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PREPARATION OF FOILS

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The thin solid films of various elements or their compounds deposited on a backing are known as foils. These films are often of a radioactive material. They are useful in many nuclear investigations such as in the study of fission, or as targets for particle bombardment. This paper will discuss the more common methods of foil preparation as well as some of the problems presented by nuclear physics experiments to the foil maker.

The common methods of foil preparation are those of electrodeposition, painting from solution, vacuum evaporation, electrostatic spraying, and electrophoresis. The choice of a method depends on the material to be deposited, the type of backing material, the film thickness and the uniformity desired. No one method is ideal for all purposes.

The methods discussed are suitable for thin films. A radioactive source is considered thin when its effective thickness is less than the effective mean range of the alpha particle system. In actual practice, foils less than 5 mg/cm^2 are considered thin. Films thicker than 5 mg/cm^2 have been made by adaptation of thin film methods, but as film thickness increases the foil suffers in appearance, uniformity and adherence. It is believed that the field of thick foils is a separate one requiring new techniques.

ELECTRODEPOSITION

The elements of the actinium series cannot be deposited in metallic form. However, they can be deposited on the cathode as the hydroxides or other insoluble compounds. Electrodeposition of these elements is mainly used for the preparation of very thin films of a few micrograms per square centimeter. Thicker films can be made, but adherence and uniformity suffer. These very thin films are put down quantitatively and are used as standards against which thicker foils are checked by comparison fission counting.

A quantitative plating bath of uranium (1) in the microgram range is made by dissolving uranyl nitrate in 4 percent ammonium oxalate solution. The solution is made basic by the addition of concentrated ammonium hydroxide using methyl red incicator and then made just red to the indicator by drop-

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wise addition of 6M nitric acid. Plating is done at 1.1 amperes and 8 volts at 80°C for 1-1/2 hours. A rotating platinum anode is used. The acidity is checked at 10 minute intervals and maintained with 6M nitric acid using methyl red solution for the first 30 minutes. During the next hour the plating bath is allowed to be just basic. At the end, the cathode is rinsed with methanol and ignited in a burner flame. The compound on the cathode is assumed to be U_3O_8.

Plating efficiency for microgram quantities is said to be 99.7 percent, 98 to 99 percent for up to 100 micrograms, and 97 to 98 percent for up to 500 micrograms (2). Thorium and transuranic elements may be plated from this bath in 100 microgram amounts or less. Plating efficiency is said to be 75% or better.

Plutonium may also be plated from a hydrochloric acid bath wherein the solution is made just acid to methyl red indicator with 2M hydrochloric acid (1). A stationary platinum anode is used. Electroplating is done at 7 volts for 1-1/2 hours. The cathode is rinsed with acetone and ignited over a flame.

PAINTING

The painting of good foils is definitely an art and requires practice. Painted foils can be made of almost any element that has a salt soluble in a volatile solvent. Numerous thin coats are necessary to build up a deposit of the desired thickness. For this reason, it is desirable that the soluble compound be one, such as a nitrate, that can be readily decomposed to an insoluble one after each coat. Otherwise, each new coat tends to dissolve some of the previous coats.

The method has produced foils from microgram amounts to 10 mg/cm^2. Foils up to two or three mg/cm^2 are highly adherent and can withstand a light Kleenex rub. A Kleenex swipe test can usually remove visible particles from the thicker foils. Uniformity can be as good or better as electrodeposited foils in the 100 microgram per square centimeter range.

Uranium foils can be prepared by dissolving uranyl nitrate in absolute ethyl alcohol. A good quality brush which will not deposit bristles on the foil is necessary. It is usually trimmed quite short so that the bristles are almost stiff. Numerous coats are applied to the backing material until the desired thickness is built up. After each coat is applied, it is allowed to dry and then ignited using an oven, flame or hotplate to remove organic substances and to convert the nitrate layer to an oxide. The ignition temperature should be as hot as the backing material can withstand without damage which in turn must be high enough for the conversion to the desired oxide.

Ordinarily the concentration of uranium in solution is 50 mg/ml. For better uniformity, a large number of coats are necessary along with a more dilute solution, perhaps as low as 5 mg/ml. Concentrations much above 50 mg/ml yield a flaking deposit.

Foils of other elements such as plutonium, thorium and neptunium which have alcohol soluble nitrates can be made by this method.

