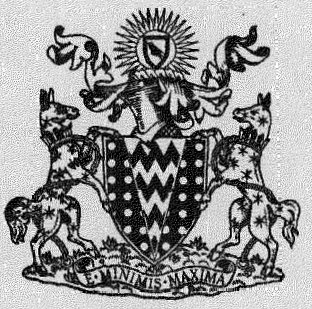

United Kingdom Atomic Energy Authority

RESEARCH GROUP

Report

PROCEEDINGS OF THE SEMINAR ON THE PREPARATION AND STANDARDISATION OF ISOTOPIC TARGETS AND FOILS

Held at A.E.R.E., Harwell on October 20th and 21st, 1965

Edited by M. L. SMITH

Chemistry Division,

Atomic Energy Research Establishment,

Harwell, Berkshire.

1965

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INTRODUCTION

PREPARATION AND STANDARDISATION OF ISOTOPIC TARGETS AND FOILS

Stable and radioactive isotopic films and foils of precise composition and dimensions are needed for measurements on a variety of particle accelerators; accurately defined films of α-active actinides are also needed as fission standards for reactors. Such standard targets are made in a number of laboratories in different countries and there was a clear need for closer co-ordination with the users in order to relate the limits of chemical purity and dimensional tolerance desirable to those practically attainable. To meet this need and also to promote an interchange of ideas and techniques the seminar of which this is the record was held at Harwell, England, on October 20th/21st. The hosts were the Electromagnetic Separation Group of the Chemistry Division of A.E.R.E. and the Special Techniques Section of the Nuclear Physics Division of A.W.R.E. Strong support was given by the Central Bureau of Nuclear Measurements of Euratom, Geel, Belgium, and the Target Preparation Centre of O.R.N.L., Tennessee. Participants from laboratories in eight other countries also contributed to the 30 papers and the discussions.

It was a very appropriate time for an exchange and participants agreed that the meeting was valuable both in giving a better appreciation of the limitations of present methods and in estimating future trends. Clearly the requirements of scientists are considerable and diverse. For some investigations individual experimenters need up-to-date information on particular techniques so that they can make up numbers of precise targets under their own control; on the other hand the larger groups explore a variety of methods, and try out more sophisticated techniques so as to be able to provide a variety of high quality targets to satisfy a wide range of needs.

The arrangement of the report follows the same order as the original programme which turned out to be a very convenient framework for the meeting but the papers have now all been re-numbered serially for ease of reference. In order to achieve quick publication the papers have not generally been specially rewritten for printing but are in the form presented at the seminar. It is hoped that the report will have enough technical detail to help all target makers. It should also be useful as a guide for those who need to understand the limitations of the art before they order from the specialised laboratories.

M. L. SMITH

SAMPLE PREPARATION AT THE CENTRAL BUREAU OF NUCLEAR MEASUREMENTS

G. H. Debus

C.B.N.M., Euratom, Geel

In 1961 during an EANDC* meeting it was stated that "The sample preparation laboratory at the C.B.N.M. is a facility to fabricate, to assay, to mount and to distribute safely samples for nuclear measurements, not only for the needs of the six Euratom countries, but for all member countries of the EANDC". This aim is unchanged, and the C.B.N.M. makes an effort to render services to nuclear physicists who are measuring nuclear constants as recommended on the EANDC priority list.

A number of nuclear constants (mainly cross sections) have to be known with an accuracy of 1% or better and consequently our main effort - as a service - is directed toward assaying, i.e. defining the chemical and isotopic composition of samples, total mass, homogeneity, total area, etc.

The activities of the sample preparation facility of the C.B.N.M. can be described by indicating the main techniques used for fabrication and assaying of samples (Tables 1.1, 1.2, 1.3).

Although application forms are provided for those ordering samples difficulties are encountered during exchange of information on samples with stringent specifications; special attention should be paid to the definition of expressions as homogeneity, acceptable chemical and isotopic impurities, acceptable errors etc.

In 1965, the total number of samples prepared and assayed by the C.B.N.M. will be approximately 5,000.

---

*European and American Nuclear Data Committee

TABLE 1.1

TECHNIQUES USED FOR THE FABRICATION OF SAMPLES

Technique	Field of application	Thickness	Remarks
Ultracentrifuge	Organic Backings	8 $\mu g/cm^2$ and up	-
Electrolysis	2π and 4π thin layers	-	Drop electrolysis
Electrospraying	2π and 4π thin layers on metal or metallized backings	0 to 1 mg/cm^2	Not in metallic form but compounds
Electrophoresis	2π layers	0.5 to 20 mg/cm^2	Oxides of all kinds
Vapour decomposition	Thin layers of ^{13}C	0 to a few $\mu g/cm^2$	-
Settling	Thick samples	About 100 mg/cm^2	e.g. HgS
Evaporation			
a. resistance heating	Low melting material	0 to 1 mg/cm^2	e.g. LiF, Au, In, etc.
b. electrobombardment	High melting material	0 to 1 mg/cm^2	e.g. B, Ti, etc.
c. high frequency levitation	Small quantities of metals	0 to 1 mg/cm^2	e.g. U separated isotopes

TABLE 1.2

TECHNIQUES USED FOR THE FABRICATION OF SAMPLES

Technique	Field of application	Thickness	Remarks
Alloying			
a. induction heating	Large quantities (up to 2 kg)	-	-
b. electronbom-bardment	High melting materials	-	-
c. high frequency levitation	Small quantities up to 15 g	-	Quantitative alloying
d. resistance heating	Up to 2500°C	-	-
Melting and casting	Na, Li, Ca	-	Different shapes and sizes
Pressing	Pellets	0.5 to 10 g/cm^2	e.g. Cr, Mn, U_3O_8
Rolling	Metallic backings and samples.	20 µm upwards	-
	Roll cladding	-	e.g. napkin rings
High precision punching	Metal foils	-	e.g. detectors

TABLE 1.3

TECHNIQUES USED FOR THE DEFINITION OF SAMPLES

Technique	Field of Application	Remarks
Weighing	All samples	High precision
Density	Composition of binary alloys, quartz detectors	High precision
Thickness measurements	Foils	Several methods available
X-Ray	Homogeneity of cast samples	-
Metallography	Homogeneity of alloys	-
Chemical analysis	All samples	-
Isotopic analysis	Isotopic composition of solids, isotope dilution	-

PREPARATION OF ISOTOPE TARGETS BY ELECTRON-BOMBARDMENT TECHNIQUES*

E. H. Kobisk

Isotopes Development Center
Oak Ridge National Laboratory
Oak Ridge, Tennessee

Problems encountered in the preparation of thin films of normal elements by vacuum evaporation-condensation techniques are significantly magnified when using isotopically enriched materials. These latter materials require maximum efficiency in evaporation and condensation and to achieve this end, the Oak Ridge National Laboratory Target Center developed an electron-bombardment vaporization source using high electron currents and low acceleration voltages. A minimum of ~20% and a maximum of 90% efficiency of vapor condensation have been obtained with this system. The vaporization source uses special crucibles to attain mechanical collimation, permitting the use of milligram quantities of evaporant in cases where previously several hundred milligrams had been required with other evaporation techniques. Materials having very high vaporization temperatures (~3000°C) have been evaporated successfully by this method, e.g., neptunium oxide, uranium oxide, plutonium oxide, and thorium oxide. Since the electron-bombardment heat source can be installed in all standard vacuum chambers at low cost and is suitable for use at pressures of 10^{-10} torr, it has proven a highly versatile tool.

The following characteristics of an evaporation system are desirable for preparing thin-film targets from isotopic materials

1. Variable evaporation temperatures between 300 and 3000°C.
2. Collimation of vapors for maximum recovery of starting material.
3. Compatibility of evaporant and crucible material to minimize loss of isotopes by chemical reaction or alloy formation.
4. Elimination or minimization of contaminants in the condensed films.
5. Maximum uniformity of film density.
6. Compatibility of the size of the evaporation system with the vacuum chamber.

Most of these criteria have been achieved with the vaporization system illustrated in Fig. 2.1.

---

*Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

From the Knudsen laws of gaseous flow through tubes, mechanical collimation of material can result if a tubular crucible is employed whose length is much greater than its internal diameter ($L/D \sim 10$). The evaporation crucible shown in Figs. 2.1 and 2.2 approximates these requirements.

However, choice of crucible materials is critical and was limited to those that would not allow during fusion and vaporization of the specific isotope. The vaporization gun uses ring-type or hairpin-type electron-emission filaments, fabricated from 0.020- to 0.040-in.-dia thoriated tungsten wire and resistivity heated with 25-100 amp ac to achieve the appropriate emission temperatures. Electrons drawn from the filament are directed toward the crucible by imposing a positive potential of 100 to 1000 volts dc between the crucible and the filament. Increased electron efficiency is achieved by surrounding the entire assembly with a 0.010-in.-thick tantalum box, electrically at earth potential, which acts as an electrostatic shield and increases the electron current to the crucible by ~30%. To raise the crucible temperature above 2000°C, an electron current of ~1.5 amp at a potential difference of ~800 volts between the filaments and the crucible was required.

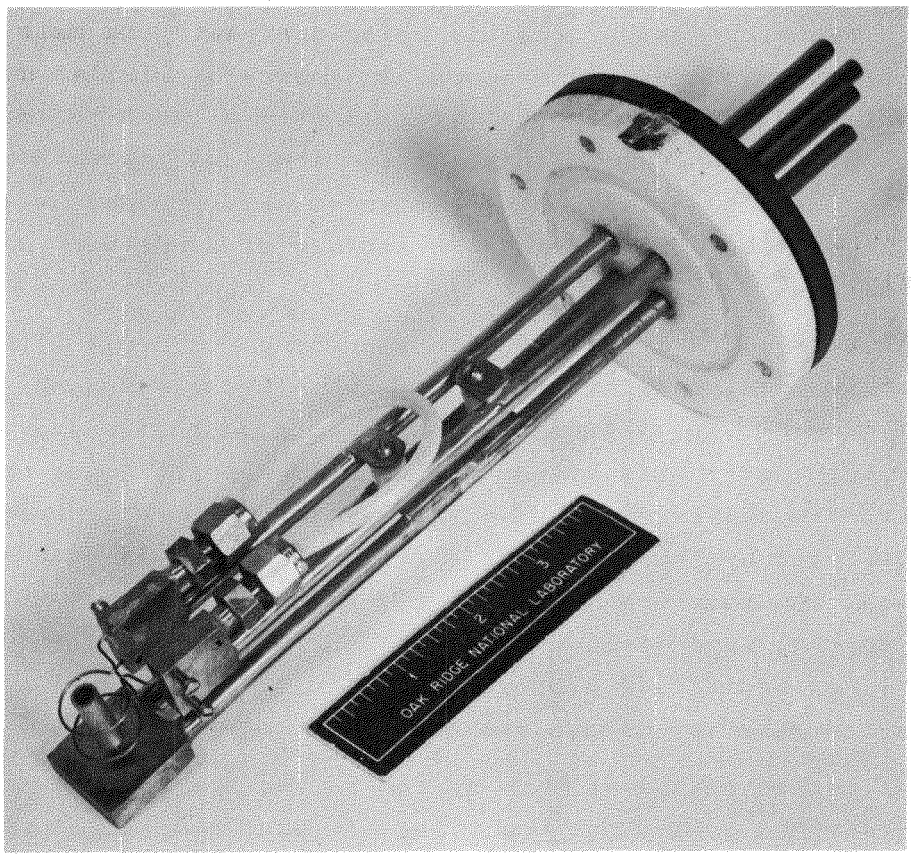
To attain appropriate heat distribution and to minimize thermal losses, the crucible configuration illustrated in Fig. 2.2 was adopted. Crucibles were made from a tungsten rod 0.75 to 1.0 in. long and 0.25 to 0.125 in. in diameter. Heat conduction from the crucible was limited by a 0.040-in.-dia tungsten wire which also supported the crucible and resulted in a more uniform temperature distribution. Because of the high temperatures required, crucible materials were usually limited to tungsten, tantalum, and molybdenum. If crucible and evaporant were incompatible, ceramic liners (Fig. 2.3) could be used. One of the most versatile materials used for crucibles was found to be spectroscopic-grade graphite. Further collimation of vapors could be achieved using an effusion plug (shown at the right of Fig. 2.2), which proved very effective at short distances between the crucible and the substrate.

A variety of evaporation techniques was found possible using this versatile heat source. For example, as shown in Fig. 2.4 it was desired to coat the inside and outside surfaces of right circular cylinders with plutonium oxide. With resistance heating, this task would have been infeasible, particularly since good uniformity of the films on the surfaces was desired. However, with our electron-bombardment heating technique, successful deposition of the oxide over the inside and outside surfaces was achieved. At the bottom of Fig. 2.4 is shown the boat-type tungsten crucible used to contain the plutonium oxide while it was heated

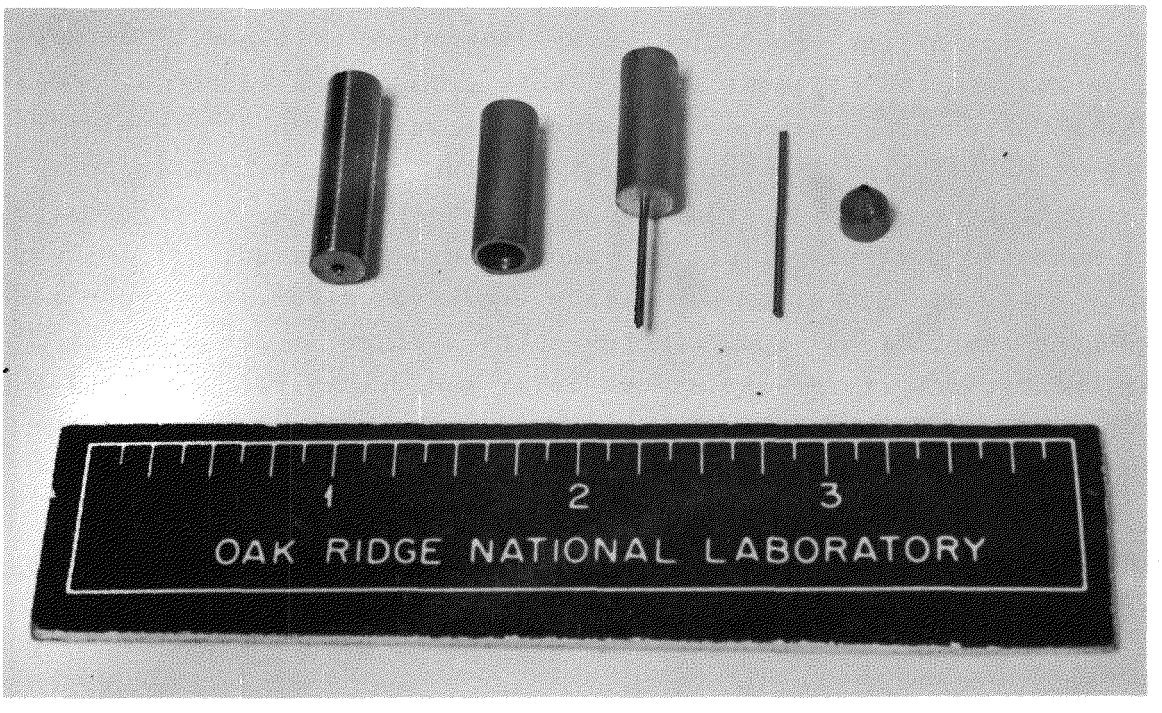
to ~2400°C by electron bombardment using a hairpin-type electron-emission filament. Each cylinder in the nest of cylinders was axially rotated at 100 rpm, with the evaporation crucible coincident with the axis of rotation of the cylinder. A second evaporation source of similar design was used to evaporate material onto the outer surface of each cylinder independently. The tungsten crucible was ~2 in. long and grooved down the center to allow even distribution of plutonium oxide powder before evaporation. Evaporation onto the outside surface of a cylinder is illustrated in Fig. 2.5.

Figure 2.6 illustrates the glove box housing the Pyrex glass "T" evaporator system designed for general use with radioisotopes. The electron-bombardment vaporization source is located centrally in the photograph. This particular system was used to deposit ^{244}Cm on the end of a 0.063-in.-dia copper wire. The versatility of this technique is further illustrated by the fact that 0.2 μg of ^{252}Cf was evaporated with subsequent condensation of 50% of the starting material on the substrate. Of course, vaporization-condensation efficiencies of this high magnitude are not ordinarily achieved, particularly when good uniformity of the deposited material is desired over a large substrate.

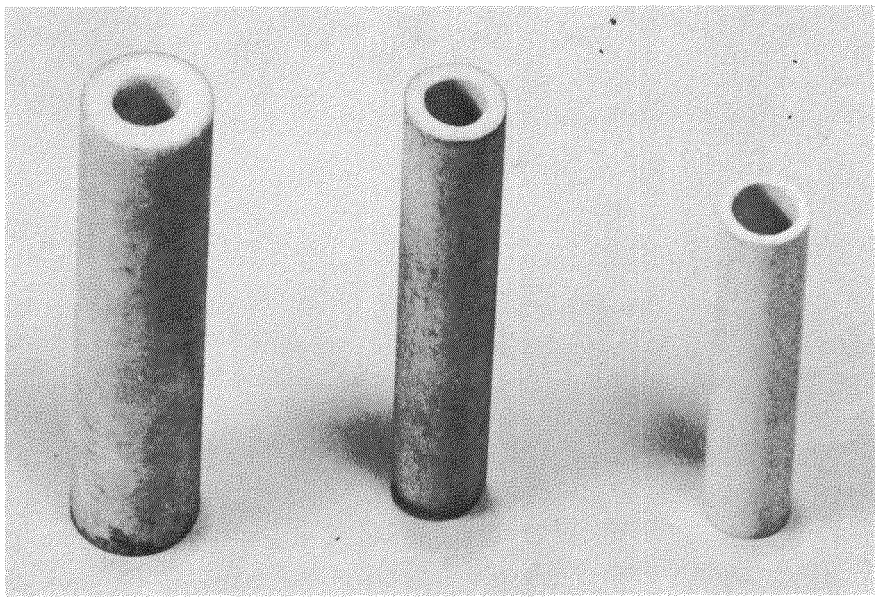
One distinct advantage of this system is the low voltage employed to accelerate electrons toward the crucible. In most commercial systems, voltages of the order of 5000 volts dc are used. In practice, commercial electron guns cause electrical breakdown or glow discharge in the vacuum system following a burst of gas from the evaporant because of these high acceleration voltages. With the electron-bombardment system developed at the Target Center, it has been observed that discharge was avoided until pressures of the order of 1×10^{-3} torr were attained. Furthermore, because of the filament and crucible geometry, a rather high degree of ionization occurs in the evaporating material causing it to glow visibly, thus allowing control by sight of the evaporation. In the future it is hoped that, by redesign of the heat source, electrostatic and/or magnetic collimation of the vapors can be realized. It is conceivable that this technique can attain enhanced uniformity of deposition by sweeping the ionized vapor beam over the surface of the substrate rather than having it focused at one point and mechanically manipulating the substrate to gain good uniformity.



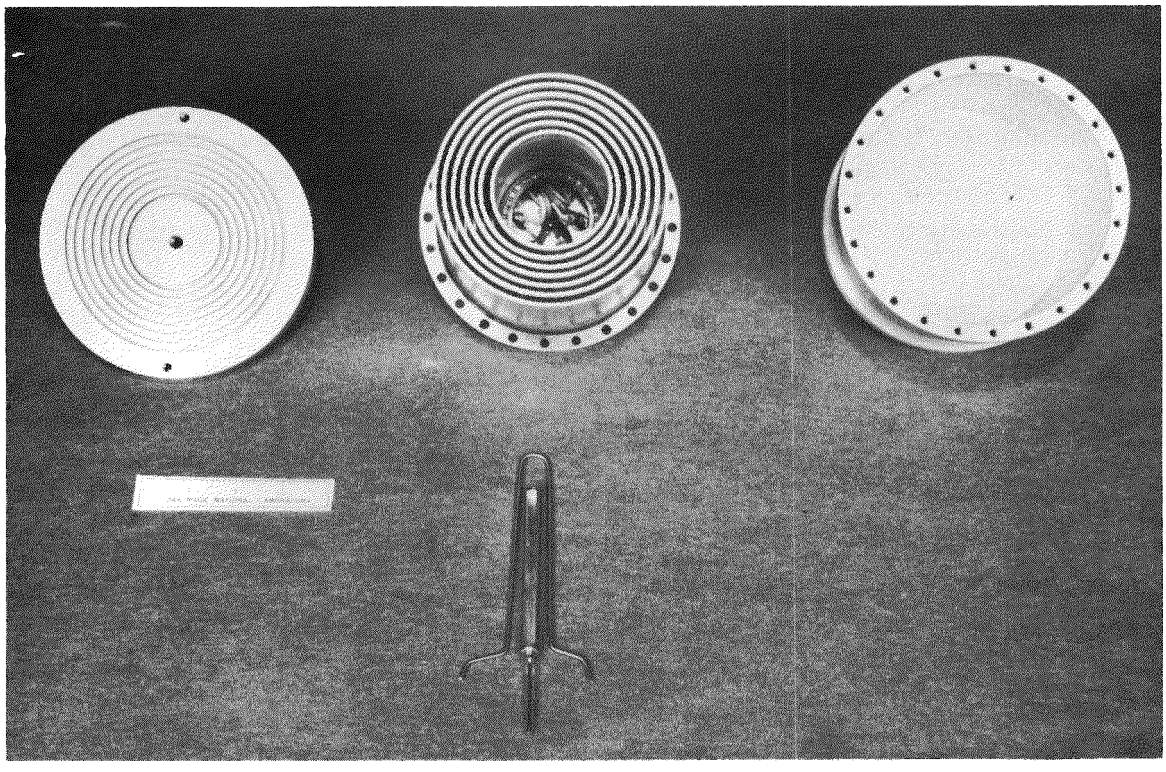
AERE - R 5097 Fig. 2.1
Electron-bombardment heat source used for evaporation from a tubular crucible



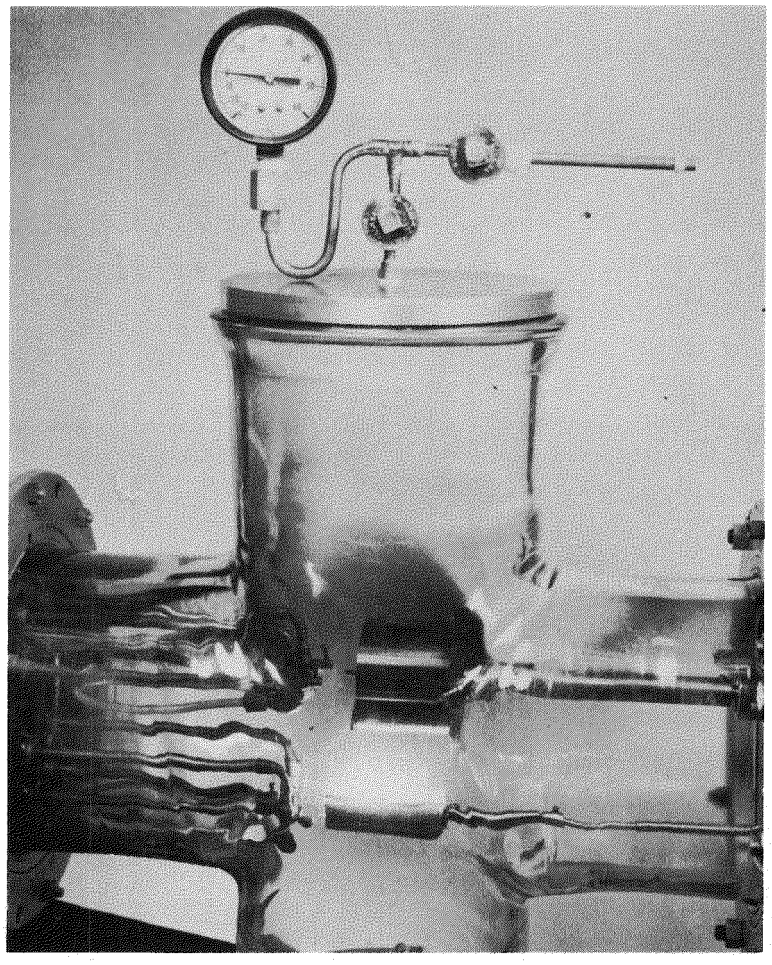
AERE - R 5097 Fig. 2.2
Tungsten evaporation crucible: components and assembly



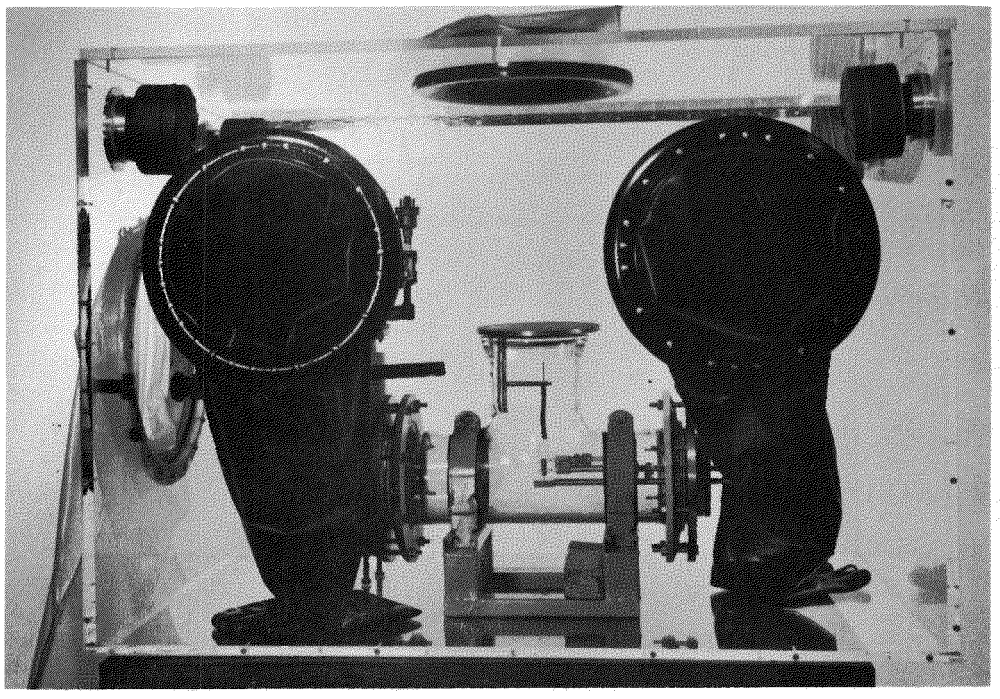
AERE - R 5097 Fig. 2.3
Crucible liners that have been used in tantalum or tungsten electron bombardment (left to right: BeO, ZrO_2, and BN)



AERE - R 5097 Fig. 2.4
Slotted tungsten crucible and electron-emission filament (bottom) used to coat fission chamber cylinders with $^{239}PuO_2$. (Fission chamber assembly is shown in the upper portion of the photograph)



AERE - R 5097 Fig. 2.5
Evaporation of $^{239}PuO_2$ onto fission chamber cylinder in a pyrex glass cross evaporator. Cylinder was rotated at 100 rpm above the vapor source.



AERE - R 5097 Fig. 2.6
Glove box enclosed evaporation system with electron-bombardment heat source in place. This particular unit was used to evaporate ^{244}Cm as oxide onto a 0.600-in.-dia copper disk (as shown over the crucible)

EXPERIENCE OF VACUUM EVAPORATED TARGETS

J. B. Reynolds and D. Boreham

A.E.R.E., Harwell.

Over the past decade several thousand requests for a wide variety of isotopic targets from physicists in many institutions, have been satisfied by the Electromagnetic Separation Group at Harwell. Experience gained in making these targets since the earlier report[1] is presented in the following notes which deal mainly with evaporation by the well-tried resistance heating method.

As most of our isotopes are stocked as oxides a tantalum filament is favoured because it is a powerful reducing agent yielding elemental deposits. Platinum is used for halide evaporations and elements or compounds with low evaporation temperatures. A number of other filaments are listed by Holland[2]. One disadvantage of using tantalum is that unless the evaporation is carefully controlled the target can easily be contaminated with tantalum due to the formation of its volatile pentoxide.

Commercial evaporation units

Nowadays all commercial evaporation units attain normal (for our purposes) evaporation pressures around 10^{-5} torr. Several firms will supply accessories, such as substrate heaters, rotating tables, racks for multi evaporations, deposit thickness monitors, etc. We have found that a "collar" with eight port holes (Fig. 3.1) is most useful for feeding in such services as those of the electron gun, water-cooled electrodes and devices for vacuum packing.

Modifications due to the use of isotopes

Because isotopes are expensive and only available in small quantities, they are used economically and the distance from the filament to the target backing normally kept to only one inch. This reduces the uniformity of the deposit to about 95% over a 1 cm. diameter circle. At this distance the efficiency of the evaporation is about 10%. The filament is made from a 1" x $\frac{1}{4}$" strip of tantalum (or Pt etc.) folded into a V shape and spot welded onto tantalum rod which is held between steel chucks. The magnetic clamp consisting of permanent magnets completely enclosed in the copper current carrying supports is still regularly used to hold the tantalum filament in its steel chucks firmly but flexibly. Various shapes of tantalum boats and crucibles are now also available for special purposes. A maximum of six milligrammes of isotope is weighed out, ground if necessary and spread over the filament using a drop of

distilled water which is then dried off. This helps to avoid decrepitation. Larger quantities than six milligrammes also tend to jump off the filament. For materials especially liable to decrepitation such as SiO_2, molybdenum gauze[3] wrapped around the filament has proved very effective in preventing losses. Higher efficiencies can be obtained by using heater pots instead of filaments as described by Bjørnholm[4].

Problems with particular elements

Iron and nickel have too high an evaporation temperature for the resistance heating method and it is preferable to use an electron gun or to electroplate. Zinc and cadmium are notoriously difficult to condense on most surfaces but suitable targets can be made on a thin layer of gold[5].

Sulphur gives a very poor yield on evaporation probably due to re-evaporation as do cadmium and zinc sulphides under our conditions. Silica and rare earth oxide reductions may result in tantalum contamination because of the high reduction temperature required.

Reactive elements (Li, Ca, Ba, Sr, etc.)

These elements are often requested in their metal form and to avoid oxidation we pack in vacuum. The method used at Harwell[6] is to mount the target substrate onto a ground glass stopper as shown (Fig. 3.2). The stopper is held by a clip attached to a rod which passes through the base via a Wilson seal. The rod can be rotated and moved up and down. The stopper is placed at the required distance above the filament. A corresponding ground glass tube which has been sealed off at one end and has a side arm with a break-seal (Fig. 3.3) is placed in such a position on the work table that the stopper can be rotated and pulled into the tube whilst still under vacuum. The bell jar is let down with argon and the pressure seals the target in vacuum. We have also tried double evaporations to protect reactive elements using gold as the protective layer. This does not appear a very satisfactory method unless the gold layer is about 200 $\mu g/cm^2$.

Evaporated targets of isotopes of the following give little trouble: Antimony, Bromine, (KBr, NaBr, AgBr), Chlorine, Chromium, Copper, Germanium, Indium, Lead, Magnesium, Molybdenum Trioxide, Potassium salts, Rubidium salts, Selenium, Silver, Tellurium, Tin, Titanium, Tungsten Trioxide, and Vanadium.

Unbacked targets and stripping techniques

Self-supporting targets of Copper, Silver, Silicon, Germanium, Carbon, Tin and Titanium can be made by evaporating the element onto a microscope

slide which has been pretreated with release agent. Detergents, sodium chloride, cesium chloride and sugar are some of the more popular ones. Detergent-prepared slides tend to deteriorate on standing and it is recommended that the films be floated off immediately after evaporation. If they are required to be stored it is advisable to remount them using a 10% glycerol solution or to store in a damp atmosphere[7].

Elements which are not attacked by chromic acid or trichloracetic acid/ammonia mixture (Fe, Ni, Si, Ge, Sn, Ta), can be evaporated onto copper and the copper stripped by using one of the two solutions mentioned[7].

Self-supporting targets can also be made using soluble plastics but this method can be troublesome as the evaporated film tends to sink in some solvents.

Thin carbon backings

These are made by arcing between carbon electrodes placed about two millimeters from detergent coated glass slides. They provide a useful backing because they can be made as thin as 10 $\mu g/cm^2$ and have considerable mechanical strength. In evaporations where the element is not attacked by water it is safer to store the carbon backing on its glass slide but floating off should not be too long delayed. Because of the close proximity of the filament some evaporations may cause the carbon film to peel. This may be avoided by 'flashing', that is by setting the variac above evaporation temperature then switching the current on and off in very short bursts. When dealing with elements which are attacked by water the carbon film has to be floated off and mounted onto the target holder before evaporation. It is advisable to preheat the carbon film in vacuum, using radiant heat from the filament. Freshly cleaned mica without any release agent has been used as a substrate for carbon. This has an open shelf life of about two months and considerably longer when stored in a desiccator.

Films evaporated directly onto mirror-finish stainless steel can be flexed off intact providing they are thicker than a few hundred $\mu g/cm^2$.

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2. L. Holland. Vacuum Deposition of Thin Films. 1956.

3. Molybdenum gauze is obtained commercially from SHERMAN CHEMICALS LTD., Downham Hills, Chestnut Road, Tottenham, London, N.17. (Agents).

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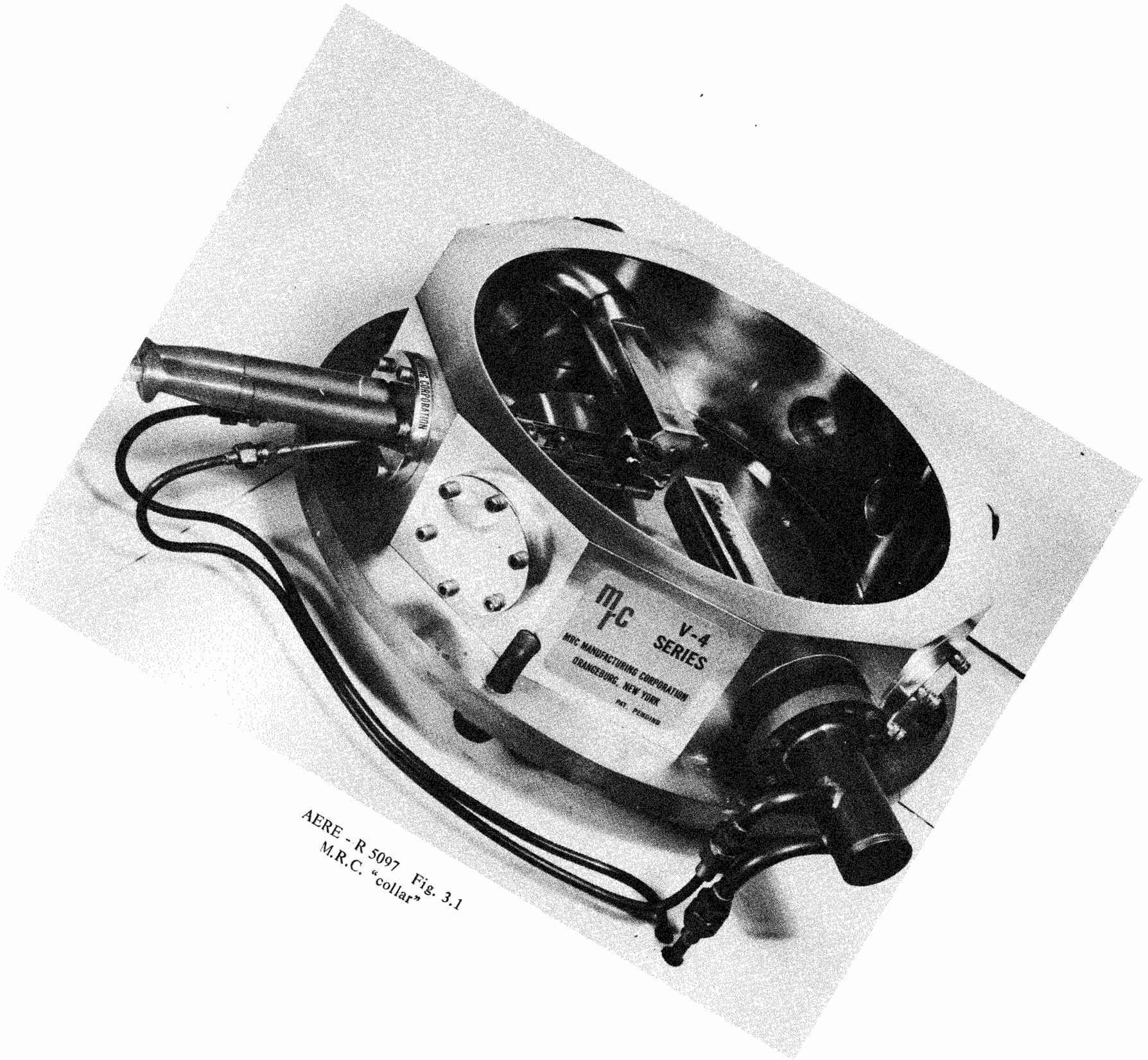
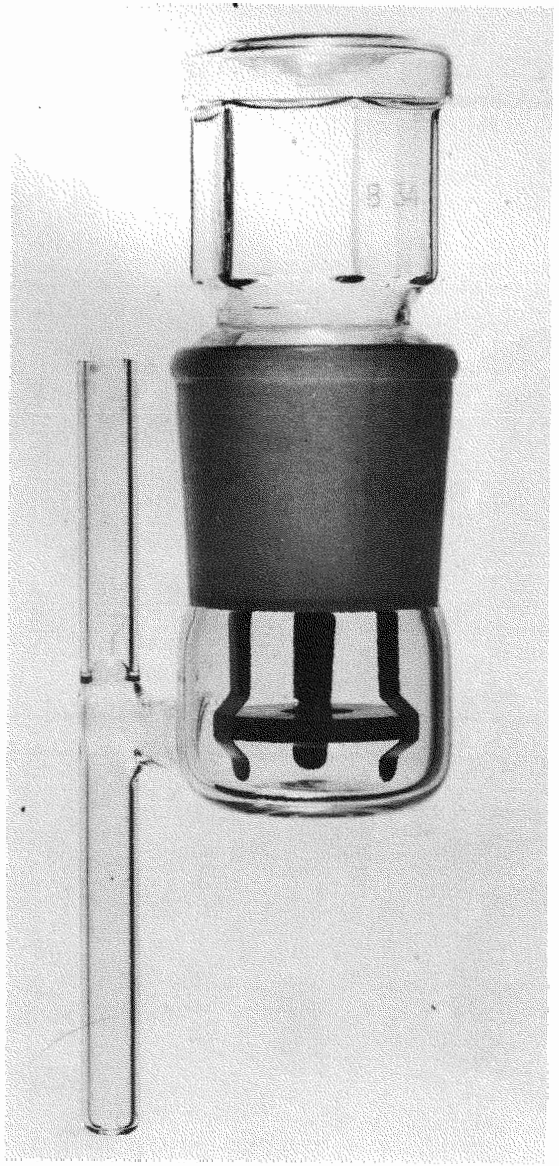
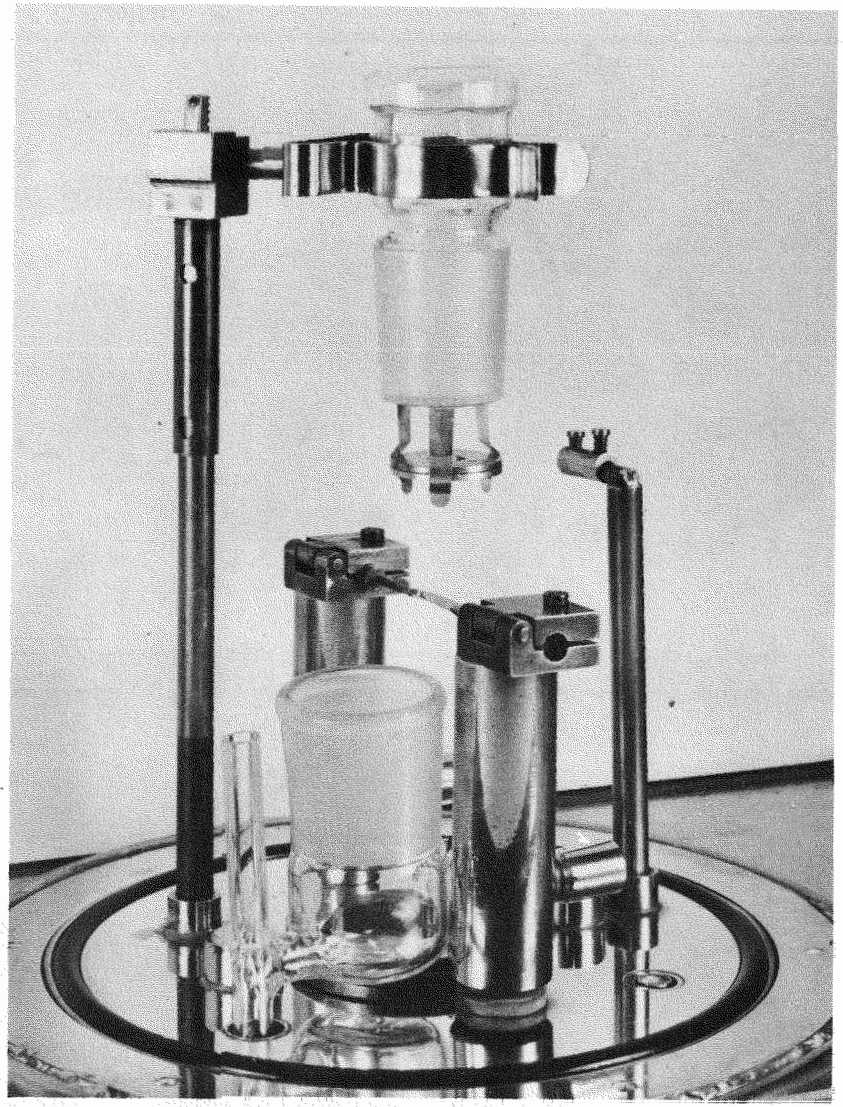
7. M. Nobes. J. Sci. Instrum. 38, 1961. p.410.



AERE - R 5097 Fig. 3.1
M.R.C. "collar"



AERE - R 5097 Fig. 3.2
Ground glass stopper for vacuum packed targets



AERE - R 5097 Fig. 3.3
Break-seal container

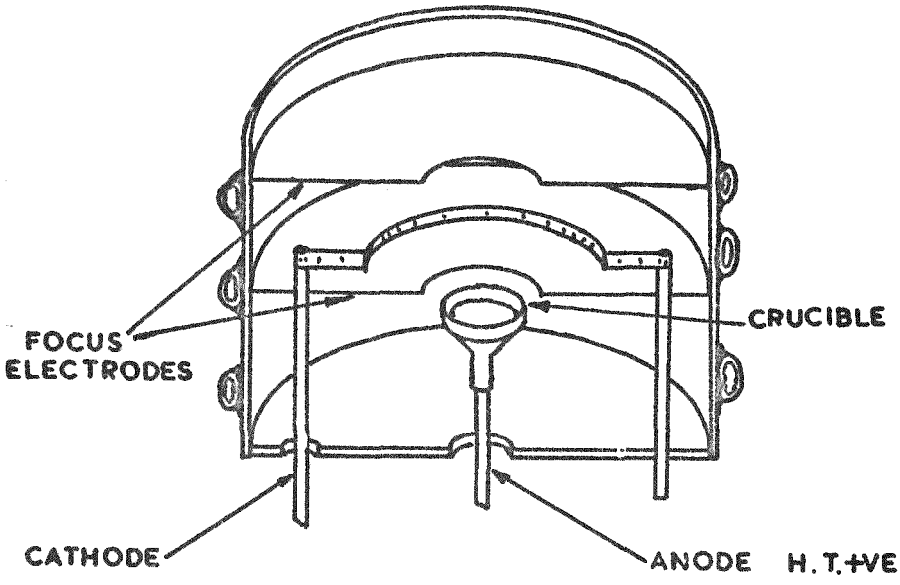
VACUUM EVAPORATION BY ELECTRON BOMBARDMENT

G. T. J. Arnison

A.W.R.E., Aldermaston, Berks.

An analysis is provided of the experience gained in the use of several electron bombardment methods of both laboratory and commercial origin. These methods include magnetic and electrostatic focussing as well as simple direct bombardments.

The salient features of each method are given in tabular form.



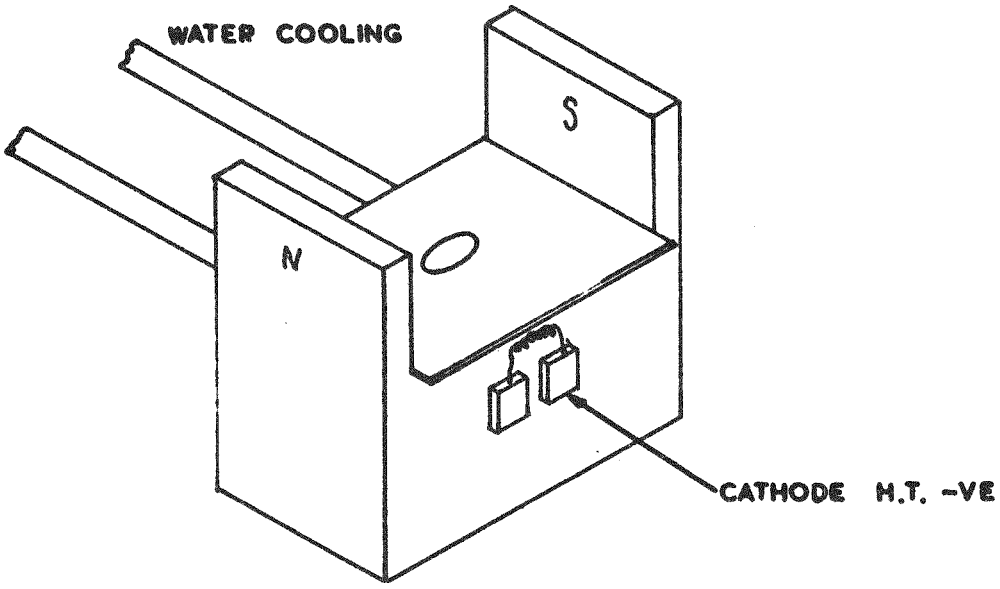
4.1 AWRE GUN

1. Anode crucible is made from Tantalum, since it is easily machineable to any chosen shape. The $\frac{1}{2}$" diam. crucible is mounted on a 2 mm diam. tungsten rod which is mechanically stable at high temperatures.

2. Large area tantalum ribbon cathode (0.125" x 0.010") gives high emission, hence large power outputs are available.

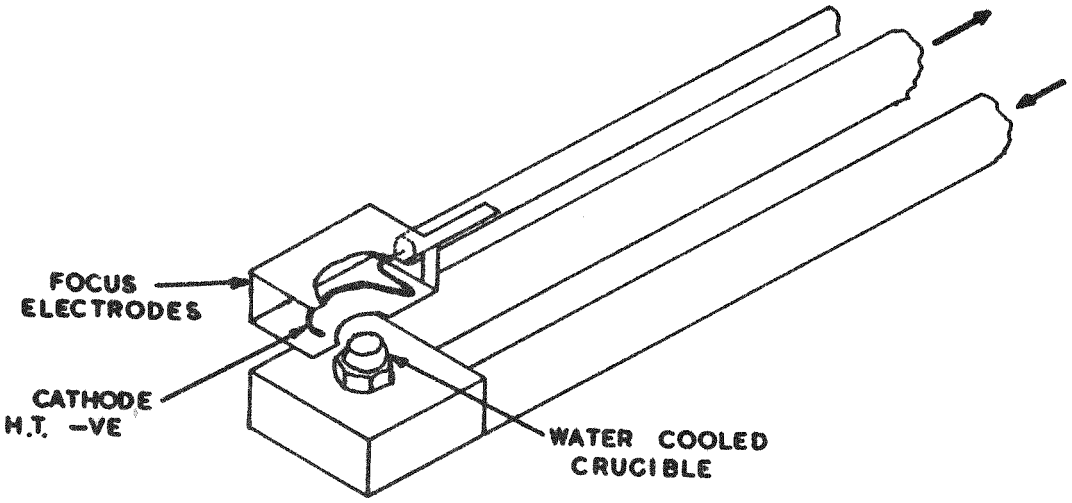
3. The lining to the water cooled copper shield is made from molybdenum, similarly the focussing electrodes.

4. The water cooled shield is necessary to prevent over-heating of the surrounding vacuum chamber.



4.2 VARIAN GUN

1. The water cooled stainless steel crucible minimises contamination of the evaporant.
2. The electron beam is magnetically focussed by a permanent magnet incorporated in the crucible housing.
3. Wide solid angle evaporation enables large surface areas to be covered.
4. The cathode is hidden from the crucible and is not poisoned by the vapour stream.

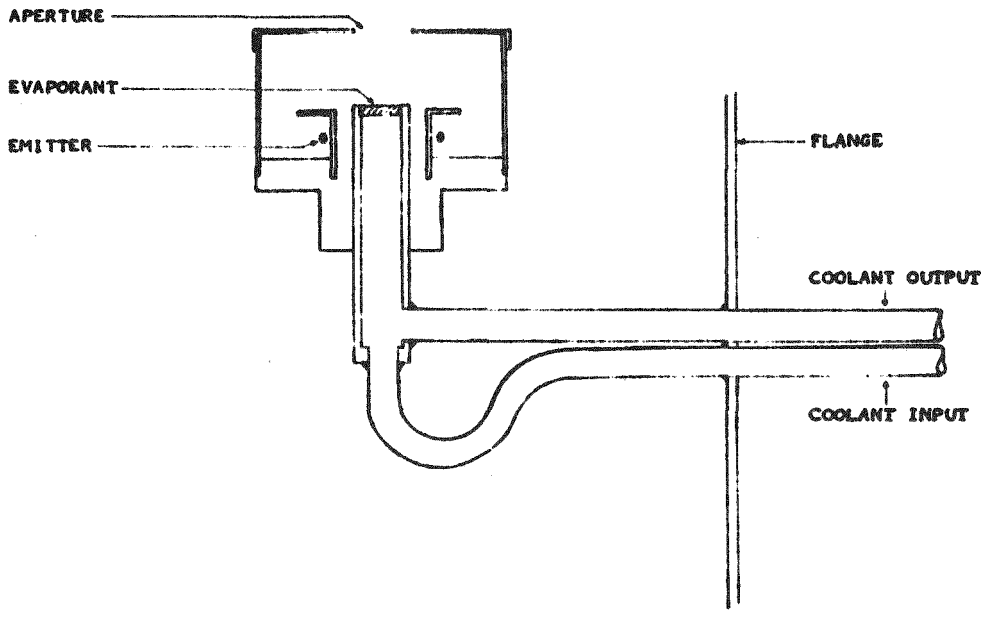


4.3 MATERIALS RESEARCH CORPORATION GUN

1. Interchangeable crucibles fit in the water cooled copper hearth.

2. It is possible to change the focus electrodes and hence evaporate isotopic quantities from this gun by narrowing the electron beam focus.

3. The cathode is a tantalum wire which is easily renewed by undoing three screws.



4.4 PLANER UNVALA GUN

1. This has a variable focus facility which is operated outside the vacuum system. Insulating powders can be evaporated.
2. The crucible is water cooled and contamination of the evaporant is minimised. The crucibles are interchangeable.
3. This is a new gun and little user experience is available.

4.5 ISOTOPE GUN

1. A small compact gun employing direct bombardment and requiring low power supplies.
2. Adopted from a gun published in Nuclear Instruments and Methods 1964 31, Pg. 25 by Menti, Martin et al.

4.6 T.V. GUN

1. Simple modification of an electron tube gun provides a useful multi source evaporator.
2. The beam can be deflected and steered by magnetic and electrostatic fields.
3. Potential X-Ray generator.

Summary

Comparison of electron guns

TYPE OF GUN	APPROX COST £	MAX POWER REQUIRED	FOCUS METHOD	SPECIAL ADVANTAGES
AWRE	50	5 KV +VE 300 MA	ELECTROSTATIC	HIGH TEMP POSSIBLE
VARIAN	450	4 KV –VE 500 MA	MAGNETIC	LARGE SOLID ANGLE, NO CATHODE POISONING
M.R.C.	150	5 KV –VE 400 MA	ELECTROSTATIC	LOW CONTAMINATION FROM INTERCHANGEABLE CRUCIBLES
PLANER	180	7 KV –VE 500 MA	VARIABLE ELECTROSTATIC	DIELECTRIC MATERIALS & POWDERED SAMPLES
ISOTOPE	50-200	400 V 25 MA	DIRECT BEAM	HIGH YIELD FROM SMALL SAMPLE
T. V.	10	15 KV 5 MA	MULTIPLE	STEERING OF ELECTRON BEAM

PREPARATION OF THIN FILMS OF UO_2 AND PuO_2 BY VACUUM EVAPORATION

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New Mexico

UO_2 and PuO_2 film preparation takes place in conventional all metal vacuum systems. The material is evaporated from a resistively-heated tungsten boat clamped between water-cooled electrodes. Fig. 5.1 is a shot of the electrodes. They pass through the base plate and the vacuum seal is made with Teflon gaskets. The boat is fashioned from tungsten sheet 1" X 2" X .005" thick. The sheet is folded into a V-shape and clamped across the electrodes. The base plate is grooved to accommodate either an 8 inch or a 12 inch diameter chamber.

There are separate vacuum systems for UO_2 and for PuO_2. They are equipped with 700 liter per second oil diffusion pumps and freon-cooled traps. The chamber of each system is enclosed in a stainless steel box with a plexiglass front. Fig. 5.2 shows the UO_2 and PuO_2 chambers in position. This photograph was taken when everything was shiny and new and not as cluttered as they are now. There is a 7" X 32" opening in the front for manipulation and loading of the chamber with gloved hands. Air flow through the opening is greater than 200 linear feet per minute. This serves to keep the activity within the box.

Every part of the system exposed to radiation from the evaporating source is water-cooled. Copper tubing is soldered around the chamber, base plate, and lid.

High-fired UO_2 or PuO_2 is loaded into the boat. The high-fired material is non-gassy and no shutter between the boat and the target appears to be necessary. The amount to be loaded into the boat is determined from a chart where thickness of the deposit desired, in mg/cm^2, is plotted against load for the commonly used boat-to-target distances. This chart is the result of many evaporations and is probably valid only for our particular geometry. It approximates the relationship $m = 0.45t\Pi h^2$ where m is the weight of the material to be loaded into the boat in mg, t is the thickness of the film in mg/cm^2, and h is the boat-to-target distance in cm.

The power supply consists of a transformer with a 120/240 volt primary and 12/24 volt secondary controlled by a 15 kva motor-driven variable transformer.

The boat-to-target distance depends largely on the substrate material and the area of the deposit. The usual distance is 5 inches or greater. At 4 inches or less, the radiated heat from the boat which is at 3000°C can ruin the substrate and warp the mask and the holder. Water-cooled holders are seldom used since they cannot be rotated. The substrate is masked to the desired size and shape and mounted in a holder made of stainless steel. The substrate assembly is then attached to a threaded rod projecting through the lid of the chamber by means of an O-ring type vacuum seal.

The chamber is pumped down to 10^{-5} mm Hg or less. Cooling water is started through the electrodes, pump-out throat, and the chamber. The boat is slowly brought up to an estimated 3000°C and held there until all of the material is evaporated. The density distribution in this arrangement is quite irregular. These irregularities are probably caused by the boat shape, warping of the boat when heated, and movement of the evaporating material in the boat. The irregularities can be smoothed out by rotating the substrate.

