Title

RECOVERY AND ESTIMATION OF RADIOISOTOPES FROM BIOLOGIC MATERIALS. II. THE ELECTROPLATING APPARATUS. PROCEDURES FOR COPPER, SILVER, ZINC, MERCURY, IRON AND COBALT

Author

Dunn, Rayburn W.

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Recovery and Estimation of Radioisotopes from Biologic Materials II. The Electroplating Apparatus. Procedures for Copper, Silver, Zinc, Mercury, Iron and Cobalt

Rayburn W. Dunn

September 27, 1950

Berkeley, California

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Recovery and Estimation of Radioisotopes from Biologic Materials

II. The Electroplating Apparatus. Procedures for Copper, Silver, Zinc, Mercury, Iron and Cobalt

Rayburn W. Dunn

Division of Medical Physics, Donner Laboratory
Radiation Laboratory, Department of Physics
University of California, Berkeley, California

September 27, 1950

Following the work of Ross and Chapin,[1] Hahn,[2] and others[3] with radioactive iron, a considerable number of procedures have been developed for the preparation of thin metallic films by means of electroplating. Inasmuch as particular interest has been shown in the 12-cell electroplating equipment which is currently being used in this laboratory, it seems advisable that the apparatus should be described in detail. In view of the large number of individual radioactive samples which had to be prepared in carrying out our investigational work, purchase of several of the 2 or 4 cell units which are commercially available was considered uneconomical. In consequence, a relatively inexpensive apparatus was constructed which would plate up to 12 samples simultaneously.

Most of the work in this laboratory has been concerned with the recovery of cobalt[4] and iron.[5,6] However, procedures for additional elements have been worked out for use in activation analysis[7,8] and distribution studies,[9] and these are reported herewith. Methods of ashing samples prior to separation of the pure elements, are to be reported elsewhere.[10]

Electroplating Apparatus. The electrodeposition assembly which was previously described by us[11] has been completely redesigned; individually speed-controlled anode stirrers have been eliminated, and separate anode-cathode current and voltage controls have been incorporated. Furthermore, a radically different anode has been devised. The electroplating cell, Fig. 1, has been modified to

permit plating on either 1-inch or 1-1/2-inch diameter planchets. The diameters of the plated areas are 13/16 inch and 1-1/4 inch respectively; either area may be plated on 1-1/2-inch planchets. As illustrated in Fig. 1, the adapter ring is in place for plating the smaller area. With this ring removed, together with the 1-inch gasket and constricted glass cell, a straight 1-1/2-inch glass cylinder and gasket may be substituted for plating the larger area, as illustrated in Fig. 3.

Fig. 2 shows the complete apparatus and Fig. 3 one electrodeposition cell, and alongside, one anode. A plywood frame supports the motor and brass tube. The electroplating cells rest on the box enclosing the electrical circuit. Twelve 1-1/4-inch holes are cut in the top of this box directly under the anodes when they are in the disengaged (left) position, in order to facilitate removal of the anodes for cleaning. A fan has been mounted at the back for venting such gases, as ammonia, chlorine, cyanide, etc. Lucite doors have been provided for easy access to the electrolysis cells.

The shaft and worm gears are housed in a 1-inch x 1-inch square brass tube, 56 inches long. Twelve brass blocks are spaced at 4-inch centers to hold the individual worm gears and anode collets and to serve as shaft bearings. An additional block is provided at each end of the shaft, and a roller bearing is incorporated at the motor end. The top and bottom, as well as the outward face of the square tube, are so cut that each of the 12 bearing blocks may be independently moved to engage or disengage the worm gear and the shaft worm. A set screw is attached to each in order to fix this position as desired. Fig. 4 shows the details of the brass block and gear assembly.

The 1/20th H.P. fan motor, obtained from radar surplus, rated at 1700 r.p.m., is connected by means of a vacuum-cleaner belt to the shaft in the ratio of 1 to 2. The worm-worm gear ratio is 10:1. The resulting anode rotation is thus approximately 350 r.p.m.