Circular foil backings can be coated by mounting them on a turntable, Fig. 1, which is rotated at about 60 rpm while each coat is being applied. Cylindrical shapes can be coated inside or out by mounting the cylinder in a chuck which is rotated by a geared-down motor. Rectangular foils can be made by mounting the backing on a cylinder and rotating with the brush held against it.

The method lends itself readily to mass production methods. Rectangular foils have been mass produced by means of a foil machine by R. Gilmore, R. Potter, and A. Rodrigues (3). Single uranium foils up to ten feet long have been made and then cut into sections of the desired size.

The backing strip is made into a continuous belt by spot-welding the ends together. This belt is placed over two rollers, one of which is motor driven at 43 rpm. The other roller is mounted on a carriage parallel to the first roller and is spring loaded to maintain constant tension on the foil. The distance between the rollers is determined by the length of the foil. The painting device is a hopper, the bottom of which contains a felt brush. It is mounted over the idling roller so that the felt brush is in contact with the belt as it passes over the roller. Uranium solution in the hopper seeps through the felt and is deposited on the belt. A row of burners placed at the motor-roller end oxidizes the deposit as it passes through the flame.

The painting method has been used in preparing standard foils. The material is painted onto a weighed, clean, electropolished platinum backing which is fired at 800°C after each coat. These foils have been compared by fission counting (and colorimetry) with thin ones made by quantitative electrodeposition and agree within 1% (4).

VACUUM EVAPORATION

The vacuum evaporation method is easily adapted to many metals and compounds. The uniformity of the films, the easy control of their thickness over a wide range and the good adherence of the films make this technique most useful. The thickness range covers from a few micrograms/cm^2 to several mg/cm^2. Adherent UO_2 foils as thick as 14 mg/cm^2 have been made. Its chief disadvantage is that the evaporating source must contain several times the amount of material that will be deposited on the backing. Therefore, it cannot be used when the active material is available only in limited quantities.

The high vacuum evaporation apparatus is generally an all metal, water cooled system. Care must be taken to build vacuum evaporation systems with adequate pumping capacities. Many materials give off absorbed gas just before evaporation temperature is reached, thus high pumping speeds are a necessity to remove these liberated gases. High pumping speeds also permit fast operating cycles.

The equipment in use by the author, Fig. 2, was designed for vacuum deposition of UO_2 and PuO_2, but is also readily adaptable to many other materials. It consists of a 2.33 l/sec mechanical pump and a 700 l/sec oil diffusion pump connected to the evaporation chamber and cold trap by a six inch pumping throat. The cold trap is necessary to prevent the diffusion of pump oil into the evaporation chamber and in this case is a commercially available freon-cooled baffle supplied by a separate refrigeration system. The evaporation chamber is a 12 inch long cylinder cut from 8 inch diameter brass tubing of 1/8 inch wall. The bottom plate of 3/8 inch brass is attached to the pump-out throat and has a recessed O-ring groove for the chamber to fit into. The top plate is also of 3/8 inch brass with a recessed O-ring groove. Bolted flanges are unnecessary as atmospheric pressure provides adequate force for a good vacuum tight joint. The chamber is equipped with a 4 inch diameter port for viewing the evaporation operation. Wilson rotary shaft seals attached to the chamber and the top plate provide for shutters, movable baffles and rotating targets. An ion gage is located in the bottom plate. A system of valving permits dismantling of the evaporation chamber without shutting down the pumps and also provides for quickly roughing out the system when pumping down.

Every part of the evaporator exposed to radiation from the evaporating source must be water cooled if the system is to be used for high melting point materials. The chamber, top and bottom plates, and the upper part of the pumping throat are cooled by 1/4 inch copper tubing soldered to the outside. The electrodes or filament stems are drilled out so that water may flow through them. One electrode has a water-cooled baffle attached to it so shielding the pump throat from radiation from the source. The filament stems pass through the bottom plate and a vacuum seal is made by means of a machined conical gasket of Teflon.

The filament power supply is a 5 KVA 120/240 volt primary and a 12/24 volt secondary transformer controlled by a 15 KVA powerstat. This will easily raise v-shaped boats of 5 mil tungsten, 2 inches long with one inch high walls to the melting point.

