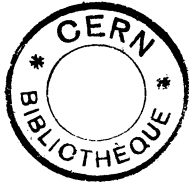


AAEC-E 512

AAEC/E512

AAEC/E512



AUSTRALIAN ATOMIC ENERGY COMMISSION  
RESEARCH ESTABLISHMENT  
LUCAS HEIGHTS

PREPARATION OF THIN TARGETS OF  $^{239}\text{Pu}$ ,  $^{233}\text{U}$  AND  $^{235}\text{U}$  BY  
THE METHOD OF ELECTROSPRAYING

by

R.L. WALSH  
I.F. SENIOR

CERN LIBRARIES, GENEVA



CM-P00067977

May 1981

ISBN 0 642 59713 8

AUSTRALIAN ATOMIC ENERGY COMMISSION  
RESEARCH ESTABLISHMENT  
LUCAS HEIGHTS

PREPARATION OF THIN TARGETS OF  $^{239}\text{Pu}$ ,  $^{233}\text{U}$  AND  $^{235}\text{U}$   
BY THE METHOD OF ELECTROSPRAYING

by

R.L. WALSH  
I.F. SENIOR

ABSTRACT

The preparation of thin, uniform targets of  $^{239}\text{Pu}$ ,  $^{233}\text{U}$  and  $^{235}\text{U}$  by the method of electro spraying is described. The technique has established advantages over other methods of target preparation, for example high deposition efficiency, ease of recovery of unused material and simplicity of operation. These targets are used for neutron-induced fission experiments.

National Library of Australia card number and ISBN 0 642 59713 8

The following descriptors have been selected from the INIS Thesaurus to describe the subject content of this report for information retrieval purposes. For further details please refer to IAEA-INIS-12 (INIS: Manual for Indexing) and IAEA-INIS-13 (INIS: Thesaurus) published in Vienna by the International Atomic Energy Agency.

TARGETS; PLUTONIUM 239 TARGET; URANIUM 233 TARGET; URANIUM 235 TARGET;  
SAMPLE PREPARATION; ELECTRODEPOSITION; SPRAY COATING

## CONTENTS

1. INTRODUCTION	1
2. THE ELECTROSPRAYING APPARATUS	2
2.1 Target Backing Material	2
2.2 Capillary Tube and High Voltage Source	2
2.3 Target Table	2
2.4 Safety Precautions	3
3. PREPARATION OF THE SPRAYING SOLUTION	4
4. METHOD OF OPERATION AND RESULTS	5
5. ACKNOWLEDGEMENTS	7
6. REFERENCES	7
Figure 1 Schematic of electro spraying technique	9
Figure 2 View of electro spraying apparatus through front of glove box	10
Figure 3 Magnified view of $\text{CuCl}_2$ target	11
Figure 4 Fragment pulse height distribution for one detector	12

## 1. INTRODUCTION

To perform fission experiments in which the kinetic energies of complementary fission fragments are measured in coincidence [Ajitanand and Boldeman 1970; Boldeman et al. 1976; Walsh et al. 1979], thin, uniform nuclear targets are required. These targets must be thin ( $\leq 50 \mu\text{g cm}^{-2}$ ) to prevent significant energy loss by the fragment during its escape from the target material (i.e. self-absorption). They must also be of uniform thickness to produce a constant fission rate across their surface, thus preventing spurious geometry effects between target and fragment detectors. Such targets can be prepared by the method of electro spraying.

The electro spraying method was first described by Carswell and Milsted [1957] and has been further developed by a number of authors [e.g. Bruninx and Rudstam 1961; Lauer and Verdingh 1963; Robinson 1966]. A high d.c. potential is applied between the target backing material and the tip of a capillary tube containing a solution of the material to be deposited in a volatile organic solvent. When the field is applied, the liquid is forced through the tip of the capillary and broken up into very fine charged droplets. The solvent must be sufficiently volatile to evaporate during passage from capillary to the backing material. The solid particles remaining after evaporation adhere to the backing; their adhesion is good because of their large acceleration in the high voltage field.