The collets shown in Fig. 4 are made from steel tubing, and are designed to take a 1/8-inch diameter anode rod. As first used, the platinum anode was fixed in 4 mm glass tubing with collets of suitable diameter. These anodes were continually being broken and had to be replaced. Since a sturdier type of anode was required, it was decided that the flat spiral of platinum wire (5 inches long x 0.052-inch diameter) could readily be welded to one end of 1/8-inch diameter wolfram rod which had been countersunk 1/16-inch deep with a 1/16-inch diameter counterdrill. Chemical attack of the latter would be negligible. An 8-inch length of this rod was far less expensive than the cost of the previous glassblowing procedure plus provisions for anode electrical connections. Experience has now shown that the W-Pt anode, shown in Figs. 1 and 3, is ideal for use in this apparatus and for this type of work.

The electrical circuit, Fig. 5, is of the conventional potentiometer type, measuring anode-cathode potential, and indicating one or more closed circuits by means of the pilot light. The power supply is 12 volts, using two 6-volt storage batteries in series. Current can be measured on either the 0 - 100 ma. or the 0 - 1 amp. scale. The anode-cathode distance, and hence the resistance between them, can be varied from about 1/4 inch to 1-1/2 inches or more, as desired.

Four units, as described above, were built for use in our laboratories. Two of these have seen continuous use for a period of about three years, and one of these two has had more use than the other three put together. The two units first referred to are still in excellent condition. The other two units had to be partially rebuilt. The critical factor in their performance seems to be in the "trueness" of the brass tube. The latter should be carefully checked before assembly. Over eight thousand electroplated samples have been prepared with these units.

Cathodes. Three types of cathodes have been used with this apparatus, namely, copper, gold-plated copper, and platinum. In general, the thickness of these

planchets is 0.002 inch, but this is not critical; thicker planchets must be used in the 1-inch diameter size when samples are prepared which are to be counted in Tracerlab's Automatic Counter.*

Although cathodes of other metals may sometimes be required, the ones listed will do for nearly all routine work. If the cathode deposit is to be weighed, platinum planchets should be used; however, gold-plated copper may be substituted for platinum in such a case, provided that the electrolyte does not dissolve appreciable amounts of copper. Experience in this laboratory has shown that the gold plate does not give perfect protection of the copper, but that under the usual conditions of use the copper attack will be small enough to allow a satisfactory gravimetric determination of the electroplated film, if needed.

In plating uranium as uranous fluoroide or oxide it is customary to calcine the deposit in order to convert it to U_3O_8.[12] Under these conditions, and also when it is necessary to recover the deposit quantitatively and pure, platinum or gold should be used.

All three types of cathode may be cleaned by immersion in the usual dicromate-sulfuric acid cleaning solution, with the precaution that the copper and plated copper not be allowed to remain in contact with this solution any longer than necessary. After removal of the excess cleaning solution, the planchets are rinsed with hot tap water as vigorously, rapidly and completely as possible. After rinsing in distilled water, each planchet should be dipped in acetone and allowed to dry. An acetone dip should also be employed after electroplating. The anodes should be cleaned in a similar fashion, although the acetone rinse is not considered necessary.

Electroplating and Electrodeposition. A general discussion of electroplating and electrodeposition for radioassay is to be found in Siri's recent publication.[13] This discussion will be of aid to those who desire to work out new

* Tracerlab, Inc., 130 High Street, Boston 10, Mass.

methods for recovery and estimation of radioisotopes by the electrolytic procedure.

Procedures for Use with Copper, Silver, Zinc, Mercury, Iron and Cobalt. All or nearly all inorganic analytical procedures for use with biologic materials are preceded by ashing. In view of the importance of ashing methods per se, these methods are to be reported separately.[10]

In general, the inorganic salt solution obtained after ashing will be rather strongly acid and may contain relatively large amounts of calcium, magnesium, sodium, potassium, sulphate, phosphate, etc., in comparison with the element or elements to be determined. The carrier element is usually added before, during or after ashing, depending upon the convenience of the operator. Whenever it is possible to weigh the final electroplated material, and thus have a measure of the amount recovered, the carrier should be added before ashing. The recovery and estimation of gold[11] is an example of the latter procedure.

