the induction power supply and the temperature of the crucible, as observed with an optical pyrometer through a hole in the shield. This calibration must be performed before each trifluoride reduction. It should be carried out at pressures of 10^{-6} mm Hg or below.

After cooling, the crucible and shield are taken to an inert atmosphere box. A piece of trifluoride is placed in the spiral attached to the cap. Enough freshly cut barium metal to provide a ten fold excess for reduction is placed in the bottom of the crucible. The crucible, cap and induction shield are reassembled and taken as quickly as possible to the high vacuum line in which they were calibrated, which must be evacuated as quickly as possible to avoid reaction of the barium with the atmosphere. Evacuation should continue until the pressure falls to lower than 10^{-6} mm Hg.

It is important during a reduction to reach a temperature sufficiently above the melting point of the product metal that the sample will agglomerate into a bead which although surrounded by BaF_2 slag, contains no barium or fluorides. When preparing relatively volatile metals such as Nd or Am, there is a temptation to use too low a temperature, or not to hold a high temperature long enough, for fear of evaporation the sample.

A "heating sequence"is important in the production of good metal. A typical sequence consists of four major steps:

1. An initial outgassing by gradual increases to about 300° C. This is performed after the system has reached about $5X10^{-7}$ mm Hg or better. After outgassing, the

pressure is allowed to drop to the starting pressure or lower.

2. A short period at about 1000° C. This serves to bring the reactants to the threshhold of reaction, and minimize the time required to reach the temperature of reduction and agglomeration.

3. Reduction at a temperature well above the melting point. A volatile metal such as Nd or AM is reduced for a short time about 300° above the melting point, then allowed to agglomerate about 100° lower.

4. A short cooling period near the melting point seems to be necessary to permit the metal to agglomerate to a bead free of BaF_2. Samples which are to be used for X-ray studies are annealed for four hours at about 760°C. before cooling to room temperature.

Proper heating sequences for actinide elements are determined by using their melting point analogs in the lanthanide series, due to the abundance and lack of radioactivity of the lanthanides. Terbium (m.p. 1356°) was used for most of the preparations in this work, since it is the melting point analog of curium (m.p. 1340°). An excellent heating sequence was developed for terbium by Jere Green. The author has developed a sequence for Nd (m.p. 1024), which has been used successfully in the preparation of americium metal (m.p. 994°), although the temperatures of reduction and agglomeration should be reduced by about thirty degrees in the case of Am. These sequences appear in table 4.

TABLE 4
HEATING SEQUENCES

Step	Duration and Temp., °C.
	Tb and Cm
1	20 min. @ 300°
2	1.0 min. @ 1100°
3	2.0 min. @ 1385°
4	2.0 min. @ 1200°
	Nd and Am
1	20 min. @ 300°
2	1.0 min. @ 1000°
3	1.0 min. @ 1320°, and 2.5 min. @ 1230°
4	2.0 min. @ 1100°

Note: for Am prep., step (3) and (4) temperatures should be 30° lower than for Nd.

The system requires about thirty seconds to reach an equiblibrium temperature after a change in power to the induction coil. This time lag is included in the duration column in table 4 and does not need to be further accounted for.

C. Results

As stated above, the mechanical manipulation of the starting trifluoride is facilitated if it is first precipitated from aqueous solution and then allowed to dry slowly to produce a hard compact mass. To check the completeness of drying of the wet precipitated trifluoride, a study was made of the oxygen content of metallic terbium prepared from TbF_3 which had been dried for various lengths of time. (Terbium was selected because the reduction conditions are the same as those used for curium.)

The results are given in Table 5. These results seem to indicate that consierable amounts of oxygen (presumably as water) remain in wet precipitated trifluoride even after very extended periods of drying over P_2O_5 or in high vacuum.[10]

TABLE 5. OXYGEN CONTENT OF TERBIUM METAL MADE FROM WET PRECIPITATED TRIFLUORIDE

TbF_3 drying conditions	O content of Tb metal, ppm
1. 9 days over P_2O_5	6400
2. 18 days over P_2O_5	3380
3. 27 days over P_2O_5	3070
26 days at 10^{-7}mm	
4. 27 days over P_2O_5	2090
43 days at 10^{-7}mm	