The target backing material must be electrically conductive for the electro spraying process to work; therefore, non-conductive backings must be coated with a thin metallic layer before use. The base of the capillary is commonly restricted by a wire with a diameter slightly smaller than that of the capillary. This is to ensure that the flow of liquid during the spraying is slow enough to permit complete evaporation of the droplets. Any liquid which strikes the backing will spoil the targets by producing non-uniformities, i.e. 'blobs' of target material. The area of the target deposit can be chosen by geometrically masking the backing. The electro spraying technique can be used to prepare deposits of thicknesses ranging from a fraction of one  $\mu\text{g cm}^{-2}$  to several  $\text{mg cm}^{-2}$  and areas from a few  $\text{mm}^2$  to hundreds of  $\text{cm}^2$ . For the very large area deposits, the capillary is tracked mechanically over the backing in a grid pattern. A schematic diagram of the electro spraying technique is shown in Figure 1.

This technique has a number of distinct advantages over other techniques of target preparation, e.g. vacuum evaporation and electrodeposition. It has high deposition efficiency (90 to 100 per cent), ease of recovery of unused material (from capillary and mask), and simplicity of operation. A disadvantage is that a chemical compound of the target material is deposited.

## 2. THE ELECTROSPRAYING APPARATUS

### 2.1 Target Backing Material

The target backing material used at the AAEC Research Establishment is a layer of VYNS, a polymer comprising 86 wt % vinyl chloride and 14 wt % vinyl acetate, having a thickness of  $15 \mu\text{g cm}^{-2}$ . The layer is self-supporting and relatively robust. To make the backing material electrically conductive it is covered with a layer of gold-palladium (90% Au-10% Pd) of thickness 10 to  $15 \mu\text{g cm}^{-2}$ . It is then mounted on a 1 mm thick aluminium support ring (o.d. 3.2 cm x i.d. 2.0 cm). Several spots of silver paint at the perimeter of the ring ensure that it is in good electrical contact with the gold layer.

### 2.2 Capillary Tube and High Voltage Source

A 21 s.w.g. stainless steel hypodermic needle with bore diameter 0.053 cm and needle length 3.5 cm is used as a capillary tube. Such needles are better than glass capillaries, having a uniform bore and ready availability, but they preclude the use of some chloride solutions. The bore of the needle is restricted by a 0.046 cm thick platinum wire of about 2.5 cm in length. Needles with tapered and blunt tips have been used but no qualitative differences were found. The needle is attached to a 1 mL graduated 'Luer' hypodermic syringe which serves as a container for the spray solution. A zero to 15 kV positive d.c. supply, located outside the fume cupboard (see Section 2.4), is connected to the body of the needle. The target table is held at earth potential.

### 2.3 Target Table

The first target table to be used was centred approximately 2 cm below the hypodermic needle and rotated at a constant speed of  $2 \text{ rev. min}^{-1}$ . Blank targets were positioned at the centre of the target table. As the target was not physically masked, for a fixed voltage on the needle the diameter of the

actinide deposit produced depended solely on the distance from needle tip to target. The diameter of a typical deposit was 1.5 cm for a needle-to-target distance of 2 cm. However, this type of table often produced non-uniformities in the actinide deposits, typically the appearance of concentric 'rings' near the outer edges, due to a non-uniform spray cone.

Therefore, an improved moving target table was constructed to give maximum uniformity of target deposition. If the fixed spray direction is called the Z-axis, this table moves simultaneously in the X and Y directions with greatly dissimilar speeds, viz  $10 \text{ cm s}^{-1}$  (i.e. 1 cycle  $\text{s}^{-1}$ ) in the X-direction and  $1 \text{ cm min}^{-1}$  (1 cycle per 10 min) in the Y-direction (see Figure 2). The movements are controlled by two small, reversible, synchronous electric motors, mounted on the outside walls of the glove box (see Section 2.4). Up to four target support rings can be mounted on the target table. As each target spends the same amount of time under the spray, four identical targets can be prepared in each run. The target backings are physically masked to produce a vacant, central circular area of diameter 1.3 cm; the mask is a brass plate which can be accurately and reproducibly positioned on the table.