The amount of carrier which is to be used varies between one and ten milligrams and will depend upon the method of separation employed, the area electroplated (with reference to self-absorption), and upon whether or not a final gravimetric determination is to be made. Five milligrams of carrier, plated on one-inch diameter planchets, and weighed to the nearest 0.1 milligram is the general rule. Taking into consideration the fact that there is usually a small weight loss when gold-plated copper cathodes are used, the error involved in following such a gravimetric procedure will usually be less than plus or minus five percent, which is quite satisfactory for this type of work.

Whenever the amount of ashed material is low, e.g., one to ten milligrams, a separation procedure prior to electroplating may not be necessary, and this is particularly true if the element is electroplated from an acid solution. However, since an alkaline condition nearly always exists within the cathode

boundary, the presence of inorganic ash salts often leads to the production of an inferior plate due to inclusion of some insoluble material with the metallic deposit. Whenever this occurs the plate will not firmly adhere. Furthermore, quantitative recovery under these conditions is frequently impossible.

All the procedures which follow include a separation before electroplating. Whether this procedure is followed, however, will depend upon the judgment of the operator. Inasmuch as each of the methods is based upon accepted analytical procedures, no quantitative data are presented.

Copper: With five milligrams of carrier copper present, the ashed material is converted to the choride by the addition of excess concentrated hydrochloric acid and evaporation nearly to dryness if a nitric acid digestion has been used, although complete removal of nitrate ion is not essential. If a sulfuric acid digestion has been employed, the excess acid must be fumed away. The resulting chloride or sulphate ash is dissolved in dilute hydrochloric acid and transferred to a centrifuge cone of suitable size, depending upon the amount of ashed material. The final acid concentration should not exceed 1 N and may be as low as 0.01 N provided that precipitation does not occur. With five milligrams of carrier, the final solution volume may be as great as 100 ml and still give excellent recovery.

The solution in the centrifuge cone is next treated with hydrogen sulfide gas to saturation. After allowing the solution to stand for a short time, the cone is centrifuged and the supernatant liquid discarded. The precipitate is washed by resuspending in water, etc.

The precipitate is dissolved in a minimum of concentrated nitric acid with slight heating, and transferred to an electroplate cell containing 20 ml of a solution made up to be 0.2 N in nitric and 0.7 N in sulfuric acid. Electroplating is carried out at 0.1 amp. for three hours.*

* Procedure devised by Mary Ann Danielson, Donner Laboratory, Univ. of Calif.

Silver: The ashed material is dissolved in dilute hydrochloric acid and transferred to a centrifuge cone containing five milligrams of silver as the nitrate unless this amount of carrier has been added before ashing. In the latter case, the ashed material will not be completely soluble due to the presence of silver chloride, phosphate, etc., and it will be necessary to transfer the incompletely dissolved material to the centrifuge cone and then to wash the ashing vessel with concentrated ammonium hydroxide if all the active silver is to be recovered.

Excess ammonium hydroxide is then added in order to dissolve the precipitated silver salts and allow the active silver to become mixed with the carrier. If much inorganic ash is present it may be difficult to observe the point at which the silver is dissolved, due to the simultaneous precipitation of phosphates, etc. In such a case, an indicator changing color between pH 9 and 10 may conveniently be employed; otherwise excess ammonia may be determined by odor. After addition of excess ammonium hydroxide, the solution is reacidified until it is about 0.1 N, followed by centrifuging. The supernatant is discarded, the precipitate redissolved in ammonium hydroxide and re-precipitated with hydrochloric acid, as above.