Deposition of UO_2 and PuO_2 onto most metallic materials one mil or thicker presents no special problems. The problems arise when it is desirable that a deposit be as nearly self-supporting as possible and extremely thin substrates are necessary. In general use is nickel which has been electroformed on a copper backing. The nickel is available in various thicknesses down to about 3 micro-inches, about 100 $\mu g/cm^2$. This material is mounted between ring-type holders and the PuO_2 or UO_2 is evaporated onto the nickel side. The copper is then dissolved in a stripping solution leaving the PuO_2 or UO_2 coated nickel. The evaporation usually takes place at boat-to-target distances of 6 inches or greater. Deposits as thick as 800 $\mu g/cm^2$ have been made on this thin material.

The copper-stripping solution consists of 50 grams of trichloroacetic acid in 250 ml of ammonium hydroxide and 250 ml of water. The stripping technique depends on whether the deposit is UO_2 or PuO_2. UO_2 films on the nickel-copper substrate can be immersed in the copper stripping solution by slowly easing the holder into it. When the copper is dissolved, the holder is eased out of the solution and washed several times by easing into beakers containing water and finally rinsed in acetone. After rinsing the holder is hung in a protected place to dry.

Unfortunately the PuO_2 film will dissolve in the copper stripping solution. To strip the copper from the PuO_2 nickel foil, the foil holder is mounted horizontally with the copper surface up. The solution is carefully pipetted onto the copper surface and after a few minutes removed with a syringe. Fresh solution is placed on the copper surface

and this process is repeated until the copper has been dissolved. Then the PuO_2 and the nickel substrate can be washed by easing into water and finally rinsed in acetone.

More recently, carbon films down to thicknesses of 30 $\mu g/cm^2$ have been used as substrates for UO_2 and PuO_2 films. The carbon film is made by first evaporating sodium chloride onto a glass slide and then evaporating the carbon onto the salt layer. After deposition of the active material, the carbon film may be floated off the slide by immersing in water. The film can then be picked up on a ring-type holder. The carbon film often has a blistered appearance after the UO_2 or PuO_2 has been deposited on it, but this does not seem to harm the film for it flattens and smooths out when floated off the glass slide. The carbon-salt-glass assembly can be used down to $4\frac{1}{2}$ inches uncooled and $3\frac{1}{2}$ inches if mounted against a water-cooled holder. UO_2 and PuO_2 films as thick as 600 $\mu g/cm^2$ have been put on these carbon films.

We are currently in the process of modernizing the systems just described by installing ion pumps to get cleaner, oil-free vacuums and hopefully lower pressures than the 10^{-5} range we are now operating in. We are also looking at electron beam heating (fig. 5.3).

The electron gun made by Varian Associates has recently been used to make a number of UO_2 and ThO_2 films. This particular electron gun is a water-cooled copper crucible, nickel plated, in which the material to be evaporated is contained. The filament is mounted on the side of the crucible and below its lip. The electron beam is bent by a magnetic field so that it impinges on the material to be evaporated. Thus the filament is not contaminated by the evaporating beam. Evaporation times are considerably shorter than with the resistance heated boat. However, nearly twice as much material has to be evaporated to get a desired film thickness for the same source-to-target distance than is required in the boat system. Also we have experienced difficulty in getting adherent films thicker than 0.5 mg/cm^2 with the e-gun. Fig. 5.4 is a shot of the e-gun mounted in the pumping throat.

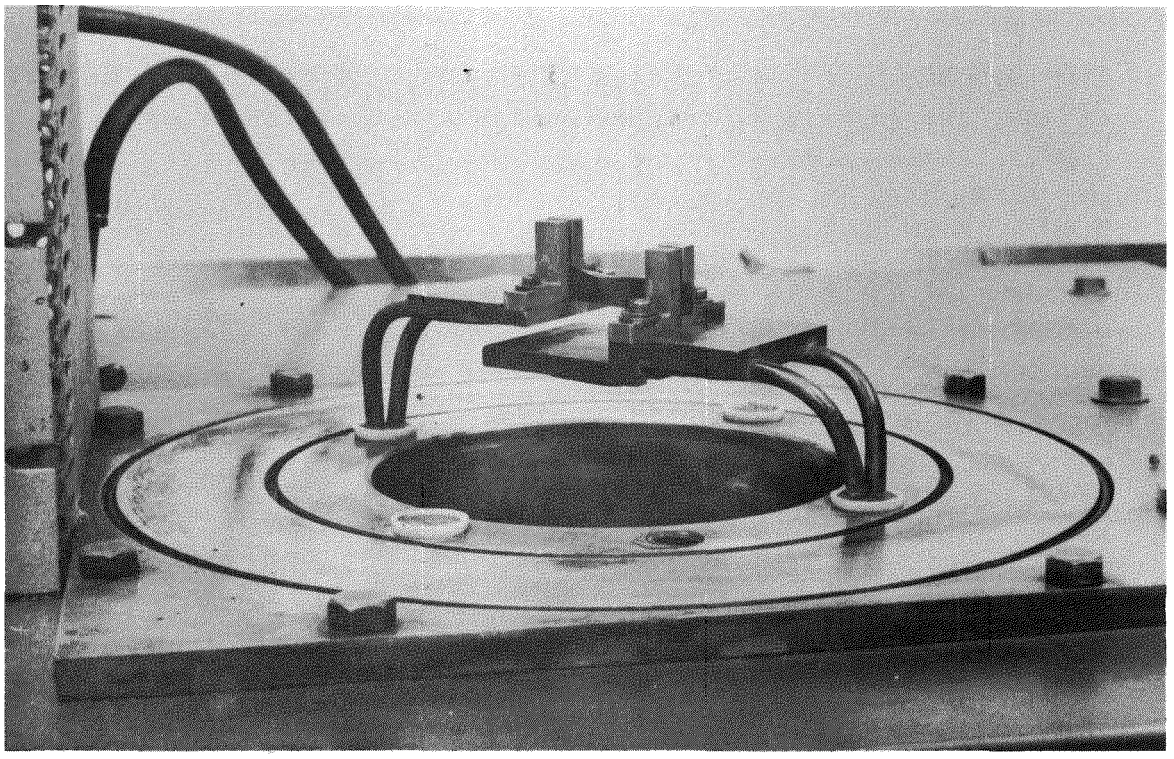
The electron beam systems are used with a deposit thickness monitor of the vibrating quartz crystal tape. The crystal is mounted on a sensor head which is installed in the vacuum system near the substrate. Before starting deposition, the variable frequency oscillator is tuned so that the beat frequency between it and the crystal oscillator in the system is zero. When deposition begins, the crystal frequency changes and a difference frequency is heard and indicated on a meter. A thickness versus frequency calibration is made for the material evaporated. A relay can be set to the frequency representing the desired thickness. When the indicated frequency is reached, the source power supply is shut off and evaporation stops

Often more than one target of a given size and thickness is required. To make them individually is time consuming and wasteful of material. To make several at once by simply grouping them above the source, markedly decreases the uniformity of each film. Fig. 5.5 is a view of our planetary gear set for making uniform multiple targets. Each target is rotated about its own axis as well as the central axis. The density distribution is smoothed out making it as good as that for a single centrally mounted target located at the same distance from the source.

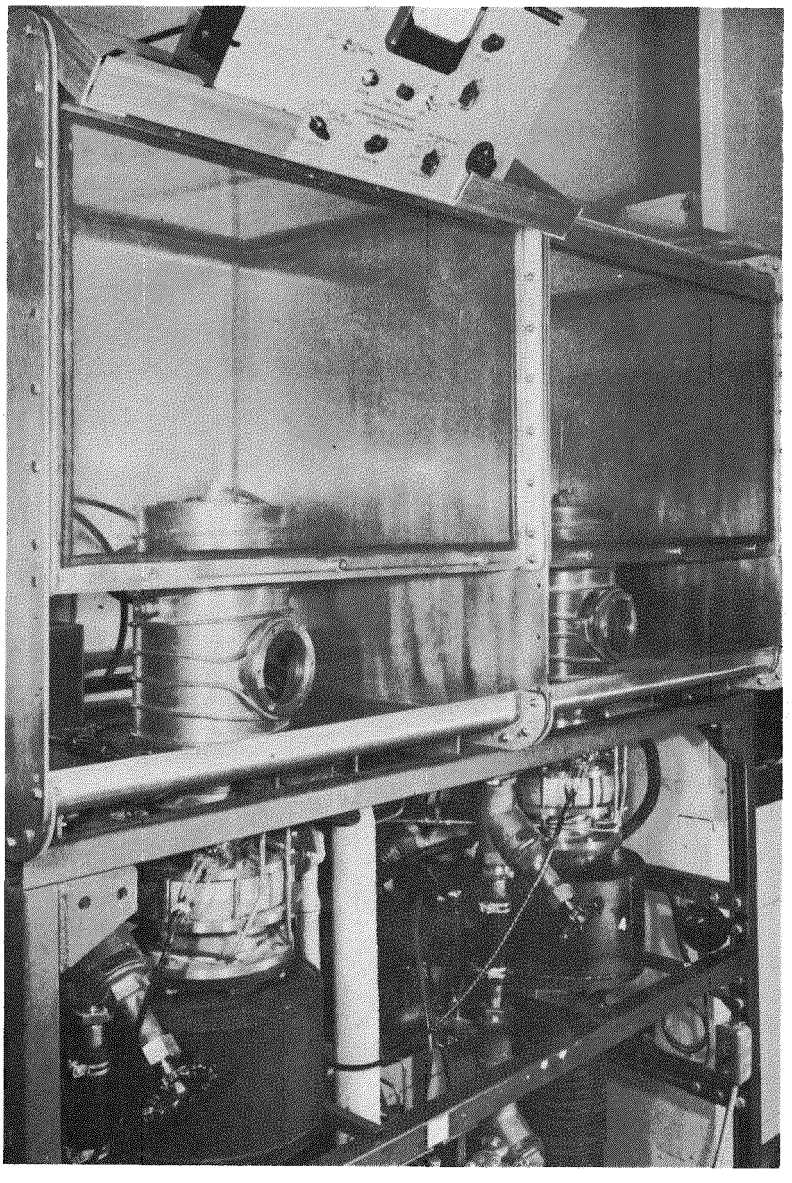
Fig. 5.6 shows the planetary gear set disassembled. The sun gear is installed on the chamber lid and is a 2 inch diameter spur gear with 48 teeth. The stem of the mounting plate for the planetary target holders passes through the sun gear centre and through the chamber lid via an O-ring seal. The motor to rotate the target holders is mounted on the outside of the lid. The planet gears are one inch diameter spur gears with 24 teeth. The mounting plates and target holders are fabricated from stainless steel. The central shaft is rotated at 6 rpm.

The sun and planet gears must be carefully aligned and lapped to operate smoothly. Even so, so much heat is absorbed from the boat during evaporation that the gears tend to bind resulting in a jerky rotation unless they are lubricated. A thin film of Octoil S brushed on the gear and bearing surfaces worked well. Also molybdenum disulfide rubbed into the metal surface is effective as a lubricant. This arrangement permits the simultaneous preparation of 3 targets up to 2 inches in diameter or 6 targets up to 1 inch in diameter.

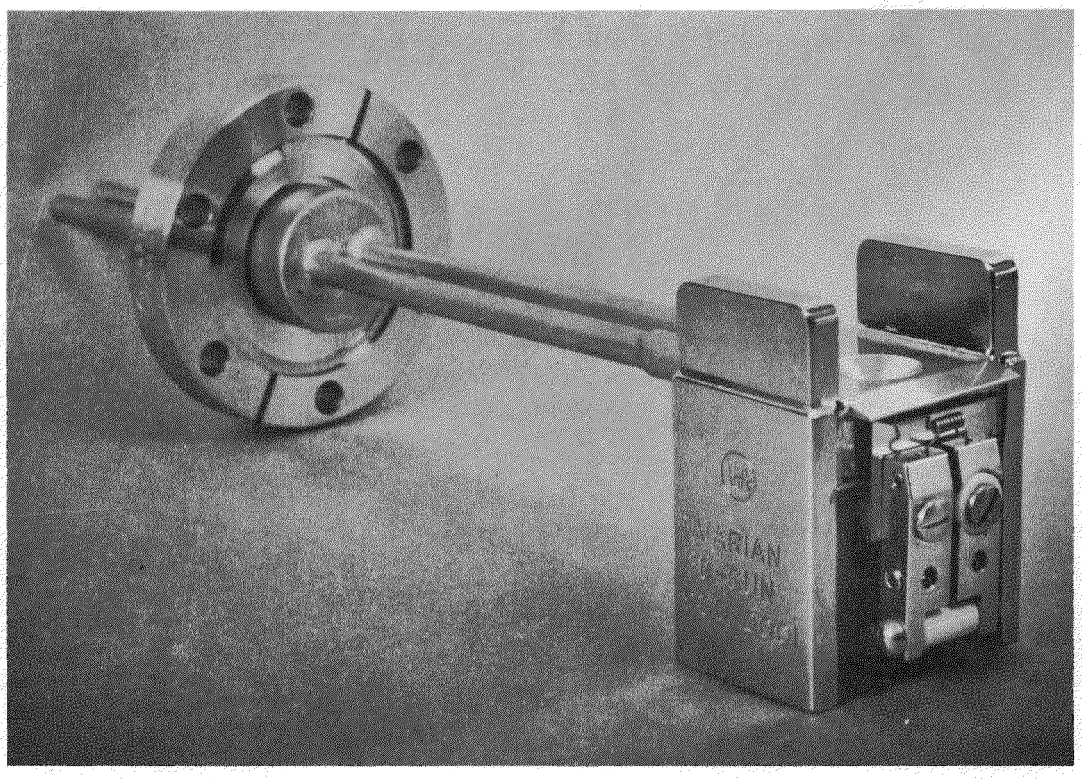
The uniformity of a number of targets was checked by alpha counting small areas (7.94 mm^2). The standard deviation for a single centrally mounted and rotated target, 11.4 cm^2 in area, located 5 to 6 inches from the source was about 3% (3.0-3.4). The standard deviation for targets made in groups of three with the planetary gear set was somewhat better, 1.8 to 2.8%, also for the same source-to-target distances.



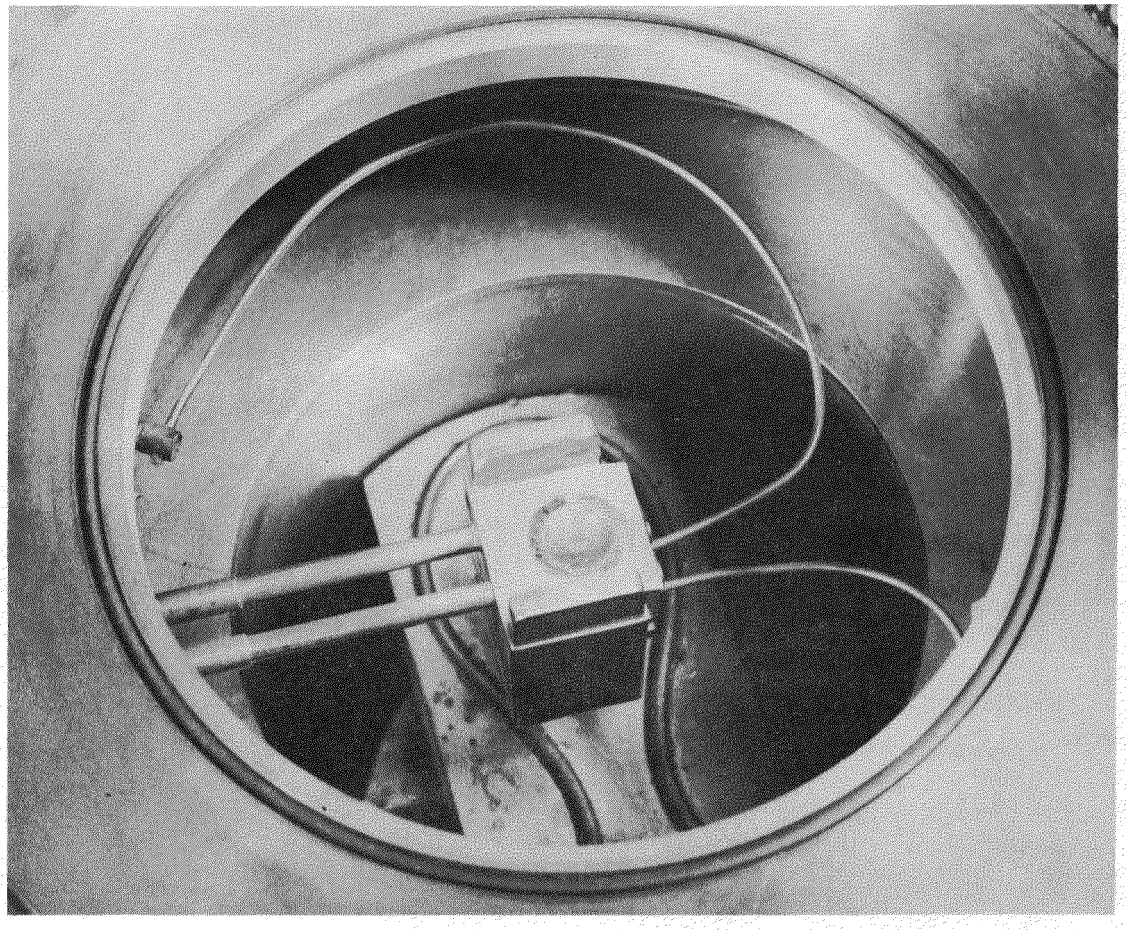
AERE - R 5097 Fig. 5.1
Water-cooled electrodes



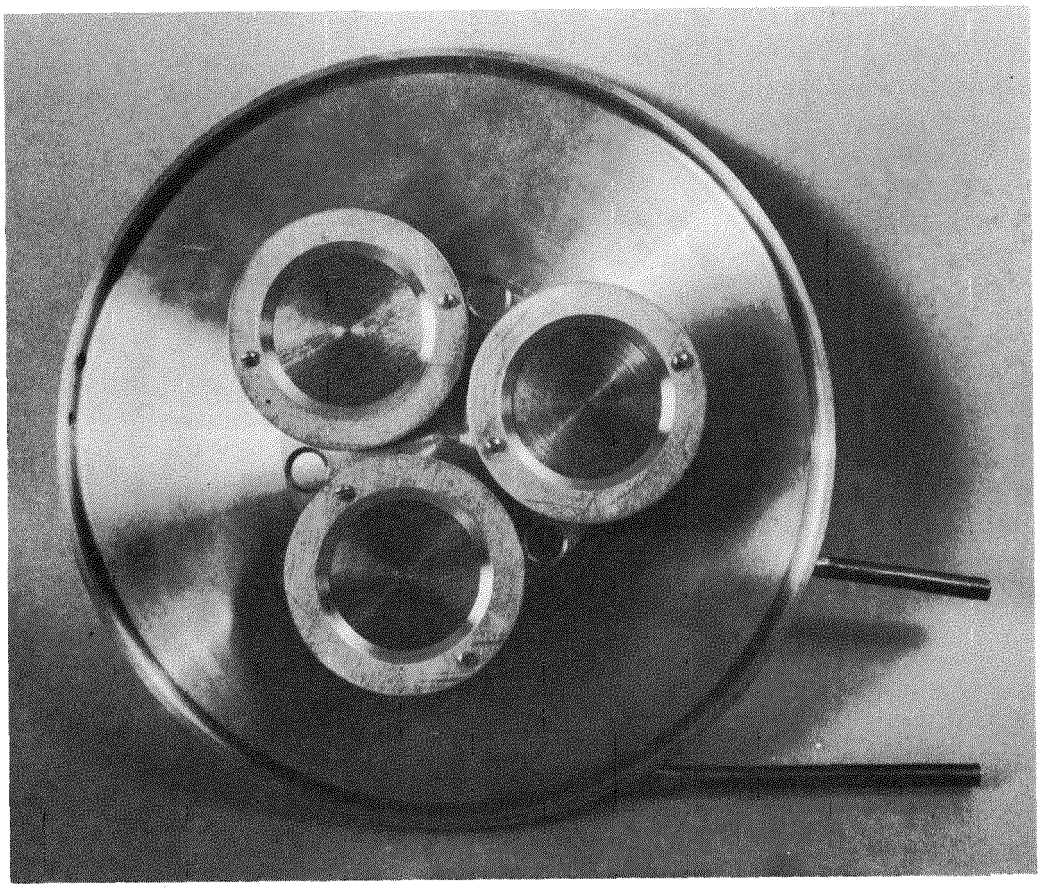
AERE - R 5097 Fig. 5.2
UO_2 and PuO_2 Vacuum chambers



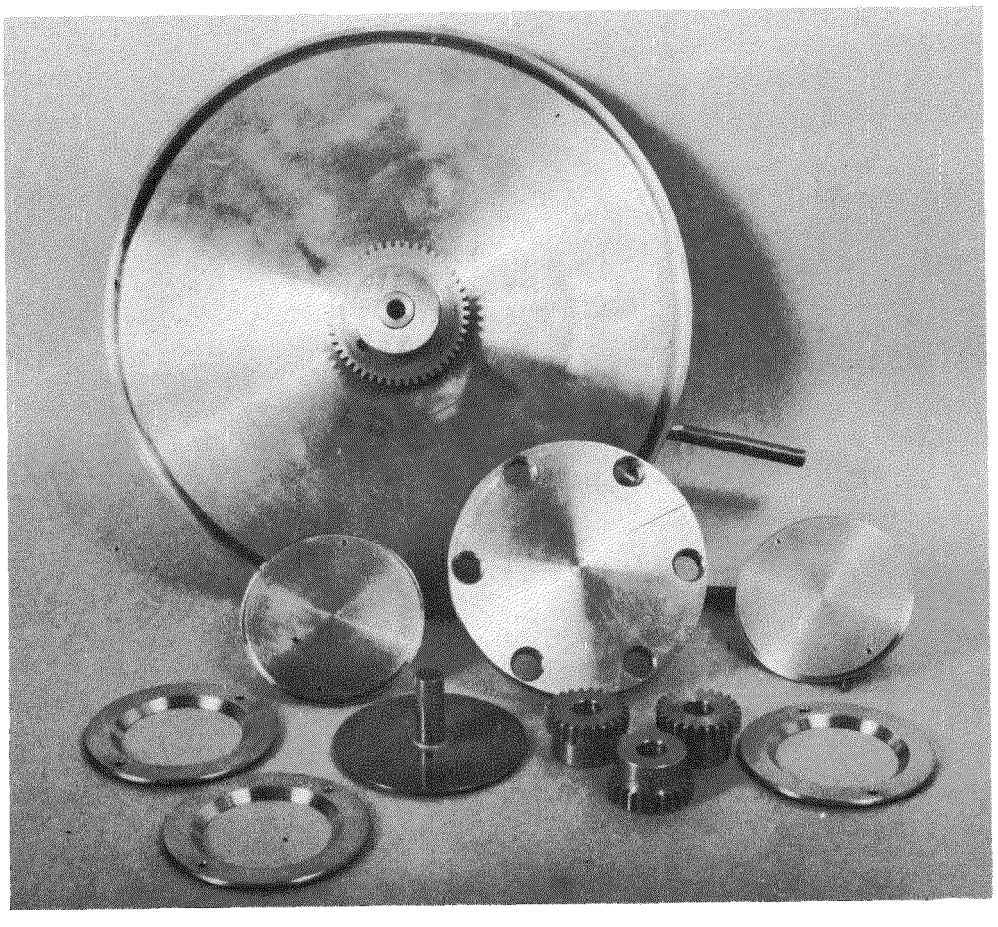
AERE - R 5097 Fig. 5.3
Varian electron gun



AERE - R 5097 Fig. 5.4
e-Gun mounted in pump throat



AERE - R 5097 Fig. 5.5
Target rotator assembled



AERE - R 5097 Fig. 5.6
Target rotator disassembled

PREPARATION OF EVAPORATED TARGETS

F. C. Ernè

Physics Laboratory, University of Utrecht, Netherlands

In the Utrecht laboratory resonance reactions on light nuclei are investigated with bombarding-particle energies up to 3 MeV. Enriched targets are frequently used in order:-

1. to investigate elements with low natural relative abundance;
2. to eliminate competing reactions from more abundant isotopes.

Enriched targets in the form of a chemical compound are preferably evaporated in the laboratory not long before the experiment, as absorbed water will contaminate the targets and promote dissociation during proton bombardment. Moreover chemical reactions with the backing may occur. The evaporation of compounds will be considered in more detail. A few remarks will be made regarding the evaporation process, the backings used and the composition of the material after evaporation. Regarding this last point we have some experience at Utrecht, as G.A.P. Engelbertink is standardizing the yields of resonance reactions in sd-shell nuclei. Absolute yield measurements on compounds are difficult. The relative yields of resonances in several elements in stocheiometric compounds are however compared, and these are tied to a few absolute yield determinations of resonances in the reactions $^{27}Al(p,\gamma)^{28}Si$ and $^{25}Mg(p,\gamma)^{26}Al$.

The melting point of most compounds is lower than 1000°C. This temperature can be easily obtained with the simple device shown in Fig. 6.1. It can be quickly installed in an evaporation bell-jar, which is used also for several other purposes. A small tantalum tube (length 20 mm, inner diameter 3 mm) filled with about one milligram of the enriched material is heated by a surrounding 50 μm thick and 1 cm broad tantalum foil (A in Fig. 6.1). The tube is placed on thin (0.3 mm diameter) tungsten wires (B in Fig. 6.1) in order to keep the heat conduction small. A current of 30-50 amperes through the foil produces enough heat to evaporate chemical compounds as CdS and $BaCl^2$, which last compound has the melting point at 962°C. One obtains a circular, sufficiently homogeneous, target spot with a diameter of 5 mm at a distance of 2 cm from the tube. The target thickness can be calculated by evaporating a known amount of material; in practice, however, it is often determined by counting the number of Newton rings to be seen on the backing.

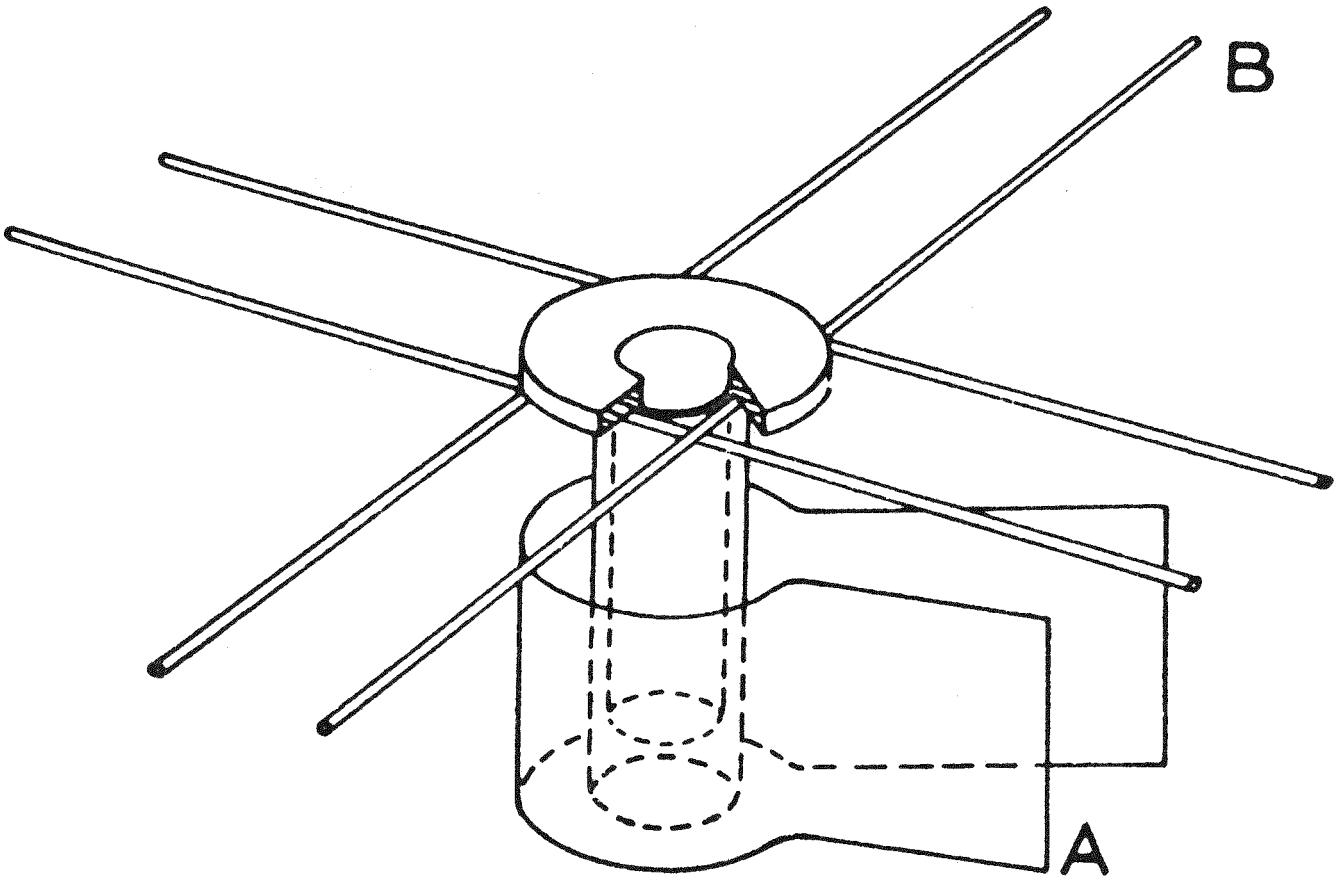


Fig. 6.1. Arrangement for evaporation of very small quantities of target material. The tantalum tube is surrounded by a thin tantalum foil A for indirect heating and supported by tungsten wires B.

The enriched material is evaporated on foils or backings, depending on the experiment. (The carbon foils used were shielded from the heat source during the evaporation process except for the target spot.) Backing material is carefully selected and cleaned in order to eliminate strongly competing reactions, for example from traces of fluorine and sodium. At proton energies below 1 MeV rolled copper backings are used, 0.5 mm thick. These are cleaned and smoothed by etching with concentrated ammonia with a few per cent hydrogen peroxide. At higher bombarding energies a material with higher Z-number, tantalum, is used. Sheets of 0.3 mm thick rolled tantalum, free from such contaminants as ^{23}Na, are obtained from the Drijfhout & Co. Corp., Amsterdam. The backings from this material are simply degreased with alcohol or acetone and gloved out.

The target composition should be known in many experiments, as the yield from a reaction is calculated using the stopping power for charged particles of the target material. However one is not always sure that the composition of the evaporated material is the same as before evaporation. Compounds may dissociate at high temperatures before evaporation, or under the influence of light (AgCl). Dissociation appears to result also from hydrolysis in crystal water. From $AlCl_3.6H_2O$

for example HCl is evaporated. In order to maintain the stocheiometric structure one should start with throughly dried material. Furthermore the crystal water can be liberated at relative low temperatures (50-200^{o}C depending on the compound) before the evaporation process starts. Engelbertink found that dry sulphates, pyro sulphates, pyrophosphates and alkali halogenides could be evaporated without dissociation.

PAPER 7

DEPOSITION OF UNIFORM EVAPORATED FILMS ON PLATES AND CYLINDERS

G. Müschenborn

C.B.N.M. Euratom, Geel

Uniform layers of gold and indium on aluminium and quartz backing materials are required for pile oscillation measurements. The backings are plates (100 X 25 X 1 mm) and cylinders (25 mm diameter, 100 mm length, 1 mm thickness) with a large surface area, so that if material is evaporated from a single source a very great distance between source and target would be needed to meet the requested uniformity in mass distribution (± 5%). To lessen this distance and thus the great loss of evaporated material we have calculated and constructed a multiple source arrangement. The agreement between calculated and measured film thickness is very good (about 0.3%) within the area of interest.

Calculation of the source arrangement

The installed evaporation sources are resistance heated molybdenum sheet of 0.1 mm thickness and 6.2 mm width. Such sources may be described as small surface sources with a cosine distribution of the evaporated material. A simple generalization of the well known formula of Holland and Steckelmacher yields for i evaporation sources lying in the plane z=0 the relative distribution function in the parallel plane $z=z_o$

$$F(x,y) = \sum_i \frac{1}{\left(1 + \frac{(x - a_i)^2 + (y - b_i)^2}{z_o^2}\right)^2}$$

where the coordinates of the sources are a_i and b_i. For a better comparison the calculated curves are normalized to x=o and y=o.

The targets to be prepared required a linear arrangement of the sources, thus all a_i=o, and the sources are mounted on the y-axis parallel to the long axis of the backing. The distributions for several arrangements with 2,3,4 and 5 sources equally loaded were computed with variation of the parameters b_i and a z_o of 50 to 60 mm. The best results were obtained with 5 sources and the following parameters b_i

$b_1 = -72$ $b_2 = -40$ $b_3 = 0$ $b_4 = +40$ $b_5 = +72$

Experimental installation.

The whole assembly for the preparation of cylinder targets is to be seen in an exploded view in Fig. 7.1, showing the ceramic base plate A, the copper mountings B, and the molybdenum filaments C with a special support to take up thermal expansion. Above this filament arrangement the stainless steel plate D is mounted with a driving mechanism for two

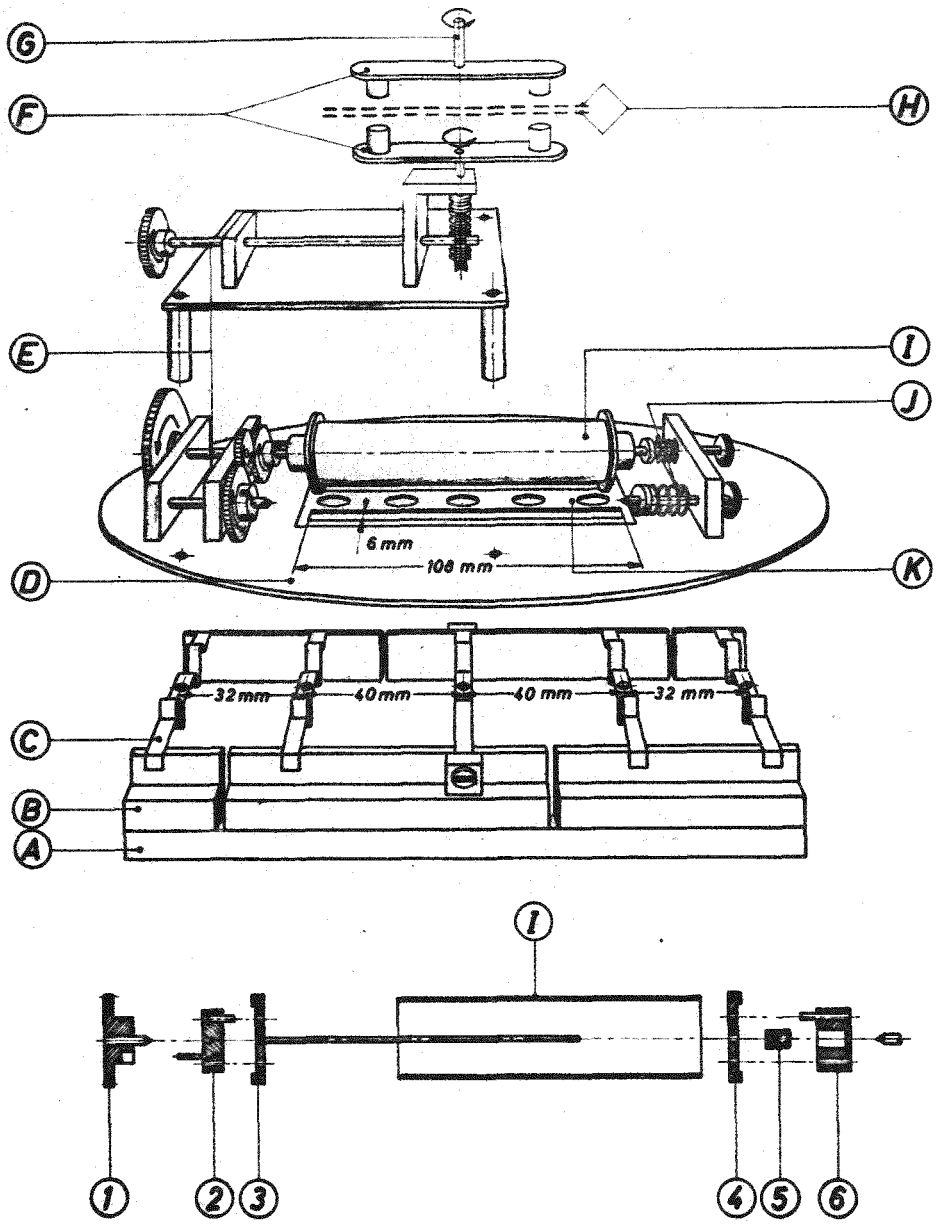
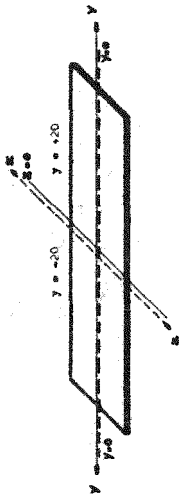


Fig. 7.1



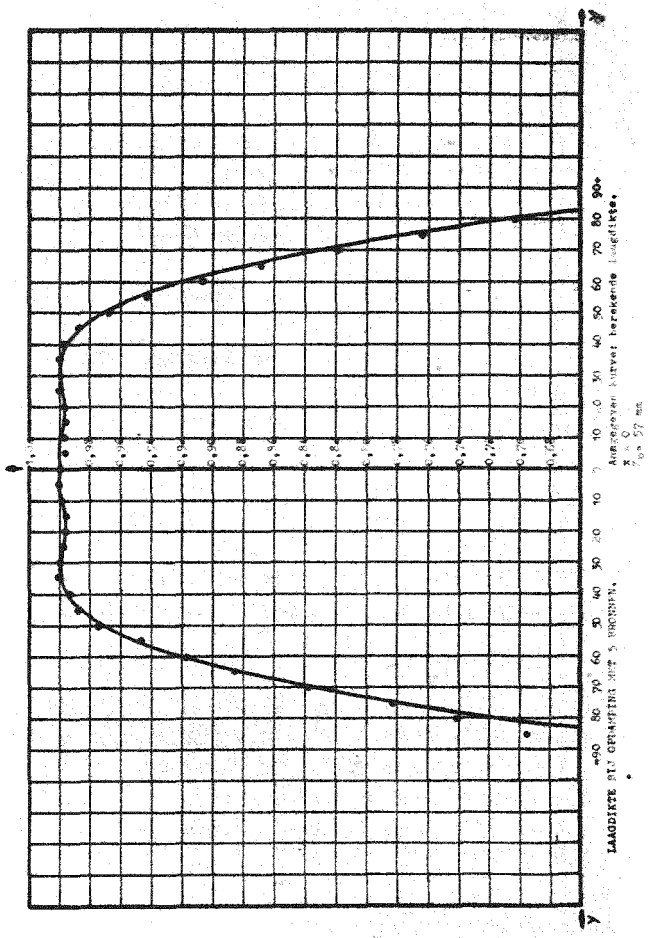


Fig. 7.2

cylinders. These are coated through two beam defining slits symmetrically arranged to the sources of 6 mm width and 108 mm length. The total condensed mass per cm^2 and a rough measurement of the uniformity were estimated by five test targets K. The cylinders run at 15 turns per minute which is satisfactory for good uniformity in x-direction. F,G,H represent the magnetically coupled vacuum feed through the driving mechanism. A similar version has been constructed for the preparation of the plate targets. A drum which can be loaded at 8 places with the aluminium plates and the test plates for uniformity rotates at 15 turns per minute above a beam defining slit with the same dimension as before.

Results

To compare the distribution of the evaporated gold films with the computed one several experiments have been done with a plane parallel quartz plate (100 X 200 mm^2) at the desired distance z_o. The filaments were loaded equally with spectrally pure gold. It takes some care to ensure that the total amount of gold has been evaporated from the filaments. The film thickness on the quartz plate has been photometrically measured. A calculation shows that for distances of 50 to 60 mm the filaments have to be loaded only with a few milligrams of gold to give film thicknesses which can be photometrically measured. But for a mass determination better than 1% the handling of the material is very difficult. For ease of measurement the filaments were then loaded with 80 to 100 mg and the source shielded with a rotating stainless steel cylinder having a diameter of 104 mm and a beam defining slit of 10 mm. The filaments were mounted on the axis of this cylinder which rotates at 60 turns per minute.

Fig. 7.2 shows the calculated distribution curve in y-direction for x=o and z_o=57 mm. The photometrically measured values are marked by points. Fig. 7.3 shows the same results for a distance z_o=50 mm. The agreement between the calculated and measured distribution lies within O.3%. Fig. 7.4 shows the calculated and measured film thickness in x-direction for y ±20. For a beam defining slit of ±3 mm the relative film thickness varies less than O.5%.

Conclusion

With the described five source geometry a series of targets has been fabricated with indium in the thickness range of O.1 to 2 mg per cm^2 and with gold between 1 and 10 mg per cm^2.

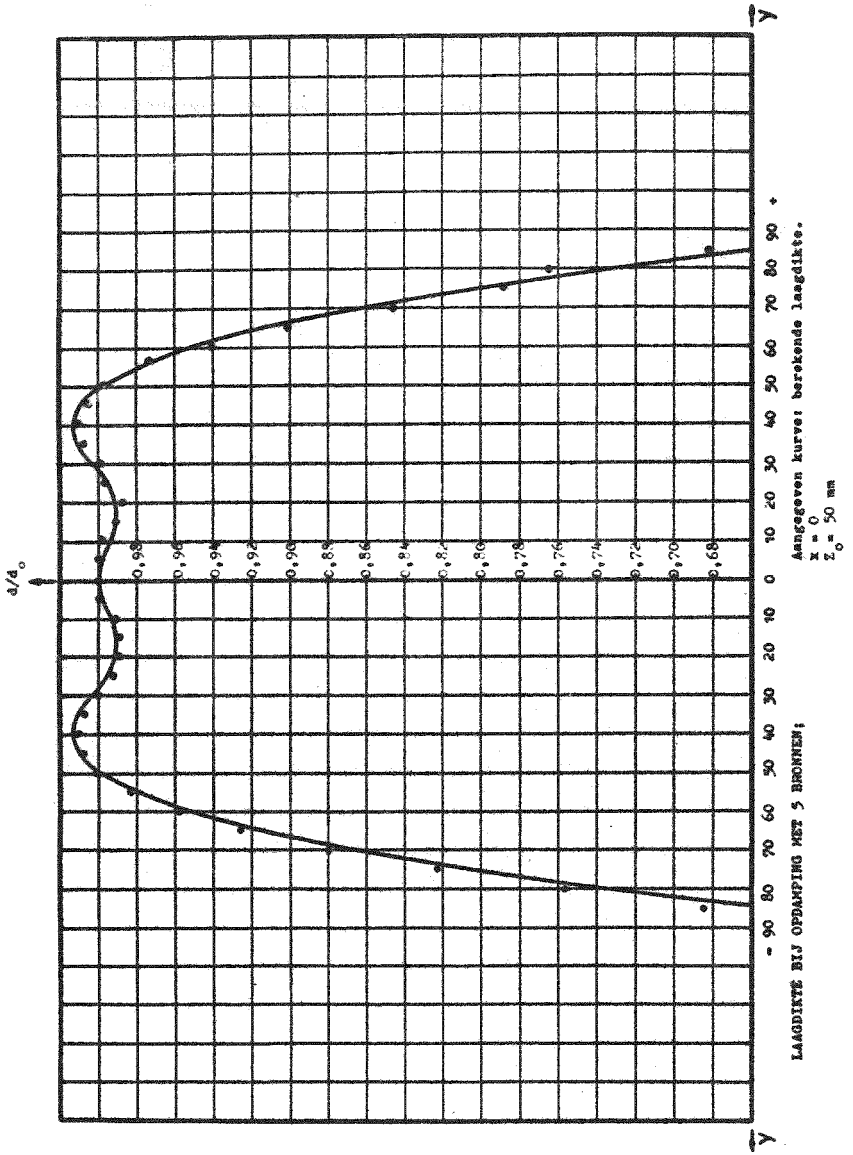

LAAGDIKTE BIJ OPDAMPING MET 5 BRONNEN;
Aangegeven kurve: berekende laagdikte.
x = 0
Z_o = 50 mm
d/d_o
y
y

Fig. 7.3

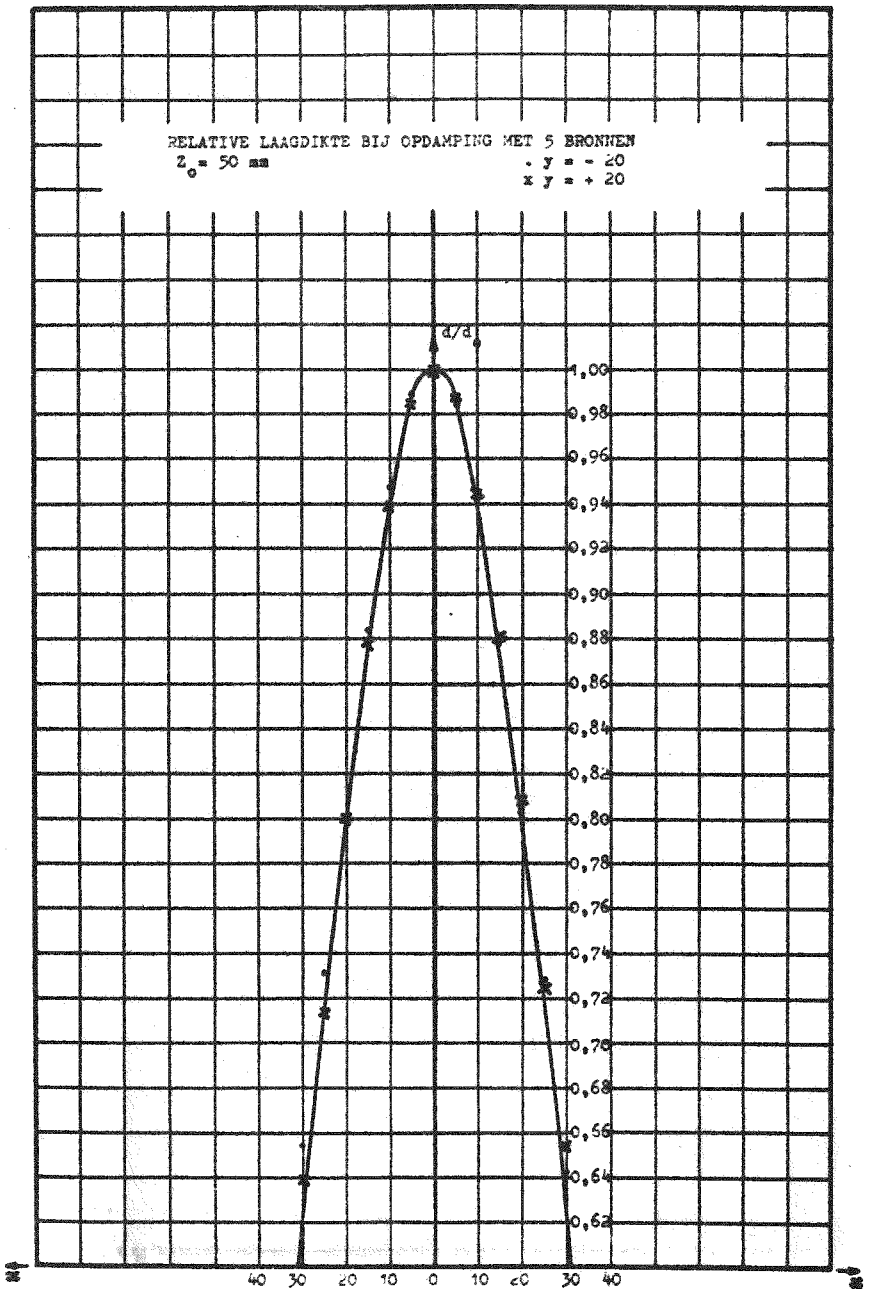

RELATIVE LAAGDIKTE BIJ OPDAMPING MET 5 BRONNEN
Z_o = 50 mm
. y = - 20
x y = + 20
d/d_o
x

Fig. 7.4

ISOTOPIC FRACTIONATION DURING EVAPORATION

H.L. Eschbach

Euratom, C.B.N.M., Geel.

1. Introduction

The evaporation of an element at low pressures can be described as molecular distillation. The total mass of vapour evaporating from unit area of the surface of a liquid in unit time is given by the well known Langmuir equation:

$$(1) \qquad g = \left(\frac{\mu}{2\pi RT}\right)^{\frac{1}{2}}$$

where g = total mass
p = vapour pressure
μ = molecular weight
R = gas constant per mole
T = absolute temperature.

Strictly speaking this is only true for a monoisotopic element and when the evaporated particles are atoms. When alloys or isotopic mixtures are to be evaporated, fractionation effects have to be considered[1]. These effects make, for instance, the fabrication of well defined nickel-chromium and nickel-iron layers as used for microcircuits and memory elements particularly cumbersome. An example where isotopic fractionation plays a role is the mass spectrometer with single filament thermal ion source[2].

We are concerned with the fabrication of high purity well-defined boron layers[3] to be used as standards and monitors in neutron experiments. For these purposes the ^{10}B content of the layer has to be known with high accuracy. In natural boron which is for various reasons our starting material, the ^{10}B content is about 20%, the rest being ^{11}B. The mass of the evaporated layer is determined in our experiments by weighing the backing under vacuum before and after evaporation with a vacuum micro-balance. But in order to evaluate the ^{10}B amount with high accuracy chemical impurities and fractionation effects must be known with the same precision.

2. Rayleigh Distillation

Supposing that during evaporation no concentration gradient is built up in the crucible, i.e. constant and complete mixing of the isotopes is provided, the evaporation process is formally equivalent to Rayleigh distillation[4]. Following the derivation given by Zinsmeister[5] and

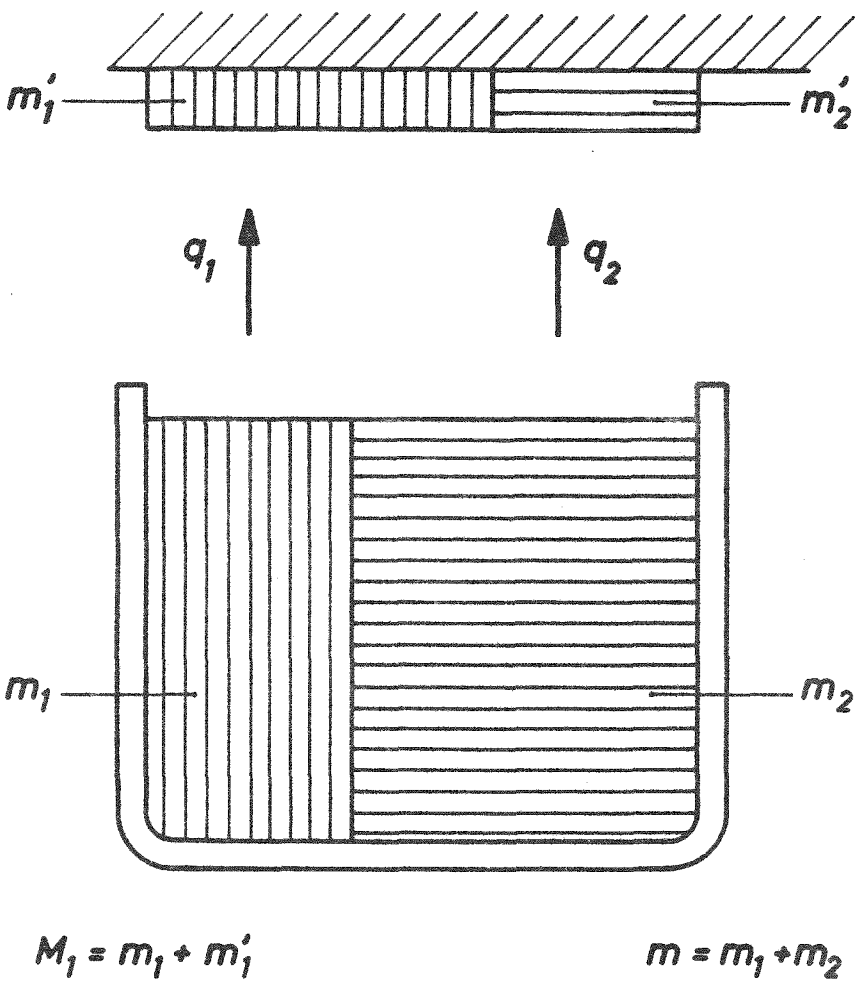

m_1'
m_2'
q_1
q_2
m_1
m_2
$M_1 = m_1 + m_1'$
$m = m_1 + m_2$

Fig. 8.1

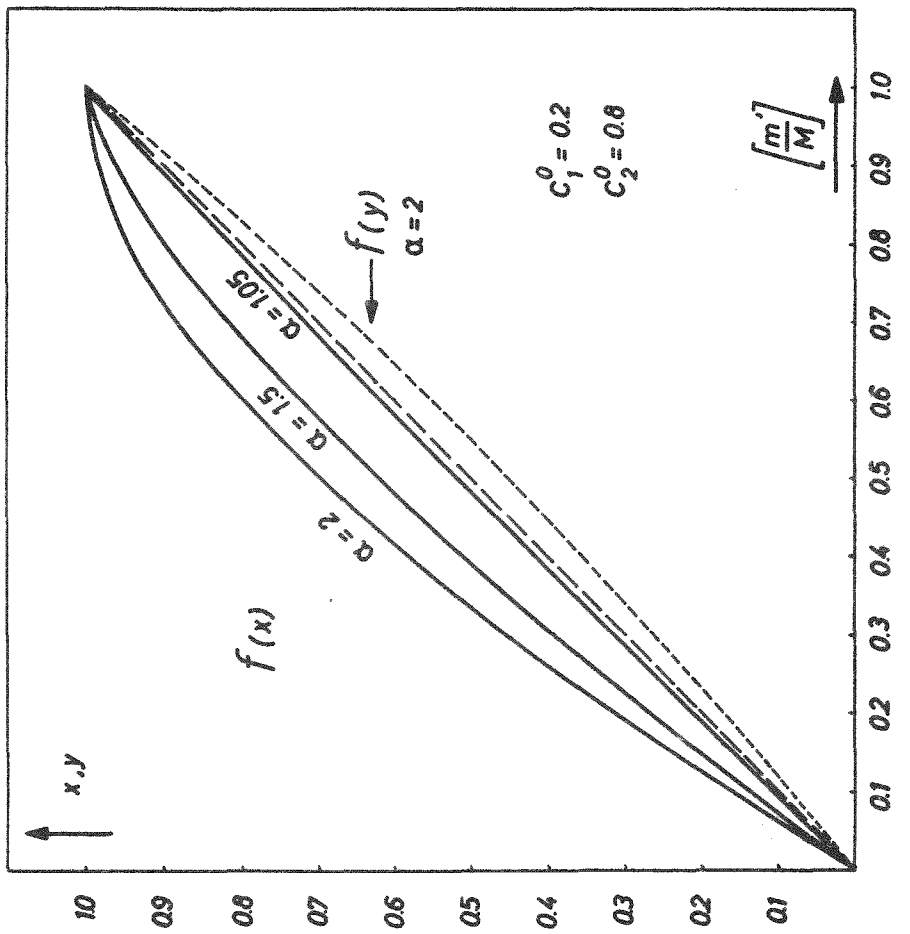

$C_1^0 = 0.2$
$C_2^0 = 0.8$
$\left[\frac{m'}{M}\right]$
$f(y)$
$\alpha = 2$
$\alpha = 1.05$
$\alpha = 1.5$
$\alpha = 2$
$f(x)$
x, y
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 8.2

using his notation (fig. 8.1) we get from Langmuir's equation:

$$(2) \quad q_i = \alpha_i \frac{mi}{m} = \alpha_i \frac{dmi}{dt} \qquad i = 1,2$$

With $dm = dm_1 + dm_2$ and $\alpha = d_{1/d_2} = \frac{\mu i}{\mu_1}$ the differential equation:

$$(3) \quad dm = 1 - \frac{1}{\alpha} + \frac{1}{\alpha} \frac{m}{m_1} \quad dm_1$$

can be derived. Integration of (3) gives:

$$(4a) \quad 1 - \frac{m^1}{M} = C^o (1-x) + C_2{}^o (1-x)^{1/\alpha}$$

with the following abbreviations: $m = M - m'$ etc.

$$x = m_1'/M_1$$

$$C_1^o = M_1/M$$

$$C_2^o = M_2/M$$

A similar equation can be found for the second component:

$$(4b) \quad 1 - \frac{m^1}{M} = C_2^o (1-y) + C_1^o (1-y)^{\alpha}$$

with $y = m_2'/M_1$.