#### 2.4 Safety Precautions

The main hazard with the operation is the radioactivity and toxicity associated with the use of  $^{239}\text{Pu}$  and, to a lesser extent,  $^{233}\text{U}$  and  $^{235}\text{U}$ . The amount of  $^{239}\text{Pu}$  used in a single run is approx. 250  $\mu\text{g}$ . If 30  $\mu\text{g}$  of  $^{239}\text{Pu}$  enters the human lung, then there is a 10 per cent chance of a fatal cancer developing over 30 years [ICRP 1980]. To safeguard against this, the spraying apparatus is enclosed in a rigid Perspex glove box, 46 cm wide by 61 cm high by 46 cm deep. The glove box is placed inside a fume cupboard located in a prescribed actinide laboratory. Equipment is transferred to and from the glove box through a port on the side of the box. After preparation, each target is fitted into a target holder which is sealed before removal from the glove box. The electro-spraying program was designed to enable the operator to gain considerable experience in the use of such inactive solutions as methanol, copper chloride  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in methanol, and the relatively inactive isotope  $^{238}\text{U}$  in ethanol, before attempting to spray  $^{235}\text{U}$ ,  $^{233}\text{U}$  and finally  $^{239}\text{Pu}$ .

A further hazard is the risk of explosion and/or fire in the glove box, due to the simultaneous presence of vaporised methanol and high d.c. voltages.

To prevent this, a slow stream of argon gas is continuously passed through the glove box during operation. The gas prevents the build-up of methanol vapour by flushing it through an exit tube at the top rear of the box and thence into the fume cupboard ventilation system.

Figure 2 is a view of the electro-spraying apparatus through the front of the glove box. The target masking plate is shown in position.

### 3. PREPARATION OF THE SPRAYING SOLUTION

For the  $^{239}\text{Pu}$  targets, the correct choice and preparation of the solution to be sprayed are of great importance. Methanol solutions are prepared with plutonium acetate rather than plutonium nitrate. Plutonium nitrate, being hygroscopic, re-crystallises after a time, to form white lumps on the target surface, and also causes the VYNS backing material to deteriorate. This does not occur with plutonium acetate since it is not hygroscopic. Methanol has low surface tension which facilitates the formation of very small drops, low vapour pressure which assists evaporation in flight, and low viscosity which permits a reasonable flow rate.

The method for preparing plutonium acetate solution from plutonium oxide is as follows [J. Pauwels, private communication].  $\text{PuO}_2$  (99.97 per cent isotopically pure in  $^{239}\text{Pu}$ ) is dissolved in a minimal volume of 7.5 M  $\text{HNO}_3$ /0.05 M HF and precipitated with a small excess of  $\text{NH}_4\text{OH}$ . After precipitation is complete, one more drop of  $\text{NH}_4\text{OH}$  is added. The supernatant solution is removed and the precipitate mixed with water containing some drops of  $\text{NH}_4\text{OH}$ . The solution is then well shaken, allowed to stand and the supernatant removed. This washing procedure is repeated at least ten times. The precipitate is dried slowly but not to excess, as excessive drying leads to the formation of the insoluble oxide. A small excess of concentrated acetic acid is then added. The precipitate is again dried and finally dissolved in methanol to a concentration of about  $0.5 \text{ mg Pu mL}^{-1}$ . During this preparation, great care must be taken to ensure that the final solution contains no traces of the nitrate.