The precipitate is then dissolved in 2 ml of 5 percent potassium cyanide solution and transferred to an electrodeposition cell containing 5 ml of 1 N sodium hydroxide, or alternatively, the sodium hydroxide and potassium cyanide may be combined and the precipitate dissolved in 10 ml 0.5 N and 1 percent, respectively, etc. The final volume in the electroplate cell should be 20 to 25 ml. Electrolysis is carried out at 0.1 to 0.2 amp. or more for one to two hours. On platinum cathodes the electroplating procedure deposits between 98 and 100 percent of the silver.

Zinc: The ashed material together with 5 mg of carrier, should be transferred with dilute hydrochloric acid to a centrifuge cone, and the resulting solution adjusted to between pH 3 and 4 using ammonium hydroxide and methyl orange

indicator. The solution should remain clear, but if a precipitate does appear, dilute hydrochloric acid may be added until the solution clears up provided that the pH is not too greatly lowered. The solution is next saturated with hydrogen sulfide, allowed to stand several minutes to allow complete precipitation of zinc sulfide, centrifuged, etc.

The resulting washed precipitate is dissolved in nitric acid, taking care that any elemental sulfur which may be formed either remains finely divided, or is completely dissolved by the acid. It has frequently been observed when dissolving sulfide precipitates in nitric acid, with the centrifuge cone in a boiling water bath, that a pellet of sulfur forms which is difficult to dissolve and which probably contains appreciable amounts of the desired element. Heating to accelerate solution of the precipitate is therefore not recommended.

The zinc nitrate solution is then transferred to an electrodeposition cell containing 10 milliliters the same alkaline cyanide solution as is used with silver, and electroplated under the same conditions of volume, current and time.

Mercury: Although very little work has been carried out with mercury in this laboratory, procedures for use with it are included here to serve as a guide for other investigators. Three possibilities are open, namely, precipitation of the sulfide under conditions similar to those employed with zinc; precipitation of the chloride in the presence of excess chloride after reduction with hydroxylamine; and reduction to the metal using stannous chloride, phosphorus or hypophosphorus acid.

The last named method has been successfully used on some pile-activated ash samples, and the recovered mercury was electroplated on platinum planchets. It was found, however, that the thin film of mercury voltalized so rapidly even when given a sulfide coating, that satisfactory radiometric determinations and decay curves could not be obtained. It is suggested that the precipitated chloride or metal be dissolved in a minimum of nitric acid and transferred to a

plastic counting cup. The cup and contents may then be placed in a suitable chamber and exposed to an atmosphere of hydrogen sulfide. The sample should be dried at a low enough temperature to prevent oxidation of the sulfide by the remaining nitrate. Alternatively the same procedure may be followed omitting hydrogen sulfide, but taking care not to volatize the mercury salt upon drying.

Iron: Huff's modification of Peacock's method for iron[5,3] gives very satisfactory results. In this procedure the ashed material containing ten milligrams of carrier is precipitated twice with sodium hydroxide in a centrifuge cone. The supernatant liquids are discarded and the precipitate is dissolved in a minimum of concentrated hydrochloric acid. The resulting solution is transferred directly to an electroplate cell containing 35 ml of a plating solution which is made up with one part of saturated oxalic acid plus five parts of saturated ammonium oxalate. Plating is carried out at 0.8 amp. (on 1-1/2-inch planchets) for one to two hours.

Since the procedure outlined above does not eliminate the principal ions which interfere with the electroplating of iron, it is questionable whether the precipitation with sodium hydroxide serves any purpose other than the elimination of excess acid. Because of the presence of large amounts of interfering anions such as phosphate, urine and feces samples cannot be satisfactorily determined by this procedure. No rapid method for separating iron from phosphate had been devised before this investigational work was discontinued.

Cobalt: The ashed material and carrier are dissolved and transferred to a centrifuge cone as outlined above. The resulting solution is then precipitated with concentrated ammonium hydroxide containing ten percent hydroxylamine hydrochloride. After centrifuging, the supernatant liquid is transferred to an electrodeposition cell. The remaining precipitate is dissolved in hydrochloric acid and then reprecipitated twice more. The three supernatant solutions are collected in the cell and electroplated at about 0.4 amp. for two to three hours.