As for filaments or sources, several types are considered in the literature (5, 6, 7). For the preparation of foils of the refractory oxides such as UO_2 and PuO_2, the v-shaped boat described above works very well.

For evaporating extremely radioactive materials, the chamber is enclosed in a hood-type box vented to filter towers. The design in use by the author (Fig. 3) has a plexiglass front with a 7" x 32" opening through which objects can be manipulated with gloved hands. Air flow through the opening is 100 linear feet per minute. This arrangement has proved adequate to keep radioactive dust within the box and yet is not as inconveniently clumsy as the usual dry box with its bulky gloves and airlock.

ELECTROSTATIC SPRAYING

The material to be deposited is ejected as an organic solution from a fine capillary by the application of an electric field and collected on a metal backing (8).

A glass capillary tube is drawn down to a very fine opening and the tip cut squarely. The tube is filled with a dilute organic solution of the material to be deposited. A thin platinum wire is pushed as far as possible into the capillary and forms one of the electrodes. The metallic backing forms the other electrode. The distance between the capillary tip and the backing is generally 1 to 2 cm. A potential of 3000 to 5000 volts, applied between the electrodes, causes the solution to be expelled from the capillary.

The size, shape and uniformity of the deposit depend on the bore and shape of the capillary tip and on the rate of deposition. A capillary with a squarely cut tip gives a nearly circular deposit, but these are difficult to obtain; most tips give an irregular shape. The rate of deposition depends on the bore of the capillary and the applied voltage.

A typical solution concentration is 10 mg/ml. However, only small volumes on the order of 5 to 10 microliters can be handled. Consequently, this method is useful at present only for the preparation of very thin films. However, it does have the advantage of uniform deposits and negligible losses. Possibly, foils could be made quantitatively by this method.

Much work is being done to adapt this method for the preparation of uniform, adherent foils in the mg/cm^2 range. In the method as described, if the reservoir above the tip is large enough to contain several milliliters of solution, the tip becomes plugged by dried material before all of the solution is expelled. Enlarging the tip produces non-uniform, flakey deposits since the droplets then hit the backing in liquid form which evaporates in clumps. For best deposits, the droplets must evaporate in transit. Success in making mg/cm^2 deposits has been claimed by heating the backing indirectly (9). The backing is placed on an elongated copper plate, the end of which is heated by a flame. This heats the backing by conduction sufficiently to cause the droplets to evaporate just before hitting, yet the backing does not get hot enough to cause the droplets to spatter off, a difficulty encountered with direct heating.

ELECTROPHORESIS

Electrophoresis is identified as the movement of a charged particle under the influence of an electric field. Electrophoretic deposition offers the advantages of uniformity and control of coating thickness with rapid deposition on regular and irregular shapes.

The suspension of the foil material in an organic medium is prepared by grinding the powdered material with the dispersion fluid in a ball mill. Ball milling reduces the particle size to about one micron and aids in stabilizing and activating the sol probably by distributing the impurity ions which put the electrical charge on the particles. With the backing material as one electrode, the application of a few hundred volts causes the suspended particles to migrate to the backing. Even, thick coats can be applied in a few minutes.

The dispersion fluids ordinarily used are alcohols and ketones. These liquids usually have an electrical conductivity of the same order as distilled water without the disadvantage of gas bubbles developing at the electrodes. The formation of gas bubbles at the electrodes prevents the deposition of a uniform and adhering layer. Also, these organic liquids evaporate quickly so that the coating dries within a few minutes after being removed from the bath.

Electrophoretic deposits appear to be quite uniform, though of low density. Adherence is not great since the deposit clings lightly to the backing material. Rubbing and flexing cause the material to drop off, though sintering oftentimes improves adherence. Generally, electrophoresis is useful when tight adherence is not absolutely necessary and when the inside walls of cylinders and irregular shapes need to be coated.

UO_2 is deposited from an isopropyl alcohol dispersion fluid. Dispersion takes 4 to 12 hours of ball milling. Sometimes trace amounts of tannic acid or anhydrous hydrochloric acid are added to help activate the sol, though usually enough impurities are present to serve this function. Trace quantities of zein, a corn protein, has proved effective in producing a tough coat of UO_2.