The  $^{233}\text{U}$  and  $^{235}\text{U}$  targets are sprayed with a solution of uranium nitrate in ethanol. The uranium nitrate is prepared from uranium oxide by dissolving in 8 M  $\text{HNO}_3$  and 0.01 M HF, evaporating to incipient dryness and diluting to volume with ethanol. Methanol could also have been used as the solvent with



comparable results. The isotopic purities were 99.27 per cent for  $^{233}\text{U}$  and 92.72 per cent for  $^{235}\text{U}$ .

#### 4. METHOD OF OPERATION AND RESULTS

The optimum values for the various parameters in the Pu and U electro spraying were established with inactive solutions (mainly  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in methanol -  $0.5 \text{ mg mL}^{-1}$ ) and are listed in Table 1. A small light source on the side of the spray remote from the operator allows the spray to be seen at the needle tip in the transmitted light. The d.c. voltage which produces the most stable spray 'cone' is used in a given run.

TABLE 1  
OPTIMUM VALUES OF PARAMETERS IN ELECTROSPRAYING

Concentration of solution	$0.5 \text{ mg mL}^{-1}$
Distance: needle tip to target mask	2.0 cm
Voltage	8-10 kV +ve d.c.
Spray rate	$15-20 \mu\text{L min}^{-1}$
Volume sprayed per run	approx. 0.5 mL

Slight adjustments to the voltage are usually necessary to maintain stability throughout the run. To achieve the desired parameter values, a large number of  $\text{CuCl}_2$  targets, each produced with different values for the operating parameters, were examined under a microscope for target uniformity and particle size. Figure 3 is a micrographic view of a good  $\text{CuCl}_2$  target magnified 3000 times. The particles are typically  $\leq 1 \mu\text{m}$  in size and have a good uniformity of spread. It is reasonable to assume that the particle size and uniformity of the Pu and U targets are similar to those of Figure 3.

The operational steps are as follows:

- (i) Position the hypodermic needle vertically above the centre of the target mask.
- (ii) Fill the hypodermic syringe to the desired volume and wait until a liquid drop forms under gravity at the needle tip.

(iii) Immediately set the target table in motion, then turn on the high voltage.

(iv) Spray until all the solution is spent.

Focusing the spray was investigated during the  $\text{CuCl}_2$  runs by surrounding the needle with a metal cone held at the same electric potential. As no improvements in the uniformity were observed, focusing was omitted.

About 50 per cent of the total mass sprayed in a single run went onto the four targets. This value was determined by spraying a known mass of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  onto four aluminium discs in the target positions. The discs were weighed before and after the run on a 'Mettler' micro-balance. Further corroboration was achieved by counting the alpha activity from the  $^{239}\text{Pu}$  targets with a calibrated hand-held monitor, and with a surface barrier detector in an evacuated chamber. The majority of the unused portion was deposited on the target mask.

The mass of actinide material deposited in a single run was determined by the volume of sprayed liquid. Target thicknesses were produced in the range 10 to 40  $\mu\text{g cm}^{-2}$ , a typical result for the  $^{239}\text{Pu}$  targets being 12  $\mu\text{g cm}^{-2}$  and for the  $^{233}\text{U}$  and  $^{235}\text{U}$  targets 35  $\mu\text{g cm}^{-2}$ . Table 2 summarises the physical details of the  $^{239}\text{Pu}$  targets.

TABLE 2  
PHYSICAL DETAILS OF  $^{239}\text{Pu}$  TARGETS

Diameter of $^{239}\text{Pu}$	1.3 cm
Inner diameter of support ring	2.0 cm
Mass of $^{239}\text{Pu}$ (typical)	15±2 $\mu\text{g}$
Thickness of $^{239}\text{Pu}$ (typical)	12 $\mu\text{g cm}^{-2}$
Thickness of backing foil: VYNS	15 $\mu\text{g cm}^{-2}$
Au-Pd	10-15 $\mu\text{g cm}^{-2}$

The high quality of the targets is demonstrated in Figure 4, which shows the pulse height spectrum of fission fragments from a 12  $\mu\text{g cm}^{-2}$   $^{239}\text{Pu}$  target recorded by a surface barrier detector during a study of  $^{239}\text{Pu}$  fission induced by resonance energy neutrons [Walsh et al. 1979]. The pulse height spectrum shows a high peak-to-valley ratio of about 7:1 and absence of a tail on the low energy side of the low energy peak (i.e. in the region <300 channels).