Although several procedures have been investigated, no method for sharp separation of cobalt from ash salts has been found. The ammoniacal extraction is satisfactory, however, but somewhat time-consuming.

SUMMARY

A relatively inexpensive apparatus for the simultaneous electroplating of up to twelve samples is described.

Various kinds of cathodes are listed, together with their special applications and methods of preparation for use.

A general discussion of the nature of solutions of ashed biologic material is included, together with a discussion of the use of carriers.

A brief outline is presented of procedures for use with copper, silver, zinc, mercury, iron and cobalt.

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BIBLIOGRAPHY

1. Ross, J. F. and Chapin, M. A., The electrolytic separation of radioactive iron from blood, Rev. Sci. Instr. 13, 77 (1942)

2. Hahn, P. F., Radioactive iron procedures. Purification, electroplating, and analysis, Indust. Engin. Chem., Anal. Ed. 17, 45 (1945)

3. Peacock, W. C., Evans, R. D., Irvine, J. W., Jr., Good, W. M., Kip, A. F., Weiss, S. and Gibson, J., II. The use of two radioactive isotopes of iron in tracer studies of erythrocytes, J. Clin. Inves. 25, 605 (1945)

4. Berlin, N. I., The distribution of cobalt in polycythemic rats, J. Biol. Chem., Nov. 1950

5. Berlin, N. I., Huff, R. L., Van Dyke, D. C. and Hennessy, T. G., The blood volume of the adult rat as determined by Fe^{59} and P^{32} labeled red cells, Proc. Soc. Exp. Biol. and Med. 71, 176 (1949)

6. Huff, R. L., Bethard, W. F., Garcia, M. A., Roberts, B. M., Jacobson, L. O. and Lawrence, J. H., Tracer iron distribution studies in irradiated rats with lead-shielded spleens, J. Lab. and Clin. Med. 36, 40 (1950)

7. Tobias, C. A. and Dunn, R. W., Analysis of microcomposition of biological tissue by means of induced radioactivity, Science 109, 109 (1949)

8. Wolfe, R. G., Jr., Dunn, R. W. and Tobias, C. A., Activation trace analysis, UCRL-480

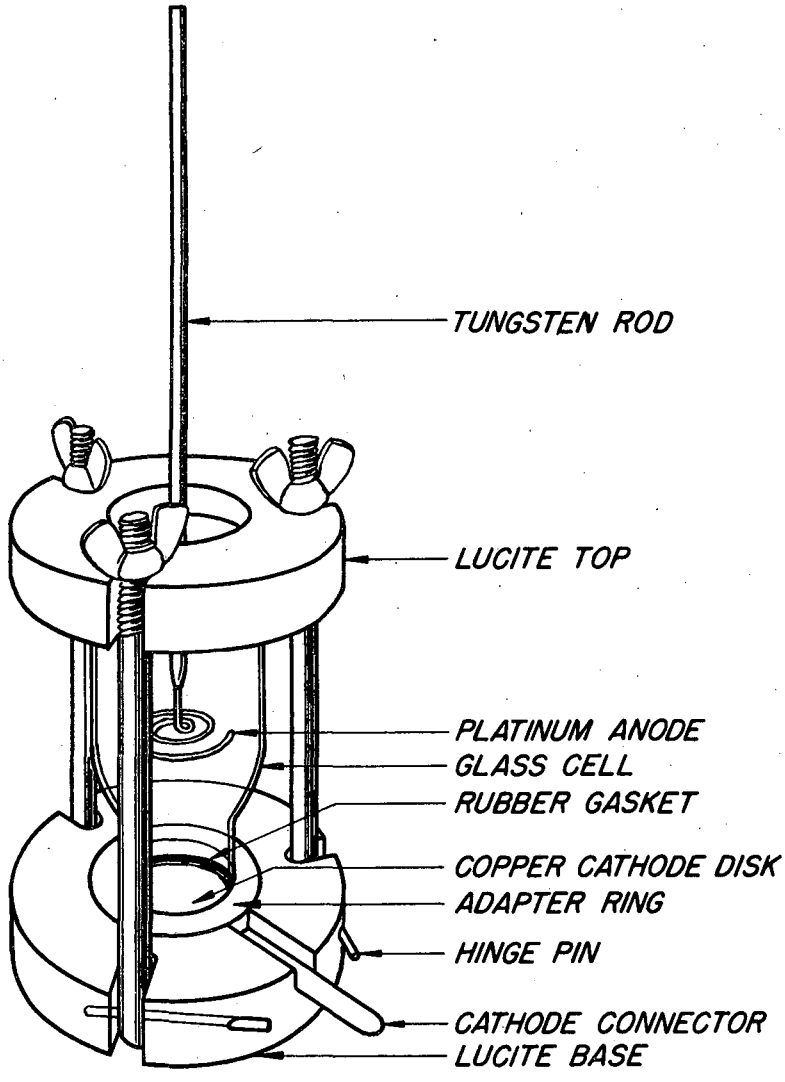
9. Rosenfeld, I. and Tobias, C. A., Studies of trace elements with radioactive isotopes. The distribution of Co^{60}, Zn^{65}, and Cu^{64} in the cytoplasm and nuclei, UCRL-480