In Fig. 8.2 f(x) and f(y) are plotted as functions of the fraction m'/M of the amount of material evaporated.
The composition of the condensed layer can be finally calculated from:

$$(5) \quad \frac{m'_1}{m'_2} = \frac{x}{y} \frac{C^o 1}{C_2^o}$$

Some curves according to equation 5 and for different parameters α have been plotted in fig. 8.3.

3. Successive Dilution

The evaporation of boron is carried out from cylinders of natural boron 25 mm in diameter and 30 mm high. Only a fraction of the total cylinder is liquid at a time, and as evaporation goes on the cylinder is gradually melted down. It is suggested that this procedure is comparable with the method of successive dilution[5] used in the evaporation of alloys, which deposits well-defined layers. With this method only a fraction of a given amount of alloy (e.g. 5-10%) is evaporated. Then the same amount of material is added to the evaporant in the composition wanted

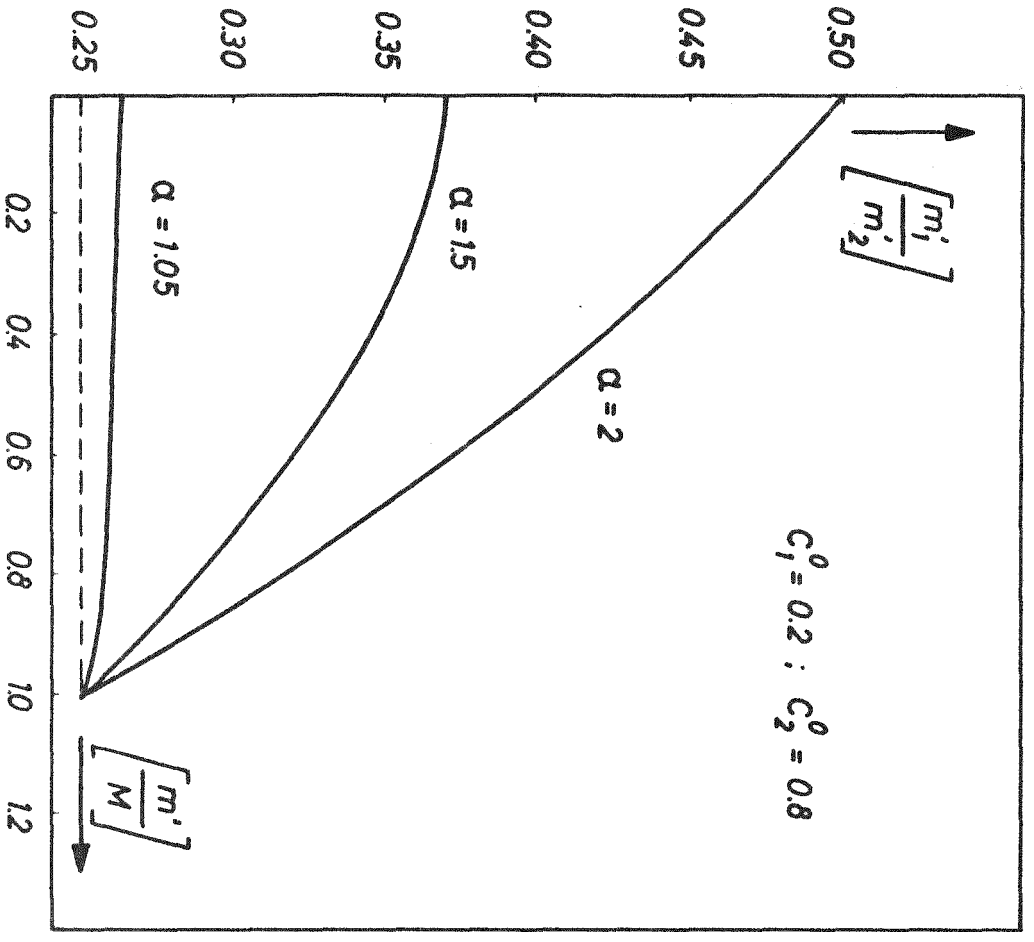

0.25
0.30
0.35
0.40
0.45
0.50
0.2
0.4
0.6
0.8
1.0
1.2
α = 1.05
α = 1.5
α = 2
$\left[\frac{m_1'}{m_2'}\right]$
$\left[\frac{m'}{M}\right]$
$C_1^0 = 0.2 ; C_2^0 = 0.8$

Fig. 8.3

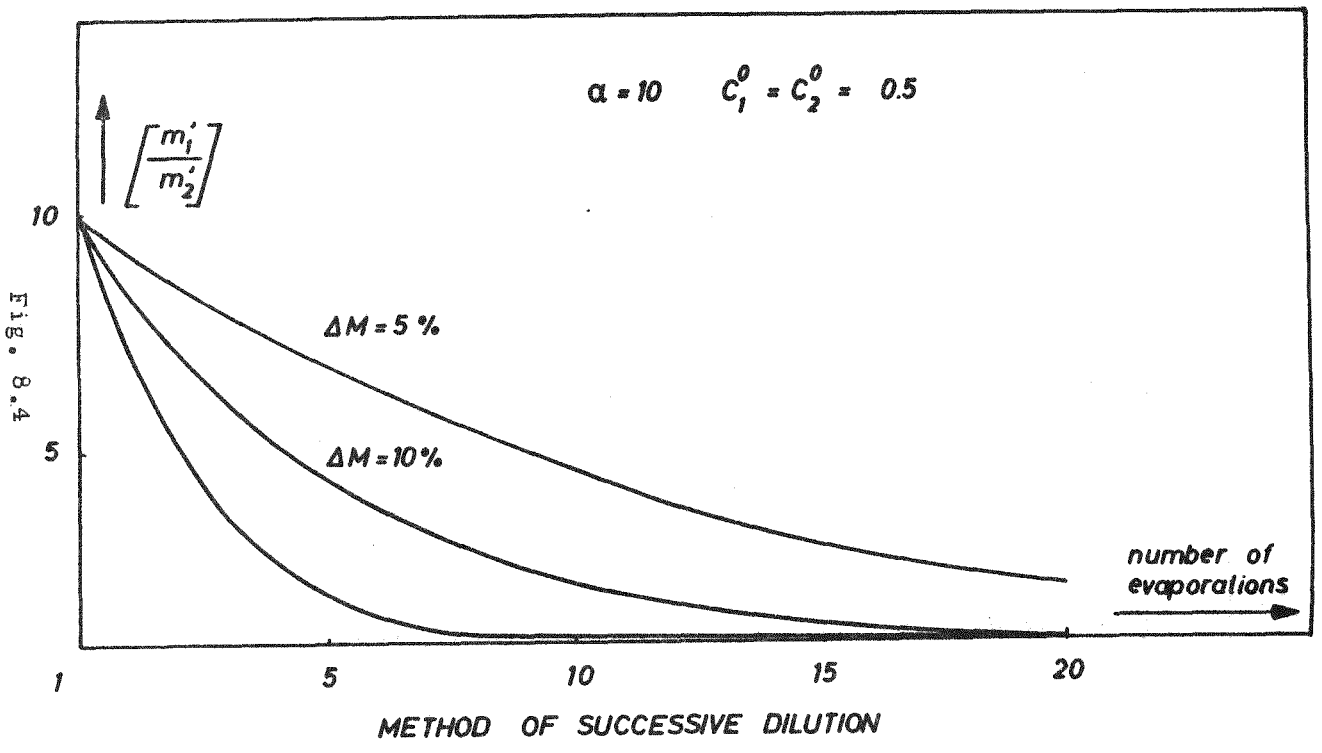

α = 10 $C_1^0 = C_2^0 = 0.5$
$\left[\frac{m_1'}{m_2'}\right]$
10
5
ΔM = 5 %
ΔM = 10 %
number of evaporations
1
5
10
15
20
METHOD OF SUCCESSIVE DILUTION

Fig. 8.4

in the layer. This procedure is repeated several times. It can be shown[5] that after a certain number of evaporations the concentration required in the layer is nearly approached.

Fig. 8.4 shows a good example (after Zinsmeister[5]). The concentrations of the two components in the starting material are $c_1^o = c_2^o = 0.5$. The composition of the layer aimed at is $m_1'/m_2' = 1$. However, due to a large α (in fig. 8.4 assumed to be 10), there will be an enrichment of the more volatile component at the beginning of about a factor of 10. By carrying out a number of evaporations and always adding material in the wanted composition, the latter is finally approached. The approximation depends, as shown in fig. 8.4 on the amount of ΔM evaporated each time and on the number of evaporations.

It is suggested that with the described evaporation of natural boron a similar curve of the ratio of $^{10}B/^{11}B$ in the layer should be observed when, instead of the number of evaporations, the time is marked on the abscissa.

4. Results

Unfortunately there are no conclusive results available at this moment. A series of measurements, however, indicates, a significant enrichment of ^{10}B in the evaporated layer. In all cases this enrichment was equal to or less than would follow from the calculation with $\alpha = 1.05$. For reasons not well understood, there is a rather wide spread in the measurements (loading technique of mass spectrometer filaments[2]?). In fact with this spread it is not possible to decide whether the predicted decrease of enrichment of ^{10}B really occurs in the course of a long evaporation run and under the prevailing conditions.

5. References

1. H. London, The Separation of Isotopes, George Newnes Ltd., London, 1961.
2. A. Eberhardt, R. Delwiche and J. Geiss, Z. Naturforschg, 19a, (1964), 736.
3. J. Van Audenhove, H.L. Eschbach and H. Moret, Nuclear Instr. Meth., 24, (1963), 465.
4. K. Cohen, The Theory of Isotope Separation, McGraw-Hill, New York, 1951.
5. G. Zinsmeister, Vakuum-Techn. 13, (1964), 233.

A WIDE ANGLE TARGET SYSTEM FOR ANGULAR CORRELATION MEASUREMENTS

P.B. Smith

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A target system will be described which combines the following characteristics:

(a) no organic materials are used after the liquid nitrogen cooling.

(b) absorption is negligeable and furthermore essentially isotropic over a range of polar angles from - 5° to 128° for a 10 cm diameter counter at 19 cm from the target spot on the front side and from 55° to 140° on the back side. This range is naturally reduced if the azimuthal angle is increased appreciably above 45°.

(c) the target backing itself forms the vacuum wall permitting cooling by means of a jet of cold nitrogen from evaporating liquid nitrogen.

(d) precision centering of the target material with respect to counters.

The target can further be rotated about the beam axis without changing the position of the target spot, permitting application of a measuring technique which eliminates errors due to differences in channel settings of the two counters in an angular correlation measurement.

The target holder was designed with the object in mind of reducing or eliminating certain shortcomings usually found in target holders used for angular correlation measurements. In this type of measurement it is necessary to measure the coincidence intensity of successive radiations in two counters, each of which can be rotated about a centre located precisely at the target spot. If one considers the beam as the axis of a system of spherical coordinates there are two polar angles (one for each counter) and one azimuthal angle[1]). This places the demand of spherically (not merely cylindrically) symmetric absorption on the target holder. Very few target holders known to the author satisfy this requirement. The target holder of the Chalk River installation does, but this fails on the requirement, that the target holder be rotatable about the beam without change of the position of the target spot. This requirement is based upon the impossibility of setting identical channels in two counters, this in turn being virtually a requirement since by means hereof the measuring time is reduced by a factor of two. If one can rotate the target without disturbing the beam spot position, one can set up a conjugated geometry

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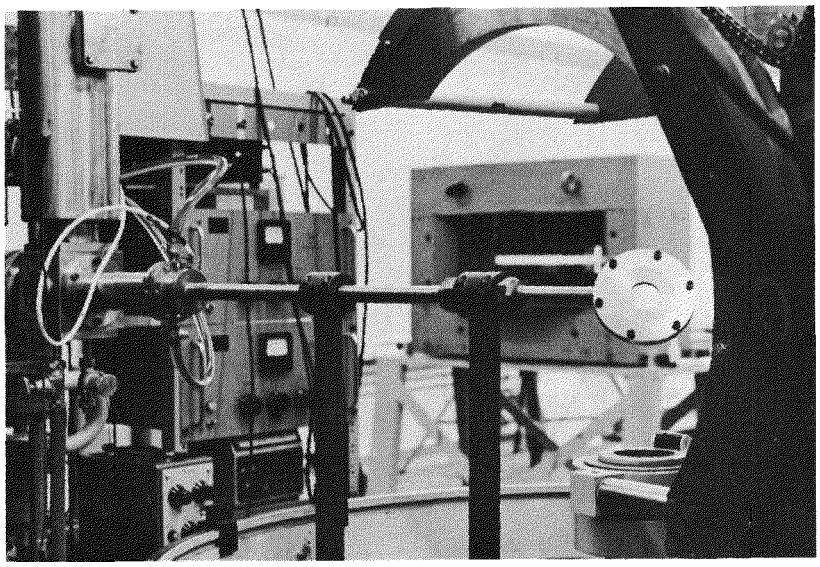
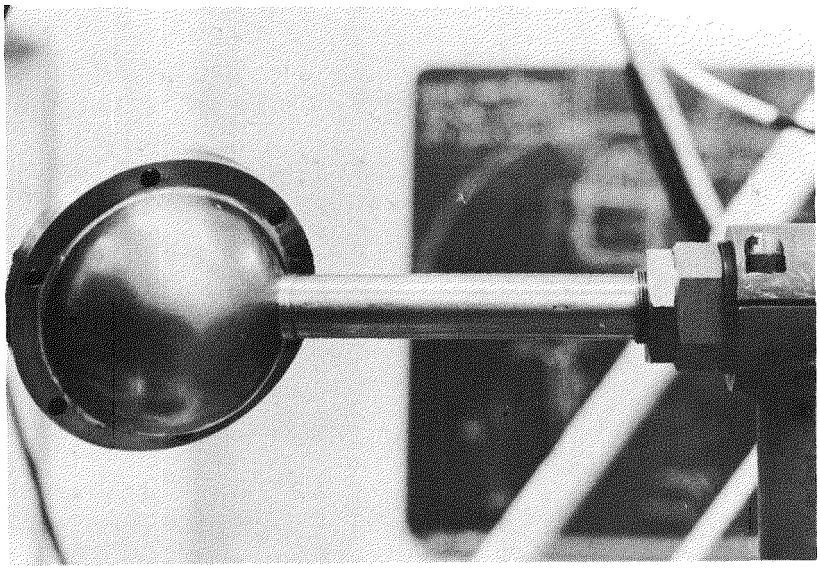
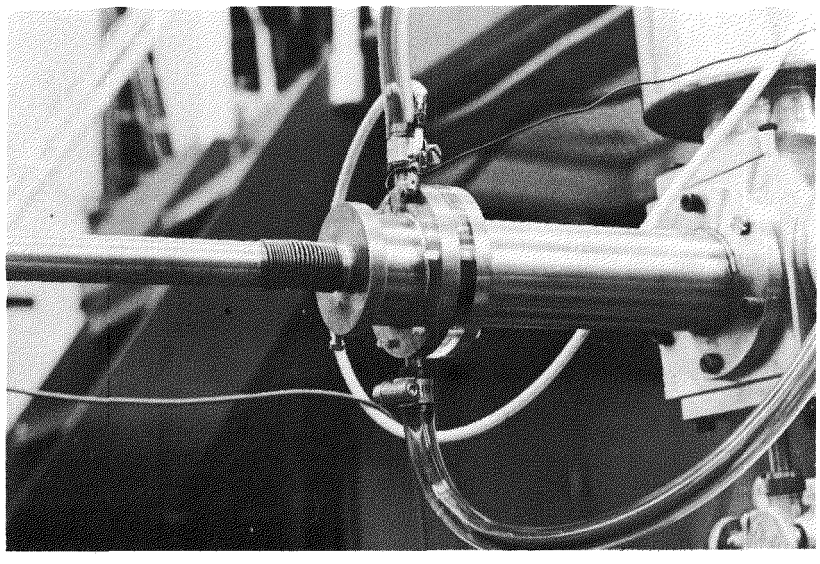
[1]) P.B. Smith, in Nuclear Reactions, edited by P.M. Endt and P.B. Smith, North-Holland Publishing Co., Amsterdam 1962.



AERE - R 5097 Fig. 9.1



AERE - R 5097 Fig. 9.2



AERE - R 5097 Fig. 9.3

(in the sense that the positions of the counters are interchanged) for every measuring point, eliminating the error due to channel settings not being identical in the two counters.

As a last requirement (besides the conventional demands on all accelerator targets of absence of organic materials and the possibility of good cooling) we mention the possibility of measuring over a range of polar angles from 0° to far above 90°. This is usually not considered to be necessary since care is taken to choose only those combinations of angles which lead to correlations symmetric about 90°. The author believes this to be an unwise policy which results in unnecessary loss of information. For that reason the angle of the target with respect to the beam was set at 30° in place of the usual 45°. This in itself placed severe requirements on the target backing thickness since at 0° and 120° the beam must traverse the backing through a distance of twice $(1/\cos 60^{\circ})$ the thickness of the material.

The completed target holder is shown in Figure 9.1. In this view the 0.3 mm thick tantalum target backing-vacuum wall is facing the camera. The reverse side of the holder is shown in Figure 9.2. The spherical stainless steel cap was pressed cold from a plate 0.5 mm thick by means of a die specially turned for the purpose. Also visible in this view is the insulating bearing (necessary for beam measurement) and adjusting nut (for centering) and lock nut. In Figure 9.3 the rotatable joint is shown. This is very simply an O-ring rotating seal made with slight extra clearance, so that the O-ring itself provides insulation. An insulating washer (not visible in the photograph) insulates the end of the bearing from the rotatable flange. In the bearing itself there is an oil cooled diaphragm, this being insulated again (by the perspex ring) for purposes of beam measurement on the diaphragm. The bellows are provided for the necessary flexibility between the rigid slit system and equally rigid target (plus counters) system.

Liquid nitrogen cooling extends around the diaphragm and ends just before the narrowing of the target tube (see piece no. 1, Figure 9.4), thus after the last O-ring. The details of the holder and in particular the metal-to-metal seal of the target backing (so far copper as well as tantalum have been used with success in this design) are also shown in this figure. This type of metal-to-metal seal was chosen in preference to a design using a metal gasket, since to the author's knowledge all metal gasket seals require a profiling of <u>both</u> surfaces to be sealed. Since it was demanded that unworked clean banks be used, in order to reduce the cost of the targets, gaskets were rejected. As can be seen the target was so designed as to reduce the thickness of the plates to a minimum so as to be able to measure over as wide as possible an angular range.

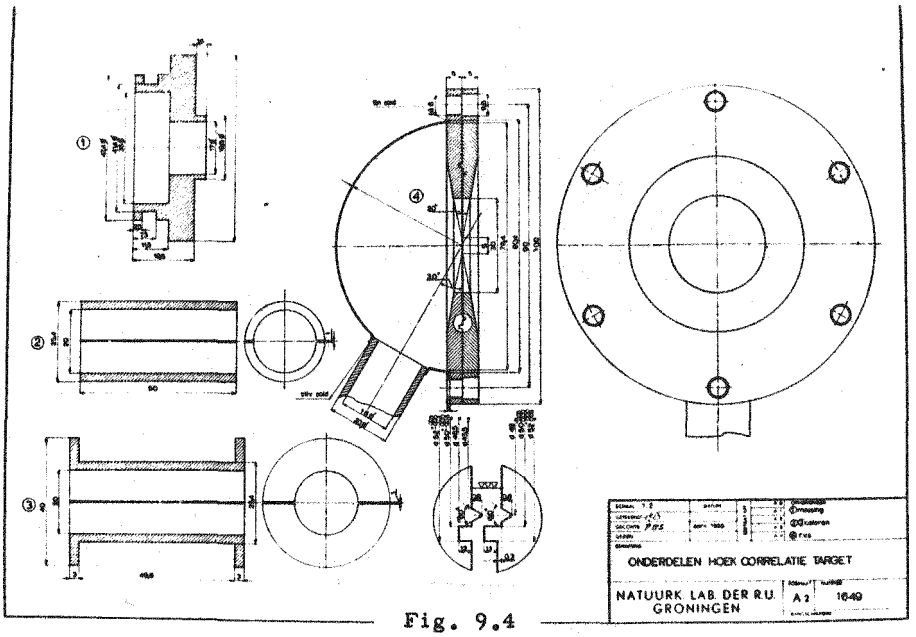


Fig. 9.4

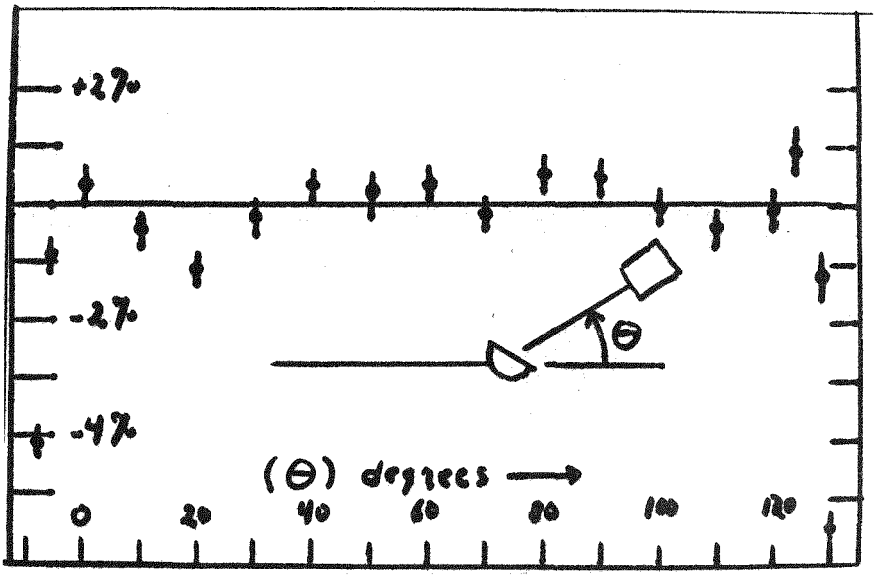


Fig. 9.5

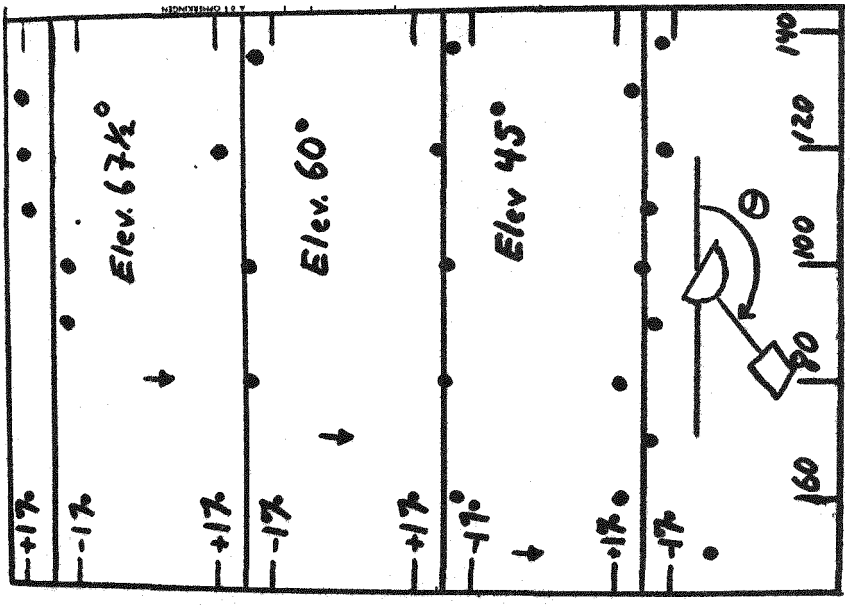


Fig. 9.6

In Figures 9.5 and 9.6 the range of isotropic measurement is shown. These measurements were made with a Cs^{137} source (1 mm diameter) at the centre of a target blank and with the target pumped out (to duplicate the slight deformation occurring in practice). The results on the front of the target (Figure 9.5) were found with the normal to the target in the plane in which the axis of the counter rotates. No systematic deviation above 1% is found for angles between $\Theta = 5^{\circ}$ and 128°. At -8° the intensity is 4% low, and at 130°, 5.5% low. The isotropic region at the back of the target is shown in Figure 9.6. The lowest curve shows the results under the same azimuthal condition as in Figure 9.5. The other three curves represent elevations of 45°, 60° and $67\frac{1}{2}^{\circ}$ (it should be noted that the counter was held at fixed elevation for the measurements, whereas in fact the true azimuthal angle is a function of the polar angle). The arrows at $\Theta = 50^{\circ}$ for 45° elevation, $\Theta = 70^{\circ}$ for 60° elevation, and $\Theta = 80^{\circ}$ for $67\frac{1}{2}^{\circ}$ elevation indicate the angles where the deviation exceeds approximately 5%. The expected isotropy to angles greater than the measured 140° would have no meaning, since the support post nearest the target prevents increasing the polar angle to more than 140°.

At this moment no qualitative results can be reported on the cooling, since the beam currents available up to the present are too small to require any cooling. It is planned to cool the target by means of nitrogen evaporating from liquid nitrogen, or with a spray of fog.

Titles of Figures

Fig. 9.1 A view of the completed target holder. In the foreground (right) one of the heavy arcs is visible upon which the counter with its lead shield can be raised.

Fig. 9.2 The reverse side of the target holder.

Fig. 9.3 A view of the beam limiting diaphragm and rotatable, insulated vacuum seal.

Fig. 9.4 A detailed construction drawing showing the metal-to-metal seal and the insulating bearings.

Fig. 9.5 The intensity as a function of polar angle measured with a Cs^{137} source at the centre of a target blank, facing the front of the target.

Fig. 9.6 The bottom curve is the same as in Fig. 9.5 except that the intensity is measured from the back of the target. The other three curves are for different elevations, as shown (see text).

ELECTROSPRAY[+]

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Chalmers University of Technology
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There are many applications for thin layers of radioactive material in the various branches of the nuclear sciences, and a great many methods and techniques have been modified, developed, and contrived as a means to this end. Generally speaking, the methods employed for the preparation of thin layers of radioactive material can be divided up into two groups, namely, physical and electrochemical. A third group can be considered under the heading "chemical" but chemical methods can not usually be considered as giving layers of sufficient uniformity for all purposes. A major advantage of using so-called electrospray is that uniform deposits can be obtained on ultra-thin backing (10 $\mu g/cm^2$) materials. Yields in the order of 70 to 100% can be obtained and if necessary, 100% recovery realised.

Here in Gothenburg we have developed a simple single lens system the details of which can be seen in fig. 10.1. The actual jet, or capillary, is contrived from a precision drawing pen unit (Rapidograph) of a type available having a selection of various bore diameters the smallest of which is 0.1 mm. diam. The jet is about 10 mm. long and made of stainless steel. The body of the pen unit is a hard bakelite-like material (C in fig. 10.1). A weighted bore cleaner B, is also provided which extends to the tip of the jet. In our case the complete unit is screwed into a brass holder so that the jet is just level with the lens aperture at D. The spring clip A holds B in position and also provides electrical contact between the bore wire and the brass holder. The backing holder F, is made from lucite and has a metal contact E, passing through the centre.

With the weighted bore wire in place, the unit can hold a little more than 50 μl of spraying solution. Using a distance of 5 to 6 cm between the spraying unit and the backing holder and applying a potential of 20KV, the above volume can be sprayed in about 15 minutes. Under the described conditions a continuous discharge can be observed between the tip of the jet and to within about 2 mm. of the backing. We have prepared samples of plutonium, thorium, and uranium having near quantitative yields on Zapon backings having a thickness of between 15 and 35 $\mu g/cm^2$. No trouble has been experienced in obtaining a radioactive area less than 2.0 mm. in diameter. In all cases ethyl alcohol spraying solutions were used.

[+]To be published in extended form in Nucl. Instr. and Meth.

The importance of humidity has been taken into consideration, and the entire arrangement can be housed in a temperature-controlled glove box. Normal operation is carried out at a temperature of 35°C. After more than 100 runs with radioactive material no trouble has been experienced with contamination of the working area.

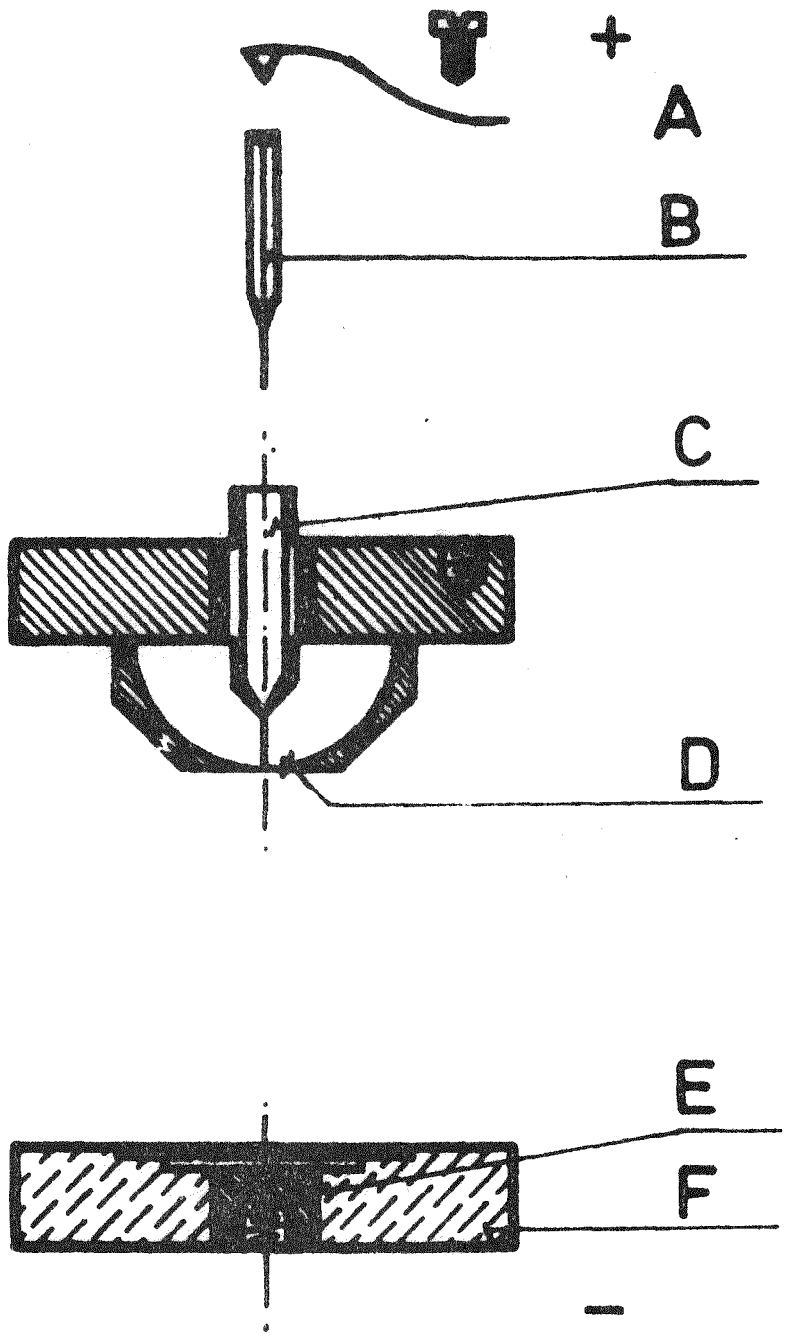


Figure 10.1 Single lens spraying gun.

ELECTROSPRAYING, VACUUM SUBLIMATION AND PAINTING

K. M. Glover (Mrs.) and P. S. Robinson

A.E.R.E., Harwell

We are concerned with the preparation of radioactive sources from the actinide elements both for high resolution alpha spectroscopy and for cross section measurements. Since quantities of only a milligram or less of many of these nuclides are available, it is desirable to have available as many techniques as possible, in order to cater for a wide variety of requirements. The three techniques which we have found most useful are discussed below.

(1) Electrospraying

Electrospraying has been developed specifically as a high efficiency method of preparing both thin uniform sources and sources of $1mg/cm^2$ thickness from nuclides which are available only in milligram quantities. The apparatus used meets these specifications, the overall deposition efficiency being about 75%. It is capable of making thin uniform sources of less than 20 keV full width half maximum peak heights for a 5.5 MeV alpha particle and can also make uniform sources up to $1mg/cm^2$ thickness. The optimum source size is 8-14mm diameter, and the activity can be deposited onto any conducting surface of suitable size and shape. Thus americium-241 has been sprayed on to the front face of a silicon gold surface barrier detector as an internal standard.

Description of the apparatus

A photograph of the apparatus is shown in Fig.11.1. The electrode assembly, consisting of jet, guard ring, collimator and collector plate, is contained in a perspex box with a front opening door. Two micromanipulators, left and right hand models, are fitted to a shelf in the box. One carries the collimator, which consists of a $^1/16$" thick brass ring, $^7/8$" internal diameter; the other carries the jet, a Luer-fixing hypodermic needle with the bore partially restricted by a 0.006" nichrome or stainless steel wire, together with the guard ring which is of the same dimensions as the collimator. The guard ring is attached to a $^1/4$" I.D. copper tube which is held in a clip on the micromanipulator arm. There is no vernier adjustment between the guard ring and the jet. The source tray is carried on a rotating table (5 r.p.m.) which, together with its motor, is housed on a second shelf on the box. The turntable is heated by a soldering iron element (125W, 230V) sandwiched between the brass top plate and a hollow Sindanyo cylinder fitted with slip rings. All metal

mountings are earthed to eliminate charge build-up. The source tray is earthed through a current measuring system to give an indication of the end of spraying. The electrical connections are made to sockets in the side of the perspex box and a microswitch relay switches off the power when the door of the box is opened.

A diagram of the electrode assembly is shown in Fig.11.2. The jet, guard ring and collimator are maintained at a positive potential above earth, and fed from individually stabilised power units via a 10MΩ safety resistor. The range of voltages applied to the electrodes are, jet, 5-8 KV; guard ring, 1-5 KV; collimator, 1-5 KV. The guard ring and collimator are used for focussing and additional focussing can be provided by the application of 50 cycles/sec A.C. to either the jet or the collimator. In general, sources are prepared by using the jet and collimator only; this arrangement does, however, produce a source with a slightly thinner area in the centre. For the best sources this is eliminated by using either the guard ring or 50 cycles/sec A.C. applied to the jet or collimator. A.C. modulation applied to the collimator results in a reduction of source area, so that this procedure is suitable for small sources of about $\frac{1}{8}$" diameter. A.C. modulation applied to the jet gives a better source with no resultant decrease in size and is therefore suitable for making sources up to 14mm diameter. For an accurately defined source area physical masking is necessary and the collimator voltage is arranged to make a source slightly larger than that required. To prepare the best high resolution sources (<20 KeV full width half maximum peak height), squared-off hypodermic needles are used. The diameter of the source increases with increasing concentration. The activity is sprayed on from alcoholic solution and the deposition times are 0.2-2μl/min for solutions of concentration 1-300 μg/ml. Up to 10% contamination of the alcohol by water can be tolerated without any deterioration in source quality. The hot plate is used only in the preparation of thick, 1mg/cm^2, sources which are prepared in one spraying. In general thick sources are built up by the application of many thin layers, igniting and rubbing down after each spraying to remove non-adherent particles.

(2) Vacuum Sublimation

Vacuum sublimation is the preferred method for preparing thin alpha sources for it consistently produces the best uniform sources with overall resolutions of the order of 12 KeV full width half maximum for a 5.5 MeV alpha.

Description of the apparatus

The apparatus is shown in Fig.11.3. The brass body (3" diameter by $3\frac{1}{2}$" long) is turned out of solid brass to eliminate leaks; the tufnol

base plate is held in position by studs, the vacuum seal being made by an 'O' ring. The top of the apparatus is of glass, mounted in a brass retaining ring, again held in position by studs and with an 'O' ring vacuum seal. The electrode rods, made in two halves for ease of decontamination, are clamped together by a tufnol bar; they are free to move vertically to allow for adjustment of filament height during firing and enter the chamber through 'O' ring seals in the base plate. The filament is made either of tantalum or ductile tungsten ribbon, 0.125" wide, $2\frac{1}{2}$" long and either 0.010" thick (tantalum) or 0.003" thick (tungsten), with a $^{1}/_{16}$" diameter dimple in the middle. Firing conditions are the same for both types of filament but tungsten gives better results. The electrodes and the filament are surrounded by a brass shield tube which supports the source backing holder; a silica baffle plate rests on the electrode rods. All of these components are replaceable to prevent cross contamination. The chamber is mounted directly on to the head of an Edwards diffusion pump type 203. The pressure in the chamber is measured by a Philips ionisation gauge and must be maintained at less than 10^{-5} cms Hg during firing. The power for the filament is obtained from a transformer the primary of which is fed from a 2KVA Variac, and the secondary delivers 60 amps at 10 volts. Firing is carried out at 2000-2400°C for five seconds to avoid fractionation, the variac setting having previously been calibrated using an optical pyrometer. Pre-firing is essential when a new filament is used; a blank tray is inserted, the system pumped down and the filament fired off to eliminate surface oxidation. This is repeated until a clean tray is produced. To make a source, the lid and the source holder are removed from the apparatus, the filament is raised and the activity pipetted into the dimple, taking care to prevent any liquid running over the edge, otherwise a non-uniform source will be produced. The activity is carefully dried off by passing a small current through the filament. The filament is lowered, the source holder with source mount and collimator in position loaded into the apparatus, the lid replaced and the apparatus evacuated. For active material with suspected organic content it is necessary to pump down and pre-fire at 3-400°C onto a blank tray, which is removed and replaced by a new one, after which the apparatus is pumped down to 10^{-5}cm and fired at 2000°C. High purity active material and solvents are necessary to obtain the best results. Nitric or hydrochloric acid solutions are used, the former being preferred if available, but essential for the preparation of thorium or uranium sources.

The efficiency of the apparatus is a function of the solid angle subtended at the source tray. The smaller the solid angle, the more uniform the deposit but the lower the efficiency. The efficiency for a

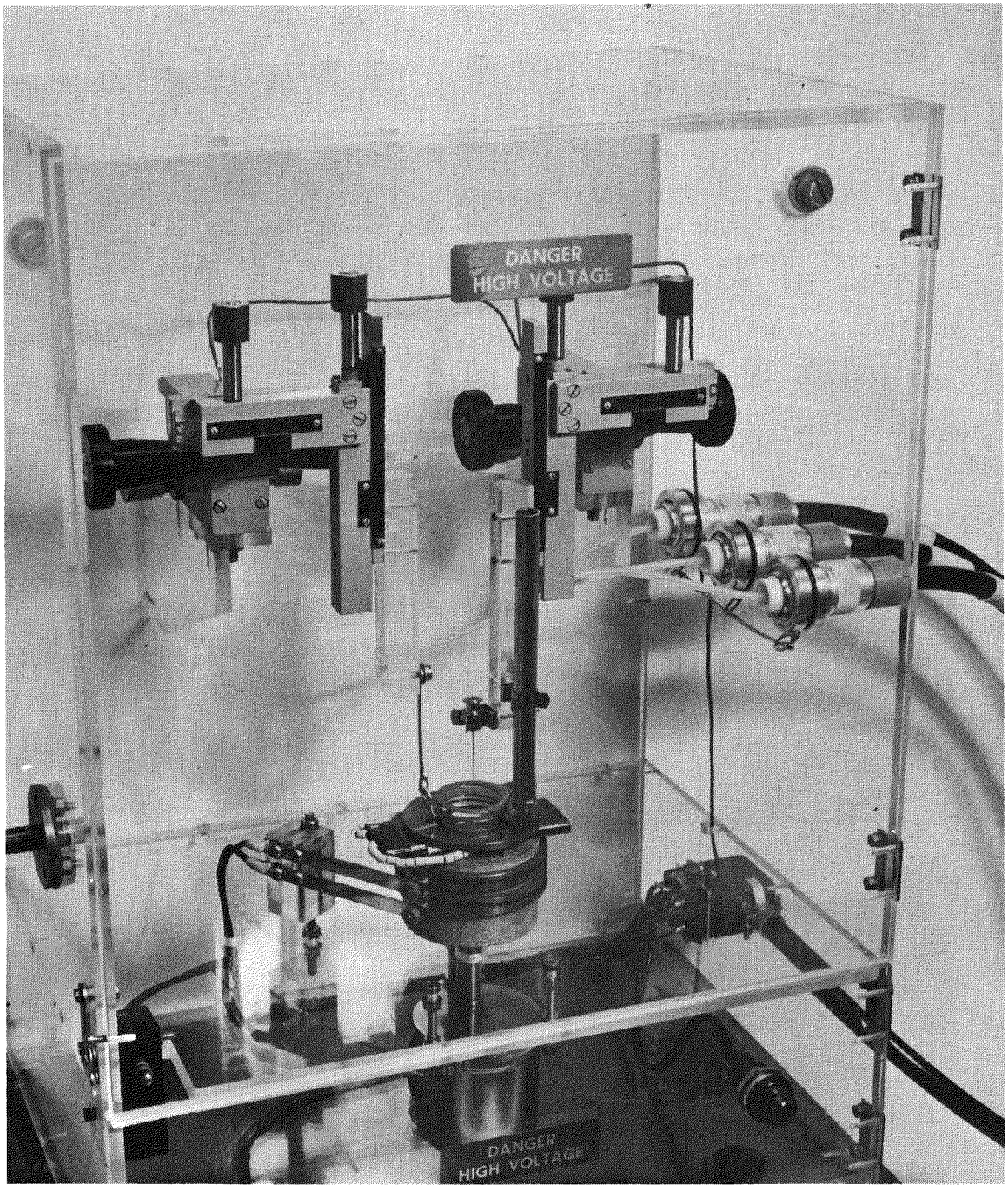
1-2mm diameter source is of the order of 1% and for a 1" diameter source 20-25%. However, this is a quick and reliable method of source preparation since it takes less than 30 minutes to prepare a 1cm diameter source of e.g. 10^6 alpha disintegrations per minute of Am241. The equipment is mounted on a mobile trolley and the exhaust from the vacuum line is connected to active extract. For high activity samples (greater than $10^6\alpha$ dis/min) the vacuum sublimation chamber itself is mounted in a glove box with an external vacuum system.

Results

Fig.11.4 is a spectrum of Americium 241 showing the alpha particle fine structure. This is typical of the best sources prepared by vacuum sublimation; electrosprayed sources do not give quite such a good spectrum.

(3) Painting

Painting is a tedious technique and is very definitely an art rather than a science, nevertheless it is still useful for the preparation of uniform deposits of up to $8mg/cm^2$ over areas of several square inches. Densitometer measurements on an autoradiograph of one of these sources indicated ± 2% variation in thickness over the source area. The active solution is evaporated to dryness on a vacuum desiccator and the residue dissolved in a few microlitres of alcohol; 3% cellulose nitrate is added and the solution is diluted with alcohol. Typical quantities used would be 10mg plutonium and 0.4ml ethyl alcohol together with 2ml cellulose nitrate and 2ml acetone. The solution is applied to the backing material with a glass woll paint brush made by cementing glass wool fibres into a glass capillary tube with Araldite and trimming the fibres to shape. The backing foil is masked to define the area accurately; a thin layer of paint solution is applied, allowed to dry and fired for one minute at 800^oC for platinum and stainless steel, ten minutes at 500^oC for Aluminium. The backing foil is removed from the furnace, allowed to cool and rubbed to remove any loose particles before application of the next coat. This procedure is repeated until the required thickness of active deposit has been built up; it can occupy many hours. In order to achieve uniformity, great care must be taken to apply the brush strokes in different directions for each successive coat.



AERE - R 5097 Fig. 11.1

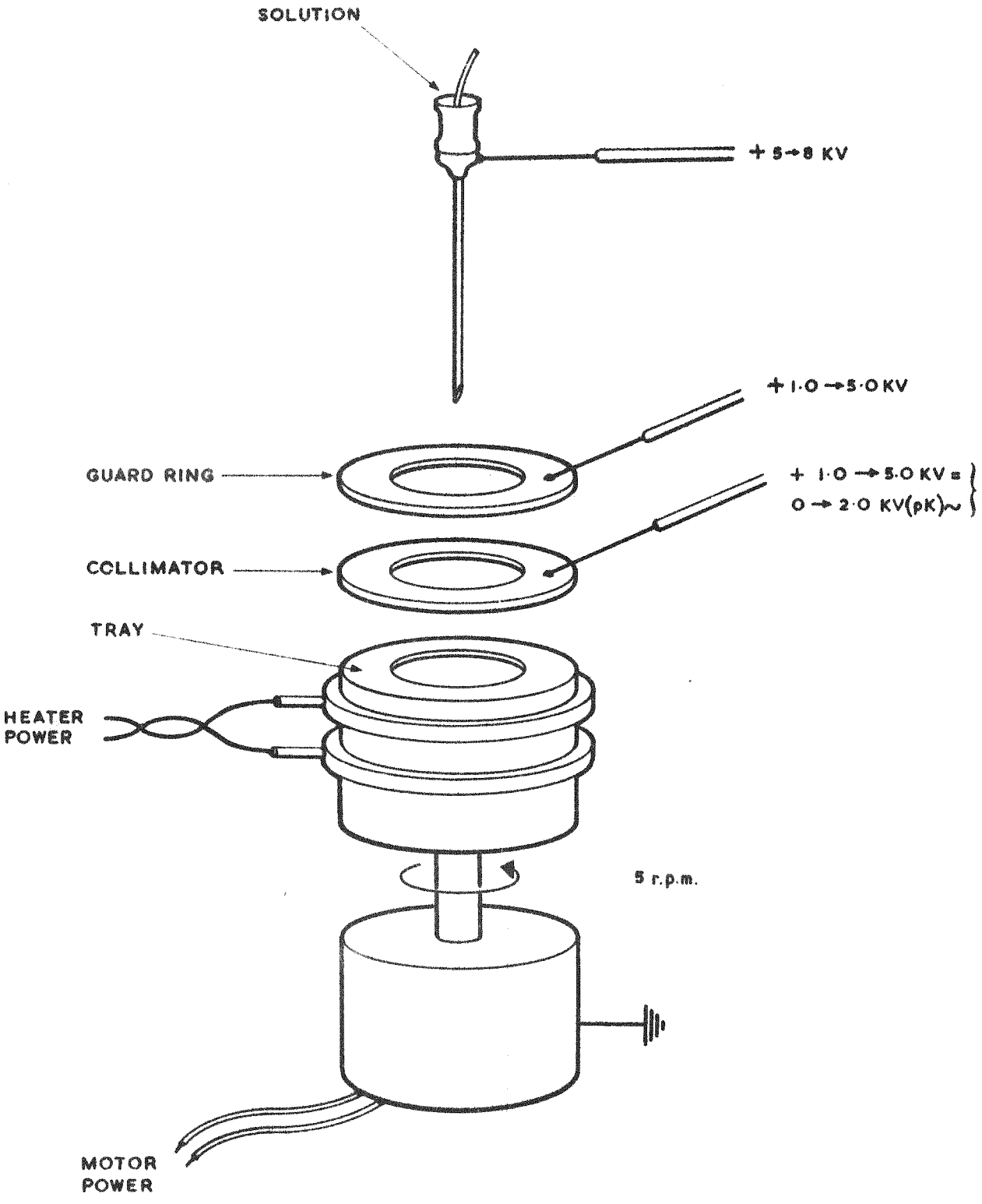

SOLUTION
+ 5→8 KV
+ 1·0→5·0 KV
GUARD RING
+ 1·0→5·0 KV ≡
0→2·0 KV(pK)~
COLLIMATOR
TRAY
HEATER
POWER
5 r.p.m.
MOTOR
POWER

Fig. II·2

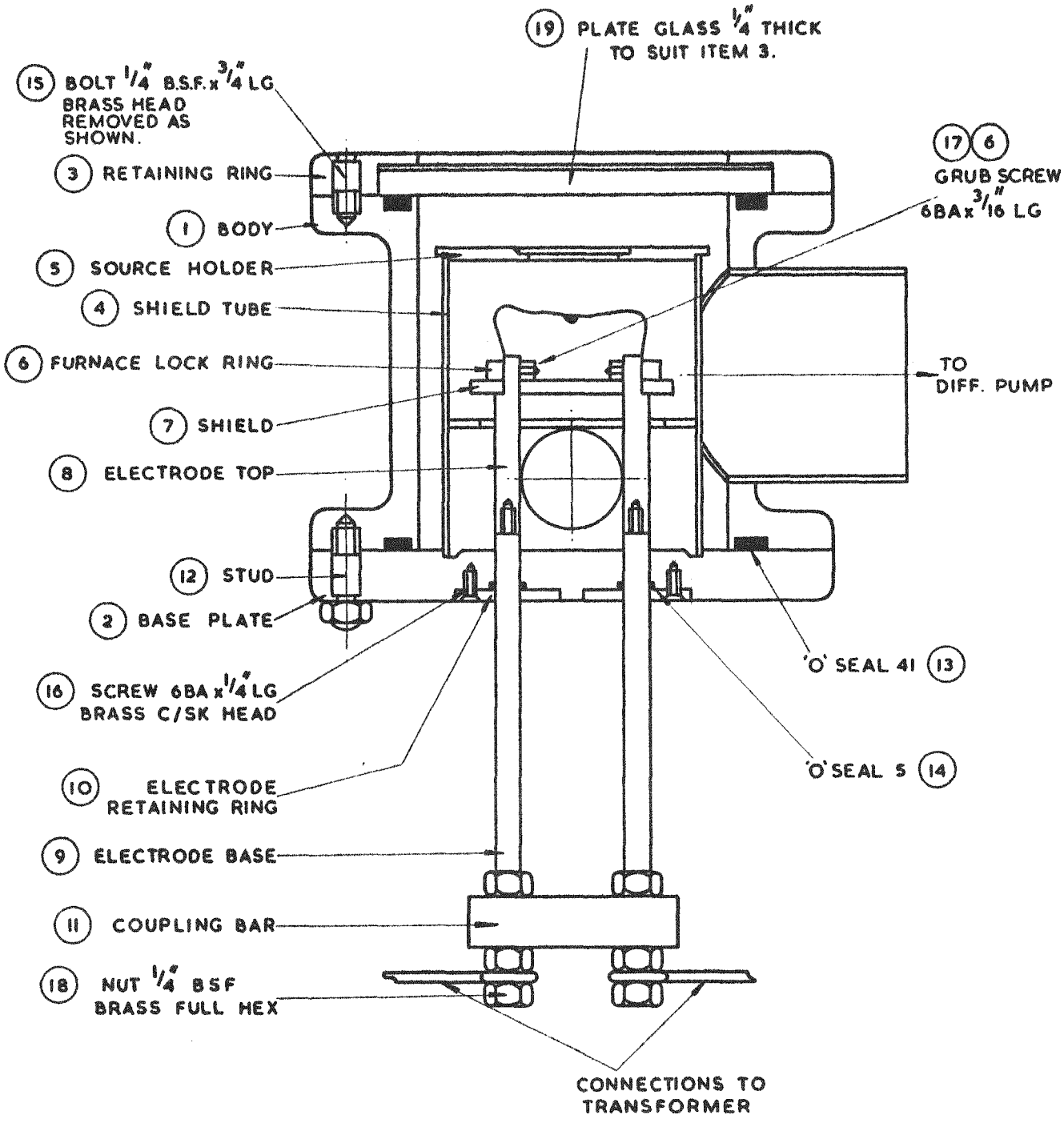


Fig. II-3.
Vacuum Sublimation Chamber.

60/30/3

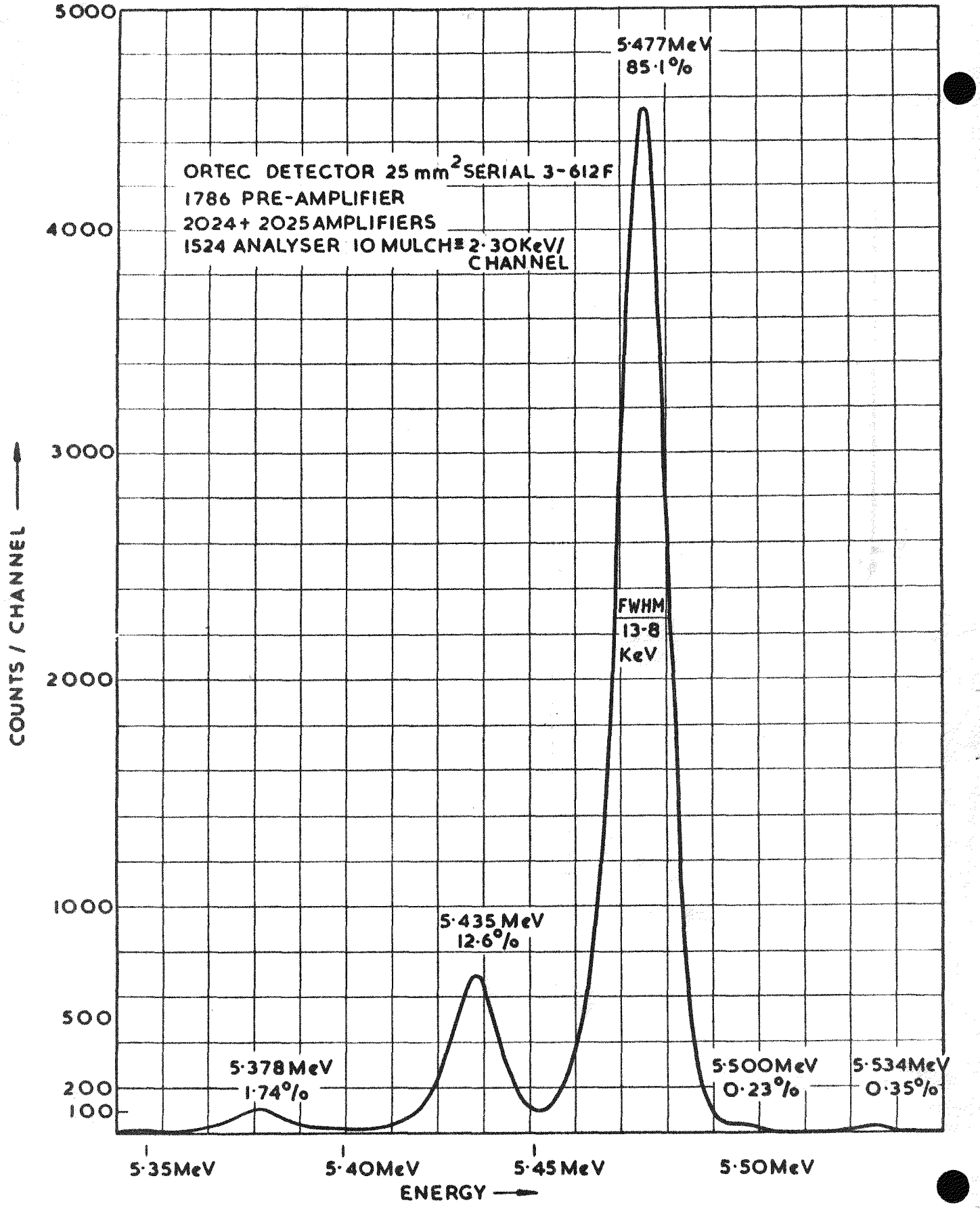


Fig. 11·4.