These features indicate that fragment self-absorption in the target is small. Several of the thinner uranium targets gave peak-to-valley ratios as high as 15:1.

#### 5. ACKNOWLEDGEMENTS

The authors wish to thank J. Pauwels (Central Bureau for Nuclear Measurements, Belgium) for advice on the preparation of  $^{239}\text{Pu}$ -acetate from  $^{239}\text{Pu}$ -oxide and on the CBNM electro-spraying technique; J.J. Fardy and C.H. Randall for preparing the uranium and plutonium solutions; V. Page for preparing the VYNS films; K.G. Watson for the electron-micrograph of the  $\text{CuCl}_2$  target; and H.A. Wyllie for discussions on electro-spraying.

#### 6. REFERENCES

- Ajitanand, N.N. and Boldeman, J.W. [1970] - Nucl. Phys., A144:1.
- Boldeman, J.W., Bertram, W.K. and Walsh, R.L. [1976] - Nucl. Phys., A265:337.
- Bruninx, E. and Rudstam, G. [1961] - Nucl. Instrum. Methods, 13:131.
- Carswell, D.J. and Milsted, J. [1957] - J. Nucl. Energy, 4:51.
- ICRP [1980] - Ann. Int. Comm. Radiat. Protect. 4:No.1/2:83.
- Lauer, K.F. and Verdingh, V. [1963] - Nucl. Instrum. Methods, 21:161.
- Robinson, P.S. [1966] - Nucl. Instrum. Methods, 40:136.
- Walsh, R.L., Boldeman, J.W. and Elcombe, M.M. [1979] - Proc. 4th IAEA Symp. Physics and Chemistry of Fission, Julich, Federal Republic of Germany, Vol. 2, p.129