10. Manuscript in preparation

11. Dunn, R. W., Recovery and estimation of radioactive isotopes from biologic tissues. I. Gold, J. Lab. and Clin. Med. 33, 1169 (1948)

12. Lilly, R. C., A non-gravimetric method for the determination of uranium on platinum discs, MDDC-430 (1946)

13. Siri, W. E., Isotopic tracers and nuclear radiations, New York: McGraw-Hill Book Co., Page 438 (1949)


TUNGSTEN ROD
LUCITE TOP
PLATINUM ANODE
GLASS CELL
RUBBER GASKET
COPPER CATHODE DISK
ADAPTER RING
HINGE PIN
CATHODE CONNECTOR
LUCITE BASE

MU 883

Fig. 1

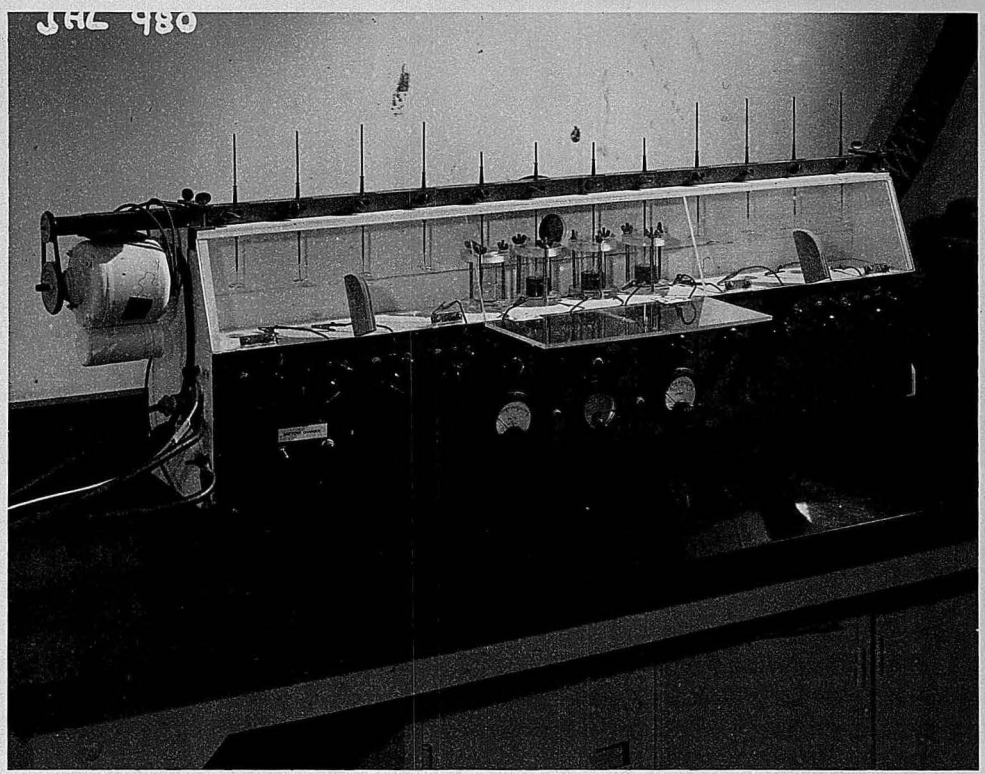


FIG. 2

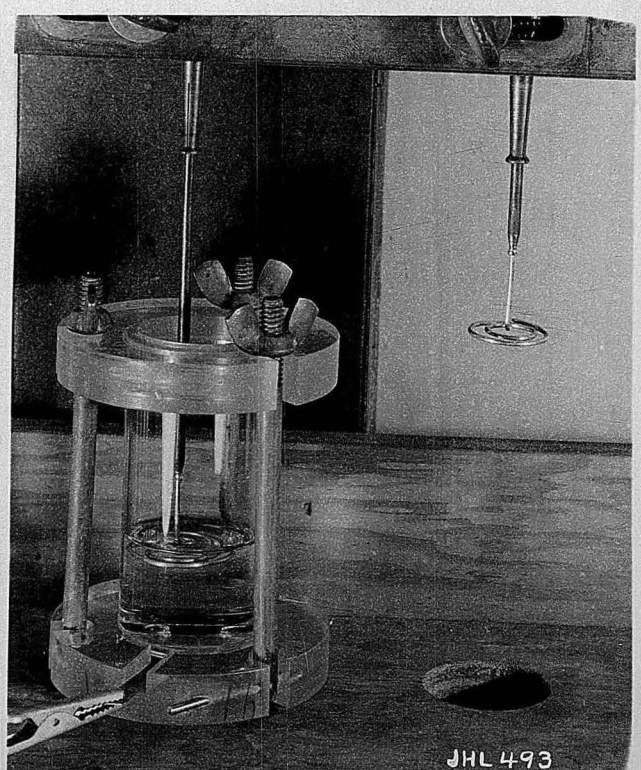


FIG. 3

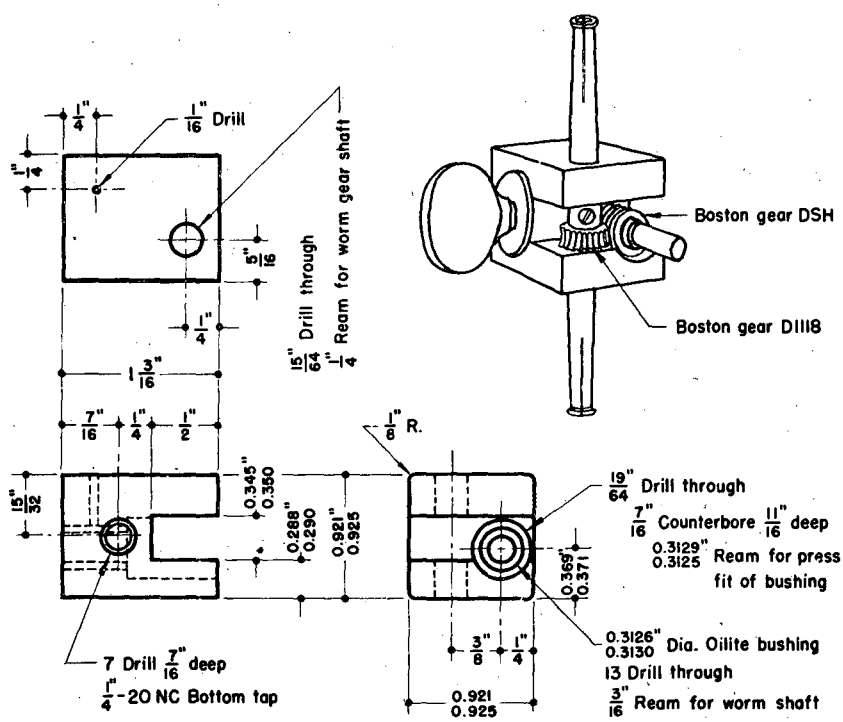

1/4"
1/16" Drill
1/4"
5/16"
1/4"
1 3/16"
15/64" Drill through
1/4" Ream for worm gear shaft
7/16"
1/4"
1/2"
1/8" R.
15/32"
0.345"
0.350
0.288"
0.290
0.921"
0.925
19/64" Drill through
7/16" Counterbore 11/16" deep
0.3129"
0.3125 Ream for press fit of bushing
0.369"
0.371
0.3126"
0.3130 Dia. Oilite bushing
13 Drill through
3/16" Ream for worm shaft
3/8"
1/4"
0.921
0.925
7 Drill 7/16" deep
1/4"-20 NC Bottom tap
Boston gear DSH