∝ Fine Structure from a Vacuum Sublimed ^{241}Am Source.

PAPER 12

THE PREPARATION OF SAMPLES BY ELECTROCHEMICAL METHODS

V. Verdingh

C.B.N.M., Euratom, Geel.

1. Electrodeposition

Advantages of preparing samples by electrodeposition are:

1. The element is deposited in its metallic state.
2. Deposits of different thicknesses can be made on a variety of backings, though generally limited to backings for measurements in 2 π geometry.

An interesting method is micro-electrolysis by which samples on thin backings can be prepared using one drop deposited on the foil. The foil serves as a cathode, the anode being a small platinum ring. A small column of solution is held between the electrodes by surface tension. We used this method for preparation of gold and cobalt samples on very thin plastic foils covered with a thin conductive gold film (total mass: 20 $\mu g/cm^2$). It may be adapted for the deposition of other substances on thin backing material.

Anodic oxidation sometimes may be used in the preparation of thin self-supporting metallic layers by etching to a specific thickness. Another application is the removal of a thick backing on which a thin film of another metal has been deposited by electrolysis or vacuum evaporation e.g. Ni on a Cu backing.

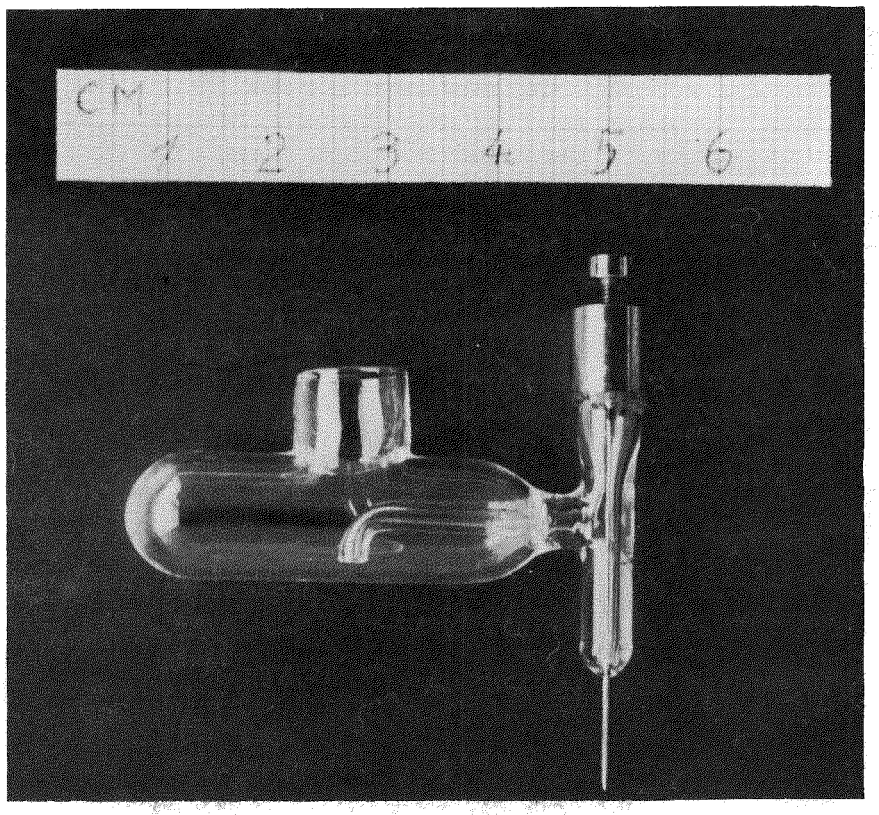
Plutonium and uranium electrolyses

We also studied the so called electrodeposition of uranium and plutonium onto stainless steel, nickel, platinum, graphite and aluminium. Very often the result of such an electrolysis is the precipitation of a complex hydroxide. The adherence is sometimes increased by baking out or calcining the deposit.

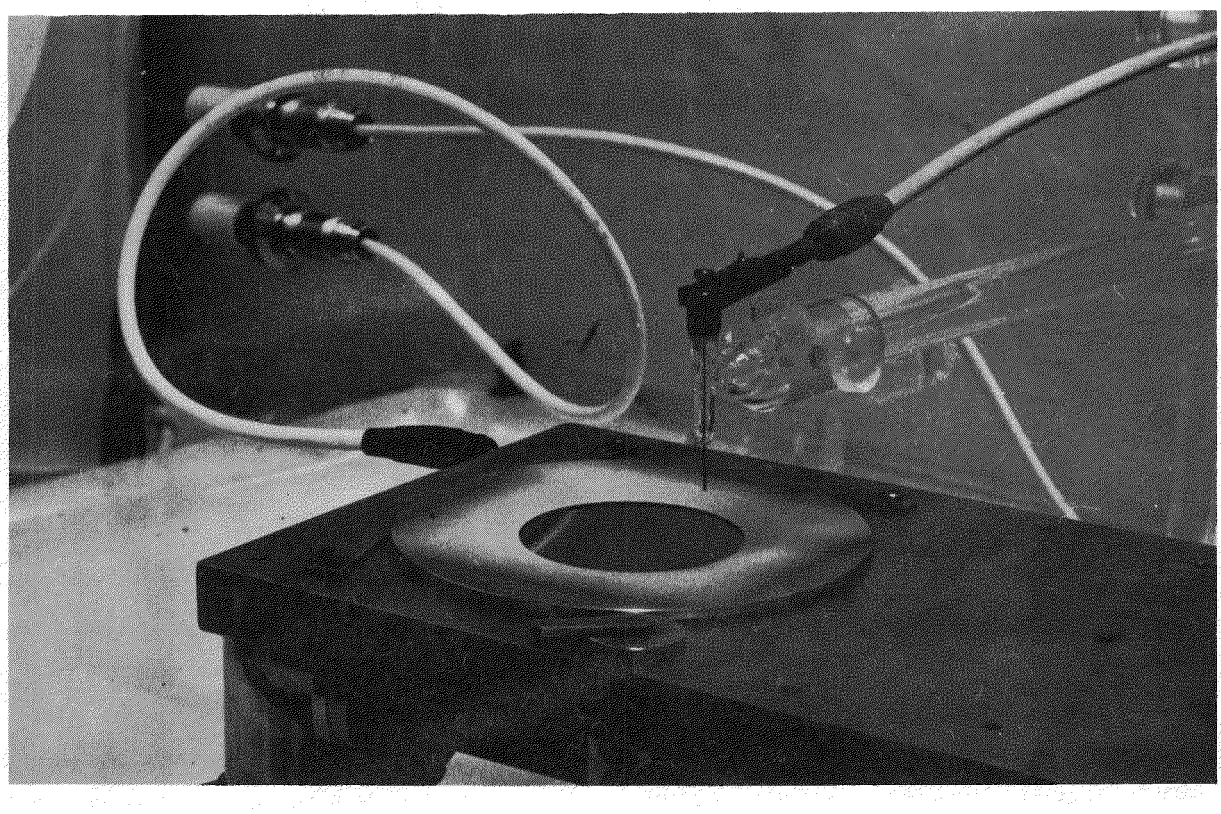
Several electrolytes were used:-

1. EDTA. This electrolyte decomposes and the maximum rate of deposition occurs after total decomposition of the EDTA. The maximal amount of Pu deposited was of the order of 250 $\mu g/cm^2$.

2. A more extensive study was made of ammonium oxalate as base electrolyte. During the preparation of such deposits the pH of the solutions changes constantly and has a determining influence on the amount of material that can be deposited. Good results were obtained by controlling the pH during the electrolysis by means of an automatic pH regulator having a special type of glass electrode with a flat end positioned in the neighbourhood of the cathode. Plutonium deposits



AERE - R 5097 Fig. 12.1



AERE - R 5097 Fig. 12.2

up to 660 $\mu g/cm^2$ were obtained on a nickel cathode of 20 cm^2.

II. Electrospraying

A quite useful method in the preparation of samples on any kind of conducting backing proved to be electrospraying. The method was especially used for deposition of the isotopes of U, Pu, Am and of B, Li, Co, Ni and Cu. The deposits varied in thickness from a few micrograms per cm^2 up to 2 mg/cm^2. Backings varied from a 10 $\mu g/cm^2$ V.Y.N.S. to stainless steel or platinum backings. The area of samples prepared in this way lay between a few mm^2 and 750 cm^2.

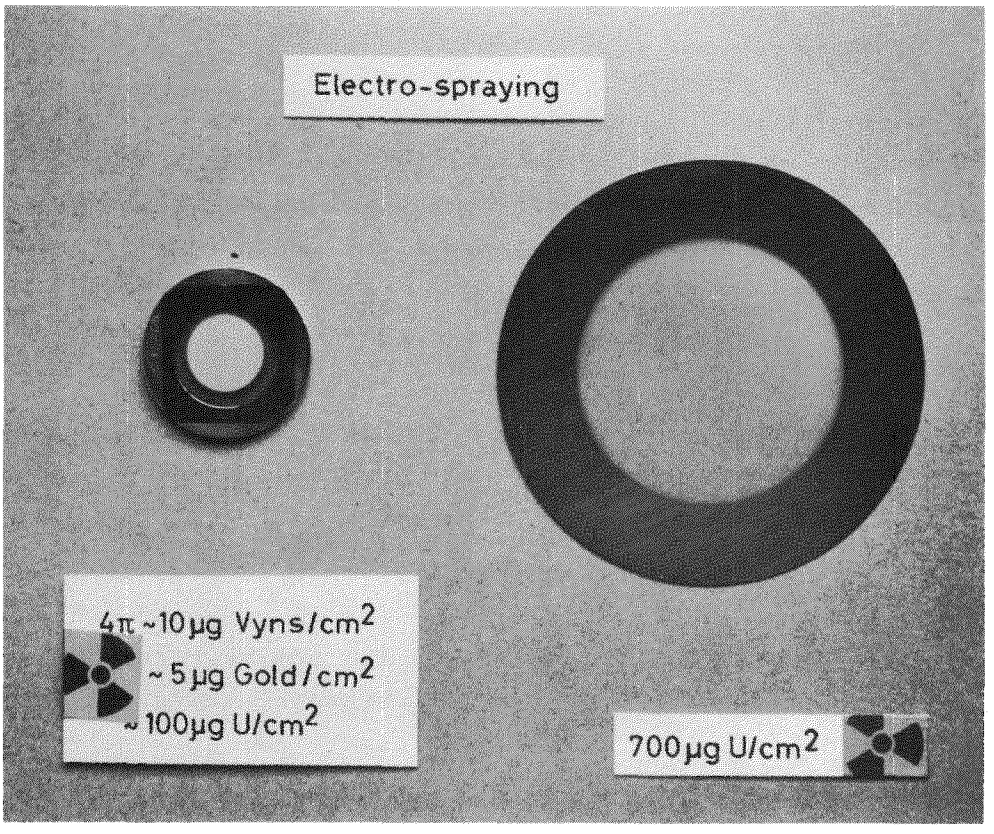
Experimental procedure

Under the influence of a high tension field - (3000 - 6000 volts) a liquid is forced through a narrow capillary. A spray of tiny droplets is projected on the backing that can be any metal or a plastic foil rendered conductive by an evaporated metal layer. Choice of compound and solvent is important. The compound has to be stable and not hygroscopic. The solvent has to be sufficiently volatile to evaporate during its passage from capillary to backing. The electrostatic acceleration in the high tension field is high enough to assure good adherence of the deposited particles to the backing. The shape of the samples is defined by masks; so an edge effect has to be expected.

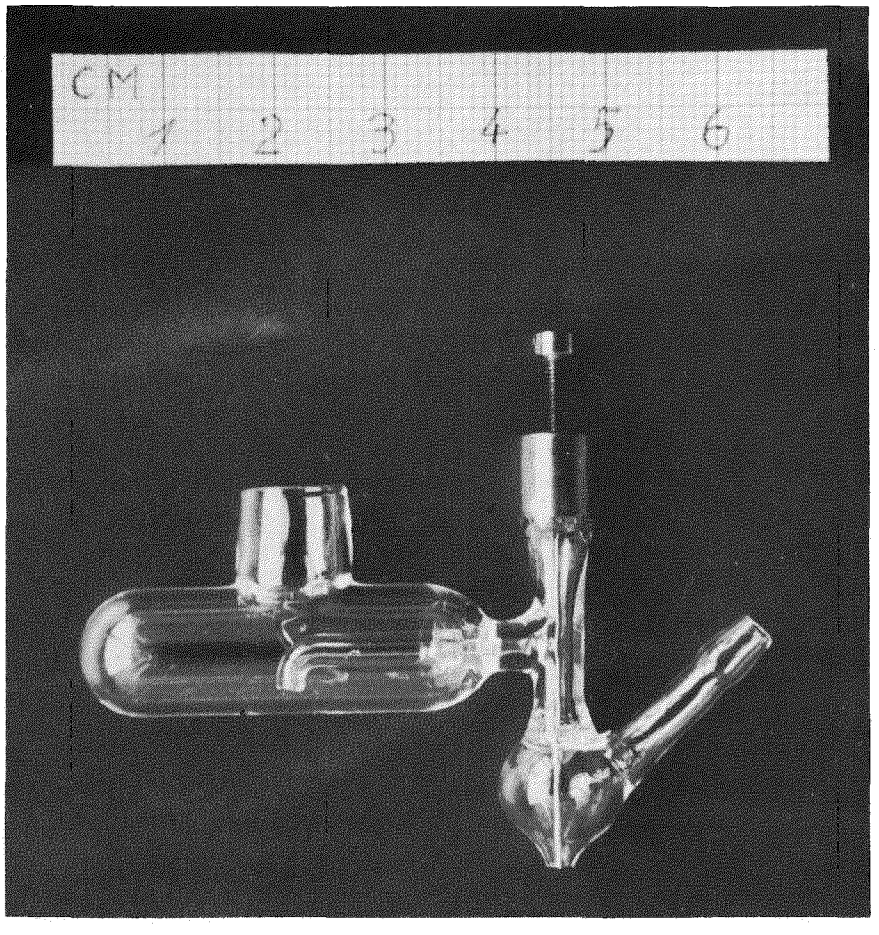
A disadvantage of the method is the fact that a compound of the needed element is deposited. In the case of targets for 2π measurements the ratio element/compound can be improved by calcining to the oxide after spraying.

An advantage is the fact that the method can be applied even when only a small quantity of target material is available as in the case of valuable isotopes.

The essential part of the equipment is the capillary which has to assure a continued regulated spray over a long period when large surfaces are to be coated. Good results have been obtained with a type of capillary shown in Fig. 12.1. Surfaces up to 10 x 10 cm can be covered using a mechanical sweeping device described below. (Fig. 12.2). Homogeneities up to $\pm$ 2% were obtained for sprayed surfaces up to 20 cm^2 with a specific covering of 100 $\mu g\ U/cm^2$. A single capillary can be used for quantities up to about 1 mg/cm^2. (Fig. 12.3). Thicker samples of several mg/cm^2 were prepared using a group of capillaries rotating with the aid of a synchronous motor. However the demand for still larger samples (25 cm x 25 cm) covered with several mg U/cm^2 forced us to modify our capillaries in order to obtain a bigger yield and a steady flow over a long period. For this we used the capillary shown in Fig. 12.4. This is a normal platinum capillary centered in a wider glass nozzle with an opening through which a gas stream is blown at 0.8 kg/cm^2 pressure. The opening of the platinum capillary is about 0.02 - 0.05 mm larger than the previously described ones.



AERE - R 5097 Fig. 12.3



AERE - R 5097 Fig. 12.4

The opening of the glass nozzle is 2 mm in diameter. The applied voltage lies between 8000 - 10000 V; the current passing while spraying is 5 - 10 μA. The mechanical sweeping device was modified to allow spraying of a maximum surface area of 28 cm x 28 cm (Fig. 12.5). The time needed for a complete sweep of the table is about 60 minutes. In this way U-235 samples >1 mg U/cm^2 upon scintillator-foil backing were prepared in dimensions up to 25 cm x 25 cm. (Figs. 12.6 and 12.7).

The chemical form deposited was again uranium acetate which adheres very well on the backing even under rough manipulation. The homogeneity of the layer was about 10%. The deposition rate for a normal capillary spraying with a 5% uranium acetate solution in methanol is about 50 μg compound/min; for the modified type the deposition rate for a similar deposit increases to about 150 μg/min.

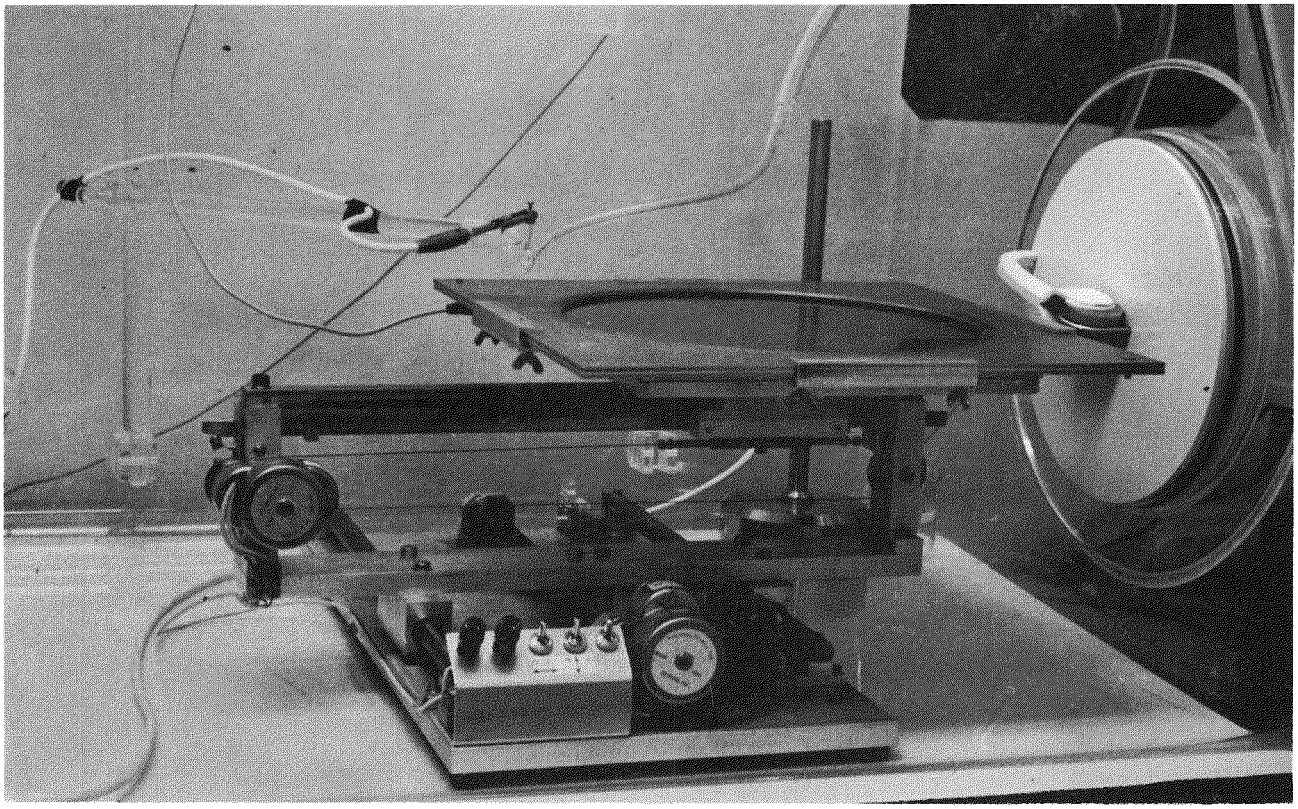
III. Electrophoretic deposition

The limiting factor in the electrospraying method is the quantity of material that can be deposited. Electrophoretic deposition proves to be a versatile coating method for quantities up to 12 mg/cm^2 and even more. Uniform coatings on different shapes of backings can be obtained. The method has been known for many years. In our case it was adapted for the preparation of samples for neutron experiments. Finely divided metals or oxides are suspended in a polar organic liquid having a low electrical conductivity. The addition of specific substances (e.g. organic and inorganic acids, etc.) causes particles to migrate under the influence of a high tension field up to 3000 V and to form quite adherent coatings on the cathode or anode. One type of cell is shown in Fig. 12.8.

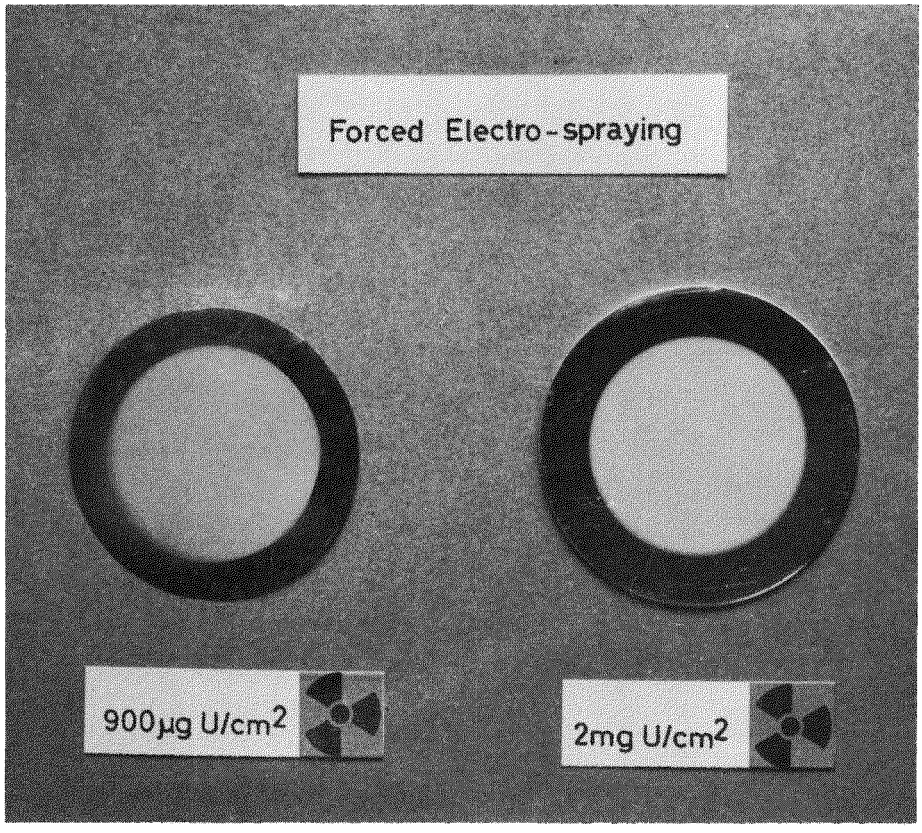
The adherence to the backing depends on:

- nature of the electrode: Al, Pt or Cu...
- quantity of deposit
- choice of the additive
- treatment of the sample after preparation
- nature of suspension (size of the particles).

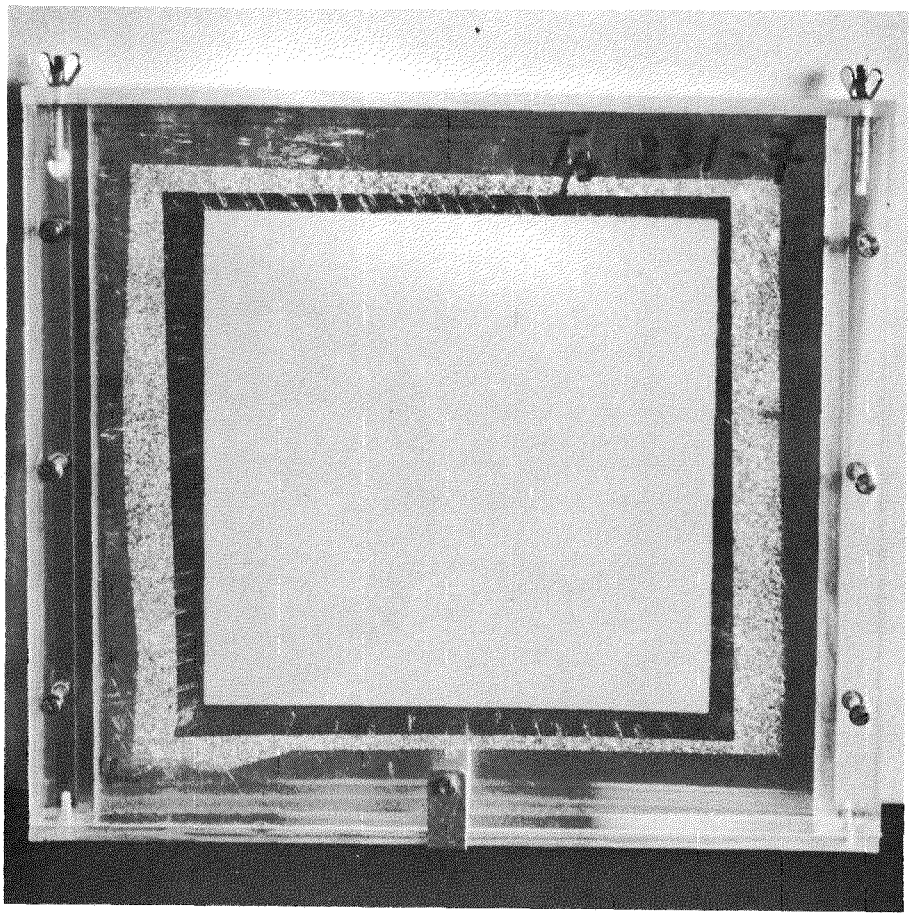
The last cited factor is of primary importance but reduction of particle siz is a complicated and dangerous operation especially when using highly radioactive isotopes. Here grinding was excluded and a method of chemical preparation of the powder had to be looked for. The method as adapted to our purposes worked quite successfully for the preparation of various samples of natural and highly enriched uranium of different shapes and dimensions. Fig. 12.9 shows deposits on shaped backings and Fig. 12.10 on 8μ Al foil.



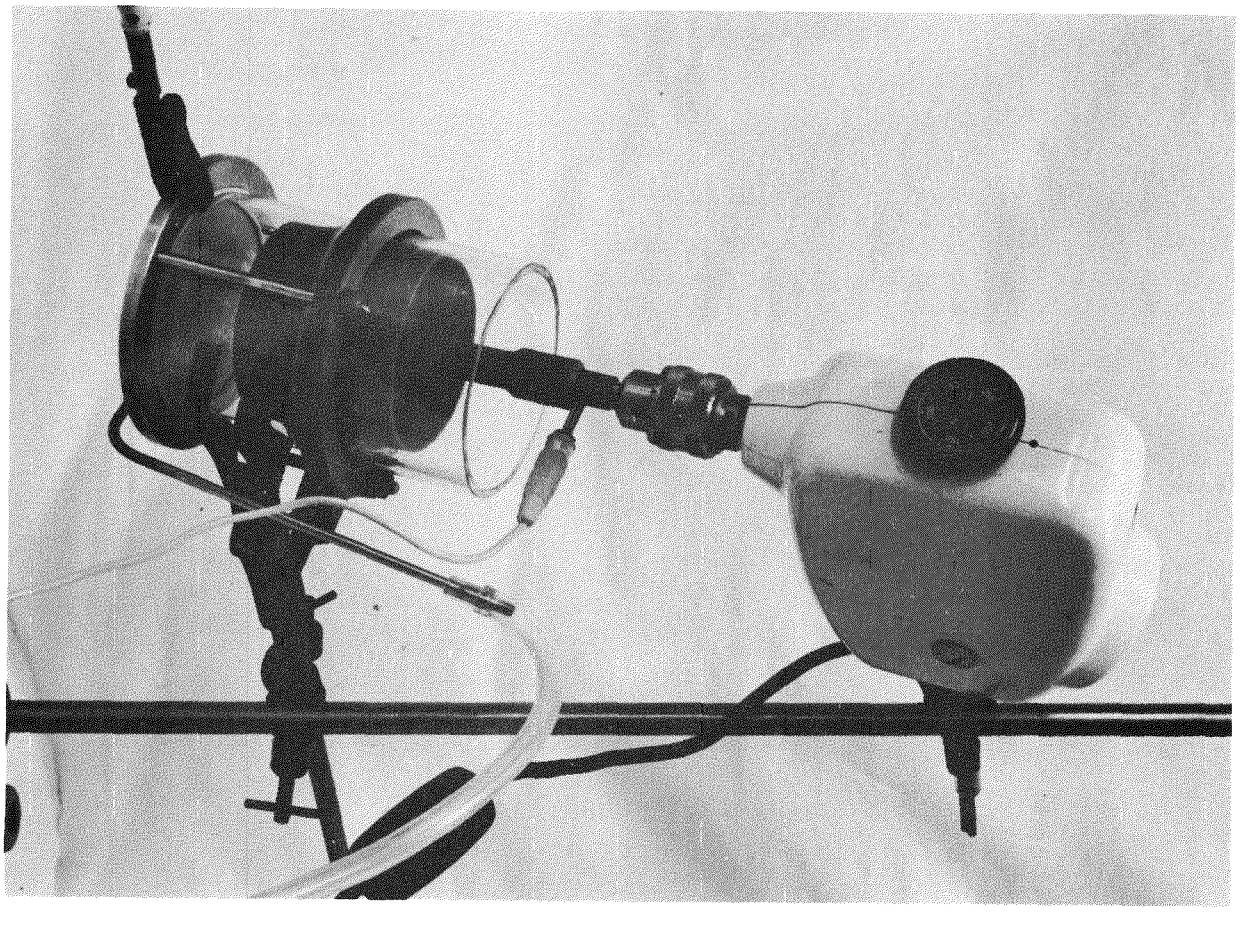
AERE - R 5097 Fig. 12.5



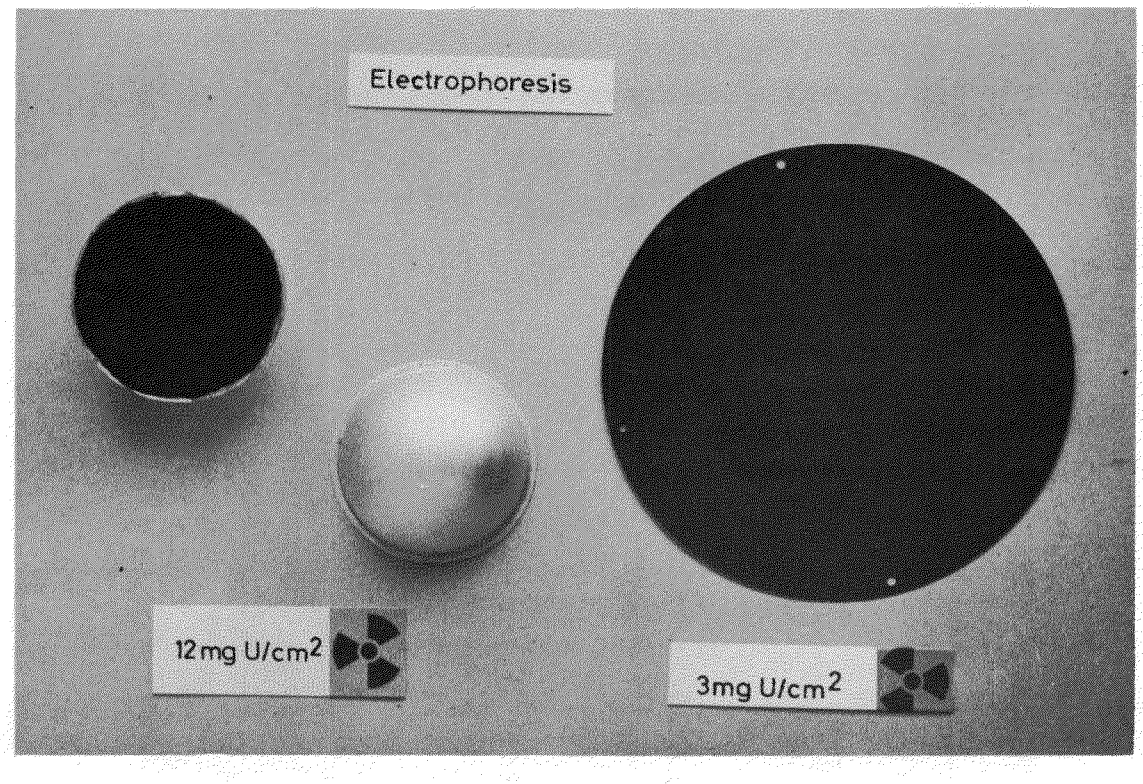
AERE - R 5097 Fig. 12.6



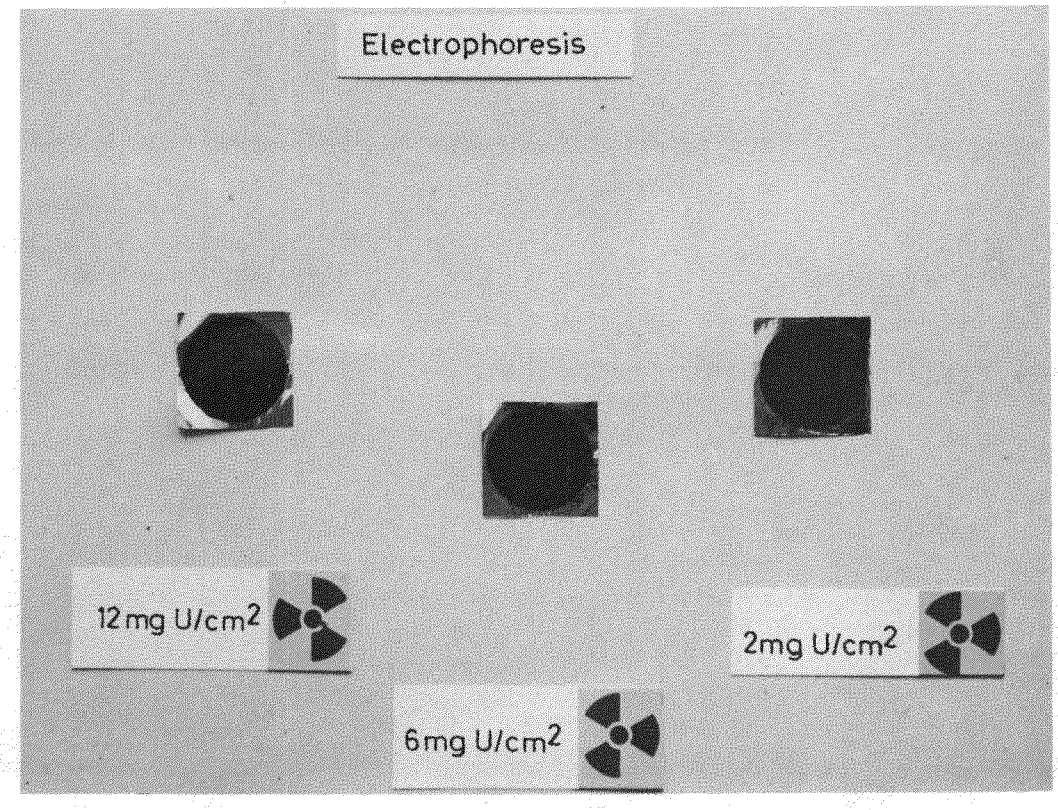
AERE - R 5097 Fig. 12.7



AERE - R 5097 Fig. 12.8



AERE - R 5097 Fig. 12.9



AERE - R 5097 Fig. 12.10

ELECTROPLATED ISOTOPIC TARGETS

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A.E.R.E., Harwell

1. Introduction

Electroplating is a very suitable technique for the preparation of elemental isotopic targets of a variety of metals over a wide range of thickness. The Electromagnetic Separation Group at Harwell has used this method extensively over the past 15 years and has sent out many hundreds of targets prepared in this way. Although rolling is now the preferred technique where applicable, electroplating is still frequently used for the preparation of a variety of targets.

The method is basically simple and efficient and can be used for the preparation of both backed and self-supporting foils. A high degree of uniformity can be obtained by taking suitable precautions and any unused isotope can be readily recovered.

The factors governing the deposition process are discussed briefly below and the experimental procedures for a wide variety of elements are also listed.

2. General considerations

a) Estimation of the weight of the deposit

In an ideal case the cumulative current flow will give an exact measure of the weight of element deposited but in practice, because of secondary electrode reactions, the process is rarely quantitative. For this reason we normally estimate the target weight by plating a solution of known concentration to exhaustion. Where possible the loading is checked by weighing on an accurate microbalance. This last technique is of limited value however in the cases of very light targets, reactive deposits such as lithium and targets plated onto masked or massive backings.

b) Quality of the deposit

On the industrial scale, using concentrations of between 3 g/litre and 30 g/litre and current densities of 50 amps/sq. ft. (32.5 ma/cm^2) satisfactory deposits of a wide variety of metals are obtainable. But in the preparation of isotopic targets we are generally limited to the amount of isotope available and concentrations of 30 mg/litre to 300 mg/litre are more usual. Attempts to deposit from these dilute solutions at around 30 ma/cm^2 generally result in

a powdery and non-adherent deposit. This effect may be due to the precipitation of basic salts at the cathode surface which become included in the deposit [1] or to the liberation of hydrogen on the cathode surface. By reducing the current density to around 10 ma/cm^2 more satisfactory deposits are obtainable in a number of cases.

Controlled potential deposition which is used to advantage in obtaining reproducible deposition in analytical electro-chemistry is generally not applicable to target preparation. This is because of the incompatibility of the lay-out of a practical plating bath with the requirements of a meaningful reference electrode measurement. In consequence the plating voltages and current densities used are those which have arbitrarily been found to give the best results.

In our experience, in the absence of controlled potential techniques, the most consistent results can be obtained by using carefully designed power supplies. By eliminating the very large a.c. ripple which is present on many commercial rectifier systems it is possible to reduce the degree of hydrogen formation and to obtain better quality deposits.

The surface finish of the backing material will also affect the quality and uniformity of the final deposit and it is essential to prepare the backing with care. Because of the very poor adhesion of electro-deposits to highly polished supports these should be avoided unless a self-supporting foil is required, and the surface should be electro-polished or etched prior to deposition.

c) Purity of the deposit

The very high quality and surface finish of industrial plating is frequently due to the use of small quantities of additives to the plating bath. These include:-

[i] wetting agents used to prevent pitting by facilitating the release of gas bubbles from the deposit.

[ii] buffer solutions used to maintain a constant pH during the deposition thus preventing the precipitation of hydroxides and basic salts. The most common buffer solutions contain borates, fluorides, fluoroborates, oxalates and citrates.

[iii] levelling agents used to obtain a smoother deposit. These include a wide range of high molecular weight organic compounds, such as gelatin, which are preferentially absorbed on the high active spots on the deposit and which may form impurity inclusions in the deposit.

[iv] brightening agents which modify the character of the deposit and are frequently foreign metal ions. Nickel, cobalt and copper are all used to improve the quality of cadmium plating.

Because of the stringent purity requirements of most isotopic targets the techniques listed above cannot generally be used. For certain elements such as iron and tin the use of buffered solutions appears to be unavoidable. In these cases only pure organic complexes are used and undesirable compounds such as fluoroborates are carefully avoided.

d) Uniformity of the deposit

In our experience the following points must be observed to ensure maximum uniformity of the target

[i] The anode should be a perfectly plain, flat piece of inert metal.

[ii] It should be parallel to the cathode and as far removed as practicable.

[iii] It should be as big as or bigger than the cathode.

As a further precaution the anode or cathode should be rotated during the deposition. We in fact rotate the whole electrolysis cell and keep the anode stationary (see section 3(a)). This rotation also provides the effective stirring action which is essential for good quality deposition.

3. Experimental

a) Electroplating cell

The electroplating cell is shown diagrammatically in Fig. 13.1. The cell is made from a section of standard Pyrex pipe-line which is bolted onto a brass plate using normal pipe-line connections. By the use of different diameter cells and masking techniques a wide range of target shapes and sizes can be made on the same apparatus. The cathode backing material (D) is clamped between the cell body (A) and the base (B) using a rubber 'O' ring (C) to effect a seal. The whole assembly, which is shown in Fig. 13.2, is mounted on a variable speed turntable to provide the necessary stirring of the electrolyte, and to give greater plating uniformity.

The electrical connection to the cathode is made via a small bush in the centre of the turntable.

b) Electrodes

(See also Section 2 (d).

Fig. 13.3 is a photograph of the anodes which are used for target preparation. These are normally made of platinum which can be readily fabricated into the required shape and is unaffected by any of the electrolytes which are commonly used.

The main cathode materials which are used are listed in Table 13.1. In all cases care must be taken to ensure that the plating solutions will not attack the backing material or serious contamination of the target may result. The treatment of the materials prior to deposition depends on whether a backed or self-supporting target is required. Table 13.1 includes details of pretreatment.

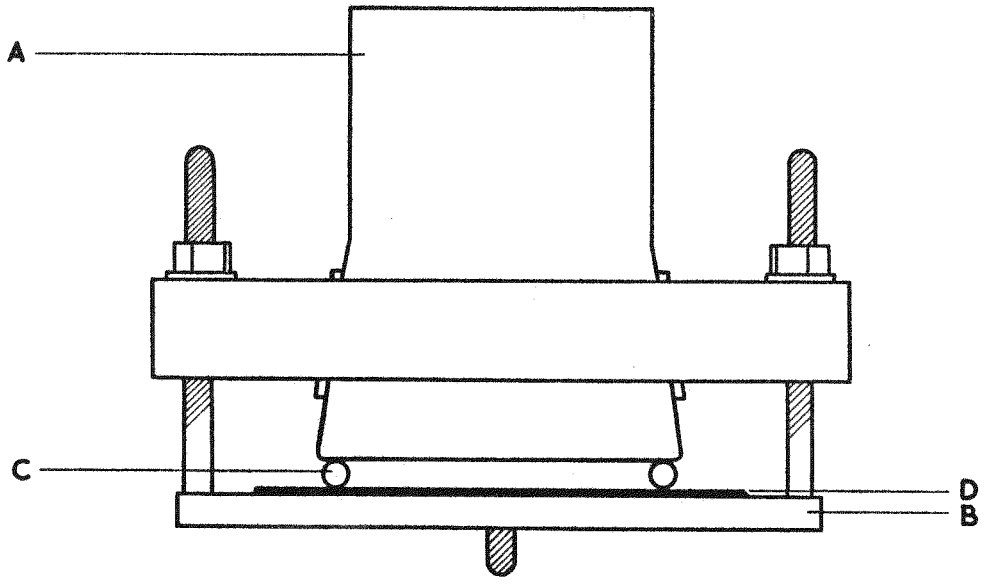

Fig. 13.1

Electroplating cell

Table 13.1

Details of pre-treatment of the more common backing materials used for electrodeposited isotopic targets

Backing material	Target details		Pre-treatment	Comments
	Backed	Unbacked		
*Copper: <0,0005"	$\lesssim$500 μg/cm^2		Degrease with acetone	Use bright side
	$\gtrsim$500 μg/cm^2		Wash with O, OIN HNO_3	Use matt side
		All weights	Wash with O, OIN HNO_3	Use matt side
Copper: >0,0005"	All weights		Wash with O, OIN HNO_3	
Stainless steel (0,040")		$\gtrsim$500 μg/cm^2	Degrease with acetone	Use 'mirror-finish' stainless steel
Platinum, Nickel Gold	All weights	All weights	Degrease with acetone	For unbacked targets use highly polished material. Use only where stainless steel is unacceptable. i.e. Fe, Cr_2 plating, Cl^- bath

*Copper foil (<0,0005") obtained from the Chromium Corporation, U.S.A.
This foil has one matt surface and one bright surface.

c) Masking techniques

Because of the high cost of separated isotopes the electroplating is normally made onto a cathode which is the size and shape of the required target. It would be quite impractical to make up different shaped plating cells to meet the many and varied target requirements and the normal practice is to mask the cathode backing material leaving only the required area exposed.

Two methods are used for this technique:-

(i) The cathode backing material is painted with Lacomit* leaving only the required area exposed. The mask can be dissolved away with acetone after deposition.

(ii) The cathode backing material is covered with a piece of self-adhesive polythene electrical masking tape which has had the required area cut out. In this case case must be taken to ensure there are no air bubbles under the tape, especially near the edge of the plating area, otherwise it may lift and expose more of the cathode backing material. The tape can be readily removed after deposition.

d) Electrical supplies

The electroplating power supply should be readily adjustable over the whole range of likely voltage and current requirements. It should have good long term stability so that the bath can run unattended, and it should give a fairly smooth d.c. output. A high a.c. ripple such as is obtained with battery chargers and certain commercial packs can give poor quality plating because of the hydrogen evolution arising from the high peak voltage.

In an attempt to satisfy these requirements we have tried circuits based on accumulators, on small motor generators and on a variety of power packs. The most suitable system and the one which we currently use is a commercial+ single phase smoothed rectifier controlled by a variac and continuously variable from 0 - 10V and 0 - 10A with only a 5% a.c. ripple.

e) Preparation of self-supporting foils

Two techniques are used to prepare self-supporting foils. The choice of method depends upon the element and the required weights of the isotopic foil.

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*Lacomit - A commercial electroplating masking paint manufactured by W. Canning & Co., Ltd., Birmingham.

+Made by Westinghouse Brake & Signal Co. Ltd.

(i) Mechanical separation of the deposit from the cathode backing material. The isotope is deposited onto a suitable highly polished backing such as stainless steel, nickel or platinum. By gently flexing the backing after completion of the electrolysis the deposit can be separated to form a self-supporting foil. This method is generally limited to foils weighing not less than 500 $\mu g/cm^2$ but with care can sometimes be employed for thinner targets.

For this technique to succeed the electrolysis must be carried out with scrupulous care. The rotation or stirring must be kept to a minimum to prevent the foil breaking away during the preparation.

(ii) Dissolution of the cathode backing material. This procedure is used for the preparation of very thin foils ($< 500 \mu g/cm^2$). Two techniques are available.

In the first a thin conduction layer (100μg) of the isotope is evaporated onto a slide of a soluble organic material such as perspex or celluloid. The required weight of isotope is then plated onto the evaporated layer and the organic backing subsequently dissolved away in a suitable solvent.

Alternatively the isotope is plated directly onto a suitable metallic backing material which is then selectively dissolved. This method is used mainly for the preparation of iron and nickel foils. These elements, which give highly stressed deposits, must generally be annealed before dissolving the backing material. Unless care is taken during the annealing stage and the lowest annealing temperature used, diffusion of the backing into the foil will cause chemical contamination of the isotopic target. Table 13.2 below gives details of stripping baths and annealing temperatures used for the preparation of iron and nickel foils by this technique.

To prevent oxidation the annealing is carried out in a special vacuum furnace.

Table 13.2

Details of annealing temperatures and stripping baths for the preparation of self-supporting iron and nickel foils

Element	Backing Material	Annealing temperature	Stripping bath	Stripping technique
Iron	Copper	580° - 620°C for 20 mins.	Dissolve 23g CCl_3COOH in 250 mls water. Add 20 mls 0,880 NH_4OH and dilute to 500 mls.	Float the foil, copper side DOWN, on the surface of the stripping bath. When the copper has all dissolved pick up the foil on a clean glass slide. Wash the foil in water by repeated flotation.
Nickel	Copper	580° - 620°C for 20 mins.	Dissolve 250g CrO_3 in 250 mls water. Add 1 ml conc. H_2SO_4 and dilute to 500 mls.	

f) Plating Baths

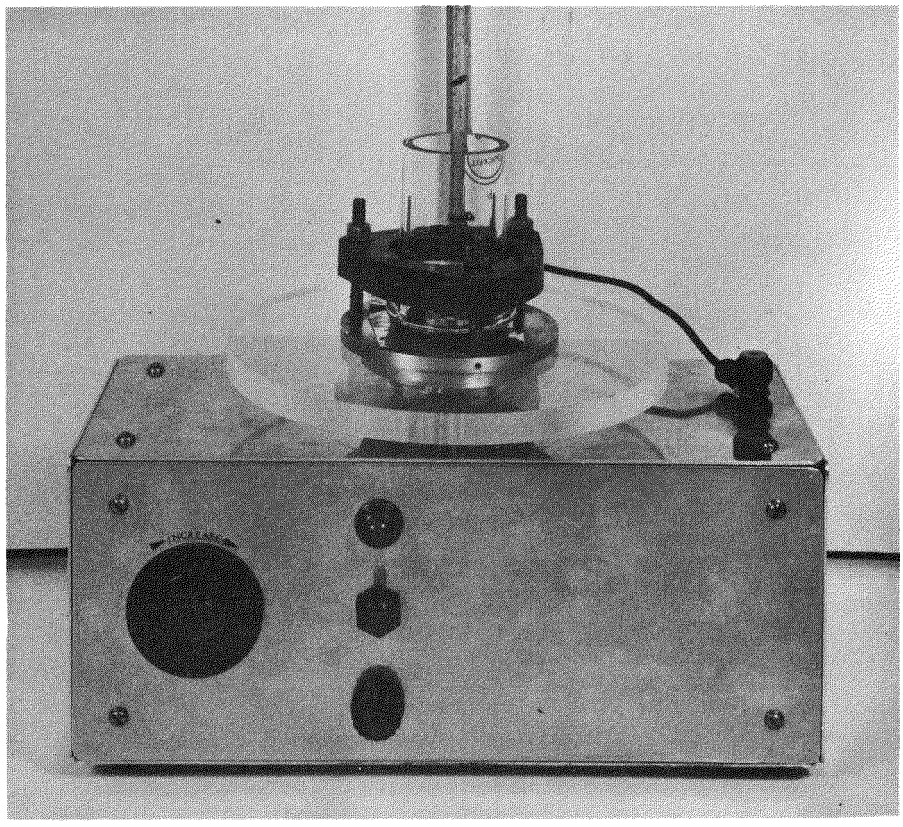
Details of plating baths used for the preparation of isotopic targets of the more common elements

Table 13.3

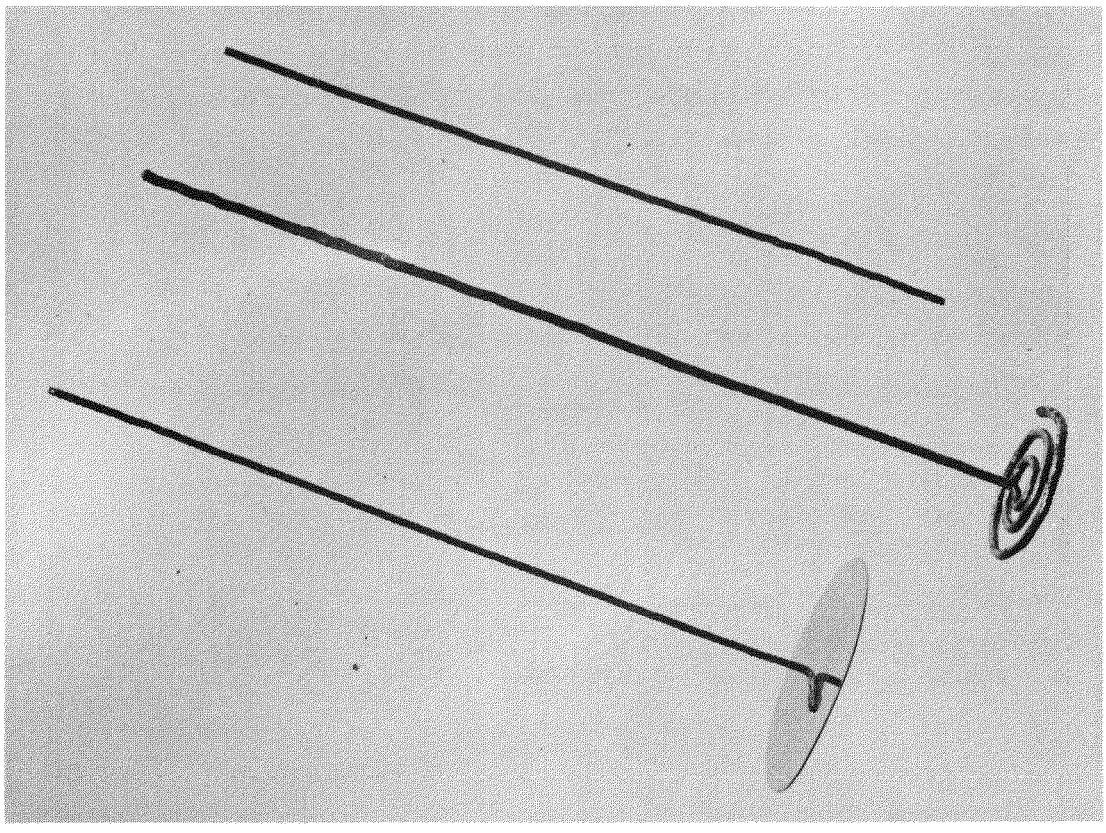
Element	Bath composition	Overall Deposition Efficiency %	Current density ma/cm^2	Target details		Comments
				Backed	Unbacked	
Sb	Sb_2O_3 dissolved in a solution of:- 7.3g citric acid 1.4g potassium hydroxide 20mls water	60	4 - 8	Cu, Au, Ni, Fe	From plastic backings	Traces of Sb_2S_3 will give a spongy deposit
Cd	(i) $CdSO_4$ in O, OIN H_2SO_4	85	30 for $\frac{1}{2}$ minute then reduce to 4-6	Cu, Ni, Pt, Au	No.	
	(ii) CdO dissolved in a solution of: 9.0g sodium cyanide 1.5g sodium hydroxide 100mls water	85	6-10	Cu, Ni, Pt, Au	Stainless steel	Only self-supporting targets heavier than 5mg/cm^2 have been made by this technique. The lower limit is not known.
Cu	$CuSO_4$ in 1N H_2SO_4 + 1ml HNO_3 (NO_2 free) per 100mls solution	>95	5-10	Ni, Pt, Au, Ta	From Stainless Steel	For unbacked targets $\gtrsim$1mg/cm^2 etch stainless steel with H_2SO_4/HNO_3 mixture
Fe	Fe $(OH)_3$ dissolved in oxalic acid. Adjust pH=6-7 with NH_4OH. Dilute to required vol. with saturated ammonium oxalate.	>95	5-10	Ni, Pt, Cu, Au, Ta	Cu Annealing necessary Table II	Unbacked targets > 5mg/cm$_2$ should be annealed every 5mg/cm^2. During electrolysis pH rises - add oxalic acid to keep pH in the range 6-7
Ni	$NiSO_4$ dissolved in a solution of:- 20mls 0,880 NH_4OH 1.2g $(NH_4)_2$ SC_4 100mls H_2O	>95	8-10	Cu, Au, Pt, Ta	Cu Annealing necessary Table 13.2	Unbacked targets $\gtrsim$ 5mg/cm^2 should be annealed every 5mg/cm^2. Use sufficient Ni to give 5mg/cm^2 and after annealing use fresh electrolyte.
Ag	$AgNO_3$ dissolved in a solution of: 5g KCN + 100 mls H_2O	>95	2	Cu, Ni, Fe, Pt, Au, Ta	From Plastic or Stainless steel	
Sn	$SnSO_4$ dissolved in a solution of 7.5g oxalic acid 3.3g ammonium oxalate 1.3g hydroxylamins hydrochloride 100mls H_2O	>95	5	Cu, Au, Pt, Ni	From Plastic or Copper Backings	Dissolve copper in chromic acid bath, Electrolyte attacks deposit. Wash by syphoning whilst maintaining current.
Zn	$ZnSO_4$ dissolved in a solution of: 1g $(NH_4)_2$ SO_4 400mg KCN for each mg of Zn. 100mls water	>95	2	Cu, Pt, Au	From Stainless steel and Gold	Only self-supporting targets heavier than 5mg/cm^2 have been made by the technique. The lower limit is not known. For targets > 5mg/cm^2 use sufficient Zn to give 5mg/cm^2 then use fresh electrolyte for a further 5mg/cm^2.