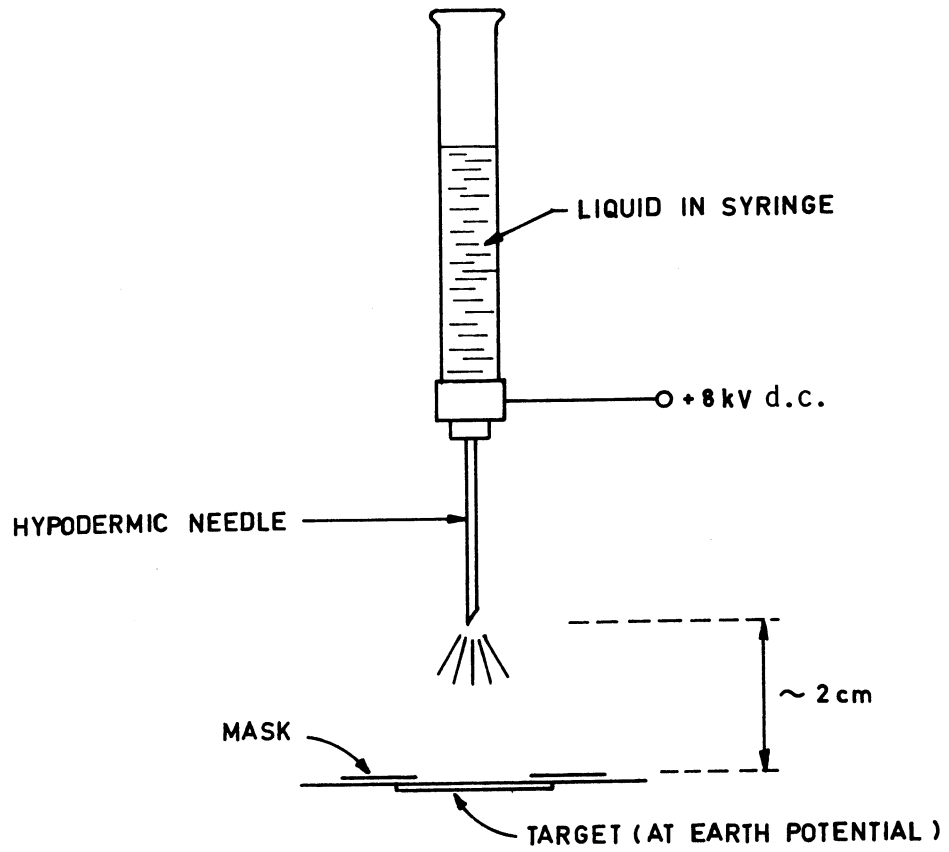


FIGURE 1. SCHEMATIC OF ELECTROSPRAYING TECHNIQUE

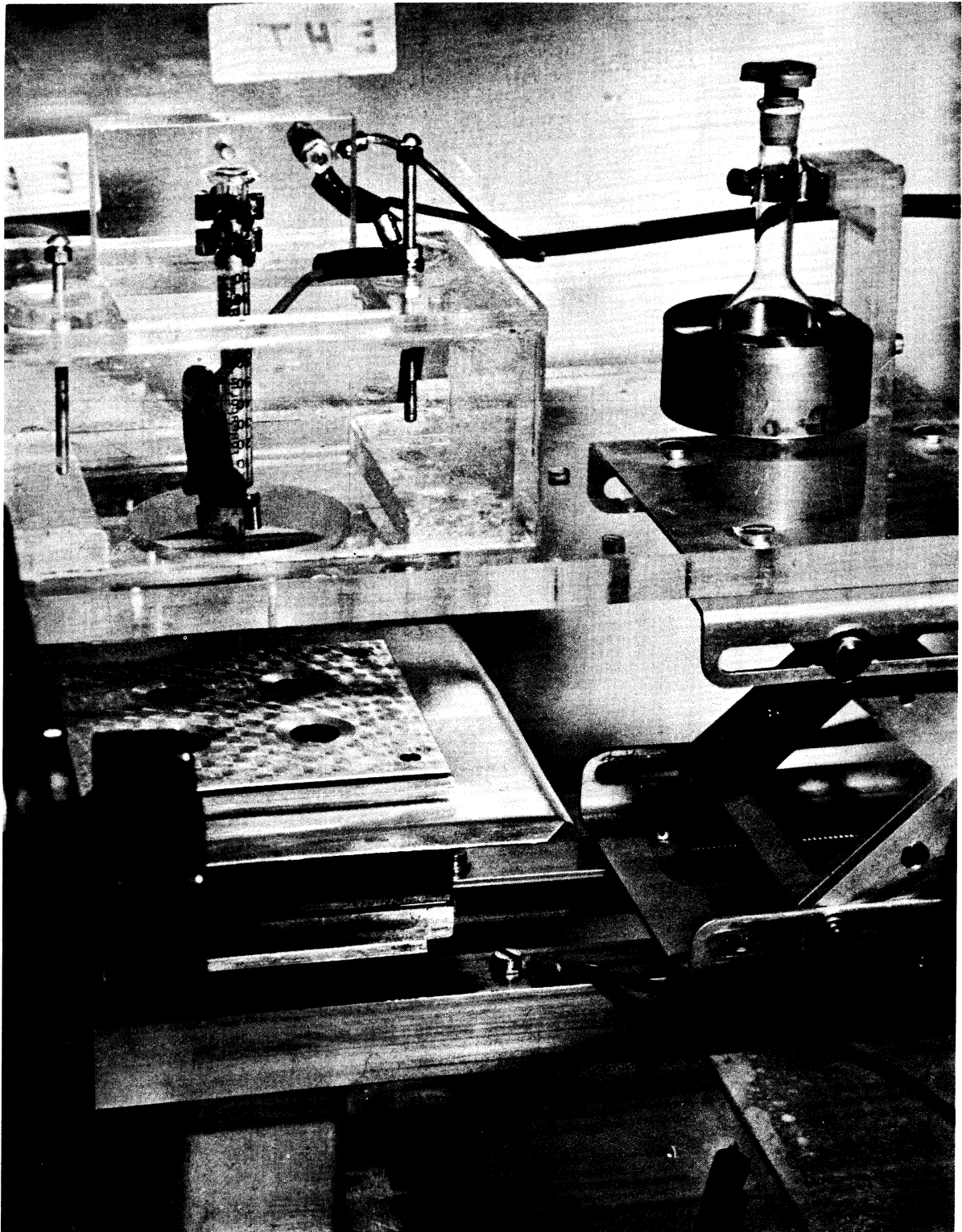
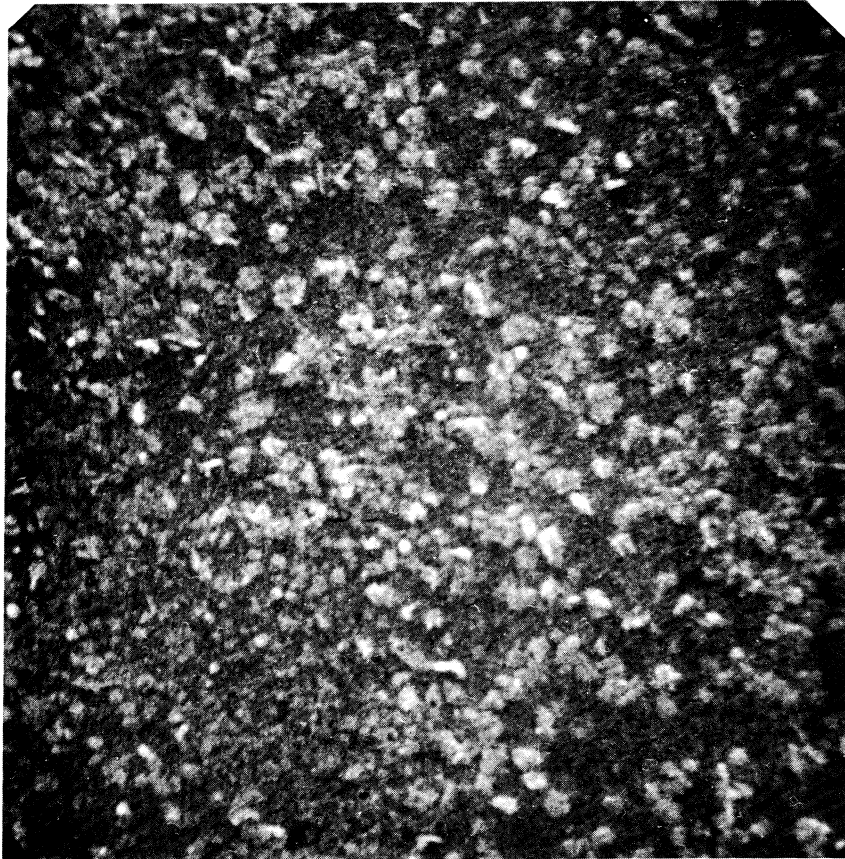


FIGURE 2. VIEW OF ELECTROSPRAYING APPARATUS THROUGH FRONT OF GLOVE BOX. The target masking plate is shown in position. The transfer port can be seen to the left of the photo. The handling glove is to the right, out of view. Y-direction of table movement is left to right, X-direction is towards back and front.