Plutonium hydride can be deposited from a suspension in n-butyl alcohol (10). The deposit is vacuum-dried at room temperature and then thermally decomposed at 525°C to yield a smooth hard coat. This coat contains a mixture of metallic plutonium and its oxides. Similarly, uranium hydride can be deposited by electrophoresis and thermally decomposed to a mixture of metallic uranium and its oxides.

METHODS OF ASSAY

The accuracy with which the amount of foil material is known often determines the accuracy of the experiments in which the foil is used. The average foil thickness is usually determined by weighing. The accuracy of weighed foils depends on the inertness of the backing material and on the stability of the foil compound. The exact nature of the compound on the foil is often not known but it can be estimated from the processes involved. Also, x-ray diffraction analysis can provide a clue to its composition. Uranium foils made by painting or electrodeposition are often ignited to U_3O_8. Vacuum deposited foils are put down as UO_2.

If the foil is too thin to weigh accurately, it is alpha-counted. The specific activity of the foil material has been determined previously by counting a thin, weighable deposit.

The completeness of a quantitative electrodeposition is checked by taking an aliquot of the residual solution and assaying it either chemically or by alpha counting.

Major constituents in foil material are determined by ordinary volumetric or gravimetric analysis. Trace impurities are estimated by spectrochemical analysis. Trace quantities are those present in amounts less than 0.001% to about 1%. Quantitative spectroscopy depends on the measurement of the intensity of a spectral line due to the sought-for constituent relative to the intensity of a line due to a standard.

The amount of fissionable material on a foil may be determined by comparison fission counting. The foil is placed in a slow neutron flux together with a known standard foil of the same material, usually back-to-back. The neutrons striking the foil produce fissions which are counted and compared with those from the standard foil.

Colorimetry (11, 12) is another method of analysis used in determining the amount of material on a foil. This method is used after the foil has served its experimental purpose since it is destroyed during analysis. The concentration of a colored substance in solution based on its absorption of light is determined by matching the color of the sample solution with that of a reference standard. The comparison may be done visually or with a photoelectric cell.

The amount of radioactive material on a foil may be determined by calorimetry when the energy of disintegration is known. Calorimetry is the measurement of the heating rate accompanying the decay of an element. This heating rate is compared with calibrated heating rates to ascertain the amount of the unknown source.

The isotopic composition of foil material is determined by the mass spectrometer.

UNIFORMITY

An estimate of the density distribution or uniformity of a foil can be obtained by the alpha counting of small areas, weighing small areas, or by exposing the foil to a nuclear emulsion.

A foil can be covered with a mask, which has a small hole which exposes a known area of the foil which is alpha counted. The mask is moved about, exposing a new area for each counting period giving an alpha distribution pattern for which the uniformity of the foil can be estimated.

The density distribution of vacuum deposited foils is often determined by mounting a number of weighed, clean cover glasses over the source in the same geometry as the target. After evaporation onto the cover glasses, the increase in weight of each cover glass is obtained and a density distribution plotted. In the case of radioactive material, each cover glass can also be counted.

A foil can also be exposed to a nuclear emulsion, the emulsion developed and the alpha track distribution determined by microscopic examination. Particles from strong sources require brief, accurately timed exposures. Reliable information on the statistical distribution of alpha tracks are obtained when their population exceeds $1000/\text{cm}^2$ (13).

The blackening of a photographic plate has also been used as a measure of uniformity. The blackening is a function of the activity and therefore of the thickness of the film.

The uniformity of a vacuum evaporated deposit is often estimated by assuming that the cosine law or some modification of it is applicable. From a point source, the uniformity of deposition onto a plane disc falls off from the center to edge in proportion to $\cos^3\theta$, if 2θ is the angle subtended by the disc at the source. However, uniformity is much better than theoretical for the source is not a point and inevitable gas collisions and collisions between vapor atoms in the evaporating beam smooth out the beam. Theoretical treatment of the principal types of sources such as point, wire and plane are adequately covered in the literature and will not be gone into here (6, 7, 14).

BACKING

The kind of backing material may be determined by the type of nuclear experiment. The possible interaction of a backing with the particles of interest, the energy of the charged particle, the detector system, the scattering problems are a few of the matters to be considered in selecting a backing. In neutron work, the backing is often unimportant. However, if as in fission studies, the energies of both fragments are to be measured as in coincidence counting and time-of-flight studies, the backing must be thin ehough to pass one of the fragments with a minimum energy loss. For instance, 0.000005 inch nickel has been used as the backing material.