References

1. Modern Electroplating 2nd Ed., p.23-25, Frederick A. Lowenheim, John Wiley and Sons, Inc. 1963.



AERE - R 5097 Fig. 13.2
Electroplating assembly



AERE - R 5097 Fig. 13.3
Electrodes used for the preparation of isotopic targets

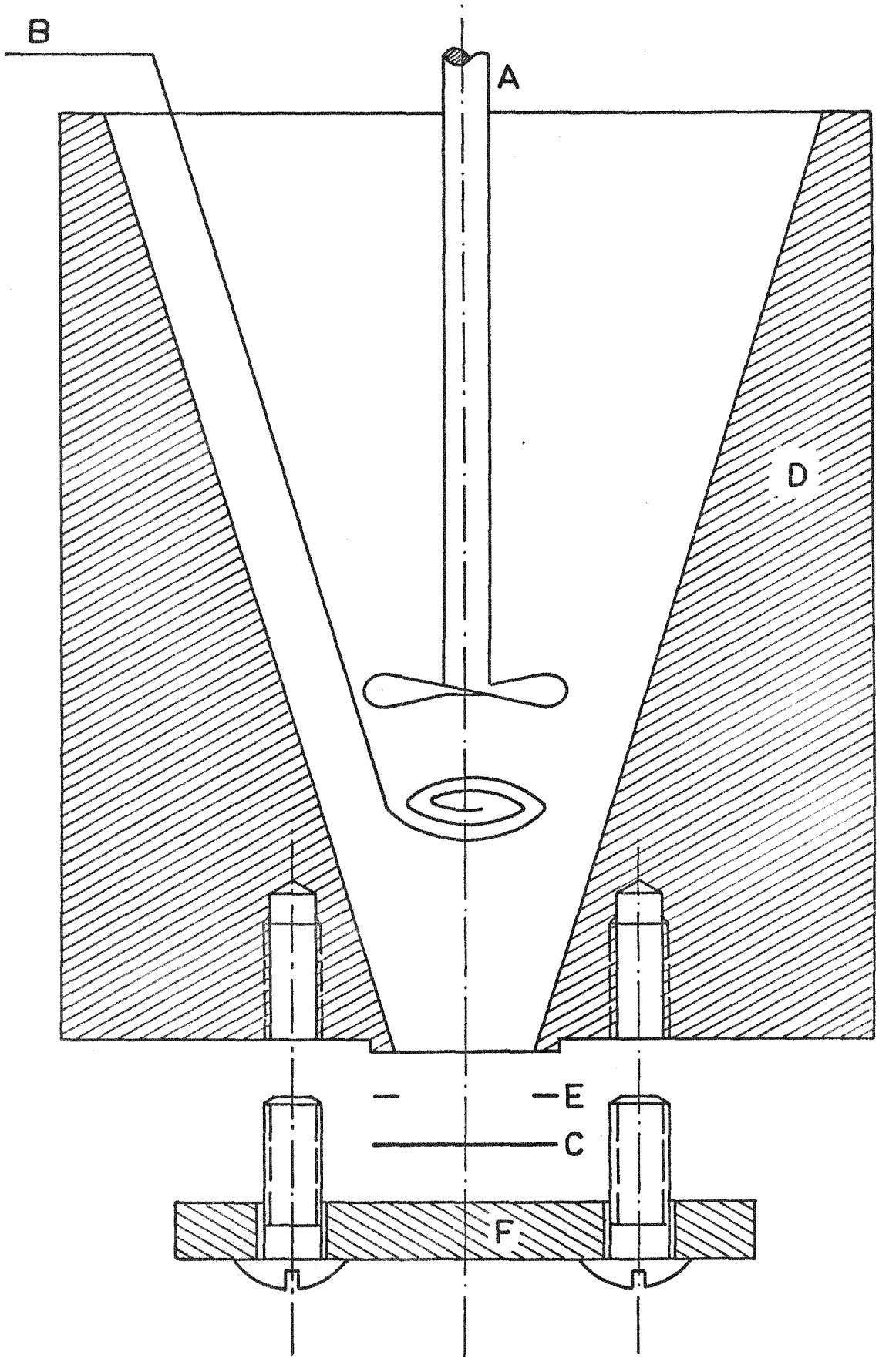


FIG. 14·1

PREPARATION OF THIN SELF-SUPPORTING ENRICHED IRON TARGETS

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INTRODUCTION

Thin self-supporting targets or sources are needed in the field of nuclear physics and nuclear chemistry. The chemical electrodeposition technique is appropriate when the requirements include,

(a) control of deposition
(b) high yield recovery (quantitative deposition)
(c) low concentration
(d) target or source homogeneity
(e) self-supporting character

Some years ago, Maletskos and Irvine[1] described a quantitative electrodeposition method with particular application to iron. However their technique did not suit the requirements a, c, d and e. Accordingly a slightly modified method was developed and optimum electroplating parameters experimentally determined. In particular the influence of the pH of the electrolyte and the determination of the rate of deposition for low concentrations of iron ions. The total removal of the copper cathode from the freshly deposited iron was also investigated.

A similar method was prescribed by Bondar et al.[2] but they did not demonstrate that their technique was quantitative. Moreover they suggested a chromic solution to dissolve the copper cathode though with thin freshly plated iron (~ 20 $\mu g/cm^2$) the film could not be successfully removed. A solvent prescribed by Richards, H.T.[3] was then tried and with this the iron film could be successfully floated off.

EXPERIMENTAL CONDITIONS

Apparatus

Iron was electroplated with an apparatus similar to that described by Maletskos and Irvine[1]. Drawn to scale the main components of our apparatus are shown in Figure 14.1. A glass stirrer "A" was used to remove the gas bubbles which might have occluded onto the surface of the cathode. The anode "B" was made of platinum (0.3 mm. diameter) with a spiral shaped end. The cathode "C" was a chemically polished copper foil (0.002 mm. thick). The interior of the reservoir "D" was conical and machined out of a cylinder of plexiglass. The diameter of the bottom was 11.3 millimeters which corresponded to an area of 1 cm^2. A teflon gasket "E" (0.006 mm. thick) and a brass plate "F" which could be tightly affixed

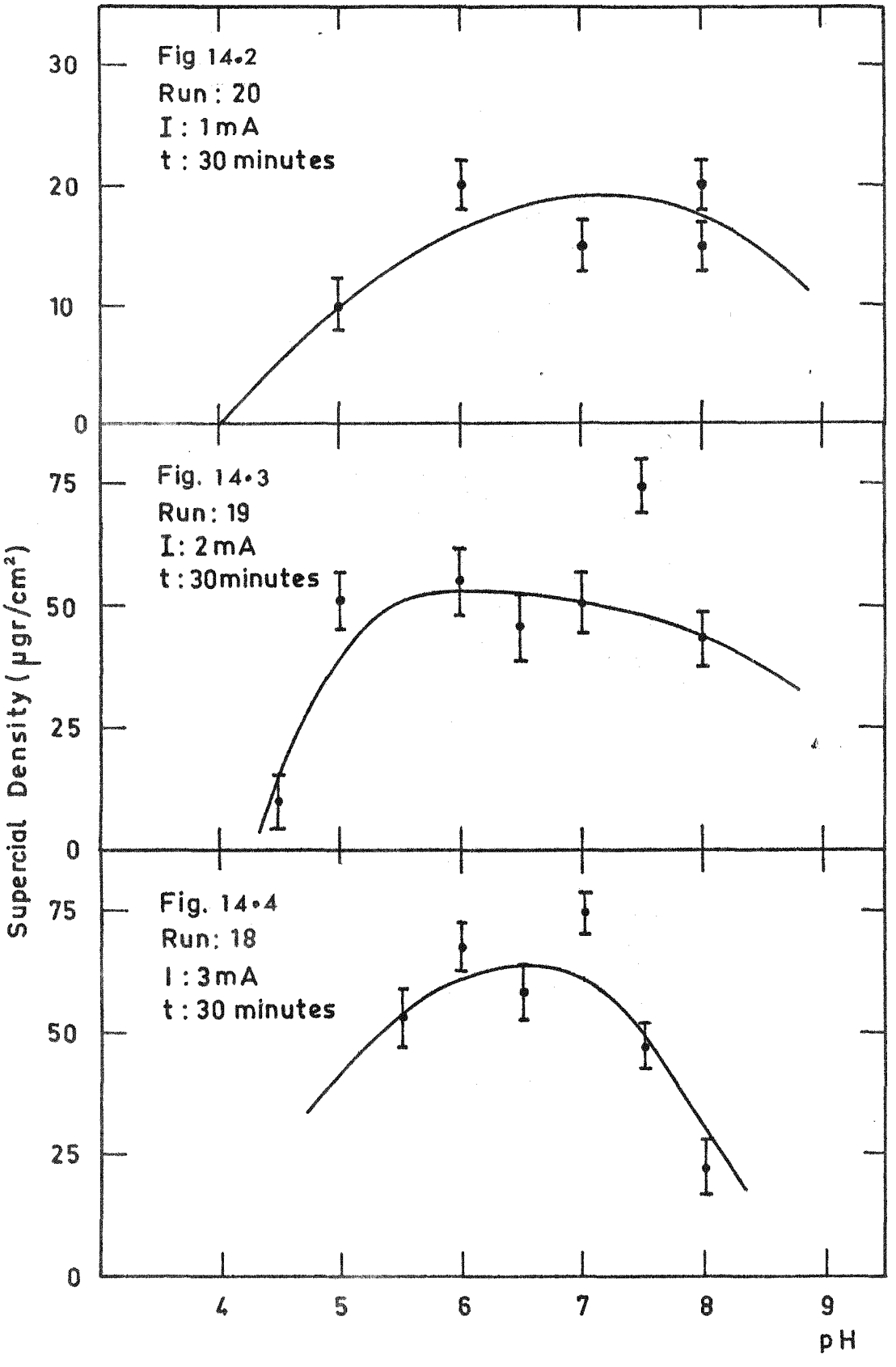
Fig 14.2
Run : 20
I : 1 mA
t : 30 minutes
Fig. 14.3
Run: 19
I: 2 mA
t : 30 minutes
Fig. 14.4
Run: 18
I : 3 mA
t : 30 minutes
Supercial Density (μgr/cm²)
30
20
10
0
75
50
25
0
75
50
25
0
4
5
6
7
8
9
pH

onto the rim of the reservoir enabled us to make a liguid leakproof contact.

Reagents

0.1 M HCl

0.1 M NH_4OH

2.0 M HCl

Saturated solution of $(NH_4)_2C_2O_4$

A trichloroacetic acid-ammonia-water solution (100g : 500 mls : 500 mls)

Recommended Procedure

7.1 mgs of Fe_2O_3 were dissolved in about 3 mls of 2.0 M HCl and the solution slowly evaporated to almost dryness. The residue was then redissolved in 16 mls. of saturated ammonium oxalate solution and the pH of the electrolyte adjusted with either 0.1 M HCl or 0.1 M NH_4OH solution. The copper cathode was mounted onto the container and rinsed twice with ethanol, once with a three-fold diluted ammoniacal solution as suggested by Richards[3] and finally several times with distilled and de-ionized water. The distance between the two electrodes was two centimeters. A regulated power supply was used and current density monitored by ammeter. The electrodes of a Tacussel pH meter (precision ± 0.002) type TS7 registered the pH of the solution. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Preliminary work and experimental conditions were determined using naturally occurring iron. First of all, dealing with a small concentration of iron (5 mg Fe^{++}), the optimum pH of the electrolyte had to be determined. The results are shown in Figures 14.2, 14.3 and 14.4. It was found that for currents of one or two milliamperes the pH of the electrolyte must be greater than 4.5 and smaller than 8.5. For pH's less than 4.5, the iron re-dissolves as soon as formed at the cathode while for pH's greater than 8.5 a brownish flocculent precipitate appears. A solution around pH 7 would seem best.

In order to determine the rate of electrodeposition for varying intensities of current and times, a second series was carried out. Keeping the pH of the electrolyte constant at 7.0 the results are given in Figures 14.5, 14.6, 14.7 and 14.8. From the data an average plating rate of 25 ± 5 $\mu g/cm^2/mA/20$ min. was derived.

Finally, at constant pH of 7.0 and fixed time of 30 minutes of electrodeposition, the rate of plating was found for current intensities ranging between 1 and 25 mA. The results are shown in Figure 14.9. Again the rate of plating was found to be of the same order of magnitude, that is 26 ± 2 $\mu g/cm^2/mA/30$ min.

The superficial density was determined by microbalance with an accuracy of ± 0.002 mg. The reliability of the method was verified by weighing the copper cathode before and after deposition. As a counter-check the copper was chemically dissolved and the iron film floated off from the bath onto a thin microscope slide which had previously been weighed. Comparison of the two methods are presented in the following table.

Run	mgms	mgms
3 a	Cu + Fe: 5.332 Cu: 5.200 Fe: 0.132	Glass + Fe: 174.315 Glass: 174.200 Fe: 0.115
3 b	Cu + Fe: 5.165 Cu: 5.090 Fe: 0.075	Glass + Fe: 163.860 Glass: 163.780 Fe: 0.080
3 c	Cu + Fe: 5.145 Cu: 5.035 Fe: 0.110	Glass + Fe: 180.515 Glass: 180.415 Fe: 0.100

According to Faraday's law and assuming that the iron exists in the ferric form, the quantity of electrodeposited iron should be about 350 μg/mA/30 min. We have experimentally found a factor which is about 14 times smaller. This shows that the law cannot be applied for the predetermination of the weight of material to be electrodeposited. On the other hand, many factors such as the valence state of the iron, the nature of the molecules (complex states), the presence of foreign ions, and the surface states of the electrodes are not well established. Also at low concentrations current may be carried by ions other than iron.

The data obtained from the above experimental results enabled us to prepare films or targets of enriched iron (^{58}Fe) with a minimum thickness of 20 $\mu g/cm^2$. Small quantities such as 2 mgs. of $^{58}Fe^{++}$ could be used in the electrolyte and the films obtained were used as targets for nuclear experiments. The reaction $^{58}Fe(p,n\gamma)^{58}Co$ was studied and no contaminants were observed.

ACKNOWLEDGEMENT

The realization of the above experiment was rendered possible with the kind collaboration of Professors J.P. Adloff and A. Gallmann.

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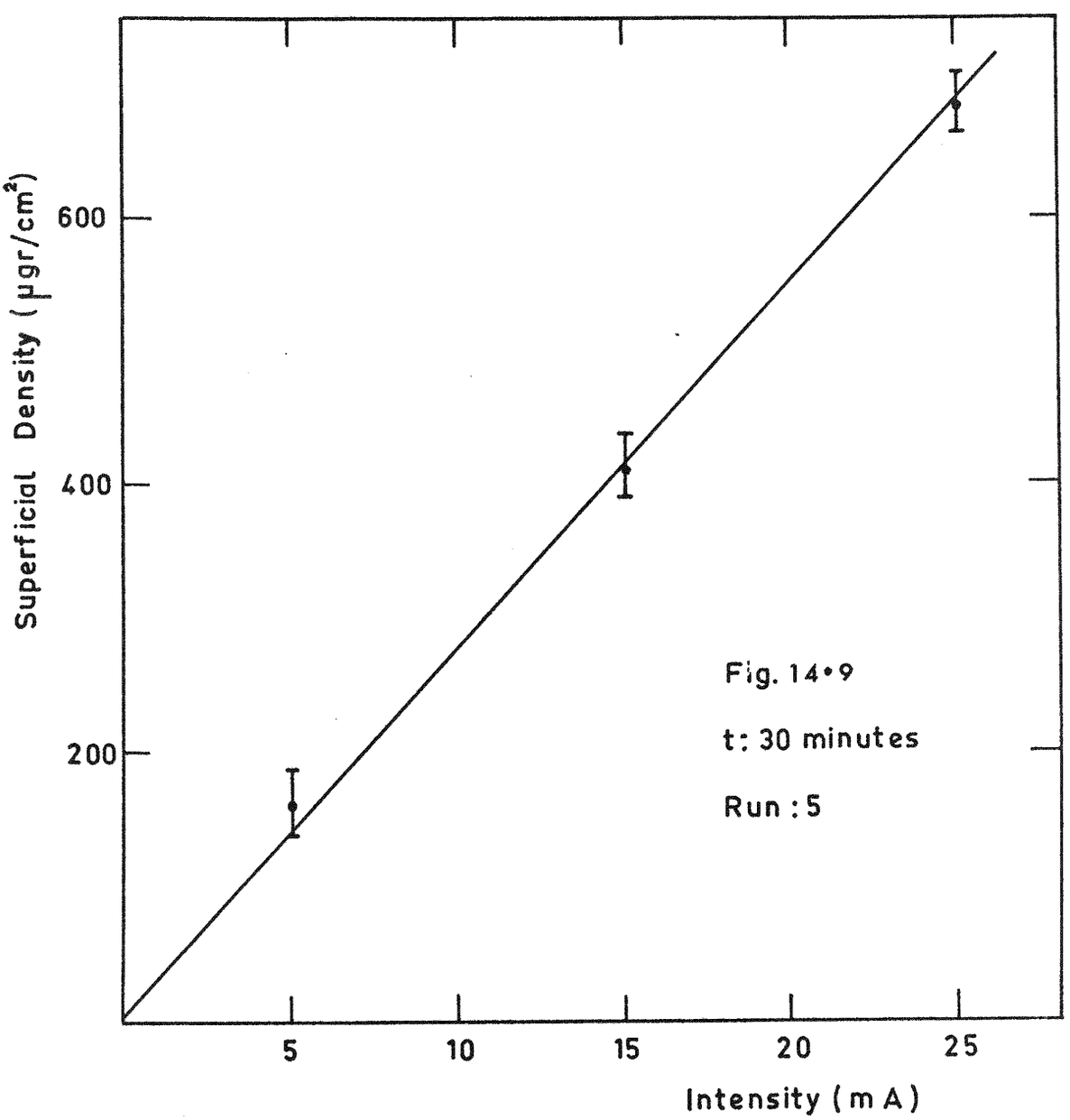
3. Richards H.T., Nuclear Spectroscopy, Part A, page 99, (1960).


Superficial Density (μgr/cm²)
600
400
200
5
10
15
20
25
Intensity (m A)
Fig. 14•9
t: 30 minutes
Run : 5

PREPARATION OF α - ACTINIDE FOILS BY ELECTROLYSIS

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1. Introduction

The electrolytic procedure depends on the actinide and operations require the following care:

- solutions must be very pure and kept in platinum containers
- the area of the anode must be the same as that of the cathode. It is wound from platinum wire and placed 10 millimeters from the cathode
- the cell, before being taken apart, must be washed with diluted ammonia and afterwards with acetone
- the cathode is made of a corrosion metal such as platinum, gold, stainless steel, nickel or copper.

2. Uranium-Neptunium foils[1]

The electrolyte used is 0.2 M ammonium oxalate. The actinide is often diluted in 0.2 - 0.25 N nitric solution and we add an aliquot to the electrolyte. pH is adjusted to 8 and we do not correct for changes during the electrolysis.

We use a rotating anode turning at 200 revolutions per minute. Current density is adjusted to 80 mA/cm^2 at the start and kept to that level for 15 minutes. It is then increased to 100 mA/cm^2 and maintained at this level for an hour when the deposit becomes quantitative. If the initial current density is lower a finer and more adhesive deposit is obtained due to less disturbance from hydrogen release. It is important to hold the temperature at 70°C. If it is higher, the deposit is powdery and not adhesive; if it is lower, the time for each deposit has to be increased.

Deposits thus fabricated have a weight per surface area up to 2 mg/cm^2 for uranium and 800 $\mu g/cm^2$ for neptunium. The black uranium foil is not ignited. If so it would become powdery and dull. The brown neptinium one is ignited when it becomes black and remains shiny.

3. Plutonium foils[2]

The same electrolyte, ammonium oxalate, is used but at a lower concentration (0.1 Molar) to give good deposition. The actinide is added in

the plutonyl nitrate form at 0.25 Molar concentration from a solution prepared by electrolysis. pH is adjusted to 7 at the start of the electrolysis and is not corrected during operation. Current density is kept at 80 mA/cm^2 for two hours.

The adhesive deposits contain up to 700 µg/cm^2 of plutonium. Yield is between 90 to 100%. We use the rotating anode at the same speed of 200 revolutions per minute. Temperature is that of the laboratory. We dry and ignite when the foil takes on the yellow colour of the plutonium oxide.

4. Americium, Curium, Californium and mixtures of elements[2]

The elements other than americium give only slight deposits. Electrolyte used is formic acid .1 M - ammonium formate .075 M. pH is adjusted to 3. Temperature during electrolysis is ambient. Current density is kept at 100 mA/cm^2 but the rotating anode is slowed down to 100 revolutions per minute. The duration for a quantitative deposit is one and a half hours. After igniting, the black file becomes colourless. Thicker deposits of americium need the following conditions. The electrolyte is a solution of ammonium formate 0.2 M/formic acid 1.5 M at pH 2. Operation starts with 80 mA/cm^2 current. After 30 minutes, pH is increased to 3 and current density up to 100 mA/cm^2 for 3 hours. For deposits averaging 400 µg/cm^2, yields are between 50 and 95%.

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MOLECULAR PLATING: PREPARATION OF SELF-SUPPORTING FILMS*

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In a previous communication Parker and Baumgartner described an electrodeposition method for the preparation of electron microscope specimens[1]. The success of the method was such that it has been extended to the preparation of larger films (0.5 cm^2) suitable for *in situ* measurements of nuclear reactions. It should be pointed out that using this particular method, one does not obtain the metal but rather a compound of the metal, e.g., carbonate, oxide, sulphite, etc. In the following, a short description will be given of the deposition cell and of the experimental work carried out up to the time of writing.

Shown in fig. 16.1 is the experimental arrangement employed for the preparation of self-supporting films. It consists of a teflon cell

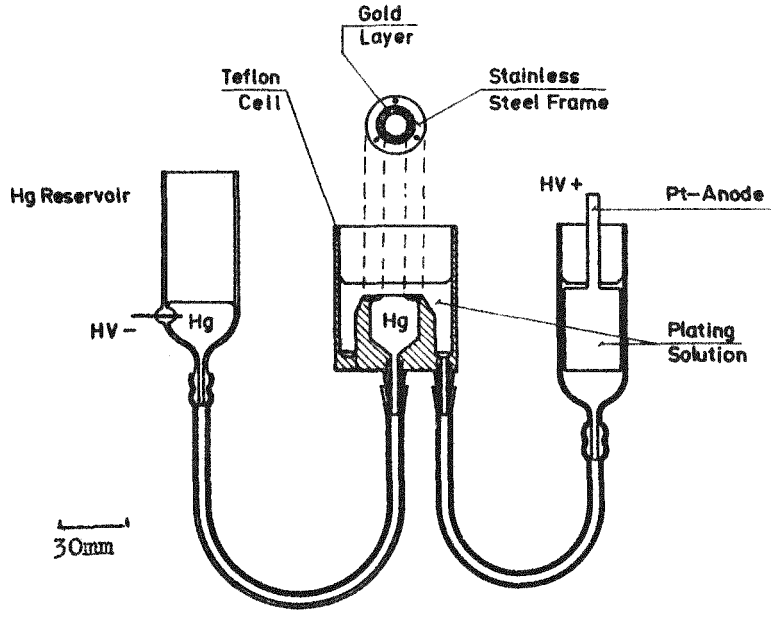
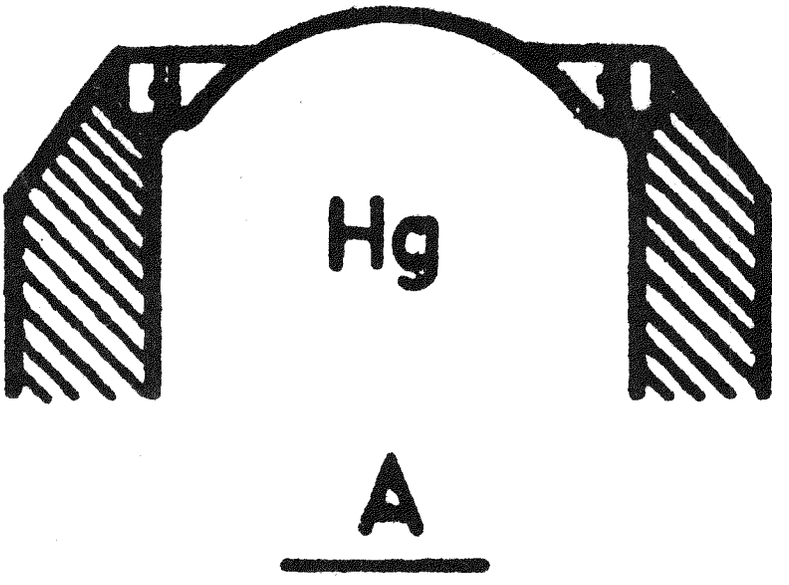


Fig. 16.1 Experimental arrangement for the preparation of self-supporting films by means of molecular plating

which is constructed in two parts forming two compartments for the mercury and plating solution respectively. Each compartment is connected by means of a polyethylene tube to a glass reservoir. These reservoirs also serve as electrode containers, a platinum electrode being

*To be published in extended form in Nucl. Instr. and Meth.



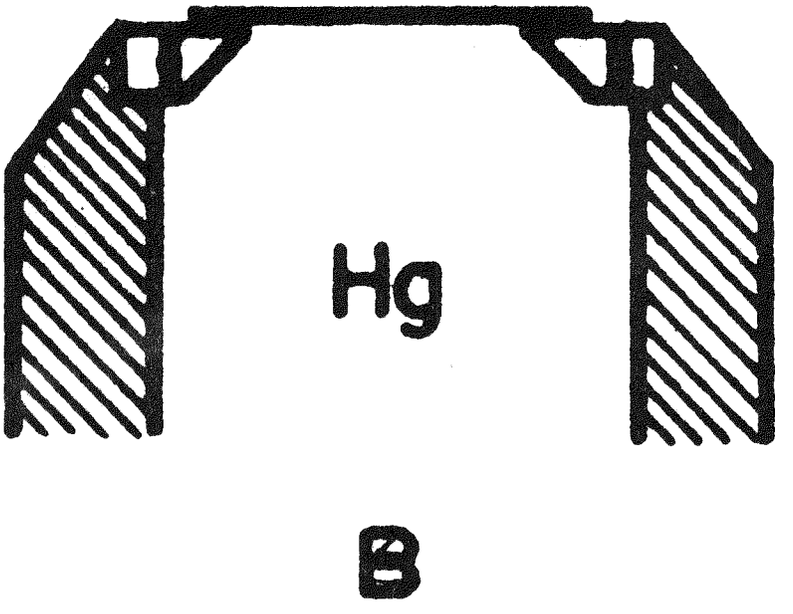


Fig. 16.2

placed in the plating solution reservoir while electrical contact to the mercury is made by means of a 1.0 mm. diam. tungsten wire. In practice, the plating cell is held in a fixed position while the height of the two reservoirs can be varied as required. The stainless steel frame is positioned, as shown in fig. 16.1 on top of the mercury compartment in which a ridge has been provided for the purpose of holding the frame in place.

In order to combat the effect of surface tension of the mercury it became necessary to prepare the frame surface with a layer capable of forming an amalgam with the mercury. In fig. 16.2, A and B, can be seen the effectiveness of evaporating a layer of gold onto the inside edge and top of the stainless steel frame. A is without amalgam formation, and B with amalgam formation. The amalgam is formed in a few sec. and for an approximately 1.0 mg/cm^2 layer lasts about 10 min. Where necessary, this time can be increased by electro-plating a thicker layer of gold onto the frame (10 to 20 mg/cm^2 will allow an effective amalgam to exist for almost two hours). Placement of the anode at such a distance from the cathode compartment, in the plating solution reservoir, results in a considerable increase in deposition time (plating current decreased). However, the advantages of not having the anode in the actual cell far outweigh any advantage of having a more rapid deposition rate. For example, positioning and withdrawal of the anode can cause undesirable disturbances which in the latter case usually result in the fracture of the film. Also, where the water content is unavoidably high, such as would be the case with compounds that are only slightly soluble in alcohol, an extremely low plating current is desirable so as to avoid as far as possible gas formation at the cathode. Trouble free observation is also facilitated in this manner. In the following is given a description of the procedure developed for preparing thin self-supporting films from a solution of uranyl nitrate.

A stock solution of uranyl nitrate is prepared having a concentration of 50 mg/ml in water. The cell is first thoroughly cleaned with ethyl alcohol, and clamped firmly in position. The two polyethylene tubes are pushed over their respective nipples and the gold-coated stainless steel frame placed in the groove at the top of the mercury compartment. The mercury reservoir is now lowered until the mercury in the cell fills the opening of the frame. As soon as the amalgam has formed, the plating solution can be introduced by adding a suitable aliquot of the stock solution to, in our case, approximately 50 ml of iso-propyl alcohol. The mixture is shaken vigorously for about 1 minute and then transferred to the anode/plating solution reservoir, the level of which is adjusted to be approximately 5 mm. above the mercury surface. A deposition potential of 1.000V.d.c., is applied between the electrodes. For a 200 µl aliquot,

a film having a thickness of 50 $\mu g/cm^2$ is obtained for a 15 minute deposition period. Removal of the film proceeds as follows: the level of the plating solution is slowly reduced until it is below the mercury compartment and about 5 minutes allowed for the film to dry. The mercury level can now be slowly reduced and the frame removed from the cell. Using the described method there is no reason why all of those compounds so far plated by means of the usual molecular plating process[2] should not be prepared in self-supporting form.

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PAPER 17

MOLECULAR PLATING: PREPARATION OF CARBON AND SULPHUR SAMPLES AND TARGETS+

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Molecular plating [1] has been applied to the preparation of thin targets and radioactive samples of carbon and sulphur. In both cases the material in question was co-deposited with sodium, i.e., Na_2CO_3 and Na_2SO_3, and $Na_2{}^{14}CO_3$ and $Na_2{}^{35}SO_3$ for targets and samples respectively. Stock solutions in water were prepared having a concentration of 10 mg/ml and a 50 µl aliquot (50 µl = 500 µg/15 µC total solids) added to 50 ml of iso-propyl alcohol in a closed separation funnel and thoroughly shaken. The contents were then transferred to an electrodeposition cell of the type shown in fig. 17.1, fitted with an aluminium cathode in the case of sample preparation and a tantalum cathode in the case of target preparation.

For an anode/cathode separation of 20 mm and an applied potential of 1.000V.d.c., a plating current of approximately 135 µA was observed. The deposition efficiency was found to be strongly dependent on the cathode material (backing) employed and in the present instance turned out to be 32 and 17% for aluminium and tantalum respectively for a deposition time of 30 minutes.

The deposits obtained in the above manner have good uniformity and mechanical stability. Determination of the yields obtained was made by m means of liquid scintillation counting and is described in detail elsewhere [2].

+To be published in extended form in Nucl. Instr. and Meth.

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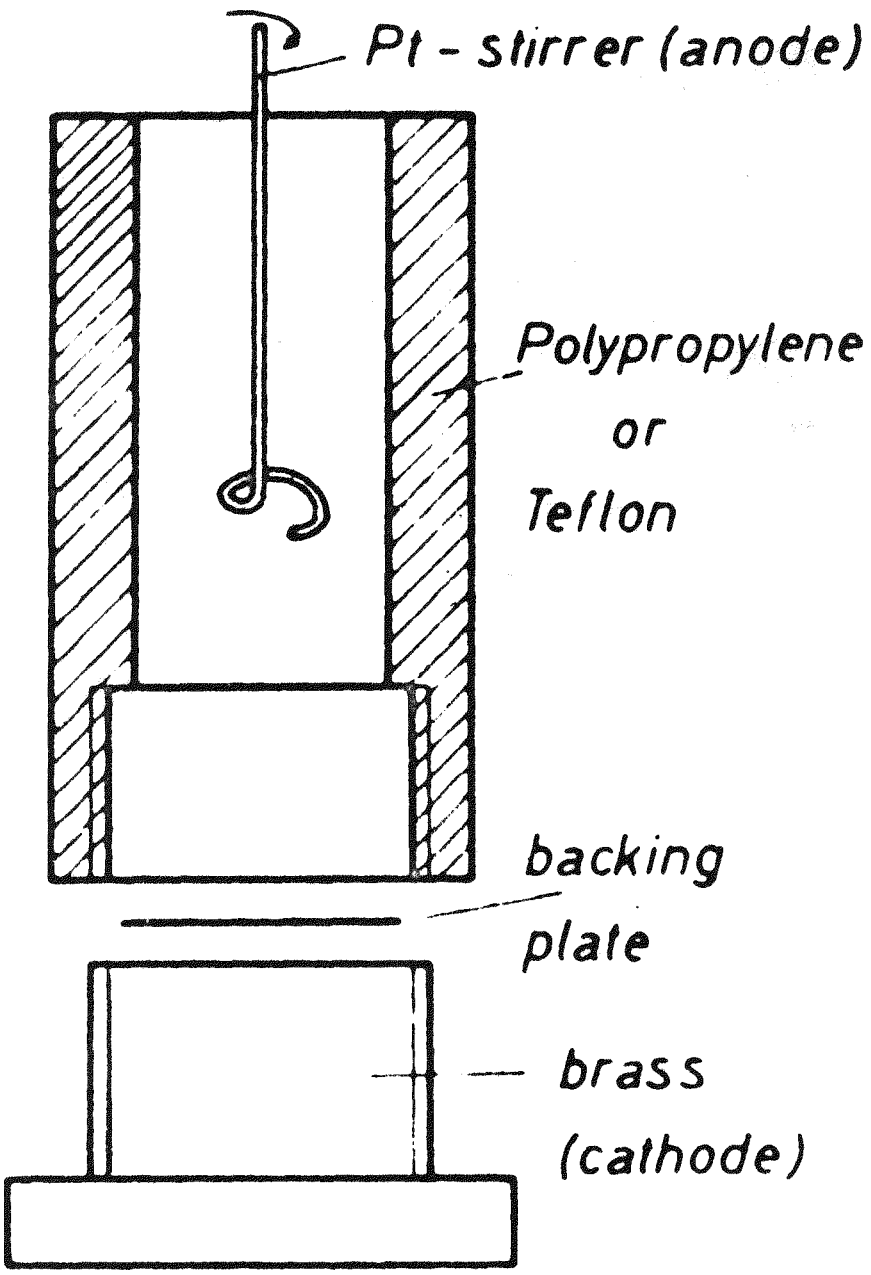

Pt - stirrer (anode)
Polypropylene
or
Teflon
backing
plate
brass
(cathode)

Fig. 17.1

PREPARATION OF THIN ^{17}O and ^{18}O TARGETS

A. H. F. Muggleton

A.W.R.E., Aldermaston, Berks.

1. Introduction

Initially enriched oxygen targets were made by a modified technique described by Holmgren et al[1], whereby a thin iron foil was oxidised by heating in a $D_2\ ^{18}O$ atmosphere. Iron was used in preference to nickel due to the greater rate of oxidation. Although a few satisfactory targets were produced by this technique the following disadvantages were encountered.

(1) Self supporting iron foils, of the required thickness (50-100 $\mu g/cm^2$) were difficult to make due to stresses set up in the foils during deposition. These caused the foils either to shred or curl during mounting necessitating an extensive annealing operation.

(2) Once mounted across the target aperture ($\frac{1}{2}$" long x $\frac{1}{4}$" wide slot) the foils were very prone to splitting.

(3) Oxidation of the iron foils was a delicate and tedious operation with a low yield of useful specimens.

To overcome these difficulties a new approach to the problem was investigated. The technique finally decided upon divides naturally into two parts.

(1) The production of a suitable compound enriched in the oxygen isotope.

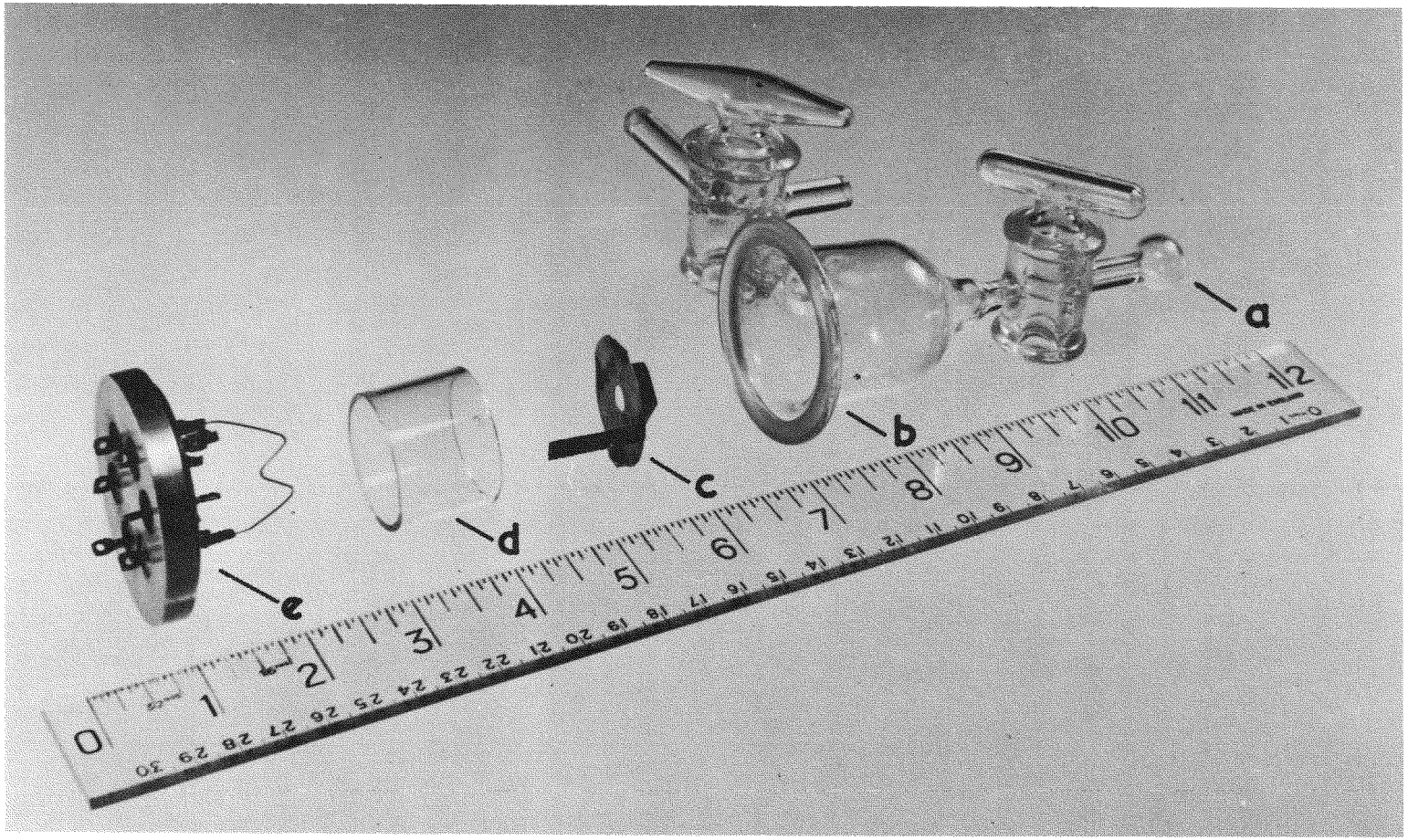
(2) The vacuum evaporation of this compound to prepare thin targets.

Tungsten oxide was chosen as a suitable compound since tungsten is easily oxidised, the oxide formed can be evaporated without difficulty and a suitable separation of mass numbers exists between tungsten and oxygen.

2. Preparation of enriched tungsten oxide

Since oxygen isotopes were more readily available in the form of D_2O[2] than as the enriched gas it was decided to produce the oxide from enriched water.

An exploded view of the apparatus used for the preparation of the enriched oxide is shown in fig. 18.1. The main vessel (b) is of borosilicate glass which is easily cleaned and allows visual observation of the process; (c) and (d) are removable shields made of nickel and glass



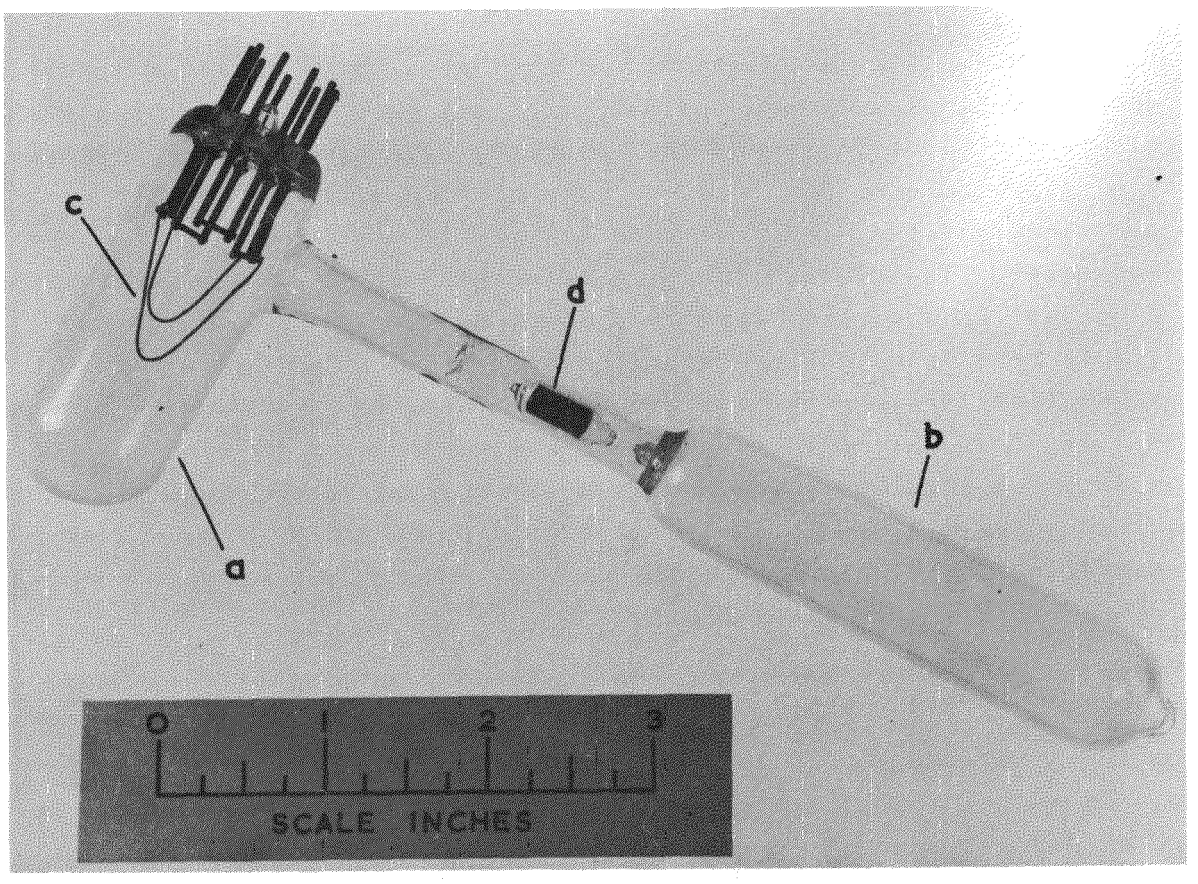
AERE - R 5097 Fig. 18.1

respectively. The top plate (e) is of brass sealed to the chamber by means of an "O" ring and contains glass-to-metal seals to which 0.5 mm tungsten filaments are attached.

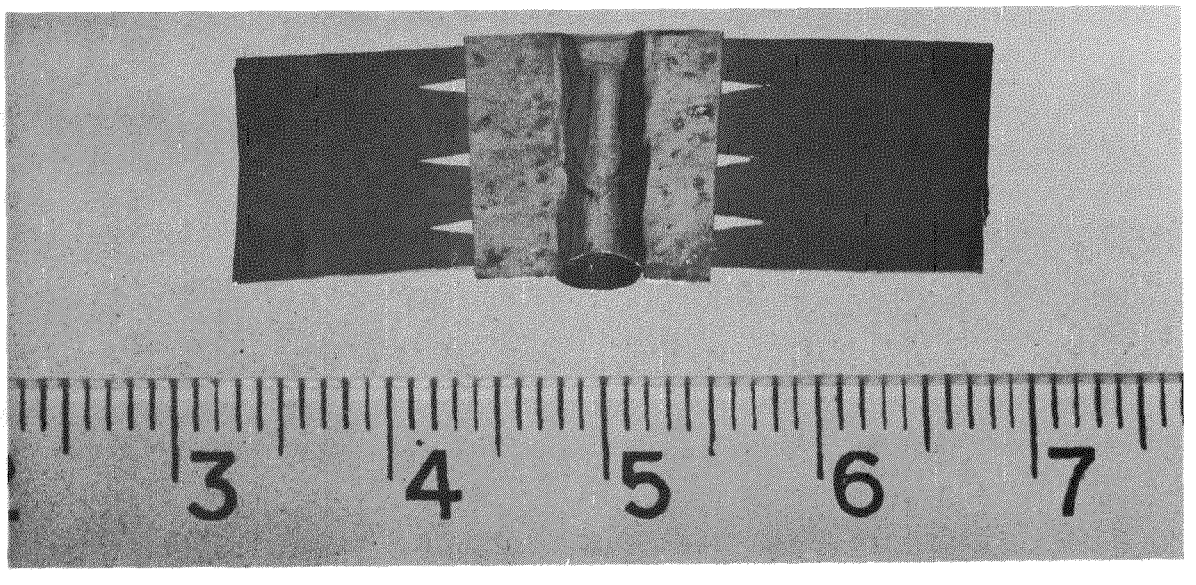
Approximately 0.2 ml of enriched water was introduced into the small bulb (a) by means of a micro-hypodermic syringe with an extended needle. This drop of water was frozen by immersing the small reservoir in a solid CO_2-trichloroethylene slush and the apparatus evacuated through the side arm until a pressure of 5×10^{-4} was maintained. With the chamber isolated from the vacuum system, the reservoir was gently heated to vaporise the enriched water. The cleaned tungsten filaments were heated to approximately 2500°C by passing a current through them. The tungsten oxide formed immediately re-evaporated and deposited on to the removable shields. Coolant applied to the reservoir caused remaining water vapour to be condensed. After isolating the reservoir from the chamber by means of the vacuum stopcock shown, air was admitted to the system. A mixture of WO_3 (yellowish-green), W_4O_{11} (violet) and WO_2 (deep brown)[3] was formed, and the removal of these oxides from the shields and top plate was accomplished by brushing with a soft clean brush.

Although the above technique was reasonably successful the oxide contained a high percentage of ^{16}O due to trapping of residual atmospheric oxygen in the frozen $D_2\,^{18}O$ and $D_2\,^{17}O$ during initial evacuation of the system and to the inability to pump the system to less than 5×10^{-4} torr. Later, when small quantities (20 atmospheric milli-litres) of highly enriched oxygen gas became available, it was decided to modify the previous technique and make the process more efficient.

The modified apparatus is depicted in Fig. 18.2. It is constructed of borosilicate glass and consists of the main chamber (a) to which is sealed a bottle (b) containing 20 atmospheric milli-litres of the enriched gas. Two cleaned tungsten filaments (c) 0.5 mm diameter x 5 cm long are spot welded to a standard glass valve base which is sealed into the main chamber. The assembled apparatus is sealed to a glass high vacuum pumping system, care being taken to ensure that the small plug (d) does not fracture the break-off seal isolating the O_2 gas from the main chamber. The system is now evacuated to a pressure of $<1 \times 10^{-6}$ torr and baked at 350°C for approximately 4 hours. After allowing to cool, the apparatus is sealed from the pumping system and the enriched gas admitted to the main chamber by fracturing the break-off seal with plug (d). Both tungsten filaments are heated in turn to approximately 2500°C and the tungsten oxide formed is deposited on the chamber walls. When no further oxide is seen to form, the apparatus is allowed to cool and carefully broken open. It is most important that no particles of glass become mixed with the tungsten oxide during this operation, otherwise during subsequent vacuum evaporations the enriched oxide film will be degraded in isotopic content



AERE - R 5097 Fig. 18.2



AERE - R 5097 Fig. 18.3

due to the evaporation of these glass particles in the form of SiO_2, Na_2O, B_2O_3, Al_2O_3 etc.

Theoretically the maximum amount of W $^{17}O_3$ obtainable from 20 atmospheric milli-litres of $^{17}O_2$ is 140 mg. This technique produced 134 mg; a yield efficiency of 94%.

3. Evaporation of tungsten oxide

Tungsten oxide has been successfully evaporated from a platinum boat (Fig. 18.3). The boat consists of a centre section made from 0.003" platinum sheet formed around a $\frac{1}{8}$" diameter twist drill shank and spot welded along the seams. Current is conducted to the boat by two tantalum strips spot welded to the platinum. Platinum was chosen to prevent the oxide being reduced, a factor which makes the usual source materials such as tungsten, tantalum and molybdenum unsuitable. This design of boat furthermore affords a saving in evaporant, since the vapour beam produced is quite directional. Evaporation of tungsten oxide proceeded satisfactorily in a vacuum of $\approx 1 \times 10^{-5}$ torr at a temperature of $\approx 1200^{\circ}C$. Typical values are, vacuum $\approx 1 \times 10^{-5}$ torr, temperature $\approx 1200^{\circ}C$, distance of boat from substrate 9.8 cm, amount of material in boat 10 mg, density of deposit 40 $\mu g/cm^2$.

Thin films up to 500 $\mu g/cm^2$ were produced by this method, the tungsten oxide being deposited on to self supporting carbon backings (5-20 $\mu g/cm^2$). The carbon backings were made by a technique developed by Bradley[4]. Deposition has also taken place on thin nickel and copper backings ($\sim$ 100 $\mu g/cm^2$)[5].

The targets produced by this technique had enrichments of > 40% from 51% enriched $^{17}O_2$ and 90% ± 10% from 99.6% $^{18}O_2$.

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A METHOD FOR THE PREPARATION OF THIN, SELF-SUPPORTING ^{13}C FOILS

A.H.F. Muggleton

A.W.R.E., Aldermaston, Berks.

Introduction

The vacuum evaporation technique [1] cannot presently be used for making isotopic carbon targets because enriched material is not yet available in large enough quantities. However various techniques have been reported for fabricating isotopic carbon targets by either thermal decomposition of a suitable organic compound [2, 3] or polymerising enriched acetylene gas in an electrical discharge [4, 5].

The technique used at AWRE is a modification of that described by Kashy, Perry and Russer [3], whereby methyl iodide, enriched in the carbon isotope, is thermally decomposed onto a thin metal substrate.

Method

A small piece of 0.0005" thick chemically cleaned nickel foil is folded in half and the edges turned over and flattened to seal one surface of the foil. The foil is then clamped between two electrodes in the apparatus shown diagramatically in Fig. 19.1.

The "carbon cracking" apparatus consists of a borosilicate glass chamber (constructed from a standard 6" diameter vacuum desiccator), to which are sealed two glass vacuum stopcocks. One leads to a small methyl iodide reservoir; the other via a vapour trap, to the pumping system. A brass top plate, into which are sealed the electrodes, air admittance valve and pressure gauge, is itself sealed to the glass chamber by means of an "O" ring.

A few millilitres of enriched methyl iodide (converted from 56% enriched barium carbonate [6] with an efficiency of 96%[7] are introduced into the reservoir and frozen by immersing the reservoir in a CO_2-trichloroethylene slush. The system is then evacuated with all stopcocks open. The methyl iodide is isolated from the main chamber and the nickel foil outgassed by passing an electric current through it until it reaches a bright red heat. When the vacuum has stabilized at a steady value ($\sim 1 \times 10^{-5}$ torr) the temperature of the nickel foil is reduced to approximately 750°C. With the main chamber sealed from the vacuum system, methyl iodide is introduced by opening the isolating valve and gently heating the reservoir until a chamber pressure of 40 Torr is obtained. After a period of approximately two minutes the reservoir is once again immersed in CO_2-trichloroethylene slush and isolated from the system. Any residual methyl iodide vapours are condensed by evacuating the system

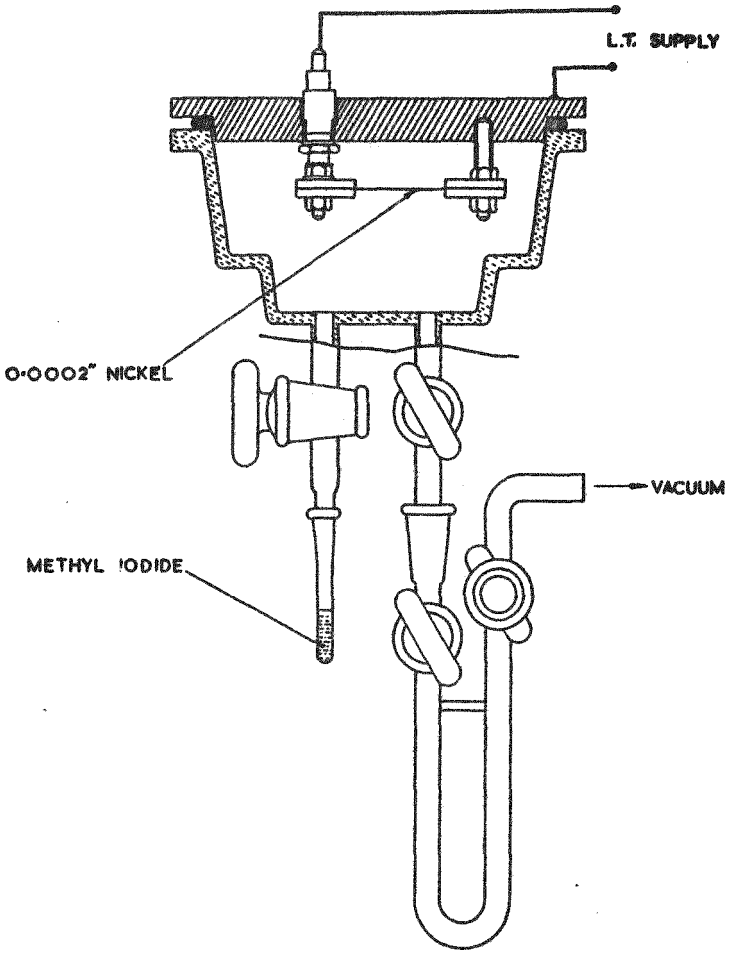

Figure 19.1 "Carbon cracking" apparatus

once more through the liquid nitrogen refrigerated vapour trap. The remaining vacuum stopcocks are closed, isolating the chamber from both the trap and vapour system. It is now possible to remove the complete trap, containing the residual methyl iodide vapour, for future recovery of the isotope. After admitting air to the chamber the carbon coated nickel foil is removed and floated, carbon surface uppermost, on a Petrie dish containing 10% H_2SO_4, 20% HNO_3 and 70% H_2O etching solution. Approximately 30 minutes elapses before all traces of nickel are dissolved from the back of the carbon foil. The solution is diluted with distilled water, until all traces of acid have disappeared, and the floating carbon foils are picked up on suitable target frames.

Conclusions

Satisfactory self-supporting foils up to 100 $\mu g/cm^2$, of both ^{13}C and ^{14}C, have been made by this technique. To vary the thickness of the carbon deposit, Kashy et al [3] varied the methyl iodide pressure from 2 to 25 Torr; we found this made very little difference and in fact 40 Torr appeared to be the optimum pressure. The upper limit of thickness appeared to be approximately 100 $\mu g/cm^2$, due to the nickel supporting foil requiring more and more current to maintain a satisfactory depositing temperature. The temperature seemed to be limited by either poor thermal transmission through the deposited carbon film, or, as suggested by Holmgren[2], the possibility of small amounts of oxygen absorbed in the methyl iodide oxidising the nickel near the supporting clamps. The poor conductivity of nickel oxide would make it difficult to dissipate sufficient power in the nickel foils. We found that overheating the nickel foil produced an insoluble deposit, perhaps due to the formation of nickel carbide. An alternative way of heating may be to focus an external light source (1000 watt lamp) onto the centre of the foil. Other workers have used chromic acid, $2:2:1/H_2O:HNO_3:H_2SO_4$ and ferric chloride solutions to strip the nickel but we found that either the etching action was too violent, resulting in gassing which punctured the carbon, or else a deposit of iron was left on the carbon due to a displacement reaction.