×3000

FIGURE 3. MAGNIFIED VIEW OF  $\text{CuCl}_2$  TARGET

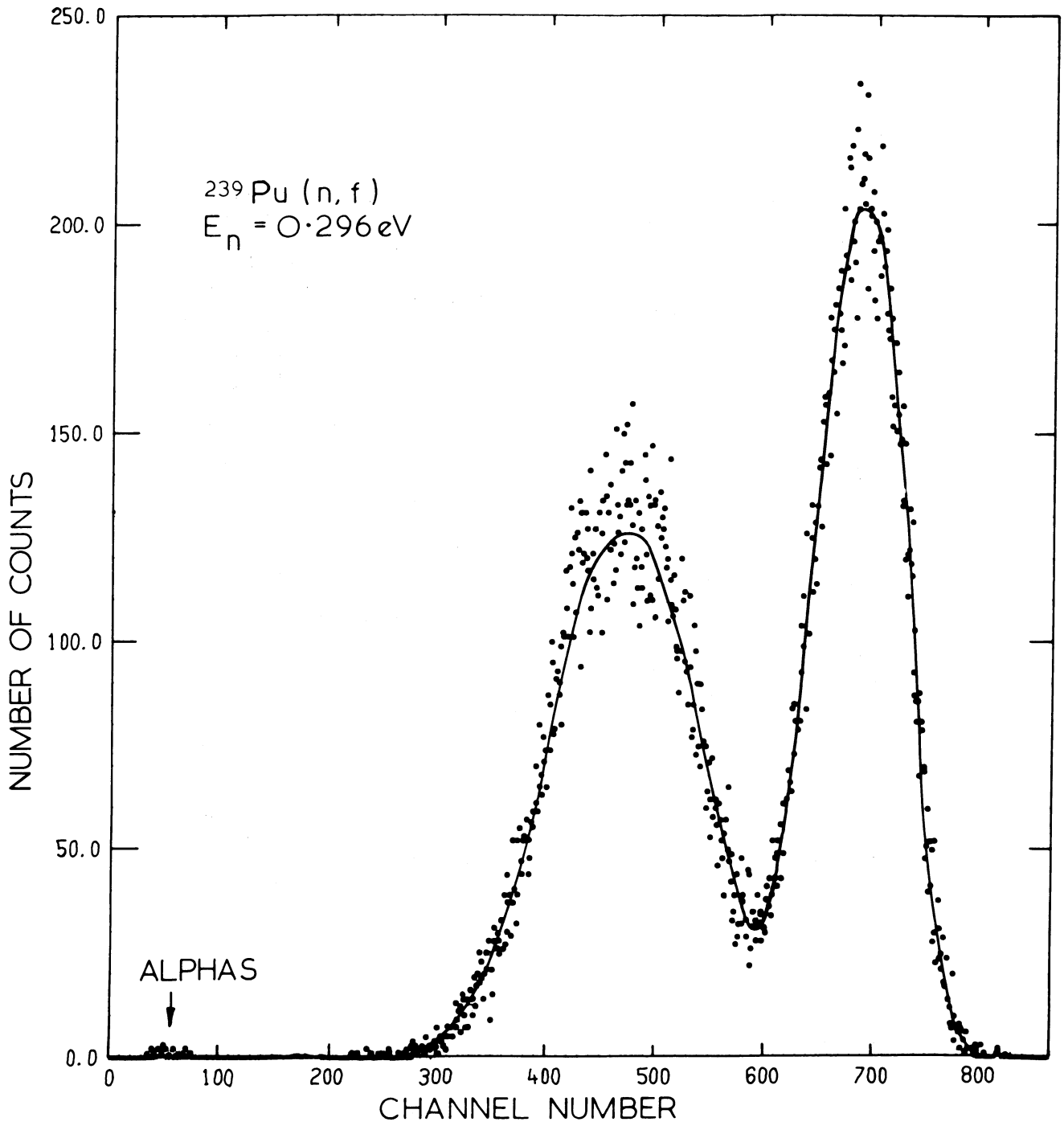


FIGURE 4. FRAGMENT PULSE HEIGHT DISTRIBUTION  
FOR ONE DETECTOR