The backing material often determines the method by which the foil will be made. For electrodeposition, the backing must be conducting, stable in the plating bath, and thick enough to be free of pin holes.

For painting, the backing must be strong enough to withstand brushing and be insoluble in the solvent used as a painting vehicle. Where each layer is to be ignited to an oxide, as in painting uranium and plutonium foils, the backing must be able to withstand the temperature used which is usually about 400°C, minimum.

Almost any backing material having a low vapor pressure can be adapted for the vacuum evaporation method. Thin or low melting point materials can be placed far enough away from the source filament so that the backing is not damaged by the heat radiation. If necessary, arrangements can be made to cool the backing. When 0.000005 inch nickel is selected as the backing, vacuum evaporation appears to be the only practicable way to put down a uniform film. A compound with a low sublimation temperature such as UF_4 or PuF_4 has to be used in the source filament.

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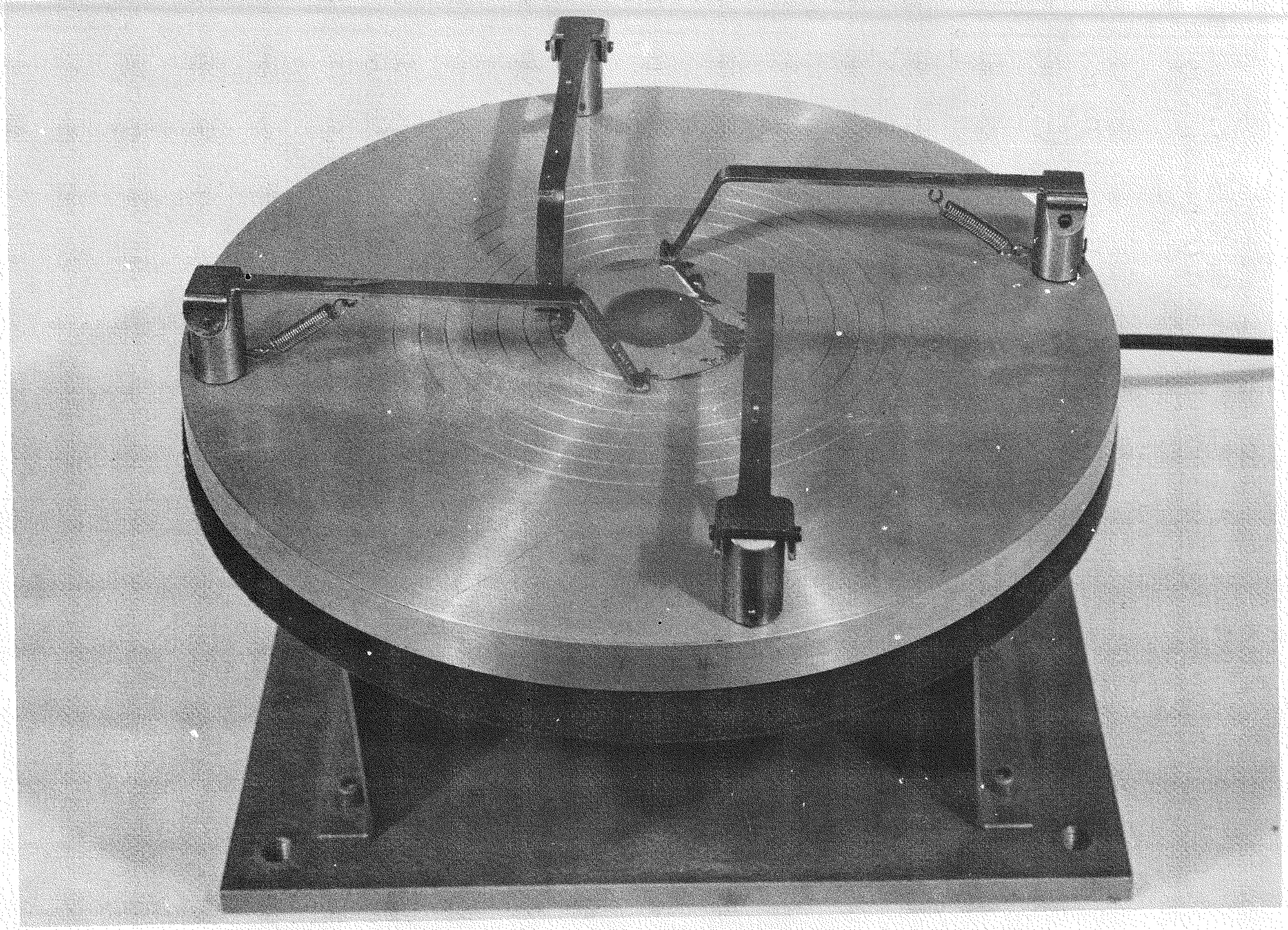