Discussion

Mr. E. H. Kobisk, ORNL, said that large quantities of ^{13}C and ^{12}C would soon be available and therefore carbon rods of these isotopes would be possible for the formation of isotopic carbon films by vacuum evaporation.

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PAPER 20

PREPARATION OF ISOTOPIC METALLIC FOILS AND BULK ISOTOPIC METALS FROM OXIDES*

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Impurities in isotopic materials used to study nuclear reactions and properties frequently cause inaccuracies in resolution by broadening observed resonances with overlapping peaks of similar energies from other isotopes of the same element or different elements, or by masking weak resonances of specific nuclei by stronger impurity peaks in the same energy region. Furthermore, the specific number of atoms in a sample must be known for accurate cross-section measurements, and impurity atoms of unknown number and type can adversely affect measurement results. For these reasons, the Oak Ridge National Laboratory Target Center initiated a program several years ago to produce high-purity isotopes for use in making targets in thin film, rolled foil, or bulk forms. Oxygen and nitrogen content have been reduced by melting metals in vacuum using electron-bombardment heating. Other techniques being developed to enhance the chemical purity of isotopes and to form them into targets include zone refining, pyrolytic deposition of metals, single-crystal preparation, and vacuum reduction of oxides to metals with simultaneous distillation of the product.

Both resistance heating and electron-bombardment heating have been used to convert various oxides to their elemental forms. The use of a variety of metal reductants has been studied, particularly for the preparation of the metals of rare-earth isotopes. Isotopes of the rare earths in metallic form for use in physical research have previously been unobtainable.

Oxide reduction at high temperature was first investigated to provide metallic magnesium isotopes either in bulk quantity or in thin film form. Powdered magnesium oxide was mixed with a slight stoichiometric excess of aluminium powder and heated on a tantalum filament to ~1100°C. Magnesium was produced by the following reaction:

$$3MgO + 2Al \rightarrow 3Mg\uparrow + Al_2O_3$$

---

*Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

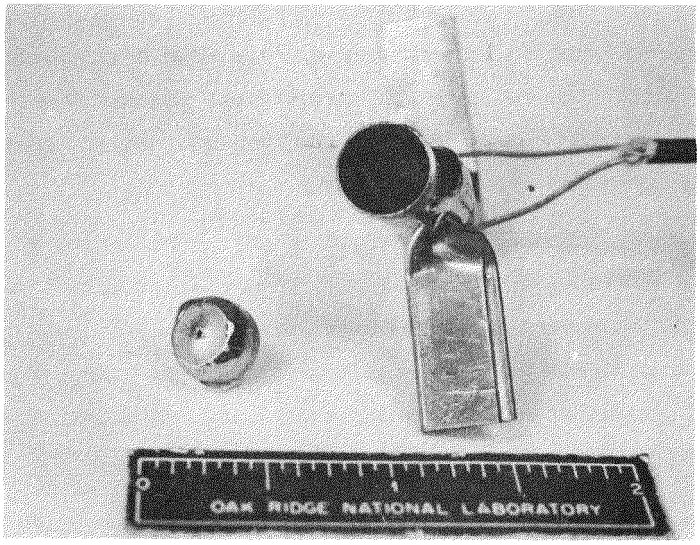
Use of a simple resistance filament, however, caused excessive loss of material and contamination of the distillate with aluminium, whose vapor pressure is $\sim 10^{-4}$ torr at $>1020^{\circ}C$. Filament geometry itself prevented good temperature control.

To obtain a high-purity product at a low distillation temperature, several resistance heating methods were studied; only the most productive will be noted here. A mixture of powdered magnesium oxide and a 100% stoichiometric excess of aluminium powder, in the form of a pressed pellet, was placed in a tantalum crucible (Fig. 20.1). Pelleting was used to achieve intimate contact of reactants and to obtain better heat conduction.

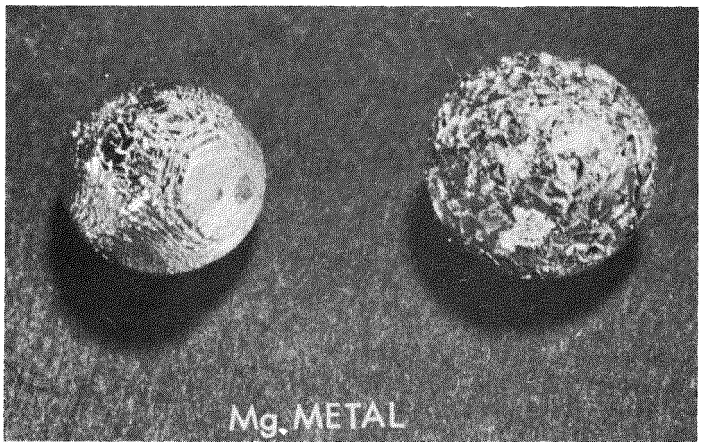
Since the pellet remained intact during the reaction, handling problems and crucible contamination were reduced to a minimum. A cap with a 40-mil-dia. effusion port was placed on the crucible so as to collimate the vapors. The crucible was heated resistively with low-voltage high-current ac power; crucible temperature was measured with a chromel-alumel thermocouple spot-welded to the crucible wall. Rapid reduction with simultaneous distillation of the product was found to occur at $\sim 1018^{\circ}C$. The metal distillate could be condensed onto a glass plate substrate and removed by peeling without using a parting agent or without exposing it to water. At $\sim 780^{\circ}C$ with a pressed pellet, a product containing <200 ppm of aluminium was routinely obtained.

To obtain bulk material, a water-cooled copper substrate was placed over the effusion port $\sim 1/16$ in. above the cap. As the metal distilled out of the crucible, a stalactitic growth formed on the substrate blocking the effusion port. Continued distillation of metal inside the plugged crucible formed a crystalline deposit inside the cap as an extension of the stalactite. The polycrystalline nature of the magnesium "flowers" can be seen in Fig. 20.2. Extremely high-purity metal was obtained in this manner because the deposits were grown in an atmosphere of the metal vapor after initial exclusion of oxygen, nitrogen, and other residual gases during the growth of the stalactite from the water-cooled substrate. Although activation analyses have not been performed on this metal, the purity level is such that foils of magnesium can be prepared by cold rolling - a feat performed only on normal magnesium having very high purity.

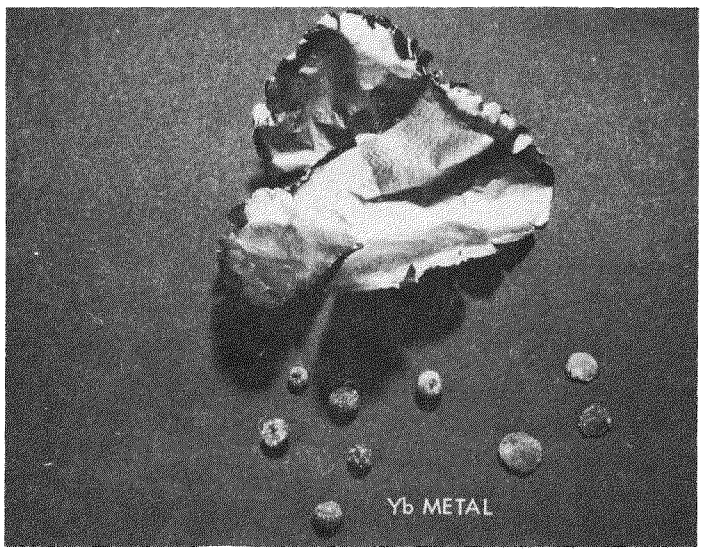
The condensation zone for the magnesium metal distillate was maintained at a lower temperature than the reaction zone so as to obtain the flower configurations. If the temperature was too low, growth did not occur, instead the entire cap of the crucible was coated with metal.



AERE - R 5097 Fig. 20.1
Tantalum Metal Crucible Used for Resistive Heating of Magnesium Oxide-Aluminium Metal Pellets. Effusion plug (left) with 0.040-in. port is used to cap the crucible during growth of magnesium "flowers".



AERE - R 5097 Fig. 20.2
Magnesium Metal Condensed from the Vapor Phase During Distillation from a Magnesium Oxide-Aluminium Metal Pellet.



AERE - R 5097 Fig. 20.3
Ytterbium Metal Condensed from the Vapor Phase During Distillation from a Ytterbium Oxide-Aluminium Metal Pellet. Metal beads are shown pressed (lower right hand corner) and finally rolled into foil 1 mg/cm^2 thick.

Single-crystal growth could be achieved, but the narrow temperature interval was difficult to maintain because of changes in the rate of heat dissipation in the crystal as it became larger. A single crystal ~6 mm in dia of ^{24}Mg was grown in this manner.

Rare-earth metals of high isotopic purity have been prepared by similar techniques and rolled into thin foils < 1 mg/cm^2 and areal density of ~50μ in. thick. Figure 20.3 illustrates flowers, pressed pellets, and a rolled foil of ytterbium metal produced in this manner. Rare-earth metals successfully prepared by reduction-condensation with < 300 ppm of reductant as impurity are Eu, Gd, Ho, Er, Yb, and Lu. The reductant used for each of the metal oxides is given below:

Metal Oxide	Reductant
Eu_2O_3	Aluminium powder
Gd_2O_3	Zirconium powder
Ho_2O_3	Tantalum filings
Er_2O_3	Zirconium powder
Yb_2O_3	Aluminium powder
Lu_2O_3	Zirconium powder

Selection of the reductant became more important when higher distillation temperatures were required so as to minimize contamination of the metal with co-distilled reductant.

Calcium metal isotopes have also been prepared as flowers using aluminium or lanthanum as reductants. Lengthy distillations at the lowest feasible temperature were required to keep aluminium contamination to a minimum. A ^{42}Ca foil of areal density < 1 mg/cm^2 was produced by reducing 50 mg of ^{42}CaO with aluminium, condensing the metal, and cold rolling in an argon atmosphere. This technique has also been applied to the production of 3 g of ^{241}Am in very ductile and bright metallic form. Similarly, strontium isotopes have been prepared as metal and rolled into foils. It should be noted that both electron-bombardment and resistance heating techniques have been used to prepare these metals by oxide reduction and vaporization-condensation of the metal products.

Another technique that has proved most useful in preparing high-purity metal isotopes is that of pyrolytic decomposition of a volatile compound, usually a metal iodide of the desired element. For example, zirconium iodide, formed by direct reaction with elemental iodine at ~350°C, can be volatilized in a chamber containing an electrically heated tungsten filament at 1200°C; the purified zirconium metal is deposited through pyrolytic decomposition on the filament and the free iodine can

return to the impure zirconium metal reservoir to react again. This technique works only where impurities do not form volatile iodides. With this technique, clasically referred to as the Van Arkel-de Boer process, we have successfully prepared samples of between 1 and 10 g of zirconium, hafnium, and titanium isotopes and purified niobium metal. In all cases the impurity levels have been < 100 ppm. Physical evidence of this low impurity content may be noted by the high ductility of the materials and our capability of rolling these purified isotopes to thicknesses of ~ 0.5 mg/cm^2.

Rolling techniques employed at the ORNL Target Center do not vary significantly from most standard rolling processes. To be rolled, a sample of the metal isotope is usually melted into a bead which is then pressed and rolled in a sandwich of Type 304 stainless steel. Two types of rolling mills have been employed: a 4-high mill having 1.5-in.-dia work rolls and another having 1.75-in.-dia work rolls. Two small 2-in. hand mills have been motorized and placed in glove boxes under argon atmospheres so that reactive metals like calcium, strontium, and rare-earth metals can be rolled to very low thickness. At present our technology has allowed a minimum thickness of ~ 250 μg/cm^2 of nickel to be rolled. Almost all materials can be rolled in the cold form rather than by using hot rolling techniques.

ROLLING AND PRESSING ISOTOPIC METALLIC FOILS

J. B. Reynolds

A.E.R.E. Harwell

1. Introduction

The rolling method can give self-supporting isotopic foils of high quality and is very convenient for production of large numbers. It is particularly appropriate for our present plan of converting a proportion of our stocks of isotopes into metallic foils.

2. Making the Bead

Metals with melting points below about 110°C can be safely melted in a silica tube using argon if necessary to prevent oxidation. Cadmium and zinc powders, however, must be fired in an evacuated, sealed silica tube heated to about 1000°C when the metal distils to the coolest part of the tube and the small droplets can be run together to form a large bead by tapping. Metals of higher melting point, e.g. iron and nickel, can be melted in silica using an R.F. furnace but there is some risk of silica contamination.

Before rolling, the bead should be pressed to a square or oblong shape not less than 0.020" thick, because it is important to start with a uniform piece of metal. The square edges ensure little wastage and a uniform piece rolls evenly. A non-uniform piece will deteriorate and will give holes when one tries to attain minimum thickness.

The more ductile metals can be pressed into uniform squares fairly easily with a laboratory press but harder metals may require pressures beyond 30 tons/sq. in. and so we have been experimenting with metal powders. These can be pressed directly after reduction - before any oxidation can take place and without chance contamination from the fusion - then sintered under vacuum at a suitable temperature (1200°C for iron and nickel). Using such compacts we have succeeded in rolling iron down to 10 mg/cm^2.

3. Rolling

The mill we use has two 4" x 2" diam. rolls and is electrically controlled to provide a reciprocating movement over 5 inches, so that a number of passes can be made with minimum attention. The technique has turned out to be a great help in dealing with small amounts of material. A strip of mirror finish stainless steel is used to sandwich the metal to be rolled. Reduction should be brought about gently, annealing where

necessary after about 40% reduction. As the stainless steel only reduces slightly, the metal foil being rolled is placed between lubricating foils of Melinex (1). Gypsum is a good lubricant with Melinex but unsuitable if slight contamination would be troublesome. Acid-free tissue paper serves well as a lubricant when rolling tantalum but must be pre-rolled until it becomes almost transparent. Everyday lubricants such as vaseline were used but did not appear to be very successful.

Using these aids foils of isotopes of the metals Cd, Ag, Sn have been rolled down to 1 mg/cm^2 and Ta to 2 mg/cm^2 with a little annealing. Cu, Fe, Ni, Pt and Pd have also been rolled to 1 mg/cm^2 using frequent anneals.

Such foils can be made even with very small amounts of starting material. For instance 2 foils 1 x 1 cm of thickness 1.2 mg/cm^2 were made starting with only 5 mg of an isotope of Pd.

4. Some factors influencing the limits of rolling

(a) Purity of metal

Because relatively small amounts of isotopes are separated a compromise is inevitable in the purification stage between chemical purity and loss of material. Impurities remaining may cause local faults in the metal which eventually lead to holes in the rolled foil.

(b) Surface dirt

Atmospheric dust will quickly damage foils during rolling so that cleanliness is essential. A method which completely envelopes the metal is a distinct advantage.

(c) Stainless steel strip

Should have mirror finish and be frequently polished. Indentations cause non-uniformity in the foil and quickly lead to holes.

(d) Care of the rolling mill

Misalignment of the rolls causes uneven films. Excessive pressure will quickly cause dents in the rolls; with small, thick beads great care is necessary at the start of the rolling process.

5. Thickness measurement

An average density is usually obtained by measuring the area of the foil and weighing. Variations in thickness across the foil can be estimated by cutting it into pieces. A more detailed measure of point-to-point variations can be determined by attenuation of alpha particles.

Fig. 21.1 shows the thickness contours of an early experimental rolled tin-foil determined by this technique. It reveals a range of thickness of ± 20% and also a gradient due to the rollers not being strictly parallel - other details of the fine structure could probably be ascribed to some of the causes mentioned in section 4 above. The alpha attenuation technique is thus valuable both in accurately delineating the target and also investigating the causes of faults.

References

1. Information from G. Whiley and Co., Ltd.
(The Author acknowledges the assistance given to him by this firm).

2. Determination by J. Turner, Nuclear Physics Division, A.E.R.E.

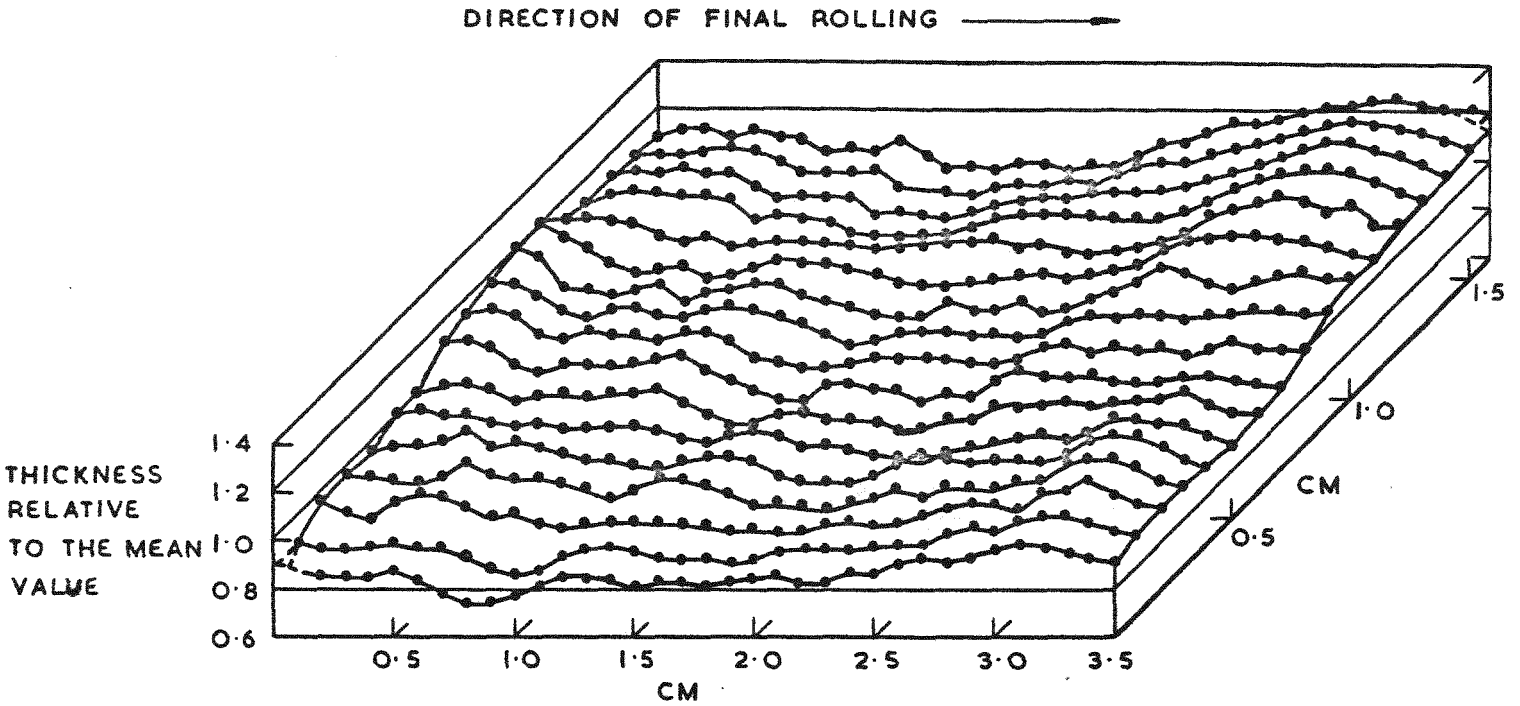


Fig. 21·1.

Superficial Density Distribution of a Rolled Sn^{118} Target.
(Mean Value 2·4 mg / cm^2)

FABRICATION OF ULTRATHIN METALLIC FOILS

Frank J. Karasek*

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Introduction

Metallic foils ranging in thickness from 5 mg/cm^2 to 50 $\mu g/cm^2$ are a necessary part of many nuclear reaction experiments. In many of these experiments self-supporting foils are preferred.

Commercial availability of many natural foils required for nuclear experimentation is for all practical purposes non-existent. This unavailability has led to development of methods of foil fabrication at the Argonne National Laboratory. These same methods have been utilized to produce the various isotopic foils that are also required. The sandwiching of foil between two sheets of stainless steel, and/or other metals has been used successfully to reduce the foil thickness well below the minimal thickness limits of the rolling mill used. One cannot in the allotted time describe fully the fabrication of all foils produced to date; therefore a general description of the procedures used is described. Production of targets from ^{24}Mg, titanium, and zirconium isotopes will also be mentioned.

Fabrication Equipment

Most of the foil rolling was done on either of two rolling mills. A 7.6 cm x 12.7 cm mill was used for rolling small cast samples or sheet. A 15.2 cm x 35.5 cm x 30.5 cm 4-high mill was used for cold rolling of sheet down to foil. This mill can roll materials directly down to 0.15mm. Either mill was used for the rolling of foil packs.

General Foil Fabrication Technique

Natural metal foils are prepared whenever possible from commercially available sheet or foil. When this is not possible (i.e., the material is not available as sheet, the sheet or foil is of limited purity, etc.) the metal or alloy is cast by arc or induction melting techniques. For the most part small melts need not be hot-worked, but can be directly rolled to sheet or foil forms with intermediate anneals.

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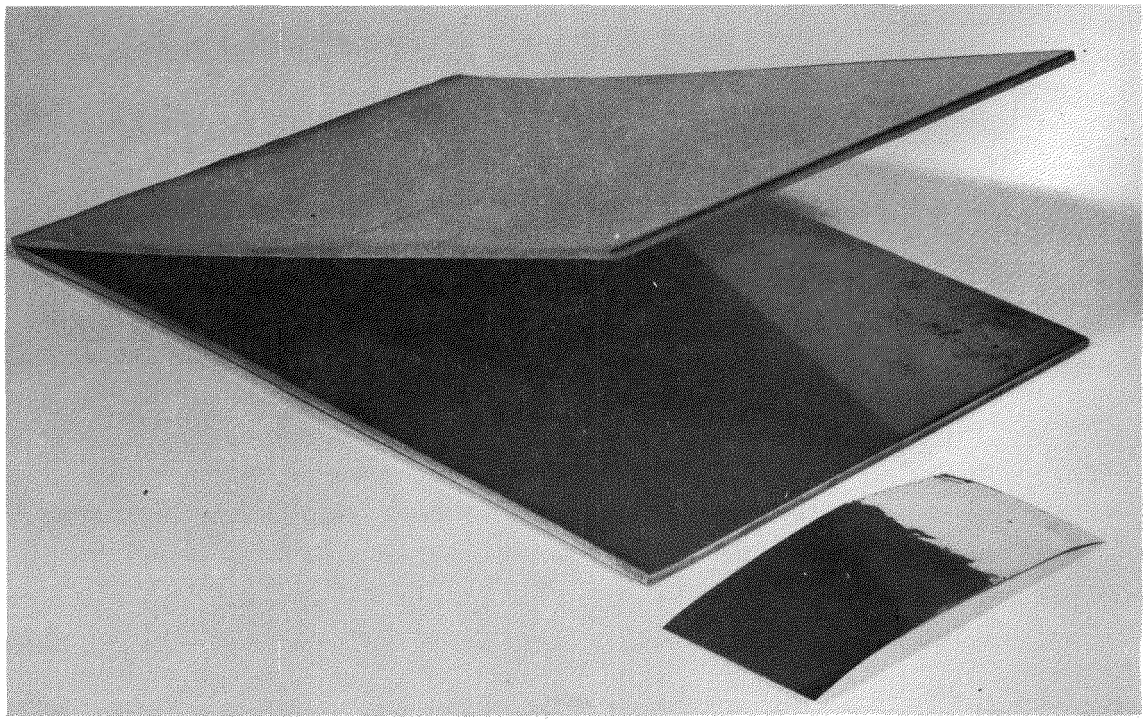
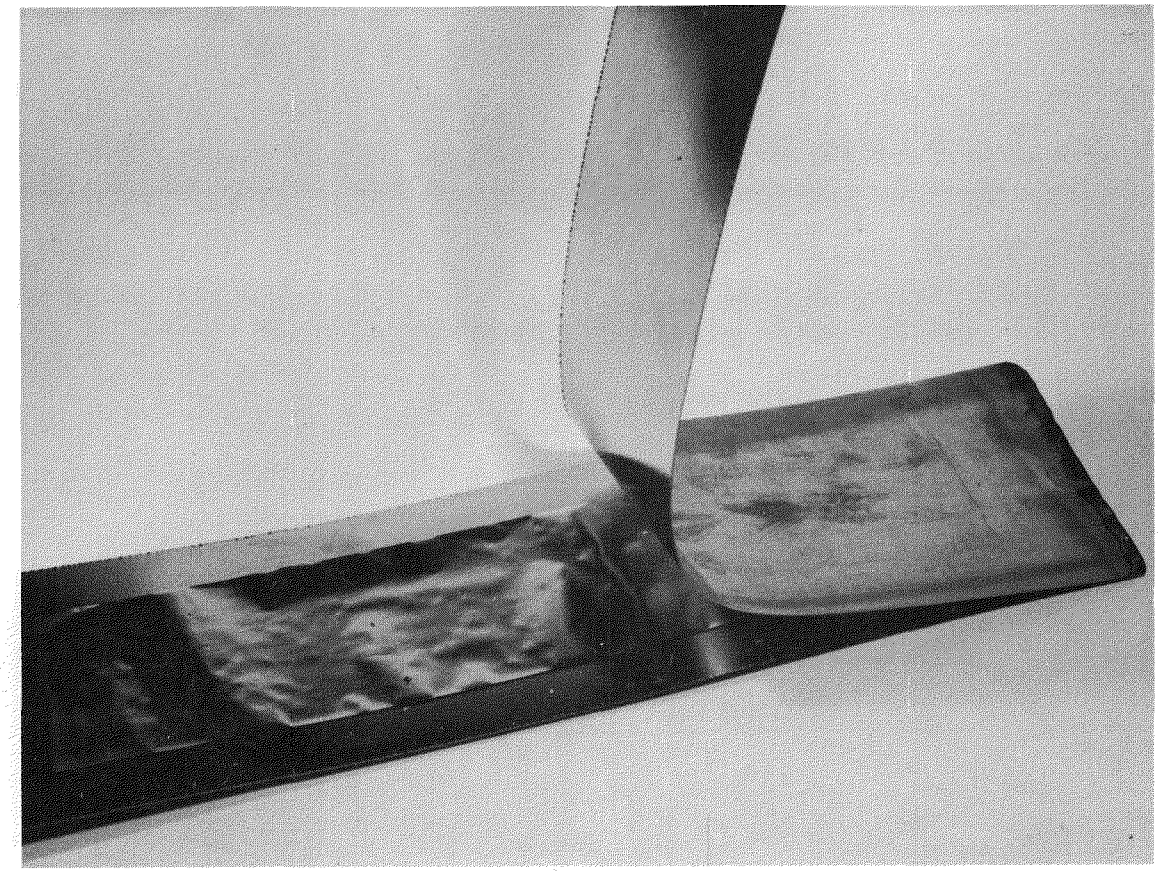
*Work performed under the auspices of the United States Atomic Energy Commission.



AERE - R 5097 Fig. 22.1 x 1
Stainless steel modified pack rolling can prior to rolling



AERE - R 5097 Fig. 22.2 x ½
Pack rolling can after rolling. Foil and pack cold rolled approximately 80% total reduction.

As previously mentioned, the existing equipment permits cold rolling directly to 0.15 mm. By modification of the commercial method of pack rolling, (i.e. the stacking and rolling of several sheets of the same material at one time), thicknesses of the order of 5×10^{-4} mm (2×10^{-5} in.) have been attained on some materials. Figure 22.1 illustrates a typical pack used for the cold rolling of foil. This pack consists of 1.6 mm thick stainless steel sheets stacked together with the lead edges welded. Copper, brass, and aluminium packs have also been used in some instances. The foil is inserted between the pack after which the whole assembly is rolled. New packs are used when necessary. Figure 22.2 shows a rolled foil and its containing pack. Reductions per pass and total reduction between heat treatment are factors that must be determined during the course of fabrication.

When necessary, intermediate heat treatments were performed either in an inert atmosphere or in vacuum. Thickness measurements of the completed foil were made by the cutting and weighing of a specific area. This method still leaves much to be desired in the way of accuracy, since calculated thickness and/or weight/cm^2 represents an average value for the overall area.

The general procedures described have been applied to the fabrication particularly of W, Y, Gd, Cu, Fe, Ni, Ti, Ag, Sc, Ta, Sn, V, Zn, Nb, Pd, Cr, Cd, Dy, and/or their isotopes down to a range of 1 mg/cm^2 or less.

For the most part natural materials are available in a high degree of purity, whereas isotopes may contain varying amounts of sulphide, oxide, and/or, interstitials. Reprocessing of the isotopic metals has, therefore, been necessary as a prelude to satisfactory foil fabrication.

The success one attains in the fabrication of metallic foils is dependent upon many factors. Purity, methods of rolling, (i.e. reduction, roll speed), heat treatment, etc., are functions of the material being worked. Factors that are the same for any foil being rolled are, in my opinion,

1. Cleanliness. Both the foil and the pack interior should be free of oils, fingerprints, dust and scratches, if defects in the foil are to be minimized.

2. Reduction per pass during modified pack rolling.

3. Amount of cold work present in the stock used in the making of rolling packs.

Reductions per pass are namely 5 to 15 per cent with occasional multiple passes at these same reduction settings. Excessive reductions per pass can generate excessive heat which may lead to the sticking of

the foil. In some cases ignition of the foil may also occur. Limiting thicknesses to which the various metals can be rolled have still to be determined.

In summary, this method of foil fabrication has been extremely satisfactory for producing self-supporting foils. Some difficulties have been encountered during the rolling of softer metals (i.e. Sn, Zn, Cd), but these for the most part can be overcome if one proceeds cautiously.

Fabrication of ^{24}Mg Foil

This isotope was obtained as vapor deposited foil fragments having a thickness of approximately 5 mg/cm^2. They were rolled in a stainless steel pack and further rolled. Several packs were utilized in order to attain the required target thickness of 50 $\mu g/cm^2$.

Fabrication of Titanium and Zirconium Isotopes

In the preparation of the foils of zirconium 90 through 94, and of titanium 46 through 49, great difficulties were experienced with the original metal powder due to interstitial contamination; therefore, purification was necessary and was accomplished by the Van Arkel hot wire method which produced a high purity metal rod with a central core of 0.08 mm diameter tungsten wire. The rods were of sufficient density and ductility, permitting one to directly work the as received rods. These were cross-rolled down to foil size, then radiographed to locate the tungsten wire which was subsequently removed by cutting of the foil. The foils were then pack-rolled down to the desired foil thickness. Because of the purity of the materials prior to rolling, no intermediate anneals were necessary. These isotopes were initially rolled to a thickness of 1 mg/cm^2. Since then, sections of these same foils have been further reduced to approximately 300 $\mu g/cm^2$.

HIGH FREQUENCY LEVITATION HEATING AND ITS APPLICATIONS TO (i) EVAPORATION OF THIN LAYERS and (ii) PREPARATION OF HOMOGENEOUS Al ALLOYS

J. Van Audenhove
C.B.N.M. Euraton, Geel

1. Principles of levitation heating

The principles of high frequency levitation heating can be summarised as follows: The eddy currents produced in a piece of metal heated in a conical induction coil interact with the high frequency field, and the metal tends to move out of this field. When the upper turn of the coil is wound in the opposite sense to the lower ones there will be a point along the axis of the coil where the opposing fields are equal thus creating a potential well. With such a coil design it is possible to obtain the conditions necessary for stable levitation melting of a piece of metal.

2. Vacuum evaporation of metals by high frequency levitation heating

2.1 Description of the evaporation equipment

Fig. 23.1 shows the design of a water cooled levitation coil (1), the turntable (2), quartz supports (4) with metal charge (5) to be evaporated and the glass manipulating rod (6) used to raise the metal into the coil or to put a refractory crucible (7) under the coil in order to receive the metal when it drops out the coil.

This fig. also shows the bakeable substrate mounting (8) and his shielding (9).

The levitation coil is connected to a 4 KW, 1 MC high frequency generator. In a first series of experiments we examined multiturn coils (up to 8 turns) similar to those successfully used by earlier investigators for levitation melting in inert gas at nearly atmospheric pressure.

With those coils the solid metals could be floated in vacuum, but glow discharge occured immediately after the melting of the metal. However, glow discharge can be avoided by reducing the maximum potential across the coil; and since the maximum potential across large multiturn coils is higher than across short coils, we use short ones consisting of 4 turns as indicated in fig. 23.2

2.2 Experimental results

With the large coil quantities from 1 g down to 100 mg of Al, Ag, Ti, Co, Cu and U can be levitated and remain in a stable molten

drop form allowing evaporation in vacuum.

With the minicoil stable evaporations with starting quantities of 3 mg upwards can be realized. Using this technique the evaporation rate is not constant, since the temperature of the metal decreases as its volume lessens during evaporation. However, experiments indicate that the weights of the deposited layers are reproducible (± 2.5%) for evaporations repeated under identical conditions, i.e. constant power input, evaporation time, pressure and charge material. During these experiments the power input was roughly controlled by the hand operated current control knob of the induction heater. Still better results can probably be obtained by using an electronic high frequency current stabilisator.

Layers of 50 to 100 microgram/cm^2 with a homogeneity of about 1.7% are obtained on substrates with a diameter of 50 mm. The distance between substrate and molten source was 230 mm. As for all single source vacuum evaporation techniques, the efficiency of this method is poor. However, during the evaporation with 200 to 1000 mg quantities, about 50% of the evaporated metal condenses on the water cooled induction coil and can easily be stripped off the coil without significant copper contamination.

In the case of evaporations with small quantities (less than 20 mg) of expensive isotopes, a funnel shaped quartz vacuum receiver can be placed inside the induction coil. This method is suitable for short time evaporations (10 sec to 1 min) and has the advantage that the metal deposited on the quartz receiver can generally be recovered in the form of a chemical compound.

3. The quantitative preparation by levitation melting in argon of homogeneous aluminium alloys for nuclear measurements

3.1 Description of the alloying equipment

Fig. 23.3 shows the design of a water-cooled levitation coil (1), a turntable (2) with metal charge (3) to be melted, a graphite mould (4), a water-cooled copper mould (5) and a glass manipulating rod (6) used to raise the metal into the coil. The levitation coil consists of 7 turns of 3 mm o.d. copper tubing arranged as indicated in fig. 23.4. It is protected by a quartz funnel on the inside and a quartz shield at the base [fig. 23.3(7)] to avoid a short-circuit by accidental metal spitting during melting or casting. Power is supplied to the coil from a 12 kW, 1 Mcps high frequency generator and aluminium alloys from 3 to 12 g in mass can be prepared with this arrangement. Water cooled cylindrical chromium plated copper moulds as well as alumina covered graphite plated split moulds suitably vented are used (see fig. 23.5).

3.2 Experimental results

10 g amounts of homogeneous Al-alloys with 0.1 to 5% of Au, Ag, Mn, Co, B, Ir, Rh, Lu or Dy and with 1 to 24.5% ^{235}U have been prepared by melting and casting in an argon atmosphere at 300 Torr.

This alloying method is highly quantitative: losses of pure Al and Al-alloys melted at ± 1300°C and cast in the Cr plated water cooled copper mould are smaller than 150 ppm (for 10 g amounts). The extremely efficient stirring of the melt and the rapid sollidification in the mould made it possible to obtain supersaturation of the alloying element in Al (e.g. Al-1.5% Mn) or to obtain finely dispersed intermetallic compounds, in an Al matrix.

Fig. 23.6 shows the Al-1% Co eutectric alloy. The as-cast alloy has a double phase structure. After heat treatment at 600°C during 14 hrs this structure globulized as shown in fig. 23.7.

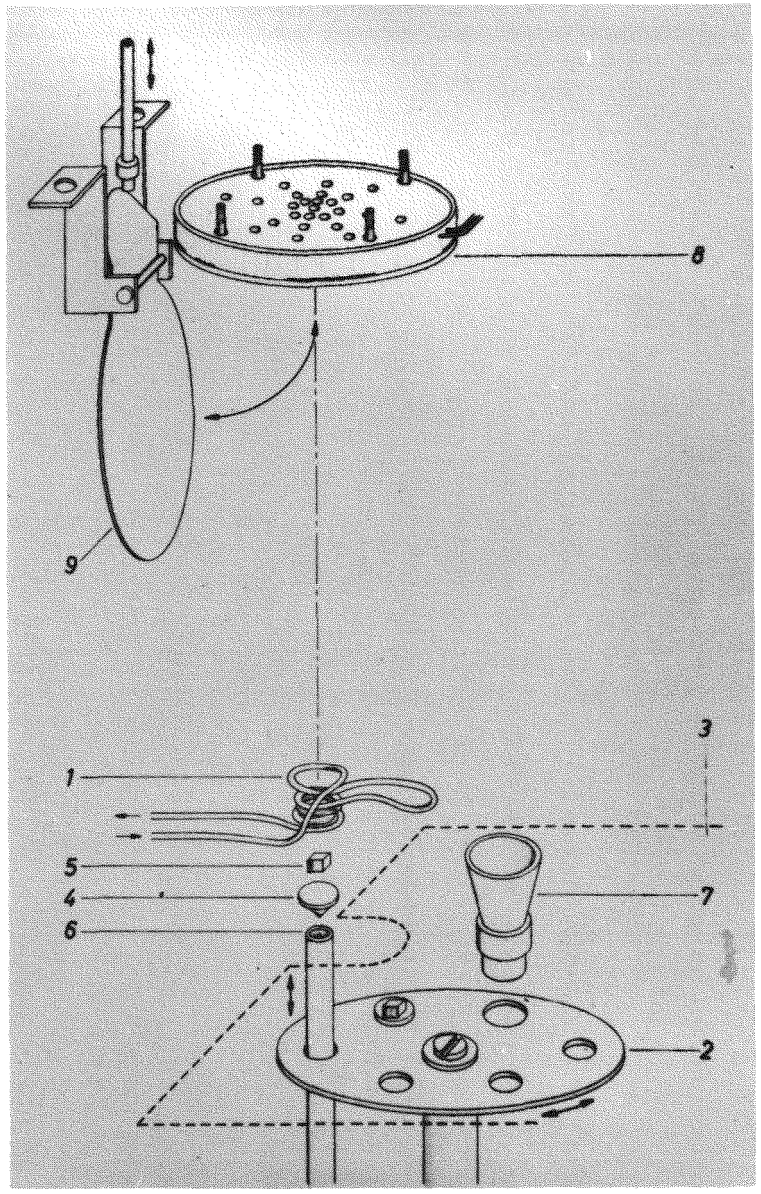
Fig. 23.8 shows the Al-0.3% B alloy with AlB_2 needles dispersed in a Al-matrix.

Fig. 23.9 shows the cast structure of Al-24 w.% U, with primary UAl_3 crystals on which fine needle shaped UAl_4 crystallized in a Al matrix. Heating at 600°C during 24 hrs gives a completely globulized structure as shown in fig. 23.10.

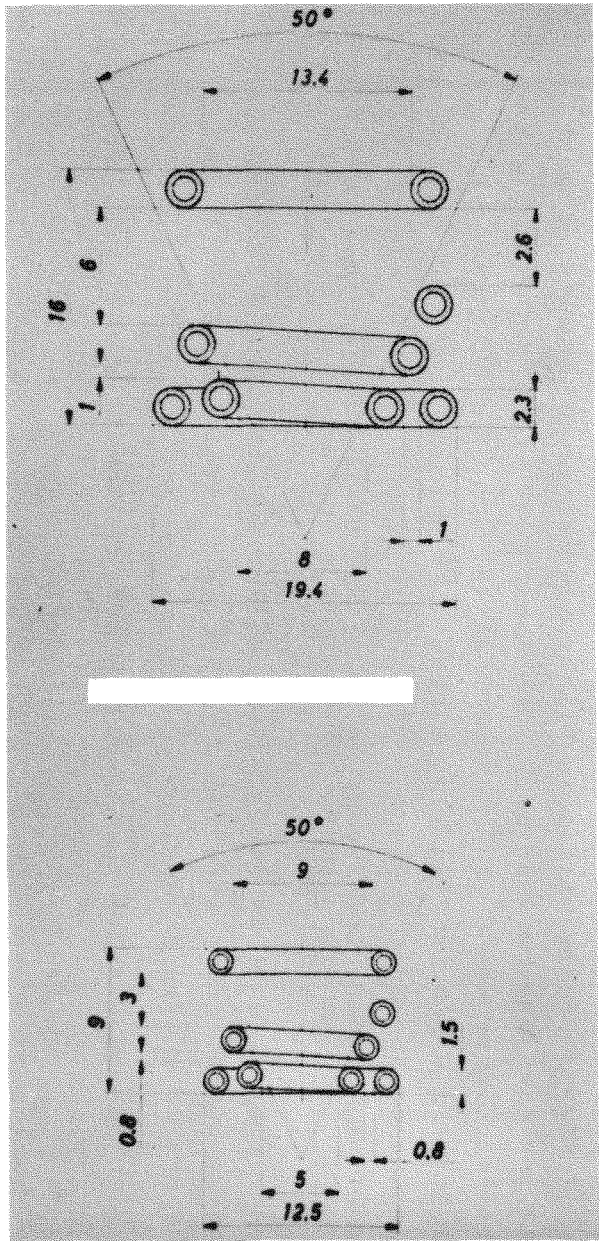
Analytical methods to define all the forementioned alloys with a precision as good as or better than 1% are not yet available; but we can conclude in the case of Al-1.5% Mn, Al-0.4% Au, and Al-20 to 24.5% U alloys that the homogeneity is better than 0.5% relative and that the maximum deviation from the nominal content is 0.5% relative.

In the case of Al-1% Co, activation analysis indicated that the homogeneity is better than 0.3% relative.

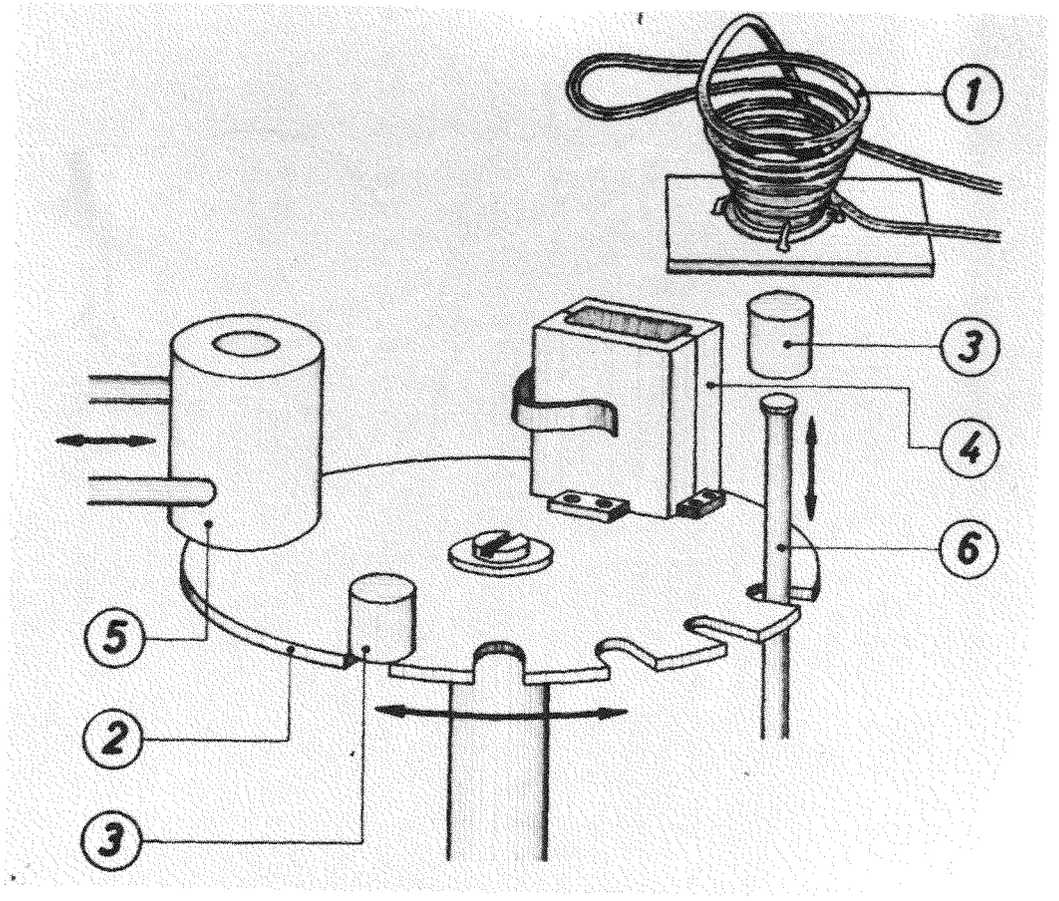
All these analysis are made on 20 to 50 mg specimens taken from different areas of different castings.



AERE - R 5097 Fig. 23.1



AERE - R 5097 Fig. 23.2



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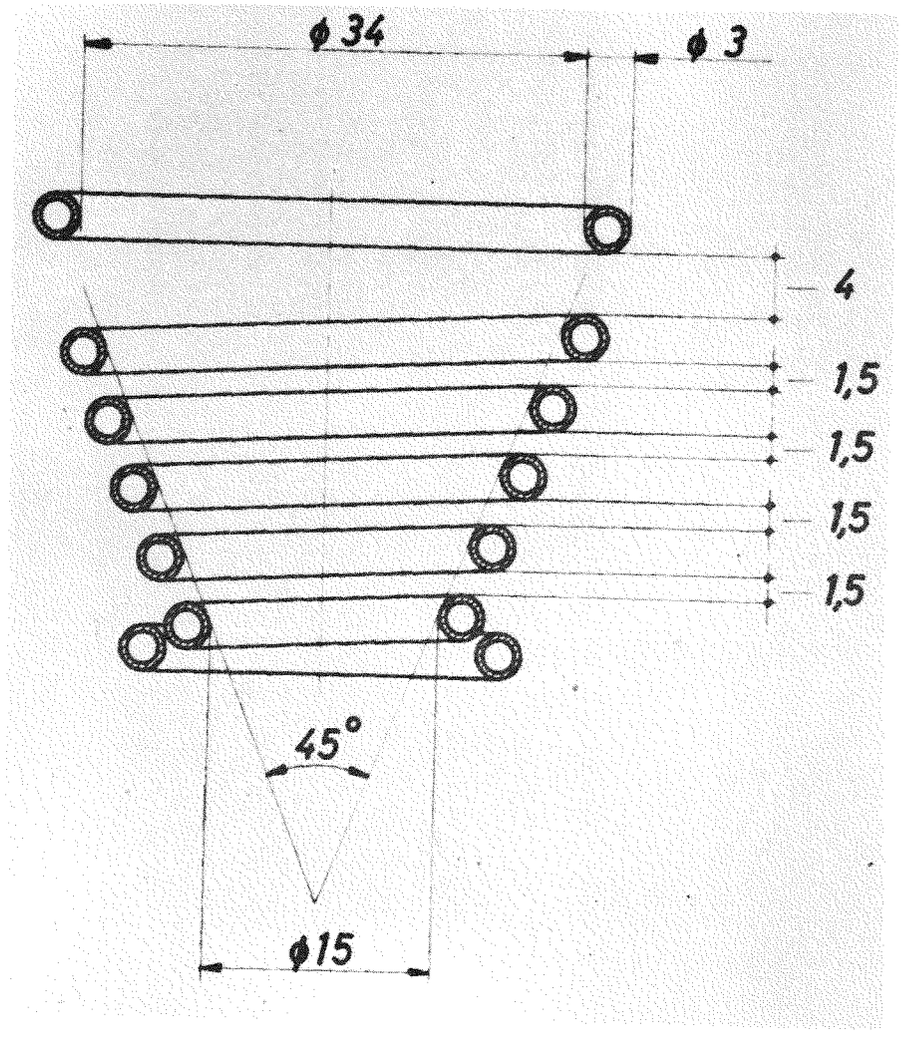

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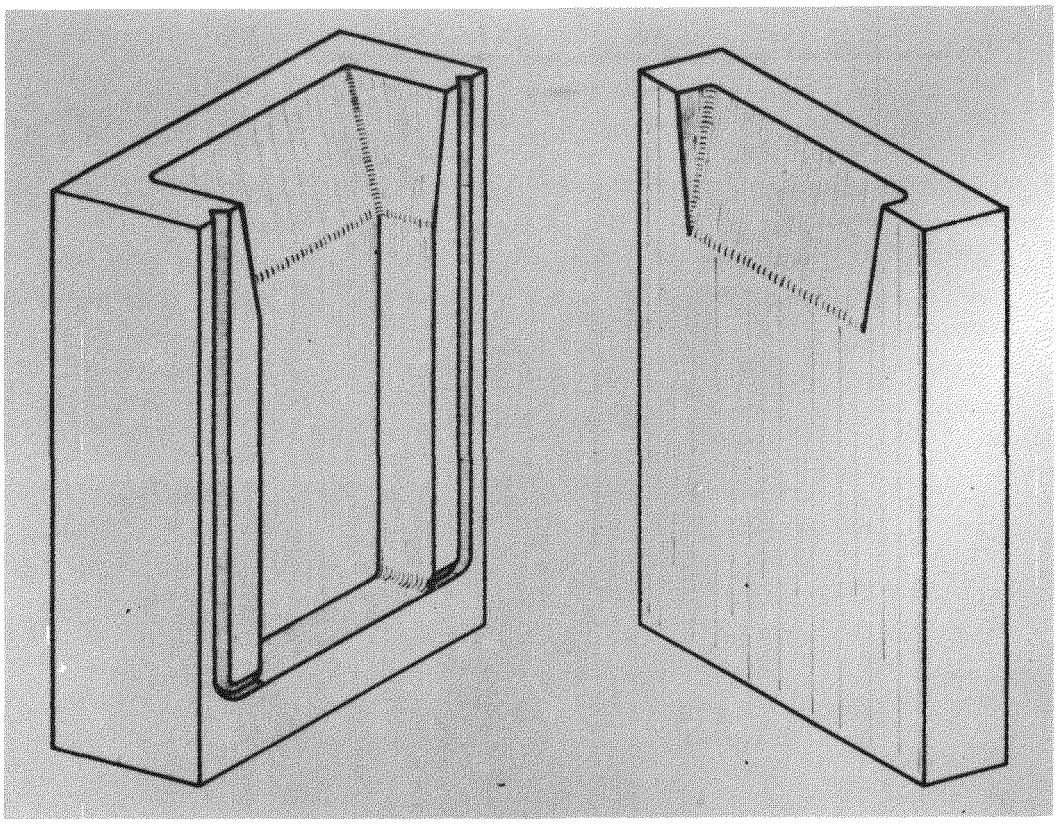

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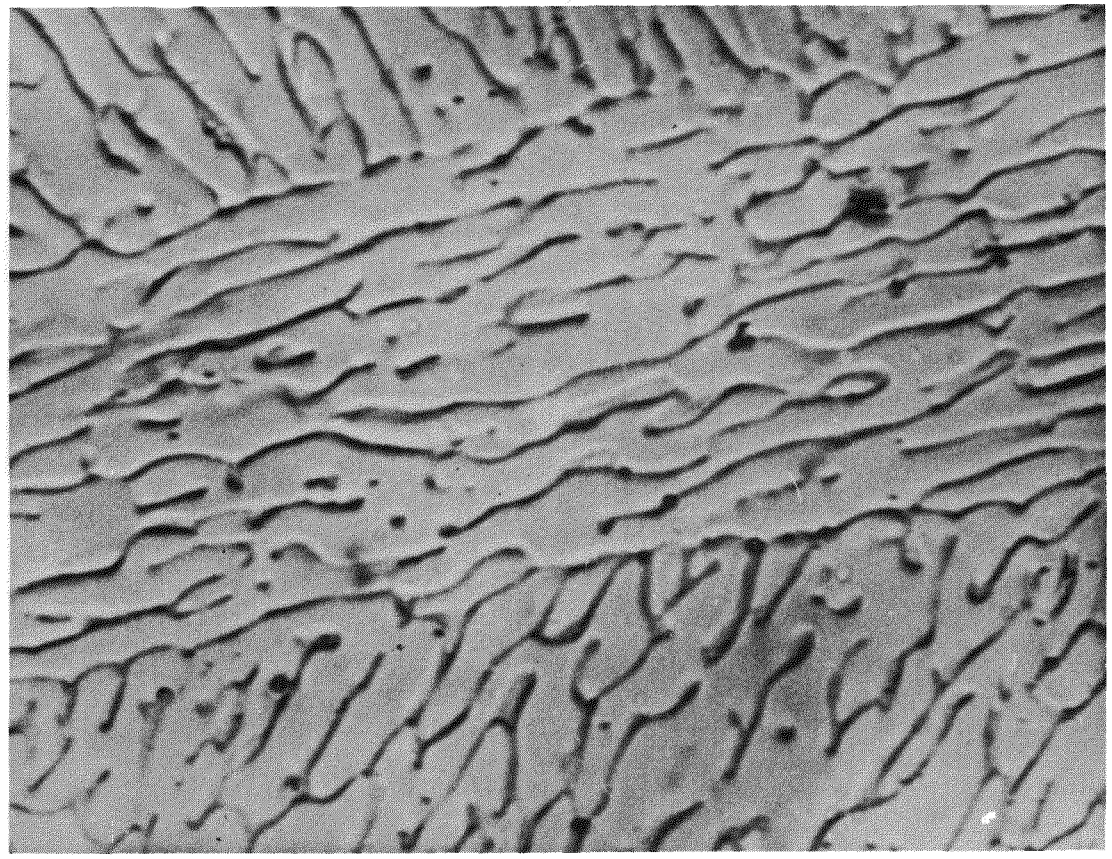
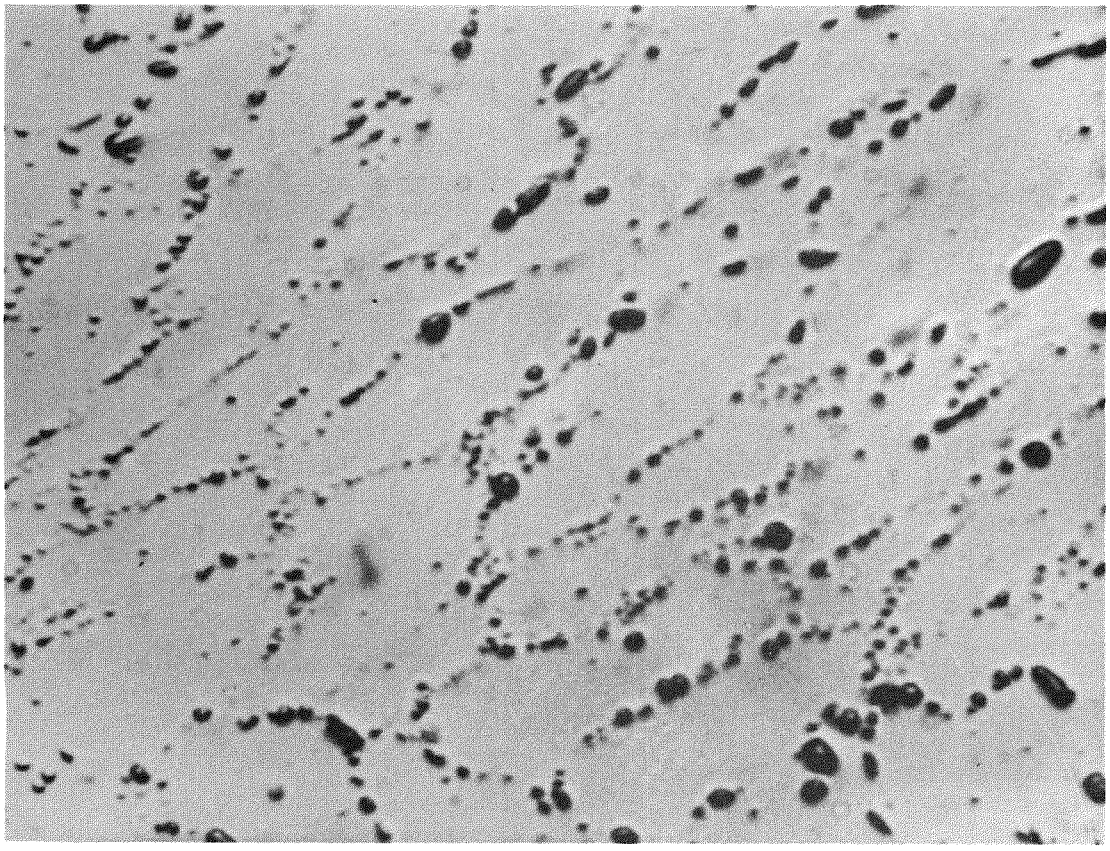