On the assumption that most of the oxygen originated from water or oxyfluoride, a sample of wet precipitated TbF_3 was treated with commercial anhydrous HF. Four reductions were made using this material and

were analyzed for both oxygen and carbon by activation analysis. The results of these analyses are shown in Table 6. The oxygen content of these preparations was substantially lower than for those derived from physically dried trifluoride; however, the carbon contents were rather high. In an attempt to remove both water and organic impurities, several batches of TbF_3 were treated with BrF_3. The BrF_3 treatment was followed by the reduction with dry H_2 of any TbF_4 which may have been produced by the oxidizing action of BrF_3. The activation analysis results for metals prepared by this method are also shown in Table 6. These results indicate that this procedure is inferior to the simple HF treatment. For this reason, further TbF_3 preparations were made using anhydrous HF purified by multiple batch distillation to remove organic impurities. The results for samples derived from this material are shown in Table 6. The results for several samples of americium and curium preparations derived from physically dried trifluorides and for americium produced from AmF_3 treated with purified HF are also shown in Table 6.

Table 6. OXYGEN AND CARBON CONTENTS OF LANTHANIDE AND ACTINIDE METALS BY ACTIVATION ANALYSIS.

Sample	Treatment of wet precipitated trifluoride	O (ppm)	C (ppm)
Tb	HF* dried at 600° 3 hours	580	1470
Tb	HF* dried at 600° 3 hours	330	680
Tb	HF* dried at 600° 3 hours	310	750
Tb	HF* dried at 600° 3 hours	480	970
Tb	BrF_3 400° for 3 hours; H_2 300° – 600°C for ten min	1440	1680
Tb	BrF_3 400° for 3 hours; H_2 300° – 600°C for ten min	1770	1530
Tb	BrF_3 400° for 3 hours; H_2 300° – 600°C for ten min	1500	1360
Tb	HF† dried, 600° for 2.5 hours	350	260
Tb	HF† dried, 600° for 2.5 hours	2200	390
Tb	HF† dried, 400°C for 1 hour 600°C for 3 hours	620	330
Tb	HF† dried, 400°C for 1 hour 600°C for 3 hours	490	600
Tb	HF† dried for 3 hours at 800°	730	410
Am	MeOH wash, vac dried 11 days at 10^{-6} mm Hg	5450	
Am	HF† dried for 4 hours at 600°	980	
Cm	dried over P_2O_5	4070	
Cm	dried over P_2O_5	4470	

*Tank warmed to 25 psig then vented to 15 psig.

†HF purified by re-distillation.

IV. Conclusion

A. He^3 Activation Analysis

The application of activation analysis to submilligram samples of easily tarnished metals requires perfect attention to detail in cleaning samples and protecting them from atmospheric contamination. While the results obtained are not highly precise, they make available data which would not otherwise be obtainable.

There are large unexpected fluctuations in the results obtained by both He^3 activation analysis and vacuum fusion analysis of thorium and gold samples. Statistical analyses of the results obtained by both methods for the oxygen content of thorium metal shows that the distribution of results of the two methods center about different means. However, the values obtained by He^3 activation analysis of small samples are close enough to the results of vacuum fusion analysis of large samples to rely on the activation technique as a fair approximation of the oxygen content of submilligram metal samples.

B. Purification of Lanthanide and Actinide Metals

Summaries of analyses of lanthanide and actinide metals prepared from variously treated trifluorides are given in Tables 5 and 6. There is an obvious decrease in the oxygen content of metals prepared from trifluorides treated with anhydrous HF, but no significant trends are observed on varying the temperature and length of the HF treatment. Bromine trifluoride does not appear to be as effective an oxygen remover as HF. It is also apparently not as good a carbon remover as HF, although the opposite result would be expected in the case of carbon. Attempts to purify commercial anhydrous HF by multiple

batch distillation resulted in samples comparable in oxygen and carbon contamination to samples prepared using untreated anhydrous HF. If a lower limit of contamination is being set by the presence of oxygen and carbon in the HF, better methods must be found for purifying the HF itself.

There is no possibility of appreciable contamination during reduction of the trifluoride; all the oxygen in the reduction system at 10^{-6} mm Hg would not contribute 1 ppm to a 1 mg. sample. Similarly, there is no chance of appreciable contamination by residual gas in the gold capsules at 1 micron Hg. Analysis of silver metal indicates that contamination during bombardment will be at worse less than about 100 ppm.

FOOTNOTES

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