Fig. 1 Turntable in use for painting circular foils

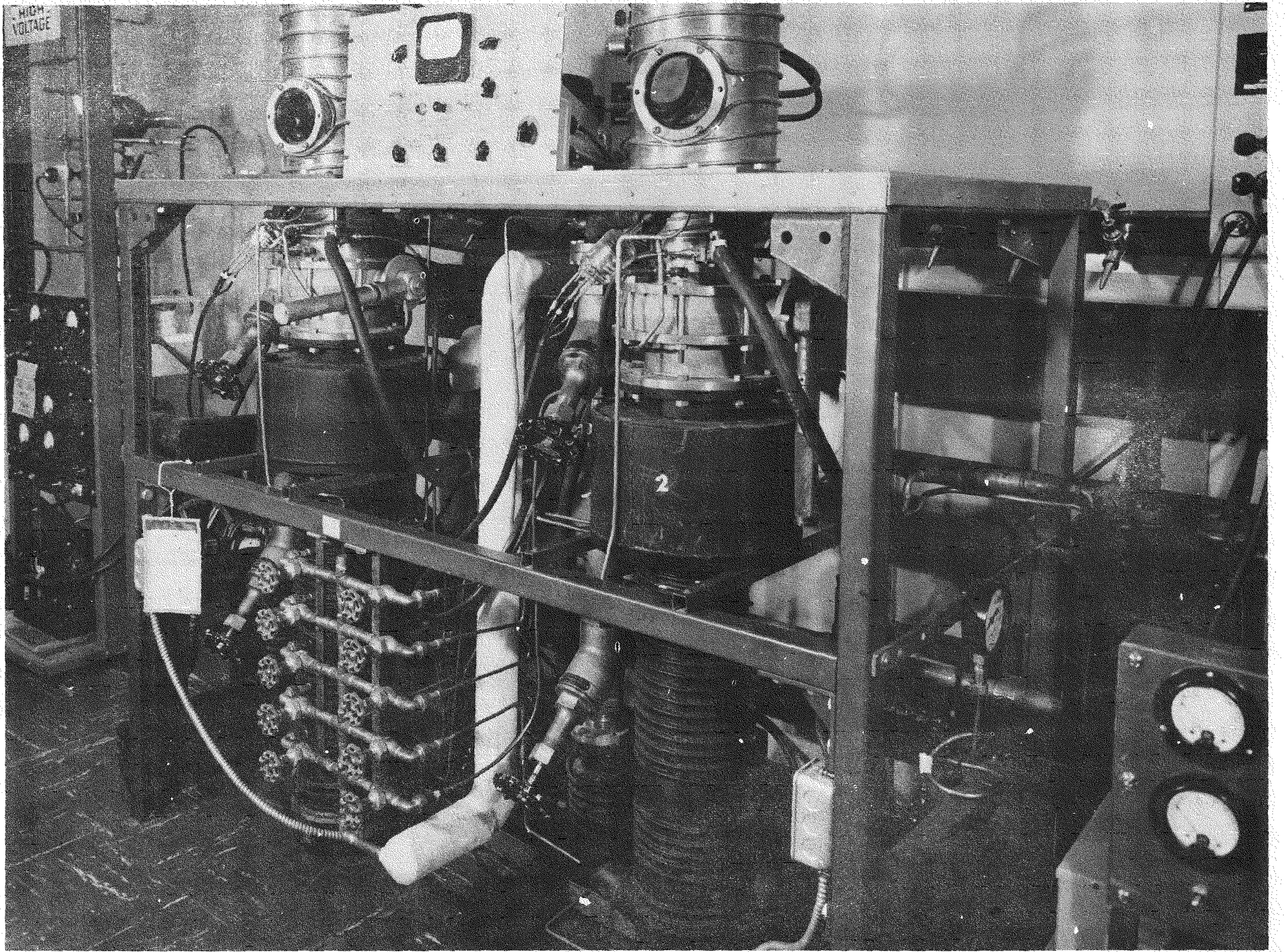

Fig. 2 Vacuum deposition equipment used in making foils of non-radioactive materials and low-level alpha emitters.