AERE - R 5097 Fig. 23.6



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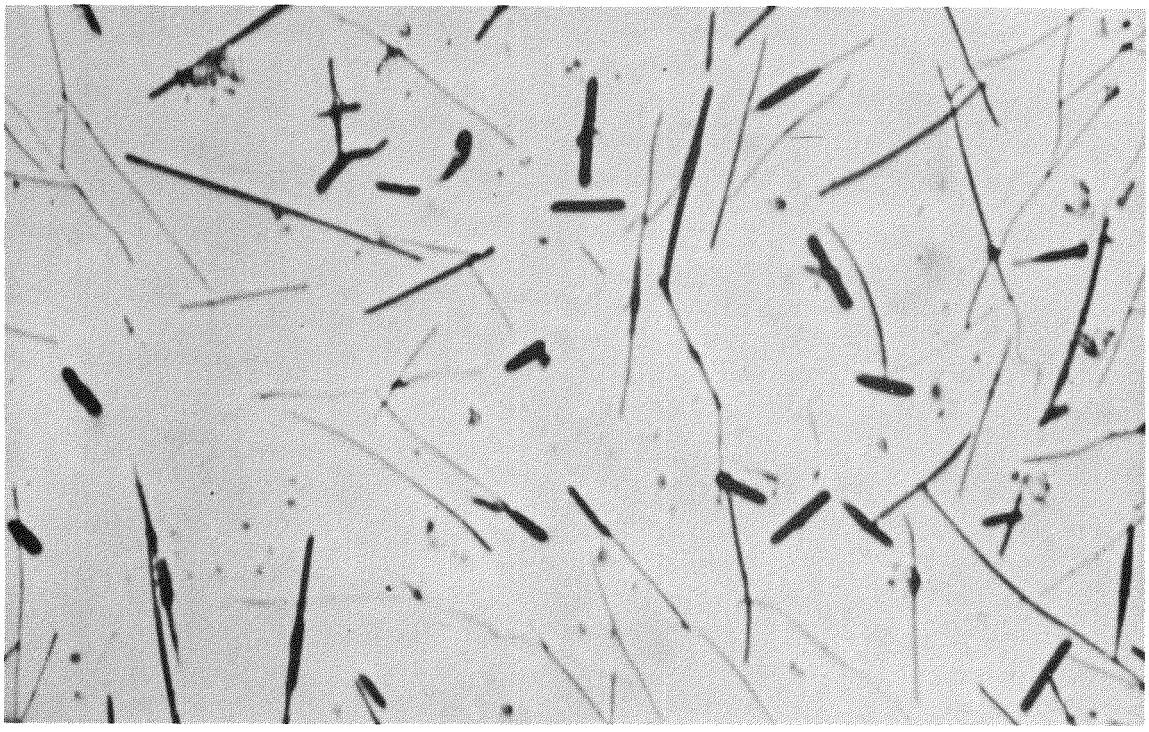
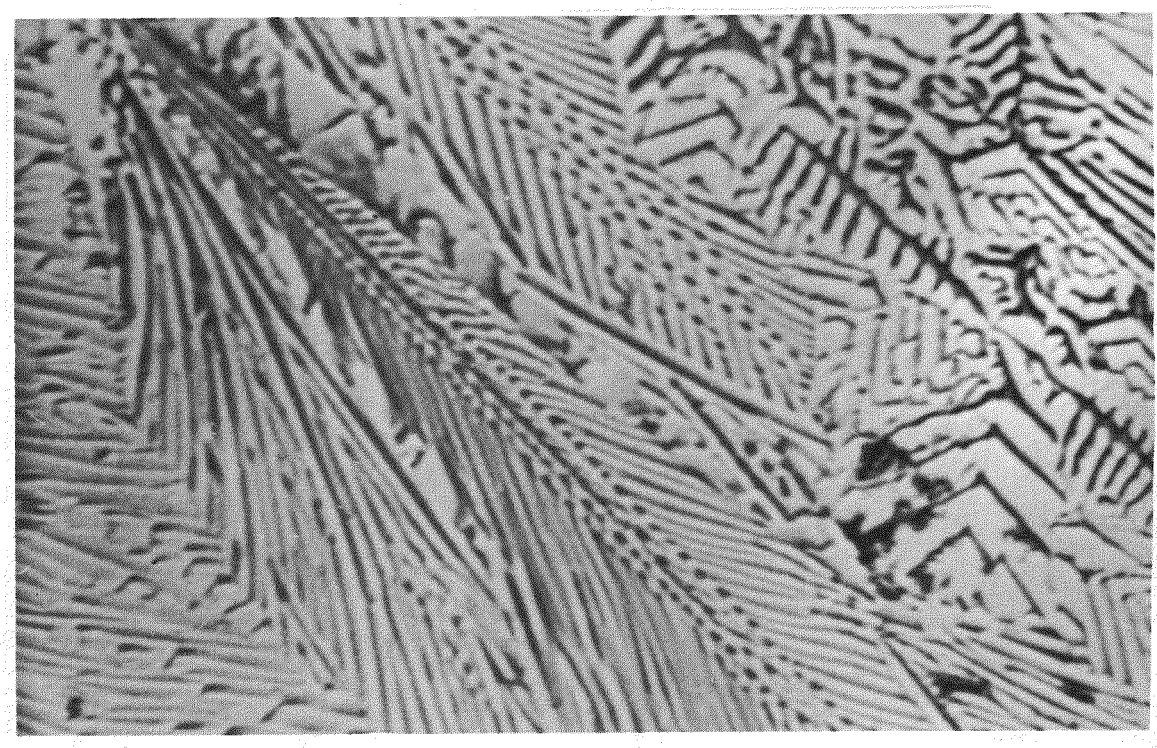
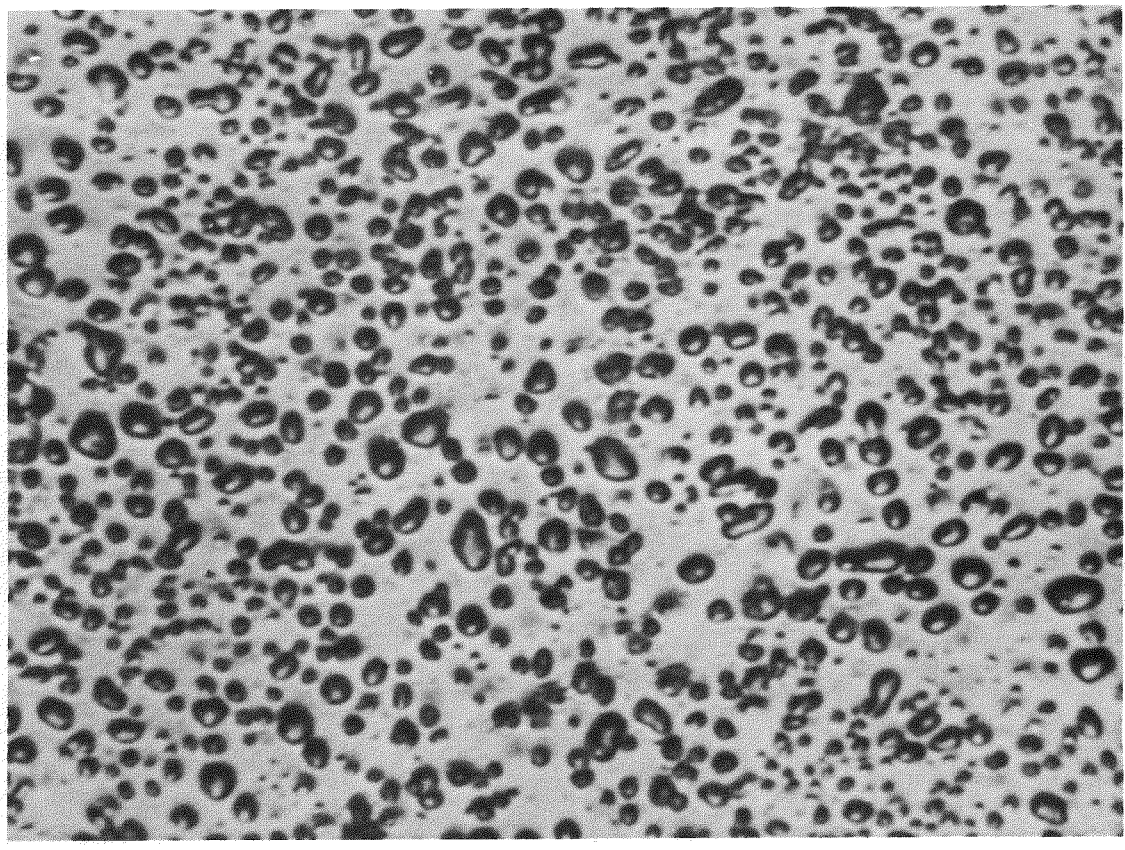


AERE - R 5097 Fig. 23.8



AERE - R 5097 Fig. 23.9



AERE - R 5097 Fig. 23.10

A CRITICAL SURVEY OF METHODS FOR DETERMINATION OF FILM THICKNESS APPLICABLE TO NUCLEAR TARGETS

F.A. Howe

A.W.R.E., Aldermaston, Berks.

Introduction

The following devices used for weight determination of stable isotopic and natural targets in our laboratory are briefly surveyed.

Balance Weighing

Alpha Particle Thickness Monitor

Modulated Beam Photometer

Densitometer

Crystal Thickness Monitor

Dynamic Balance

Vapour Beam Ratemeter

A comprehensive survey of most of the known methods of thickness measurement has been made by Pulker and Ritter[1], and an English translation is held by A.W.R.E.

Balance Weighing

When our interest in thin films began several years ago, this was the main method available, and it is still very important today. Our first few measurements of very thin films frequently produced apparently negative weights, this being tracked down to loss of weight by the substrate due to outgassing - ~10 $\mu gm/cm^2$. The difficulty was largely overcome by keeping the cover slides used as substrate at about 100°C in a vacuum oven until required; but a slight loss of weight must still be allowed for if the substrate is taken to a higher temperature during the evaporation.

The subsequent gain in weight by the newly formed film and outgassed substrate on exposure to air is also troublesome, but rapid weighing on a well-damped semi-micro balance in an air conditioned laboratory minimises this error. We find the full microbalance takes a long time to stabilise, and hence its accuracy cannot be used to advantage. Reasonably accurate measurements of films weighing less than 10 $\mu gm/cm^2$ call for considerable experience, but a typical cover slide coated to about 100 $\mu gms/cm^2$ can be weighed with better than 1% accuracy.

The method is still very widely used, especially in the calibration of the other devices to be discussed.

Alpha Particle Thickness Gauge

The paper by Enge et al[2] aroused our interest in the method. At that time information on air equivalent thicknesses of the various elements for alpha particles was lacking, and this coupled with the time taken for measurement and the embarrassment of the polonium source caused us to abandon the idea. Later however, Dr. Eccleshall of AWRE measured a 20 $\mu gm/cm^2$ iron film, on a 50 $\mu gm/cm^2$ carbon support after the method described by Ramavatarans[3], and obtained a 6% accuracy. A spread of about 20% in the actual measurements obtained was thought to be due to variations in the target thickness. The method enables mounted foils to be measured non-destructively and in this respect is rather valuable.

The Modulated Beam Photometer

This device is used by the optical industry in the production of filters, and is capable of accurate measurement of light transmission. For our purpose, it is limited to use with translucent foils and must be calibrated by chemically assayed or balance weighed foils. The calibration being non-linear, and different for each material, is a tedious process. It has however the distinct advantage of measuring film thickness during the formation process.

We have found it valuable for the monitoring of gold deposited on V.Y.N.S. plastic 4π B counter foils, where repeatable accuracy is required.

The equipment is fairly expensive ~£400 and being bulky is not particularly suitable for building into laboratory type apparatus.

The Densitometer

This is another optical device used for measuring the degree of transparency, and although specialised in its application, is well worth consideration at a cost of around £50. We have constructed simple masks for our standard target mounts. These form the light tight enclosure essential for accurate measurement, and also protect the mounted foil from damage. The device is particularly useful for the measurement of carbon and gold foils used as backings for those target materials which require support. Calibration is necessary as for the previous optical device.

The Crystal Thickness Monitor

This has justifiably received considerable attention recently and is now commercially available. Muggleton and myself reported on a single laboratory built apparatus[4] and advantages include: the facility to monitor continuously during the film formation; wide range of measurement - less than 1 $\mu gm/cm^2$ to several $milligrams/cm^2$; sensitivity variable; ease of calibration because this is linear over the working range and is the same for all materials. Calibration is best carried out with gold

and accuracy is improved if the crystal itself is weighed.

The main cost is that of the frequency meter, and a good digital type meter is ideal; this meter and the beat frequency oscillator can be used to serve several evaporators. At AWRE we have used 1 M/C AT cut crystals and evaporation onto a 3/16" dia spot; this gives some 2 $\mu gm/cm^2$/cycle, a working range up to 10 m.grms per crystal before departure from the linear law, and is quite ideal for our purposes. It is reported however that 10 M/C crystals can give 500 x more sensitivity, e.g. 4×10^{-9} gms/cm^2/cycle. The crystals are, however, temperature sensitive, some types more than others, so care must be taken to avoid undue heating.

The latest AWRE device planned will use 2 similar crystals placed side by side in the vacuum system. Only one will be exposed to the evaporant, the other will be heated independently by a small lamp filament to equalise the temperatures, so that in a dummy evaporation run very little frequency drift if any, will be observed. It is to be noted that errors may also result from heating of the oscillator components, so the location of these must be considered. The error due to the thermal energy of the vapour condensate is not sufficient to warrant consideration in normal use.

The Dynamic Balance

This is an adaptation of a Microammeter movement. When used as a balance, the torque produced in the meter balances the weight of evaporant on the vane. When used as a rate meter the torque balances the force due to impinging vapour molecules, the meter arm being maintained in the horizontal position by signals derived from 2 photo diodes. The main problems are the fragility of the movement, and drift in sensitivity from thermal effects. The range of measurement of the unit tested was limited to 100 $\mu gms/cm^2$ for full scale deflection of the meter, when resetting becomes necessary.

It is not possible to use the device as a ratemeter with electron bombardment evaporation because of the electrostatic forces involved. The unit is also sensitive to vibration. Being mass sensitive, calibration is simple.

Vapour Beam Ratemeter

The device measures the ionisation of the evaporant beam, and can therefore be used only with electron bombardment. By means of a feed back system to the crucible heater, it is possible to stabilise the rate of evaporation, but we found the motorised follow-up system too slow to be effective. We have found it useful for the monitoring of uranium and beryllium evaporation, where the calibration is unaffected by the excessive heating from the vapour source - as other measuring devices may well have been in similar circumstances. The whole coverage of the

vapour beam can be put to productive use with this device. By careful setting up and timing, good estimates of total film thickness can be obtained.

This device, and in fact most of those discussed will have errors due to variations in the sticking coefficients of the surfaces. This is particularly evident when materials such as magnesium, lithium and zinc are evaporated.

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(1) Vak.-Tech. May 1965.

(2) Enge et al. Rev. Sci. Instrum. Vol.28 145 (February 1957).

(3) Ramavatarans et al. Nucl. Instrum. Meth. Vol.4 239-242 (May 1959).

(4) Nucl. Instrum. and Meth. Vol.28 (1964) No. 2.

TABLE 24.1

Method	Measurement Capability	Accuracy	Remarks	Approximate Cost
1. Balance Weighing (in air)	Normally up to 20 grams	Using differential weighing ± 5 μgms	Basic standard almost essential.	£200
2. Alpha Particle Thickness Gauge	Few μgms/cm up to milligrams/cm^2	Typical figure of 5% for 20 μgm/cm^2 Fe. Probably 1% for larger air equivalent thickness.	Measurement of mounted foils, and checking targets after use. Very good for special applications.	£50 plus source and counter
3. Modulated Beam Photometer	Translucent film only Typical ~15 μgm/cm^2 Al ~300 μgm/cm^2 gold	That of calibration method	May be used during deposition process or in open laboratory as required. Very good for range covered.	£400
4. Densitometer	" " " "	as (3) + 5%	Accuracy limited by meter used on instrument. For measurement of completed foils on holder or glass slide.	£60
5. Crystal Thickness Monitor	< 1 μgm/cm^2 to 10 milli gm/cm^2	~1% plus calibration error which should be small	Used during film formation under vacuum and probably best method available for general use.	£250 for meter and Oscillator plus £30 for each vacuum system served
6. Dynamic Balance	0 - 100 μgm/cm^2	~5%	Sound Basic principle. Development of Device required and could be calibrated direct by calculation of electrically induced torque	£50 for sample unit plus £30 for electronic control unit
7. Vapour Beam Ratemeter	No limit	~10% 5% should be achieved with careful control of evaporation rate and timing	Useful where high temperatures during evaporation are unavoidable and where full use of vapour beam is required.	Head £30) Control) Unit £220) Automatic plus Power) Supply £750) or Simple Ratemeter about £100

PAPER 25

THICKNESS MEASUREMENT AND MASS DETERMINATION OF EVAPORATED LAYERS

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C.B.N.M. Euratom Geel

Introduction

A short survey of the most commonly used methods of thickness measurement is presented, with emphasis on methods used in Euratom (e.g. optical densitometry, alpha- and beta-absorption, mechanical measurements).

Experimental data indicate that considerable mass changes occur when substrates are exposed to vacuum and/or heat treatment, and even under normal laboratory conditions. This may seriously affect the ultimate accuracy of layer thickness definition. The instrumentation and the technique of weighing evaporated layers in vacuo is described.

1. Review of Methods

The Table 25.1 lists the techniques which are most frequently used[1-4]. Nearly all methods are applied to foil thickness measurement, whereas the first three methods are less suitable for the assay of thin layers on (comparatively thick) supports.

Table 25.1

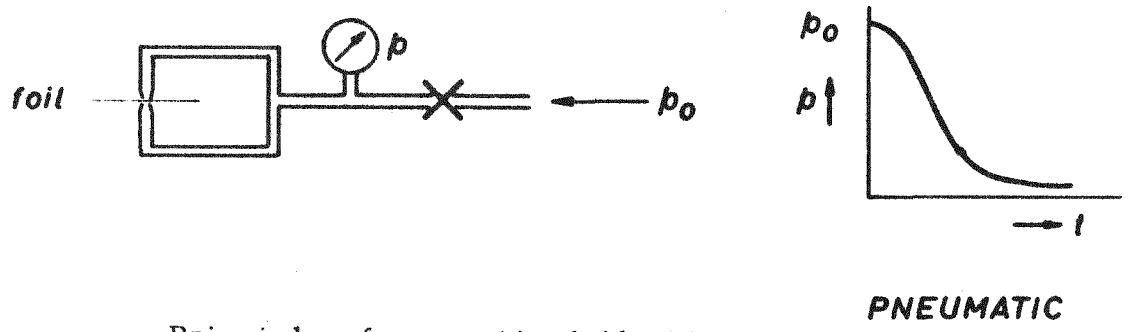
THICKNESS MEASUREMENT OF FOILS AND LAYERS

MECHANICAL	Micrometer, dial, etc. capacitive, inductive pickups
PNEUMATIC	
IONIZING RADIATION	α, β, γ, X-ray absorption
OPTICAL	interferometry ellipsometry densitometry fluorescence
GRAVIMETRIC	
CHEMICAL ANALYSIS	
ACTIVATION, ACTIVITY	
TRACER TECHNIQUES	
ELECTRICAL	

Techniques tried out in our laboratory include:

(i) Pneumatic measurement[4,5]

In fig. 25.1 the pressure p is a function of the clearance between nozzles and foil. At fixed distance between the nozzles, p is a function of foil thickness; with sufficient supply pressure p_o a region between the nozzles may be found where vertical displacement of the foil has no influence on the reading of p.



Principle of pneumatic foil thickness measurement.

Fig. 25.1

Advantages of this method are:

a. High sensitivity with simple equipment,

b. No mechanical contact with the foil.

Several serious limitations have been found:

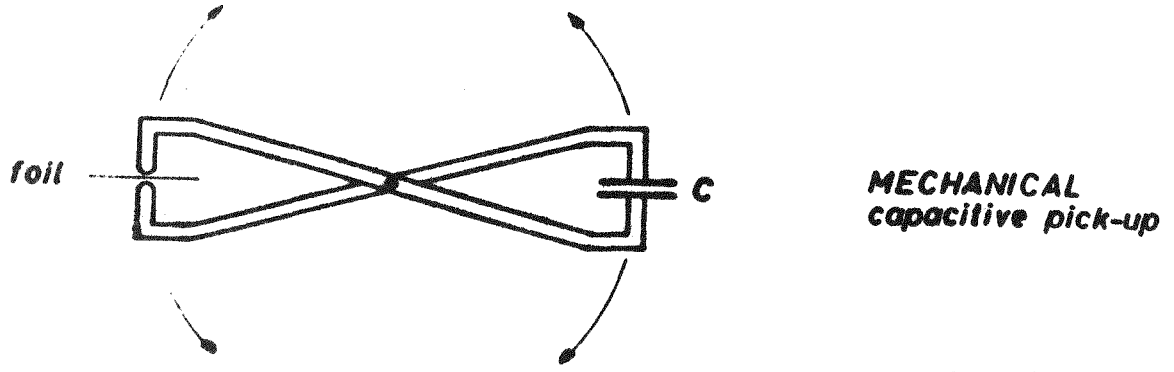
a. In order to have a region where movement of the foil between the nozzles is not sensed, p_o has to be about 2 atm. But then the air flow causes deformation and even damage of the foils.

b. Surface roughness has an effect on the reading.

Therefore, application is limited to foils thicker than about 0.1 mm. Reproducibilities better than ± 0.002 mm are difficult to obtain.

(ii) Mechanical capacitive pick-up

Adjustable contact pressure is obtained by loading with weights with the device shown in fig. 25.2. Distance between the contact points is detected with a variable capacitor and a sensitive capacitance measuring device.



Mechanical measurement with capacitive displacement detector.

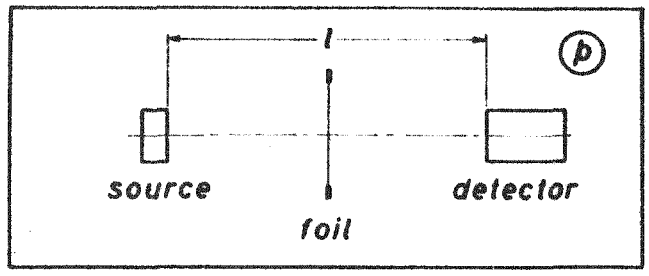
Fig. 25.2

Reproducibilities are ± 0,0001 mm. The influence of contact pressure is measured by taking readings at different pressures and extrapolation to zero. This seems a useful method for metallic foils, down to about 0.02 mm (i.e. of the order of 1 mg/cm^2).

(iii) Absorption of α radiation

This is applied to thicknesses up to about 100 μg/cm^2 with a reproducibility of ± 2 μg/cm^2.

The distance between source and detector is equal to the range of the α particles. Insertion of the foil is compensated by variation of either air pressure p or distance l.



Absorption of radiation

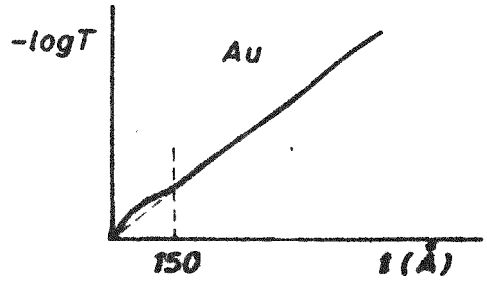
Schematic of α absorption measurements. Either pressure p or distance l may be used to express thickness in "air equivalent".

Fig. 25.3

The thickness range between 100 μg/cm^2 and several mg/cm^2 may be covered by β-absorption or X-ray fluorescence and X-ray absorption.

(iv) Densitometry

Thin layers on transparent substrates are measured with a microdensitometer. For several elements (e.g. Au) the absorbance log $^1/_T$ is proportional to thickness with the exception of a region of very small thicknesses (see fig. 25.4). In the proportional region this method is very suitable for determination of the uniformity in thickness of evaporated layers.



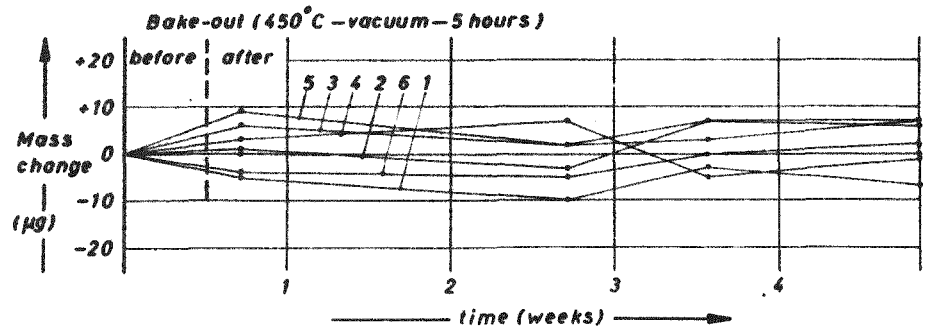
Densitometry

Absorbance of Au layer vs thickness.

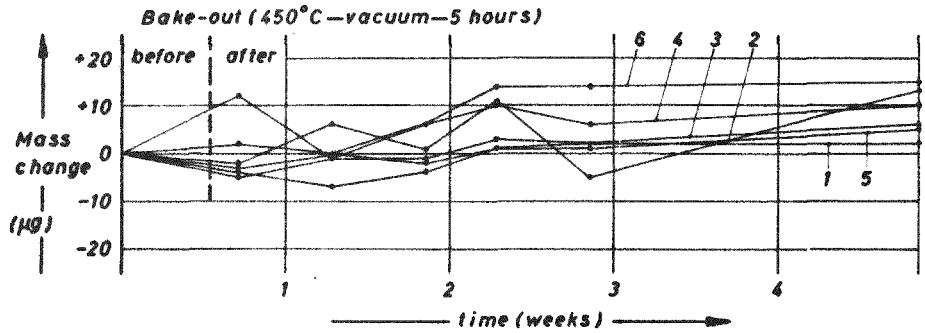
Fig. 25.4

(v) Direct weighing

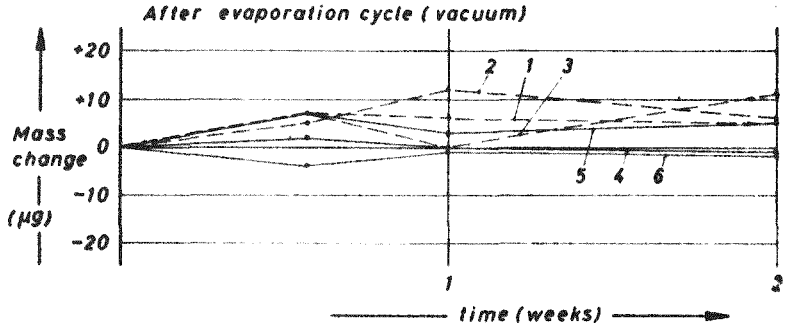
For many experiments the thickness expressed in mass per unit surface area is most important. Therefore direct weighing of foils is frequently applied. Apart from very thin foils mounted on frames, this presents no difficulties. Mass determination of layers is a difficult technique, since the relatively heavy substrates show mass variations under laboratory conditions and especially when they have been exposed to vacuum conditions and heat treatment. This is illustrated by figs. 25.5, 25.6 and 25.7.



Al-(Levitation Melting) discs ø 3 cm



Stainless steel-discs ø 3 cm



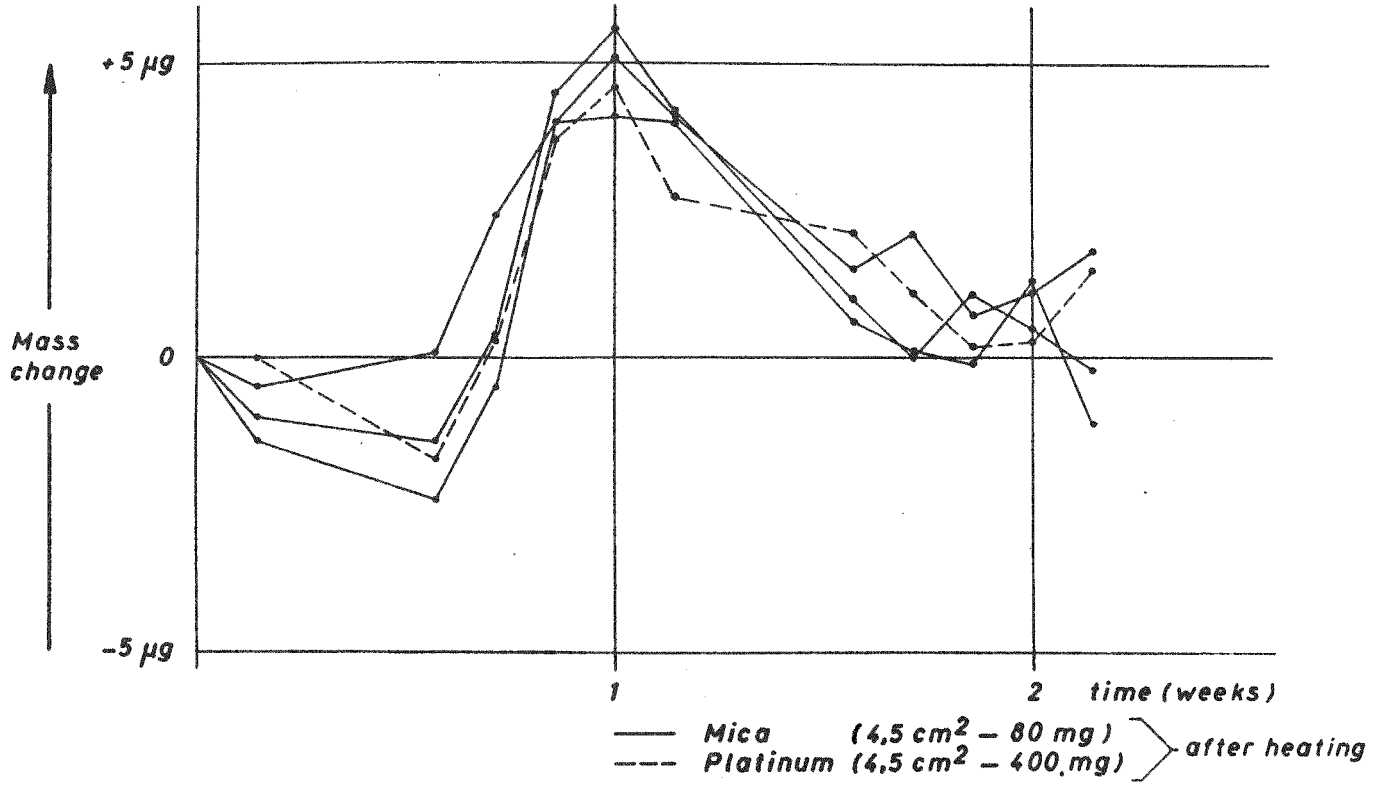
Stainless steel-discs ø 3 cm
Stainless steel + Boron (100 µg/cm²)

Mass variations of:
a) Al discs,
b) stainless steel discs,
c) stainless steel discs with B layer, compared with blank discs.

Fig. 25.5

Figs. 25.5a and b show mass variations of Al and stainless steel discs, 30 mm diameter and 0.6 mm thick, which have been chemically cleaned. First mass readings were taken; these readings are considered as "zero mass" in the figures. Then all samples were baked out at 450°C in vacuum during 5 hours. When again exposed to atmospheric air both mass increases and decreases were found. And even when kept in the weighing room at constant temperature and humidity conditions significant mass changes were observed over several weeks.

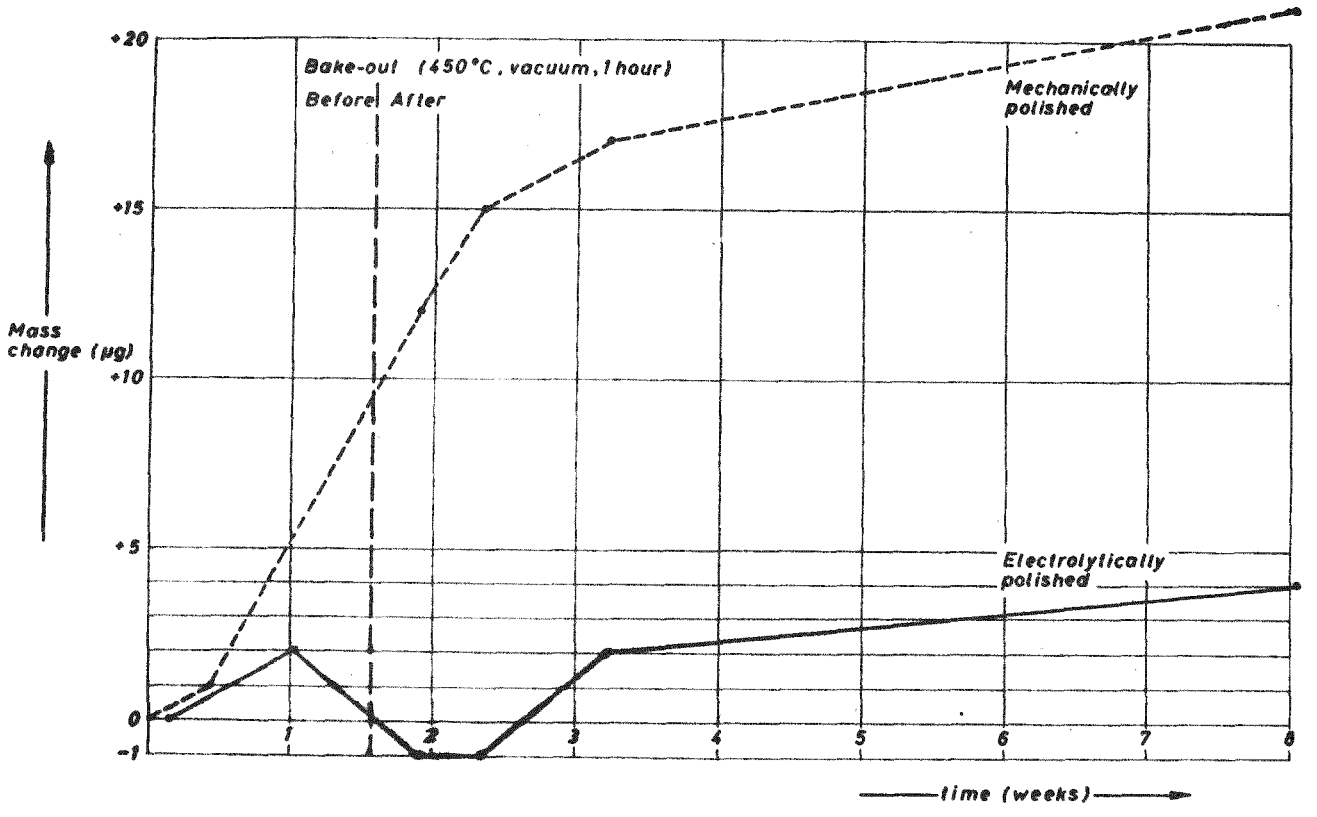
Some of the stainless steel discs (nos. 1, 2 and 3) were used as substrates for vacuum evaporated boron layers. The remaining discs nos. 4, 5 and 6 were placed back-to-back with these substrates during the vacuum evaporation cycle. After this cycle the masses were recorded (fig. 25.5c). There seems to be no difference in behaviour between the two groups of discs. In all these mass determinations the standard deviation was 2 μg. Fig. 25.6 shows the observed mass variation on 3 mica samples as simultaneously compared with a sample of Pt of about the same surface area. Despite the difference in material the samples seem to follow each other. In this case the standard deviation per weighing was 0.7 μg.



Mass variations of mica samples as compared with a Pt sample.

Fig. 25.6

Fig. 25.7 demonstrates the effect of different surface finish for equal samples (standard deviation in this case was 1.7 μg).



Comparison of mass variations of electro-polished stainless steel discs with mechanically polished disc.

Fig. 25.7

It is clear that for layer thickness determination, better than ± 1 μg, weighing in air can (at present) not be applied. If the evaporated layer reacts with air, this becomes still worse. Weighing in vacuum and ultra-high vacuum seems to be the answer.

Two methods are applied in our laboratory:

1. An uhv type microbalance was developed[6], which allows samples of 2.5 g to be weighed with 0.3 μg standard deviation per single weighing.

   Main difficulties in application of this balance are that great care must be taken to avoid dust collection on the substrate and that at high vacuum conditions (10^{-5} to 10^{-6} torr) radiometer effects and molecular flow have a direct influence on balance reading.

   At uhv conditions (e.g. 10^{-8} torr) the last two effects are negligible.

2. Quartz resonators[7,8] are very sensitive (< 0,01 $\mu g/cm^2$) and relatively easy to operate. Main limitations are, that the layer thickness of the sample might not be equal to the layer thickness on the resonator (evaporation geometry), and that the temperature of the resonator influences the indication.

Study of mass effects on substrates in ambient and in vacuum conditions will be continued because of the importance of gravimetric layer thickness determination, not only for vacuum evaporated layers but for other methods of preparation (e.g. electrospraying) as well.

For most applications the other techniques must be calibrated in surface density units but will be complementary in application to gravimetry (ease of operation, better sensitivity, etc.). Improvement of stability and development of calibration techniques are envisaged.

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PAPER 26

THICKNESS MEASUREMENT AND TARGET UNIFORMITY STUDIES*

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Mass determinations of specified areas of deposited films have been used as the standard method against which other film-thickness measurement techniques might be compared. Only two other nondestructive measuring techniques have thus far been found suitable for true thickness measurements. The first of these is the resonating-quartz-crystal method which has been most successful after suitable calibration. Thickness of deposition and associated deposition rates have been calibrated for several elements and compounds with excellent results. The second thickness-measuring device, useful for self-supported films of $< 1000\ \mu g/cm^2$ areal density, is an alpha-ray energy attenuation system. In this case the true value of the stopping coefficients for alpha particles in most materials is known to a limited extent and, therefore, most film thicknesses can be expressed only in terms of the alpha-energy attenuation, i.e., kv-energy loss of 5-Mev alpha particles. However, these values have direct application to charged-particle accelerator studies and can be mathematically converted to energy attenuation values for most charged particles. It is emphasized that both of these techniques can be used for areal density determinations only after calibration against the basic standard of mass determination.

Since there are so many techniques applicable to thickness measurement of thin films and/or mass determination of evaporated layers, it appears that some discussion concerning the use of these films in physical and nuclear measurements would be worthwhile to permit selection of the methods most applicable to the physical measurements for which the targets are fabricated. Usually the physicist requires a mass determination so that the actual atom count within the film might be quantitatively obtained; for example, films used for cross-section measurements require accurate atom count and the impurity atom count must also be determined.

In determining these two characteristics of thin films, it is important first to note that evaporation and condensed thin films do not necessarily have theoretical densities and, in fact, can have densities as low as ~0.4 of the theoretical value. Because of this peculiarity, measurements depending upon the physical thickness of the specimen do not give

*Research sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation.

correct atom counts. Techniques such as stylus measurements and interferometry depend upon the physical thickness of the film and not upon the atom count within the film nor upon film density. Of course, mass determination by weight measurement, alpha-particle energy attenuation, the resonating-quartz-crystal technique, and various radiation counting techniques do yield specific atom counts. A newer technique that seems particularly applicable to a thickness determination from which a specific atom count can be calculated is ellipsometry.

Although usually of parenthetical importance in making nuclear measurements, the structure of the film used as the target should be well understood by the target fabricator. If one were able to look at a thin film of material on a microscale, one would find many voids, aggregations, and rarifications, as established by Pashley and others, using electron microscopic techniques. Studies in the semiconductor industry have indicated that growth of epitaxial films occurs only at relatively high substrate temperatures compared to the condensation temperatures normally employed by target fabricators. Epitaxy requires temperatures of from 350 to $>1500^{\circ}C$, depending on the element being condensed. For the most part, this high substrate temperature is necessary to gain high mobility of the condensing atoms on the surface; condensed atoms move on the surface and nucleate at points not uniformly distributed across the surface. Evidence obtained from electron-microscope studies of epitaxy, performed by Pashley in England, indicates that even after 30 or 40 average monolayers of material have been condensed only ~50% of the surface is actually coated. Nucleation sites form islands on the substrate and only after average thicknesses of 1 to 10 $\mu g/cm^2$ are reached is the surface completely covered with condensed atoms. Of importance to the target fabricator therefore is the fact that these films do not have uniform density or atom count in any one section of the film, although gross physical measurements indicate that the film is uniform to $\pm 5\%$ of a reported thickness.

Recent solid-state radiation damage studies have indicated that particles traversing a thin film show an energy loss dependent upon the direction which the particle takes with respect to the crystal orientation of the target. Therefore, energy losses in a polycrystalline film can be greater than in a specifically oriented single-crystal film. It would seem that, in the near future, oriented single-crystal films of isotopes may be required in some research programs and then the inherent problems of target manufacture will become magnified in diversity and complexity. It becomes equally apparent that knowledge of the specific atom count and impurity atom count will be even more important than they are now.

The program of the Oak Ridge National Laboratory Target Center has made future provision for study of these problems using electron microscopy, electron and x-ray diffraction, and related techniques (e.g., microprobe studies). In the past two years some development work has been performed in growing single-crystal films of silver and gold having specific orientation. This work is not unique, but constitutes an initial effort to grow more uniform films of all isotopes in which the film density approaches the theoretical value for the bulk material and where an accurate atom count can be achieved to $< 1\%$. It is hoped this work will accelerate in the future and provide a basis for better film integrity and uniformity.

In summary, the thickness measurements employed by target fabricators require careful scrutiny as to exactly what physical characteristic is being measured and whether or not the measurement has significance to the physicist using the target foil. Furthermore, more sophisticated techniques need development in order to enable the physicist and the target fabricator to closely define films as to atom count and crystal orientation.

PAPER 27

CHEMICAL METHODS OF ASSAYING TARGETS

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C.B.N.M. Euratom, Geel

The assay of samples involves several different kinds of measurement including chemical analysis, isotopic analysis, and metrological determination of weight, thickness, etc.

The CBNM is a Bureau of Standards limited to the nuclear energy field, having its main interest in neutron data measurements. Furthermore, as a bureau of standards, it is particularly concerned with absolute values.

The CBNM possesses, therefore, laboratories for sample preparation, analytical chemistry, mass-spectrometry, and classical metrology. Samples are prepared and assayed for laboratories from the Euratom Community and sometimes even for outside laboratories. These activities are limited to substances of interest to the nuclear field, such as boron, thorium, uranium, plutonium, lithium etc.

Experience at CBNM shows that the accuracy of absolute determinations of nuclear data and very often even of relative measurements are limited by the uncertainties in the assay of the sample. One typical example is a long-standing request from reactor physicists to measure the thermal fission cross-section of fissile isotopes to an accuracy of 0.5 %. We should realize that we are far away from this aim when we look at some uncertainties which still subsist in the sample definition.

Let us assume that the uranium-235 fission cross-section at thermal energy is to be measured relative to Boron-10. Well-defined samples of boron and of uranium-235 are needed. For the boron samples the largest uncertainty lies now with mass-spectrometry and the boron-10/boron-11 ratio for natural boron is certainly not known to better than 0.2 %. But this uncertainty again is due to the uncertainty in the mass-discrimination factor, which in turn can only be improved if the chemists can prepare known blends of highly enriched boron-10 and boron-11 with very high accuracies. Looking at uranium-235 we find that physicists like to assay their foils by alpha-counting, but alpha-counting presupposes that the half-life is well-known. Taking all this together, one realizes that measuring a fission cross-section to 0.5 % is a formidable task.

So there is a need for improvement of chemical analysis, especially of small quantities of the elements of interest, and furthermore there is a pressing need for precise assessment of the real accuracy of chemical analysis; a point on which there is currently much confusion. Many neutron measurements, performed at the CBNM, pertain to absolute standards. This, of course, means that with the growing refinement of physical measurement methods in nuclear physics the requests of the physicists to the analytical chemists are increasing every day. Many measurements of nuclear constants or of neutron reactions have reached such a stage of refinement that one of the main errors in the completed measurement consists of the uncertainty in the chemical composition of the sample.

This means that the analytical chemistry department of the CBNM has to provide for all elements of interest, analytical methods that allow the main constituents of a sample to be measured with a precision so that this uncertainty is no longer important for the complete nuclear measurement. Depending on the type of neutron measurement to be done, this might require precisions ranging from 1 % down to 0.01 %.

If we say "precision" we might as well say "accuracy", because many of the measurements being done at the CBNM, are supposed to be absolute measurements, and even if we only make relative measurements there has to be a primary standard to which one can compare his actual measurement.

Because the sources of interferences in high precision chemical analysis are nearly innumerable, the physicist should during his first feasibility studies consult a specialised chemist.

If accuracies in the order of 0.1 % are to be attained in the final chemical analysis, information on the quantity of element available, its chemical purity in its final physical state and its isotopic analysis is needed, furthermore in many cases the same properties of its support will have to be known before any conclusions can be reached.

The analytical facilities existing at the CBNM are set up in such a way as to provide for all kinds of analysis. This includes of course analysis for trace impurities by modern physico-chemical methods as well as high precision analytical methods for the determination of main constituents of substances used for neutron measurements. The following methods are currently used for the analysis of trace impurities: emission spectrography, spectro-photometry and oscillographic polarography. These methods are used for element concentrations from 0.1 % down to fractions of parts per million. Certain methods have been perfected, so that the analysis of parts per billion is possible in certain substances[1].

For the analysis of main constituents any one of the great number of classical or modern physico-chemical methods of analysis could be used. Choice from this host of methods will be governed by the relative precision as well as by the accuracy that will be required. In general it can be said, that the analytical work at the CBNM aims actually at accuracies of about 0.1 % or even better. The long term goal will be the improvement of these methods to accuracies of about 0.01 % and the diminution of the quantities necessary for an analysis. The introduction of systematic errors, despite high reproducibilities is an ever present danger.

It will have to be made clear to the scientist using the samples that all the values are only relative to certain reference substances. The precision of any physico-chemical measurement, like simple emission spectrography, spectrophotometry, polarography is limited by the inherent precision of the equipment, being optical or electronic. We can assume that normally these methods will not give much better reproducibilities than about 0.5 % and there is practically no way to use these methods as absolute methods, because we always have to standardize the method with the identical substance and under the same conditions as we will have during the final analysis. Certain of the physico-chemical methods have been refined in the last few years so that they can now be used for precise differential measurements[3, 2, 5]. When using such methods, which are very often not so difficult to apply, one has to dispose of a very good and comparable primary standard and one has to prove that the method in itself is really adaptable and useful in the ranges one uses.

The analysis of uranium and plutonium has been perfected to such a point that reproducibilities or better, relative standard deviations of 0.01-0.03 % can be reached with many methods. Such methods have been used extensively for the analysis of high purity uranium metal and oxide. The agreement of all these methods including methods of primary standardisation as applied to the NBS 950 series of oxide standards or the USAEC "Dingot" high purity metal allows the conclusion that the true uranium content of these two standard materials is surely known to better than 0.05 %. Some additional studies now being done at the NBS and NBL might soon allow this very safe limit to be lowered to about 0.01 %.

The agreement between the many methods used for the definition of the NBS 949 plutonium metal standard is also so good that the certified plutonium content of this sample can also be accepted to be accurate to better than 0.05 %. Using these standard materials as reference, it should under favourable conditions be possible to define chemically pure uranium and plutonium samples with comparable accuracies.

For the precise determination of boron and thorium we are in a much less favourable position. Although very reproducible methods exist for these analyses, there is not yet sufficient evidence for their accuracies. We can probably say that a pure solution of either element can be analyzed with an accuracy of about 0.1 %.

No high precision methods exist for the accurate determination of lithium, americium, neptunium and protactinium.

The choice of the method will depend very much on the type of sample that has to be analyzed, the quantity of element present, the accuracy required and last but not least on the past experience of the laboratory with these methods. If sufficient sample material exists and if there are no interfering elements present, the definition of a sample with an accuracy of better than 0.1 % is still a very lengthy business and might take up to a month or two for a very experienced team of technicians.

In many cases the small quantity at our disposal ($\leq$ 1 mg element) or impurities present might make it totally impossible to reach such accuracies.

The accurate chemical determination of the above mentioned elements has been discussed lately[4] at a round table. In the following we give some tables, that show the type of accuracy stated to be obtainable[4]. It should be remembered that the tables are only valid in connection with very specific conditions. It is advised to consult a specialized analytical chemist before any generalization is attempted. Very small changes in the operational conditions or trace impurities might influence the methods strongly. The number of determinations is mostly 10 - 15.

METHODS FOR THE DETERMINATION OF BORIC ACID

Method	Laboratory	mg Boric Acid per Determination	Coefficient of variation	Estimated Accuracy
Volumetric	A.W.R.E.	150	± 0.25 %	± 0.2 % (pure boric acid solution)
	C.B.N.M.	1000	± 0.02 %	± 0.1 % (pure boric acid solution)
	C.E.A.	300 - 3000 mg/l	± 0.1 %	± 0.3 % (routine anslysis of pure boric acid)
Coulometric	A.W.R.E. C.B.N.M.	20 - 90 150	- ± 0.02 %	- bias possible, depending on working conditions
Gravimetric	C.E.A.	50 - 100	-	± 0.1 % (pure boric acid solution)
Diff. Spectro-photometric	N.B.L.	170 µg	± 0.08 %	relative to a standard boric acid solution

METHODS OF THE DETERMINATION OF THORIUM

Method	Laboratory	mg Thorium per Determination	Coefficient of variation	Estimated Accuracy
E.D.T.A. Titration	F.O.A.	2 - 12	± 0.1 %	relative to a standard zinc solution
	C.B.N.M.	50 - 250	± 0.05 %	relative to a standard zinc solution
Differential Spectrophotometric	N.B.L.	15 µg/250 ml	± 0.2 %	relative to a standard thorium solution
Gravimetric	N.B.L.	-	-	± 0.1 %

METHODS FOR THE DETERMINATION OF URANIUM

Method	Laboratory	mg Uranium per Determination	Coefficient of variation	Estimated Accuracy
Constant Current Coulometry	A.W.R.E.	30 - 50	± 0.05 %	± 0.05 % (based on the accuracy of the timing and constant current units)
	N.B.S.	100 - 500	± 0.016 %	± 0.01 % (based on the combined results of CCC and precise titration with potassium dichromate)
		500 - 1000	± 0.006 %	± 0.01 %
Controlled	O.R.N.L.	5 - 30	± 0.1 %	± 0.1 % routine analysis, based on agreement
		30 - 50	± 0.05 %	± 0.1 % of electrical calibration and stan-
		2 - 50 µg	± 0.8 - 0.2 %	± 1 % dard uranium solutions.
	C.B.N.M.	0.7 - 45	± 0.07 - 0.02 ±	± 0.05 % only for very pure solutions of uranium
	A.W.R.E.	10 - 5(1)	± 0.09 %	± 0.1 % (for small targets ±0.5%)
Gravimetry combined with titrimetry of the different oxidation states	C.E.A.			± 0.01% (overall accuracy, larger quantities needed)
Redox titration potentiometric end point	O.R.N.L.	30	0.1 %	0.1 % relative to a reference solution of given oxidising power.

Method	Laboratory	mg Uranium per Determination	Coefficient of variation	Estimated Accuracy
Redox titration potentiometric end point	A.W.R.E.	-	± 0.02 %	± 0.05 % relative to a reference solution of given oxidising power
Redox titration indicator end point	A.W.R.E.	50 - 100	better than 0.1 %	± 0.1 % intercomparison with ORNL
	C.B.N.M.	1000	± 0.06 %	Bias of - 0.1 % used for routine only
E.D.T.A.	C.B.N.M.	0.012 - 9	± 5 - 0.1 %	relative to a standard uranium solution
Differential Spectrophotometry	N.B.L.	0.2 mg/100 ml	± 0.1 %	relative to a standard uranium solution
Differential Polarography	A.W.R.E.	100 - 1000 µg	± 0.2 %	relative to a standard uranium solution
	C.B.N.M.	10 - 500 µg	± 0.2 - 0.1 %	relative to a standard uranium solution

METHODS FOR THE DETERMINATION OF PLUTONIUM

Method	Laboratory	mg Plutonium per determination	Coefficient of variation	Estimated Accuracy
Redox titration potentiometric end point	C.E.A.	10 - 30	± 0.1 %	relative to a standard cerium solution
	A.E.R.E.	4	± 0.12 % (pure Pu) 0.20% (5% Pu in U) 0.20 % (ion exchange separation), small positive bias	relative to a standard cerium solution
	L.A.S. L.A.S.	300 25	± 0.03 % 0.06 % (Different method)	relative to a pure standard Pu-solution
	A.W.R.E.	-	0.06 %	relative to a pure standard Pu-solution
	A.E.R.E.	6	± 0.5 (after ion exchange separat.)	relative to a standard Ce-solution
	FOA	15 - 50	± 0.13 - 0.04 %	
Redox titration spectrophotometric end point	L.A.S. (Rocky Flats)	500	± 0.03 %	relative to a pure standard Pu-solution
	A.W.R.E.	-	± 0.06 %	relative to a standard Ce-solution

Method	Laboratory	mg Plutonium per determination	Coefficient of variation	Estimated Accuracy
Redox titration amperometric end point	L.A.S.	10 - 20	± 0.03 %	relative to a pure standard Pu-solution
Redox titration amperometric end point	A.E.R.E.	15	± 0.07 %	positive bias after ion exchange separation
	F.O.A.	1 - 10	± 0.1 %	-

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CONTINUOUS OBSERVATION OF ACTINIDE ELECTRODEPOSITION

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A.E.E. Winfrith

One of the main responsibilities of the A.E.E. Winfrith is the assessment of reactor assembly performance by precise experimental methods. These methods frequently require samples for irradiation, and samples prepared for post-irradiation counting, of high isotopic and chemical purity in the form of thin uniform deposits (of finite area) to avoid or minimise self-shielding effects.

We have found electrodeposition techniques highly suitable in this preparative field and to investigate the deposition conditions of a wide variety of isotopes of interest, e.g. ^{231}Pa, ^{234}U, ^{235}U, ^{236}U, ^{237}Np, ^{241}Pu, ^{242}Pu and ^{243}Am, we have developed an electrodeposition apparatus which gives us chart recorder profiles of α-activity as it builds up on the cathode during deposition. This enables us to observe immediately changes in the deposition rate as a function of changed electrolyte or cell parameters and is an extremely valuable tool for investigating electrode processes. Our approach to this problem has been the thin end-window cathode technique in which short range radiation passing through the very thin metallic foil electrode is continuously monitored by an adjacent detector.