Boston gear D1118
MU 881

Fig. 4

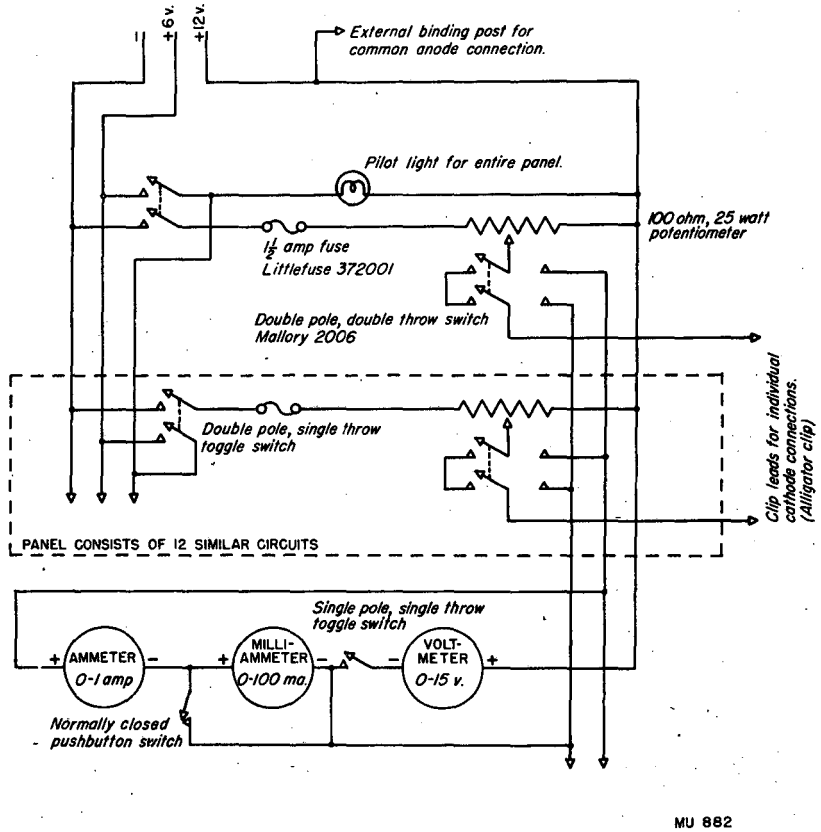

+6 v.
+12 v.
External binding post for common anode connection.
Pilot light for entire panel.
100 ohm, 25 watt potentiometer
½ amp fuse
Littlefuse 372001
Double pole, double throw switch
Mallory 2006
Double pole, single throw toggle switch
Clip leads for individual cathode connections. (Alligator clip)
PANEL CONSISTS OF 12 SIMILAR CIRCUITS
Single pole, single throw toggle switch
AMMETER
0-1 amp
MILLI-AMMETER
0-100 ma.
VOLT-METER
0-15 v.
Normally closed pushbutton switch
MU 882

Fig. 5