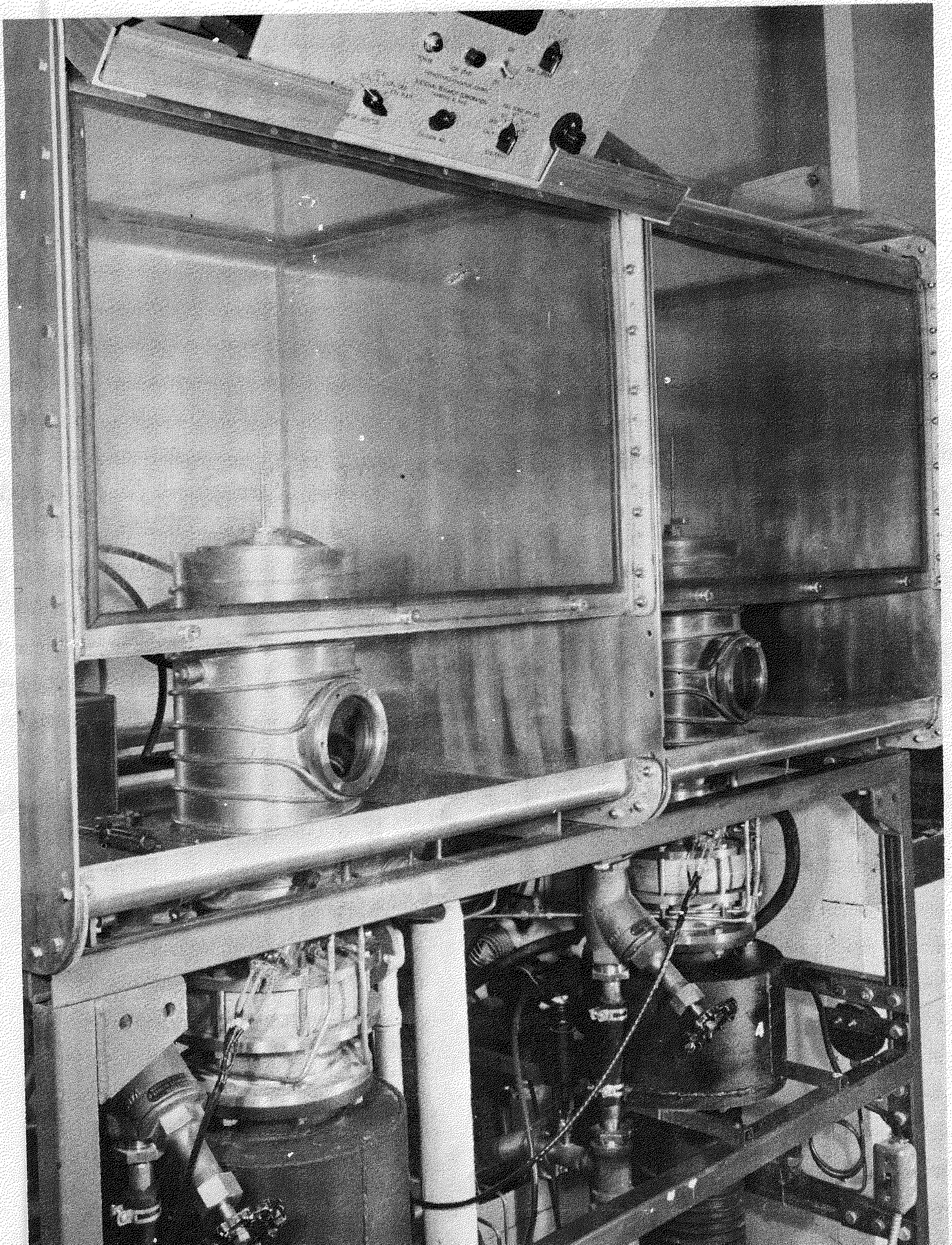

Fig. 3 Vacuum deposition equipment used in making foils of enriched uranium and plutonium

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