As you may remember, various workers, including Joliot[1] in 1930, and more recently Sinitsyna[2], Ponomarev[3] and Hansen[4] have all made contributions in this field. The commercial availability of very thin stainless steel, i.e. < 3 microns thick with a transmission of ~ 60% for 5 MeV alphas, which compares well with only ~ 30% for gold foil of similar thickness, invited its use as a thin window. Typical results are shown in Fig. 28.1 for the electrodeposition of 2 mg of enriched uranium on to gold from formic/formate/oxalate. We produced quantitative milligram level primary calibration foils for the Zebra reactor assemblies using this medium and the accuracy of the work has been confirmed by low geometry counting. Now a word or two about the equipment and conditions. The perspex or polythene cells with cylindrical platinum anodes, zinc sulphide screen, photomultiplier and electronic follow-through to a chart recorder are all quite conventional. We would recommend the use of 'VITON' sealing rings but pre-conditioned neoprene is satisfactory, although it is more permeable and less durable. As regards electrolytes, such as formic/formate, nitric acid or ammonium chloride, our experience confirms that adding initial low concentrations of oxalate is usually bebeficial in terms of source quality. We follow pH

by means of a micro sampling electrode. Current densities are anything from 0.125A/cm^2 upwards calling for external E.M.F.'s between 7 and 15 volts.

Now I would like to show you some more examples.

Fig. 28.2 - Here we see the electrodeposition of ^{231}Pa from 0.2M NH_4F. Recently G. Smith and I were able to demonstrate quantitatively the deposition of tracer Pa in 4 hours and the work was reported this Spring in the Journal of Inorganic and Nuclear Chemistry. This slide is a later study showing the electrodeposition as it takes place on to stainless steel, simulating the use of the standard stainless steel counting disc. In this case we are using a smaller aqueous volume, higher current density and higher temperature, reaching an equilibrium situation in only 30 minutes.

Fig. 28.3 - This is the electrodeposition of ^{239}Pu at the µg level using M NH_4Cl/0.01M oxalic acid on to a gold cathode. This rapid deposition, which runs very close to 100% in only a few minutes on the standard steel disc, lends itself to Health Physics surveys. This slide shows a deposition on gold because the chloride system 'pinholes' the very thin stainless steel foil.

Fig. 28.4 - Here we have the electrodeposition of ^{237}Np from formic acid/ammonium formate. I will say something later about the use of this system for routine ^{239}Np evaluation in ^{238}U neutron capture studies.

Fig. 28.5 - Here we are making changes during the deposition which is of 2 µg of ^{239}Pu using 5 ml of 1M NH_4Cl/0.01 oxalic acid with two additions of 0.25 ml of 100 vols H_2O_2. The two points at which the peroxide was added are clearly visible.

Fig. 28.6 - This system is a little unusual. It is the electrodeposition of 1 µg of ^{239}Pu from 5 ml of 1M NH_4Br/0.01M $(COOH)_2$ on to stainless steel.

Fig. 28.7 - One trace shows the deposition of 1 mg of ^{233}U and the other 1 mg of ^{238}U plus 10 µg ^{233}U in chemical equilibrium so that the higher specific activity system can be compared with the lower one. As can be seen, there is no significant difference.

A point to be noted is that these profiles merely show the rise to equilibrium conditions at the cathode surface. To demonstrate 100% deposition, one has to carry out an examination of the electrolyte for residual activity.

Fig. 28.8 - This is ^{243}Am.

I would like to mention that at Winfrith we have a well established precise analysis[6] for neutron capture in ^{238}U which calls for the simultaneous electrodeposition of ^{239}Np and ^{237}Np. To maintain the linearity of the β/α ratio of these two nuclides as a function of source mass, we

include 50 μg of natural uranium as a co-deposit. This technique has been in use for several years in a variety of water and fast reactor studies. Although $\gamma|\alpha$ -counting is now preferred on grounds of equipment stability, many hundreds of foils gave a level of precision which was more than adequate to match the everyday counting statistics. I am aware that some workers recommend the use of small additions of uranium as a panacea in actinide deposition work generally, but we have no evidence that this is normally necessary. Moreover, the great bulk of our electrodeposits on stainless steel are not flamed but only water and acetone washed. Flaming tends to produce erratic results and can adversely affect the relative $\beta|\alpha$ measurements obtained from several isotopes co-deposited on the same disc.

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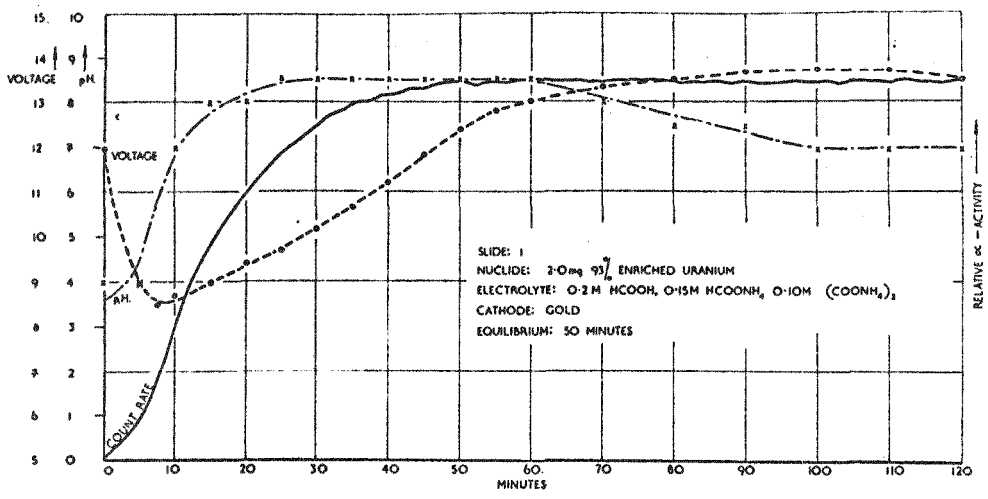

Figure 28.1

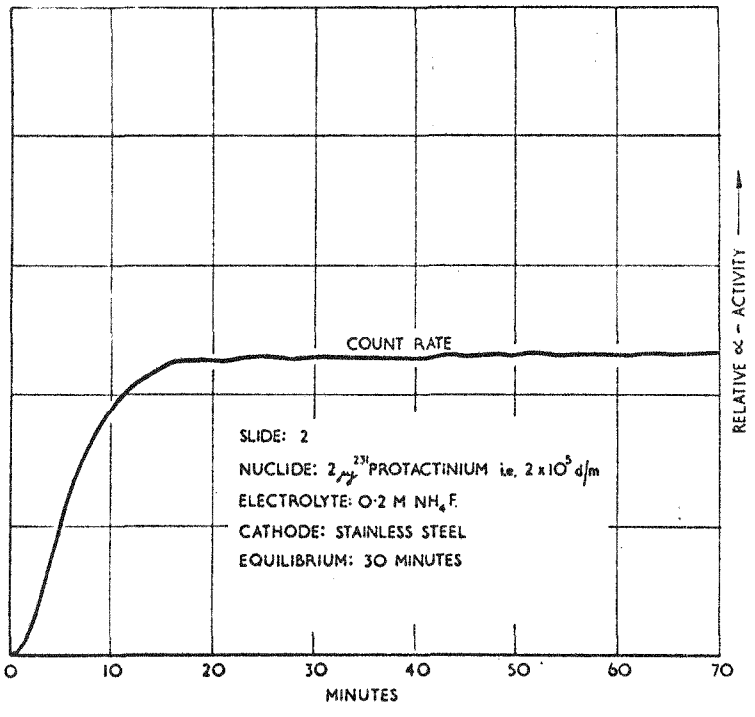

Figure 28.2

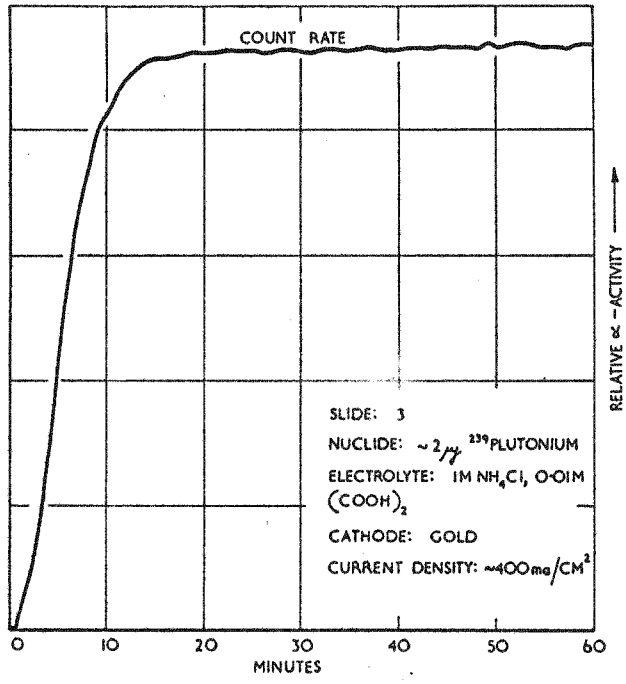

Figure 28.3

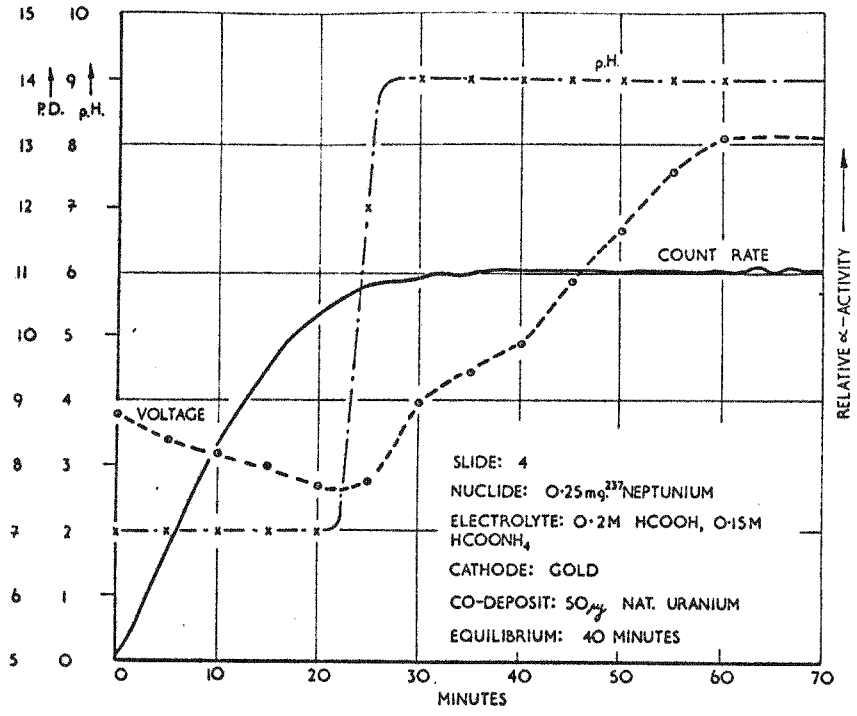

Figure 28.4

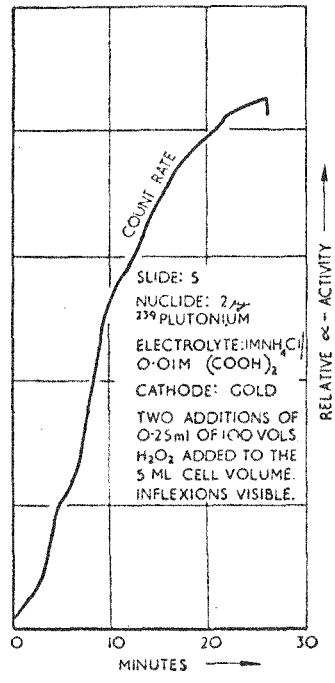

Figure 28.5

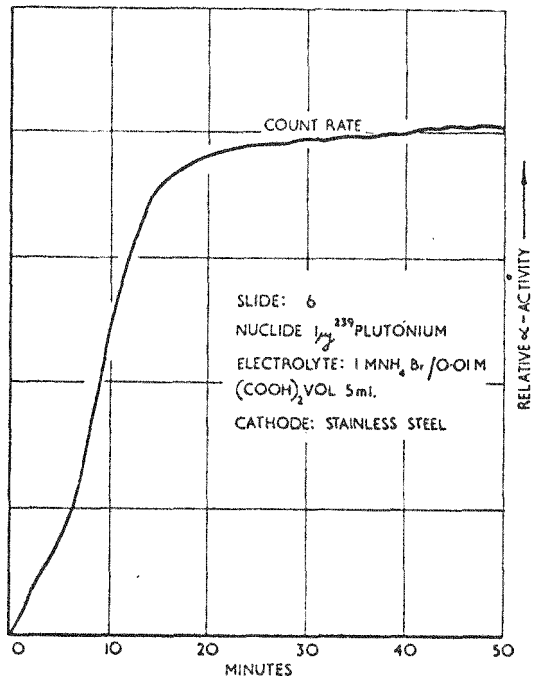

Figure 28.6

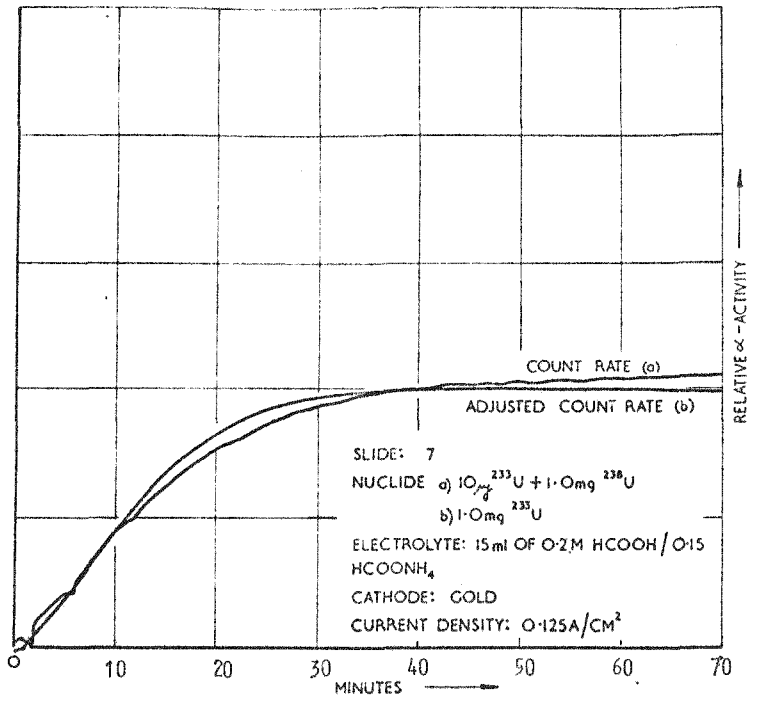

Figure 28.7

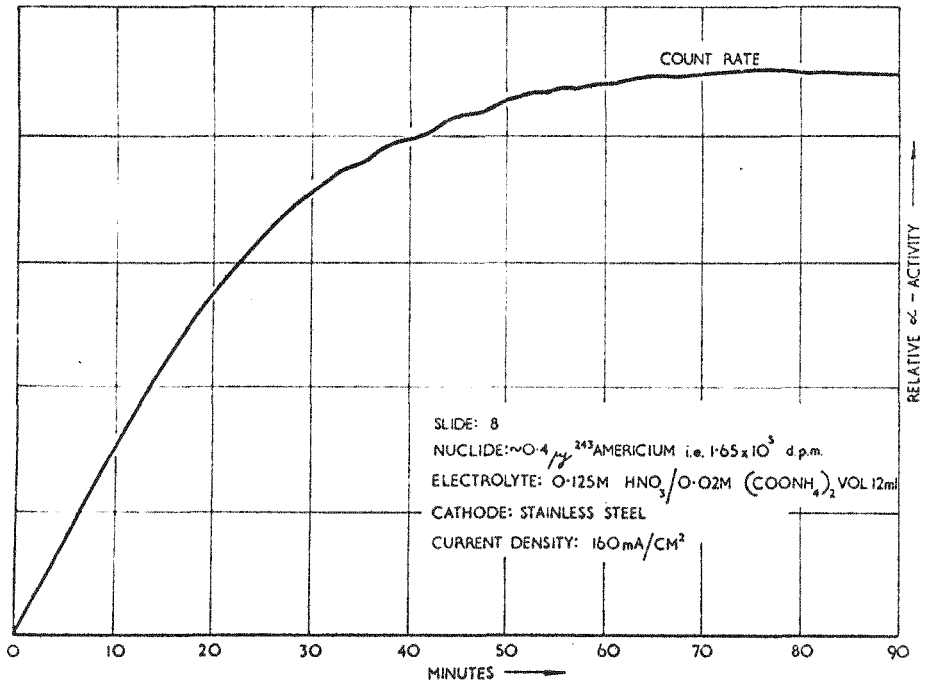

Figure 28.8

ALPHA AND FISSION COUNTING OF THIN FOILS OF FISSILE MATERIAL

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A.W.R.E., Aldermaston

1. Introduction

This paper is concerned with the assay of thin foils of fissionable material by alpha and fission counting. The discussion is restricted to foils deposited on thick backings and hence in the case of fission counting only one fission fragment is detected. This discussion is further restricted to the counting of alpha particles and fission fragments in 2π geometry.*

To make useful measurements most of the fission fragments must escape from the foil. Since the fission fragments have a very short range (~10 microns) in the foil material the foils usually have thicknesses in the range 0.1 - 1.0 microns. This thickness is of the same order as the surface roughness on most materials and the possibility that, in the past, this roughness has caused difficulties on the assay of thin foils prompted the measurements described in this paper. Also included in the discussion are the results of other work where these are relevant to the assay of thin foils.

2. Assay of alpha particles and fission fragments in 2π geometry

A small fraction of the alpha particles or fission fragments generated inside a thin foil of material are emitted at angles close to the plane of the foil and may not escape before dissipating all their energy. If particles of range R are detected in 2π geometry from a uniform foil of thickness t, the fraction F lost due to absorption is $t/2R$. If the foil thickness is not uniform the fraction F becomes $(t^2 + \sigma^2)/2tR$ where t is the mean thickness and σ the standard deviation on the variation of the thickness.

The other major correction necessary in 2π assay is one for backscattering of the particles in the foil and in the backing and has been calculated by Crawford (1949) to be of the order of 3.9% for alpha particles from uranium. This calculated value is in reasonable agreement with the 3.1% measured by Walker (1965). Because two fragments are emitted in opposite directions in the fission process, backscattering of one of them does not result in an extra recorded fission event and no correction is necessary for backscattering of fission fragments from very thin foils.

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*A more detailed paper is to be presented at a Round table discussion on "Alpha counting techniques and mass spectrometry" and will be published as an EANDC report.

3. Measurements of backscattering and foil absorption in 2π geometry

3.1 Fission Fragments

The correction for absorption of fragments in foils of U^{235} uranium oxide has been measured by comparing in a constant neutron flux the fission rate per unit mass for foils of different thickness. The results are shown in Figure 29.1. For foils prepared by vacuum evaporation the observed variation of the total fission rate/unit mass of uranium varies linearly by $7.7 \pm 1.0\%$/mg cm^{-2} with the foil thickness. This agrees within error with the value $6.7 \pm 0.5\%$/mg cm^{-2} calculated from the known range of fission fragments (7.5 ± 0.5 mg cm^{-2}). However, a small non-uniformity of $\sigma/t \sim 0.4$ would give better agreement.

The variation for painted foils which is 10.9%/mg cm^{-2} is much larger than expected for uranium foils, but could be explained if it were assumed that the uranium oxide deposit had a non-uniformity σ/t of 0.8 - 0.9. The expected small reduction in the correction for foil absorption due to backscattering was masked by the much larger increase due to the non-uniformity in the foils. Polishing or deliberate scratching of the platinum backing did not change the measured correction for absorption of the fission fragments from that of foils on rolled platinum backings.

Some of the foils produced by painting and by vacuum evaporation were examined microscopically and are shown in Figure 29.2. The absolute thickness of the foil could not be determined from the interference colour produced in the transparent uranium oxide, since its refractive index is not known. The variation of colour over the foil surface did, however, give a measure of the foil non-uniformity. For the vacuum evaporated foils the non-uniformity inferred from colour variations was reasonably consistent with that deduced from the fission measurements. The painted foils were not wholly transparent and an estimate of the non-uniformity could not be made from the colours. However, the structure of parallel ridges (Figure 29.2C) probably deposited from single hairs of the brush used for painting could reasonably be expected to give a non-uniformity $\sigma/t \sim 1$.

Figure 29.2A shows an evaporated foil on a backing deliberately scratched with steel wool. The fraction of the foil area covered by the scratches is quite small and perhaps explains why no change in the correction for foil absorption was obtained between the different surface finishes in the platinum backings.

Another effect discernible on magnification is shown in Figure 29.2B. This shows an evaporated foil on a polished backing. The uranium oxide deposit had crazed and some of the small pieces had

become detached, probably when the platinum had been flexed during its removal from a fission counter.

3.2 Alpha Particles

The series of foils used for the fission measurements described in the last section were alpha assayed in 2π geometry in a gridded ion chamber and in low geometry. Also included in the measurements were foils prepared by Dr. Lauer at BCMN, Geel, using an electrospraying technique. The ratio of the total disintegration rates calculated from the 2π and low geometry assays are shown in Figure 29.3 as a function of foil thickness. The results for all foils extrapolate to a ratio of $1.030 \pm .005$ at zero foil thickness in good agreement with the 3.1% of alpha particles backscattered measured by Walker (1965). Contrary to the results for fission fragments the variation in the foil absorption has the same value $9.5 \pm 1.0\%/\text{mg cm}^{-2}$ for painted, evaporated and electrosprayed foils. For the evaporated foils, assuming the same non-uniformity as the fission measurements, the variation calculated from a range of 11.2 ± 1.5 mg cm^{-2} is $5.2 \pm 0.7\%/\text{mg cm}^{-2}$ and leaves a discrepancy of $4.7 \pm 1.3\%/\text{mg cm}^{-2}$. This discrepancy is much smaller than the $0.8\%/\mu\text{g cm}^{-2}$ measured by Deruytter (1962) for electrodeposited foils of 10 - 50 μg cm^{-2} thickness on stainless steel backings.

It is not understood why the foils manufactured by different methods should have the same correction for foil absorption of alpha particles where different values were obtained for fission fragments. More detailed calculations of the combined effect of backscattering and foil absorption and perhaps more measurements would be required in order to understand this apparent anomaly.

4. Conclusions

Alpha counting of foils in 2π geometry whatever their method of manufacture would seem to be accurate only for foils less than 0.1 mg cm^{-2} and then only to an accuracy of ~1% due mainly to discrepancies in the corrections for backscattering and foil absorption. Deruytter (1962) has obtained much larger discrepancies than obtained here. If accurate results from 2π alpha counting are to be obtained further work is required to determine the reason for these discrepancies.

Fission counting of foils of thickness 0.1 - 1.0 mg cm^{-2} in 2π geometry can be performed to an accuracy of 0.2 - 1.0% depending upon the foil thickness, provided experimental corrections for foil thickness are used.

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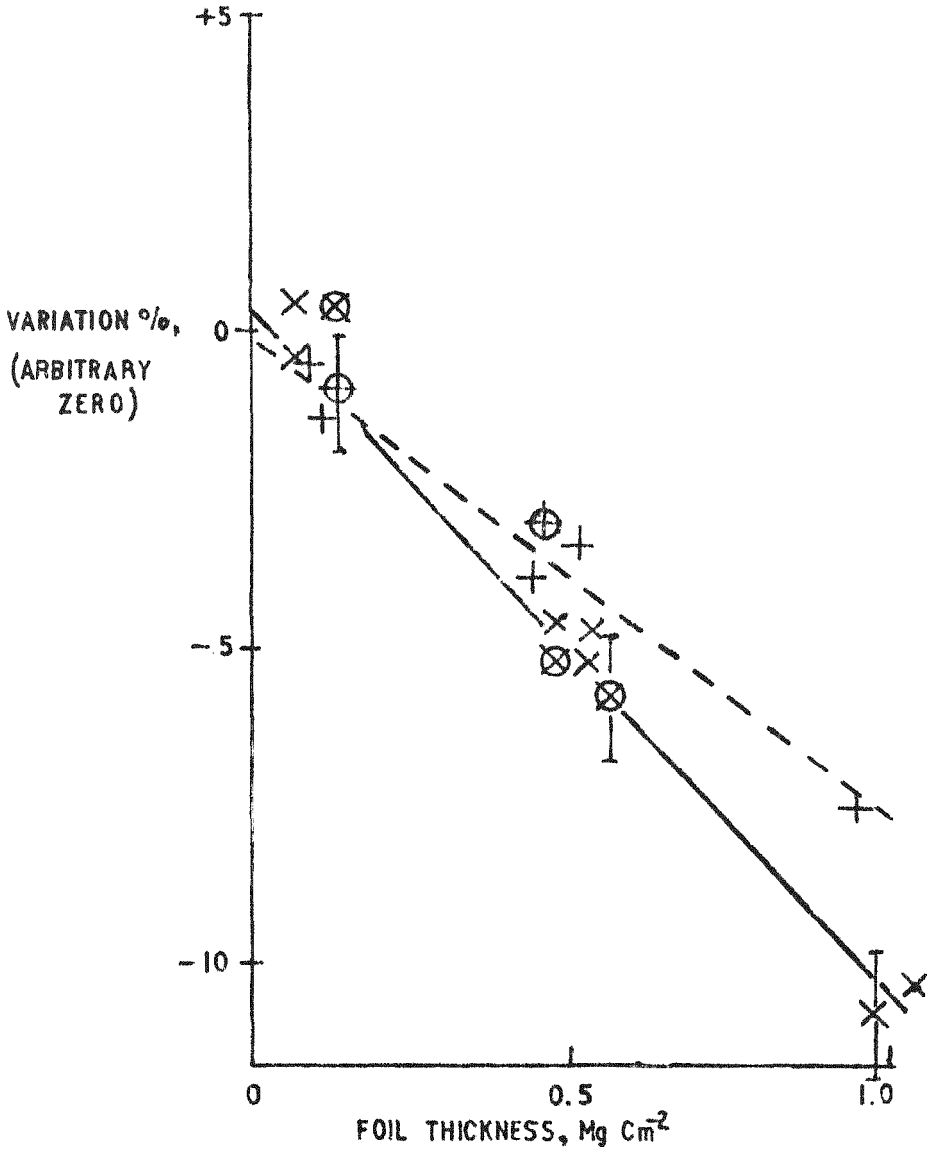
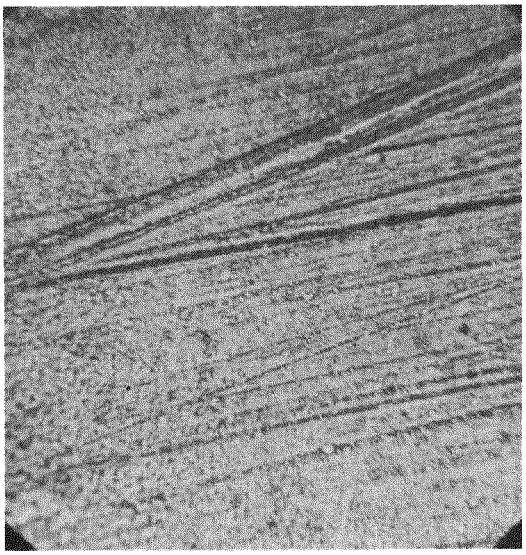


FIGURE 29.1 VARIATION OF FISSION COUNTING RATE PER Mg Cm^{-2} OF U_3O_8 WITH FOIL THICKNESS

--- All Vacuum Evaporated Foils
—— All Painted Foils
X Painted Foils
\+ Vacuum Evaporated Foils
O Highly Polished Platinum



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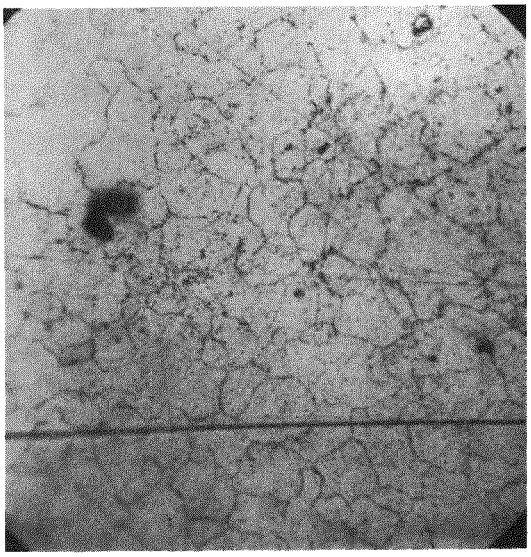
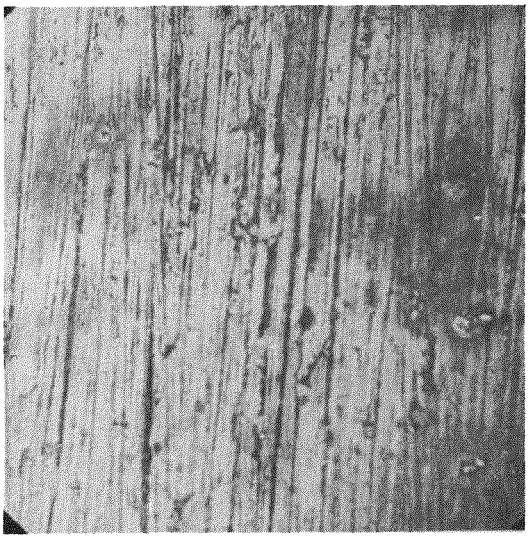


B

C



D

A. Evaporated foil thickness 0.5 mg cm^{-2} on scratched platinum
B. Evaporated foil thickness 0.1 mg cm^{-2} on polished platinum
C. Painted foil thickness 0.1 mg cm^{-2} on rolled platinum
D. Painted foil thickness 0.25 mg cm^{-2} on rolled platinum

AERE - R 5097 Fig. 29.2 x 500
Surface of foils of U_3O_8

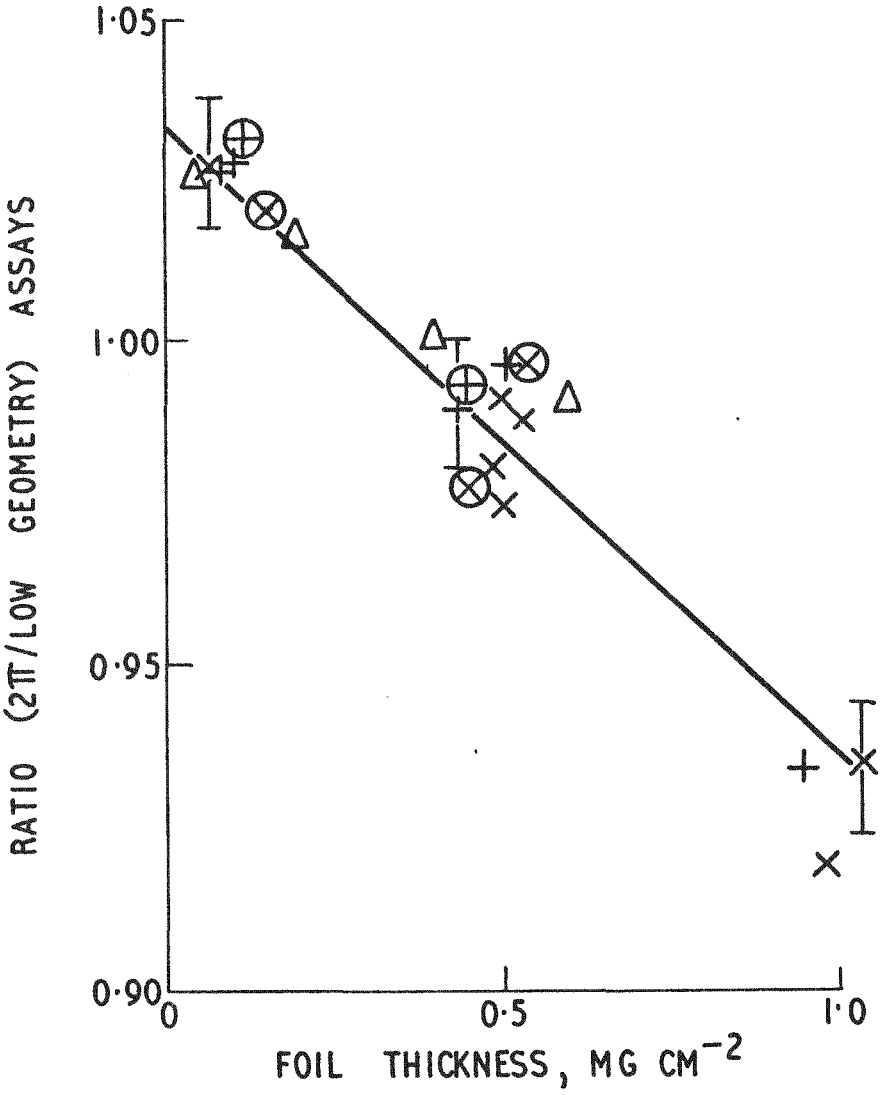


FIGURE 29.3 RATIO (2π/LOW GEOMETRY)

α PARTICLE ASSAYS AS A FUNCTION

OF FOIL THICKNESS

X Painted Foils on Platinum
\+ Vacuum Evaporated Foils on Platinum
O Highly Polished Platinum
Δ Electrosprayed Foils on Platinum

DENSITY AS A NON-DESTRUCTIVE MEASURE OF COMPOSITION OF U/Al ALLOYS

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1. Introduction

In earlier work carried out by L.R. Aronin and J.L. Klein[1] (declassified in 1957) on alloys prepared by classical vacuum induction melting, the U contents determined by an alkaline peroxide spectrophotometric method with a relative precision of ± 1% were compared with the U contents calculated from the densities measured on these alloys. The relative precision of the calculated U-content was only ± 1 % since the 0,03 wt % solubility of U in Al, and the error on the X-ray measurements of the dimensions of the UAl_4 unit cell had not been taken into account. The total error (including chemical analysis) was of the order of ± 2 % relative. However, a statistical analysis was made for about 90 samples containing 15 wt % U, and the standard deviation of the mean obtained for the difference between chemical analyses and composition based on density measurements was ± 0.085 wt %.

In the present work quantitative alloying by levitation melting is applied to achieve high accuracy with a small number of samples. Destructive chemical analysis is not needed. It is hoped that the experience gained in this work will be helpful for the future application on Al-Th and Al-Pu samples.

2. Experimental

2.1 The quantitative preparation of Al-U alloy samples

1 to 10 g amounts of Al-20; 22; 24 and 24.5 wt % U samples are prepared from:

Al-Raffinal[+]: 99.99 wt % Al; 0.005 wt % Fe; 0.005 wt % Si.
Natural U: 99.9 wt % U;
or ^{235}U : 99.9 wt % U of isotopic compositions

	234	235	236	238
wt %	0.83	89.79	0.30	9.08

All samples were prepared in the same way:

[+]Trade name for alloys prepared by Vereinigte Leichmetallwerke GMBH, Bonn, Germany.

- quantitative alloying by levitation heating (1500°C) in argon at 300 Torr and casting in a water cooled chromium plated copper mould[2]. This defines the nominal uranium content with an accuracy of 0.015 wt %;
- preparation of plates 3.5 x 20 x 50 mm by remelting at 1200°C and casting in an alumina covered graphite plate split mould;
- homogenization in vacuum at 600°C for 14 hrs and cooling to 200°C in 5 hrs;
- closing of the micropores by reducing 50 % in thickness by rolling at 450°C;
- ultrasonic degreasing of the samples.

2.2 The experimental determination of the density

The combination of the float method with hydrostatic weighing as developed by J. Spaepen[3]) is used to determine the densities of the Al-U samples, the sample tube is placed in a water thermostat stabilized within 0.005°C.

This quick method in which the sample tube is placed in a water thermostat stabilized within 0.005°C gives an accuracy of $\pm$ 2.10^{-5} g/ml for the densities of the rolled and unpolished Al-U samples. In Fig. 30.1 a curve of nominal uranium content versus density, [measured at 26.2°C and corrected to 25°C* [4]] is plotted for 13 samples of 23 to 24.5 wt % nat. U and in Fig. 30.2 another curve is given for 8 samples of 20 and 24 wt % enriched U (89.79 % ^{235}U).

3. The computed densities of the alloys

The Al-20 to 24.5 wt % U samples, prepared as indicated in section 1, show a homogeneous double phase structure of fine (<4 microns), globulized UAl_4 crystals in an α-Al matrix as illustrated in fig. 30.3 and predicted by the Al-U constitutional diagram given in fig. 30.4 [5]).

Generally speaking the density of an alloy can be computed from the amounts and the densities of the phases present.

For substitutional solutions, as in the case of α-Al and UAl_4, the calculated densities are given by the relation:

$$d = \frac{n\bar{A}}{VN} \qquad (1)$$

as indicated by Charles S. Barrett[6]) or:

---

*Linear coefficient of thermal expansion for Al-20 % U: $20.9 \times 10^{-6}/°C$, as indicated by Wilkinson W.D.[4]).

$$d = 1{,}66020\ \frac{n\bar{A}}{V} \qquad (1')$$

where n is the number of atoms in the unit cell of volume V (in A^3), N is Avogadro's number and $\bar{A}$ is the mean atomic weight of the elements. The mean atomic weight can be calculated from the atomic percentages p1, p2, ... of the isotopes present in the alloy and the nuclidic masses A_1, A_2, ... by the relation

$$\bar{A} = \Sigma\ \frac{p_i A_i}{100}$$

providing $\Sigma p_i = 100$.

The alloys here considered contain only α-Al and the UAl_4 phase, and the densities of the alloys can be calculated from the formula:

$$V\ alloy = V_{\alpha Al} + V_{UAl_4} \quad (V = volume)$$

or

$$\frac{100}{d\ alloy} = \frac{wt\%(\alpha\text{-}Al)}{d_{\alpha\text{-}Al}} = \frac{wt\%\ UAl_4}{d_{UAl_4}}$$

$$d_{alloy} = \frac{100}{\frac{wt\%(\alpha\text{-}Al)}{d_{\alpha\text{-}Al}} + \frac{wt\%\ (UAl_4)}{d_{UAl_4}}} \qquad (2)$$

where d_{alloy}; $d_{\alpha Al}$ and d_{UAl_4} are the respective densities.

The weight percent of both phases can be determined in the constitutional diagram, fig. 30.4. The relative amounts of the α-Al and UAl_4 phases are shown as $\frac{PN}{PF}$.

4. Comparison of the computed densities with the measured densities

The computed and measured densities of Al, αAl, UAl_4 and Al-20; 22 and 24 wt % U are tabulated for natural and enriched uranium in Table I and plotted in figs 30.2 and 30.3.

Table 30.1

	Nat. Uranium	Enriched Uranium ^{235}U = 89.79 %	Remarks
U content in UAl_4	(calculated) 68.803 wt %	68.558 wt %	4.1.1.
25°C d_{UAl_4}	(calculated) (6.06 ± 0.06) g/cm^3	(6.01 ± 0.06) g/cm^3	4.1.2.
25°C d_{Al}	(calculated) 2.69837 g/cm^3 (measured) (2.69831 ± 0.00015) g/ml	- -	4.1.3.
24°C $d_{\alpha Al}$	(calculated) 2.69907 g/cm^3	2.69907 g/cm^3	4.1.4.
25°C $d_{Al\text{-}20\ wt\ \%\ U}$	(calculated) - (measured) -	(3.215 ± 0.006) g/cm^3 (3.2165 ± 0.0003) g/ml	4.1.5.
25°C $d_{Al\text{-}23\ wt\ \%\ U}$	(calculated) (3.312 ± 0.006) g/cm^3 (measured) (3.314 ± 0.0015) g/cm^3	- -	4.1.5.
25°C $d_{Al\text{-}24\ wt\ \%\ U}$	(calculated) (3.345 ± 0.006) g/cm^3 (measured) (3.347 ± 0.0013) g/ml	(3.343 ± 0.006) g/cm^3 (3.345 ± 0.0012) g/ml	4.1.5.
25°C $d_{Al\text{-}24.5\ wt\ \%\ U}$	(calculated) (3.364 ± 0.006) g/cm^3 (measured) (3.3645 ± 0.0004) g/ml	-	4.1.5.

4.1 Remarks on the calculated values indicated in Table I

4.1.1 For the atomic weight of natural uranium the "unweighted average of MSAW" as indicated by P.J. De Bièvre, M.G. Gallet and G.H. Debus[7]) is used:

$$238.02894 \pm 0.00012$$

All the other atomic weights used in this paper are the values as indicated by the 1963 table of International Committee on Atomic Weights I.C.A.W.

4.1.2 The volume of the UAl_4 unit cell is calculated using the indications of B.S. Borie, Jr.[8]), who determined that UAl_4 is body centered orthorhombic with:

$$a = (4.41 \pm 0.02)\ \text{Å}$$
$$b = (6.27 \pm 0.02)\ \text{Å}$$
$$c = (13.71 \pm 0.03)\ \text{Å}$$

thus $v = a.b.c. = (379.1 \pm 3)\ \text{Å}^3$,

and that the unit cell contains four UAl_4.

4.1.3 The composition of the raffinal Aluminium used was:

99,99 wt % Al

≈ 0,005 wt % Fe

≈ 0,005 wt % Si

The density is calculated using the relations (1) and (2). The presence of 0,005 wt % Fe and 0,005 wt % Si results in a density decrease of max. 5.10^{-5} g/cm^3, and this was neglected. The measured density of the aluminium agrees very well with the calculated values.

4.1.4 P.R. Roy (1964)[9]) determined that the solubility of U in Al at 350°C is about 0,03 wt %, and we considered an αAl phase in which 0,03 wt % U is disolved substitutionally.

4.1.5 The densities of the alloys are calculated from relation (2). The error in the calculated density is about 0.2 % relative and reflects the uncertainties on the X-ray measurements of the dimensions of the UAl_4 unit cell.

The error indicated for the measured density reflects the accuracy of the weighing of uranium and aluminium and the precautions taken during the levitation melting.

It is possible to obtain a reproducibility in density up to 0.0004 g/ml for different samples containing the same U content. This is shown in fig. 30.3 for the 5 samples containing 20 wt % ^{235}U.

Special precautions taken were:

- the use of thoroughly cleaned and vacuum degassed uranium and aluminium charges;
- temperature stabilizing in inert gas of the uranium before weighing in order to avoid oxidation;
- the choice of the form for the uranium base material so that the charges have an as small as possible surface;
- levitation melting in a pure argon atmosphere.

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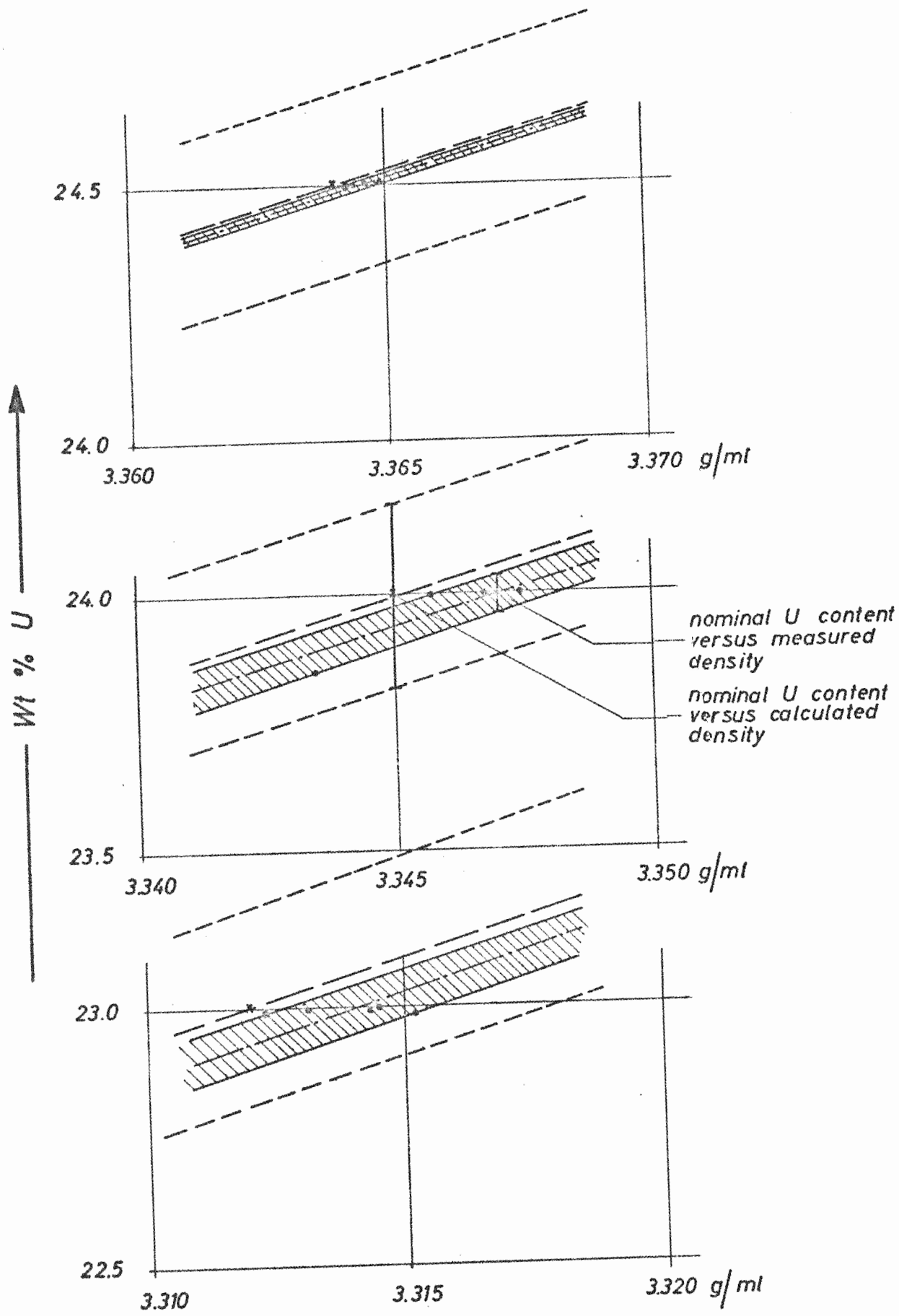

Al-U-Alloys
Wt % U
24.5
24.0
3.360
3.365
3.370 g/ml
24.0
23.5
3.340
3.345
3.350 g/ml
23.0
22.5
3.310
3.315
3.320 g/ml
nominal U content versus measured density
nominal U content versus calculated density

Fig. 30.1

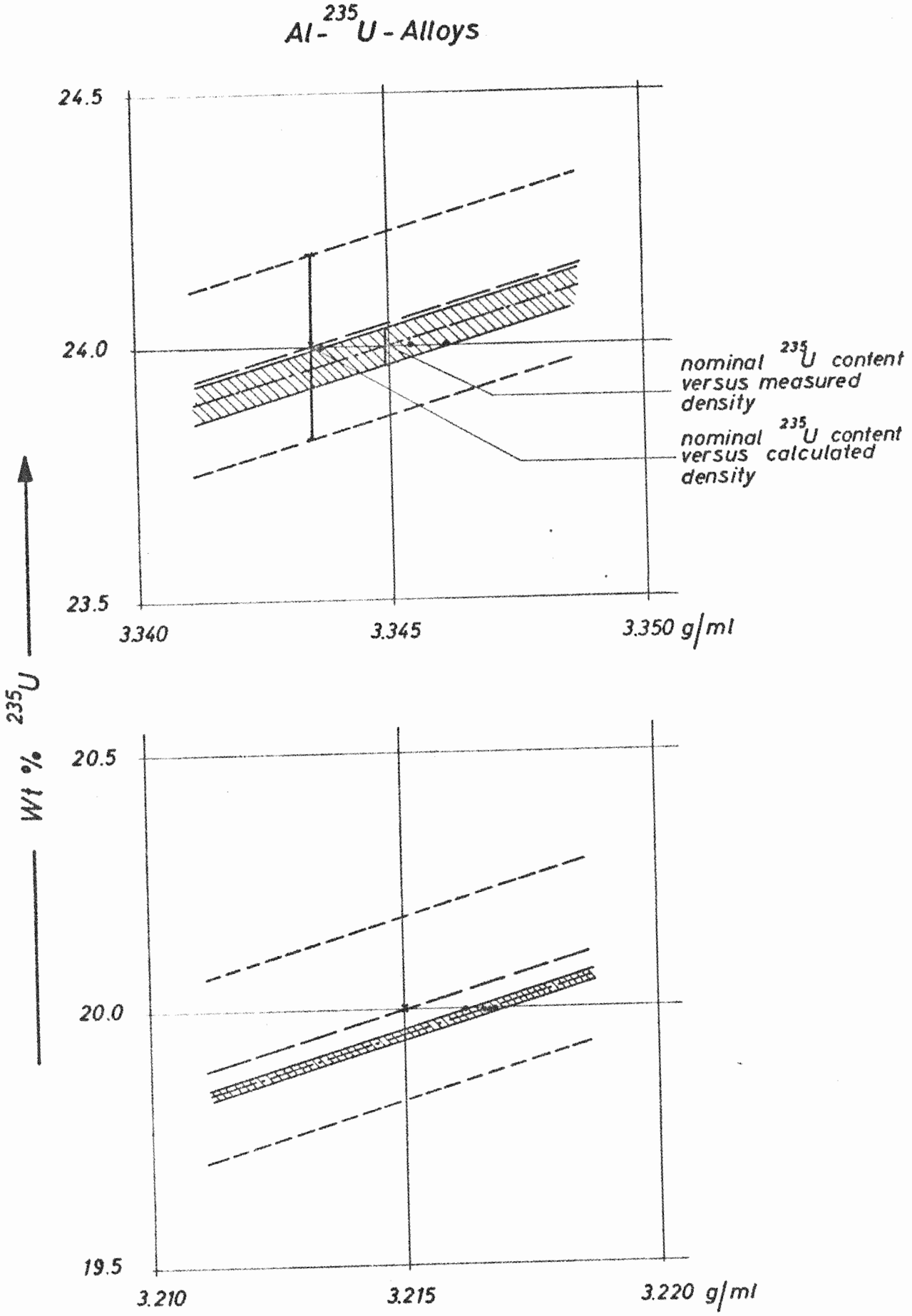
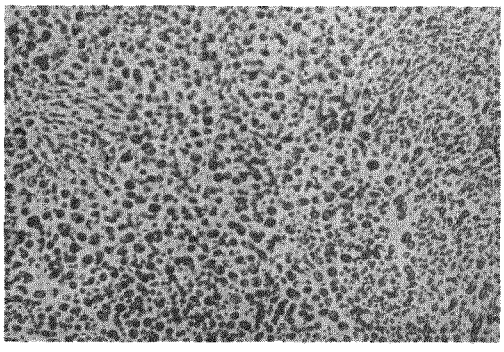

Al - 235U - Alloys
24.5
24.0
23.5
3.340
3.345
3.350 g/ml
nominal 235U content versus measured density
nominal 235U content versus calculated density
Wt % 235U
20.5
20.0
19.5
3.210
3.215
3.220 g/ml

Fig. 30.2



AERE - R 5097 Fig. 30.3
Al-24 wt % U alloy heat treated at 600°C for 14 hrs showing globulized UAl_4 in an α-Al matrix (Electropolished, x 500)

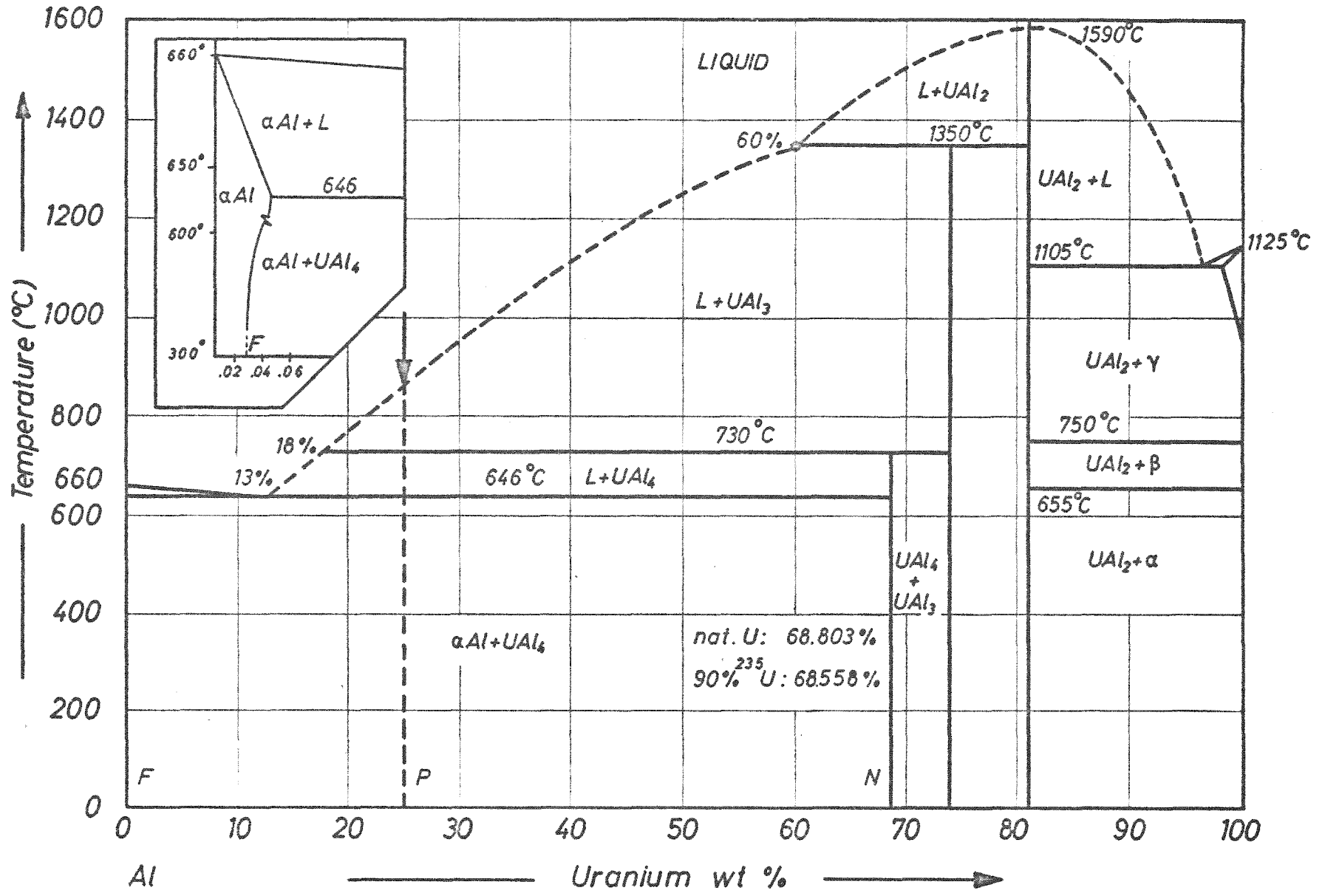

1600
1400
1200
1000
800
660
600
400
200
0
Temperature (°C)
660°
650°
600°
300°
αAl + L
αAl
646
αAl + UAl4
F
.02 .04 .06
LIQUID
L + UAl2
60%
1350°C
1590°C
UAl2 + L
1105°C
1125°C
L + UAl3
UAl2 + γ
730°C
750°C
18%
13%
646°C
L + UAl4
UAl2 + β
655°C
UAl2 + α
UAl4 + UAl3
αAl + UAl4
nat. U: 68.803 %
90% 235U: 68.558 %
F
P
N
0
10
20
30
40
50
60
70
80
90
100
Al
Uranium wt %

Fig. 30.4

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