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DETERMINATION OF TRITIUM IN URINE AND WATER

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HEALTH AND SAFETY

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ABSTRACT

The sample, water or urine, is prepared for counting in a vacuum line. Urine or water is dropped onto metallic calcium, and hydrogen and tritium are evolved. The gas flowing into the evacuated system is passed through liquid nitrogen cooled traps to remove unreacted water and condensable gases. The gas is allowed to flow into a tube similar to a Geiger-Muller tube until a pressure of 15 cm of mercury is attained. Ethylene and argon are added to give a total pressure of 22 cm of mercury. The beta activity is counted with a scaling circuit having an input sensitivity of 1/4 volt. A tube similarly filled with inert hydrogen is counted simultaneously to determine the environmental background. The background count is subtracted from the sample count to obtain the true sample count.

The method has a precision of ± 5% in the range of 1 to 250 μc of tritium per liter of sample. Samples with higher concentrations may be determined with appropriate dilutions. An experienced operator can do approximately 50 determinations per day. The tolerance used at LASL for tritium in urine is 250 μc/liter.

1. Introduction

The initial work on tritium determination at Los Alamos followed essentially the method in use at Hanford at that time.[1] Acetylene was evolved by dropping urine on calcium carbide, collected over water in a glass vacuum manifold, and passed through suitable drying agents into a glass, silver-coated electrometer chamber. The current generated in the chamber was measured with a vibrating reed electrometer. However, the only electrometer available at the time did not respond satisfactorily to small variations in tritium concentration.

Brass cylindrical chambers with Lucite insulators were substituted for the glass electrometer chambers and the measurements were made with a Lindemann-Ryerson electrometer. The tritium concentration was determined by the velocity of needle travel across the scale in a microscope field. This modification gave adequate sensitivity and good precision but proved time-consuming for samples of low activity. The brass tubes were prone to develop current leaks at the Lucite insulators and the electrometer was subject to frequent breakdown.

At this time E. C. Anderson of LASL brought to our attention the method developed by Wolfgang and Libby for counting gaseous tritium.[2] Brass Geiger-Muller type tubes were fabricated and filled with hydrogen evolved by dropping urine on calcium metal. The measurements were made with a scaler equipped with an external quenching circuit. A high vacuum manifold, similar to that used at present, was designed to fill the tubes. The quenching circuit was subject to maintenance difficulties and was finally eliminated when it was found that satisfactory results could be obtained with ethylene-argon mixtures as an internal quenching agent. This method proved very satisfactory for routine work since the time per determination was greatly decreased. This apparatus was used with little modification for many months. A second scaler for the simultaneous determination of environmental backgrounds was added to compensate for background variability.

The fragility of the glass connections on the brass tubes and the difficulty of decontamination of the brass were the chief problems with this system. To overcome the decontamination problem, glass Maze-type internal counting tubes with an external cathode were designed and fabricated. These tubes are described in detail under 5.4. They have been in routine use for two years and have proved satisfactory. They are durable when handled with reasonable care and are easily cleaned and decontaminated.

2. Apparatus

The analysis is carried out in the glass vacuum line shown in Figs. I and II.

The counter tube is shown in Fig. IV. The tube is of the Maze type[3] in which the beta particles are determined internally. The external cathode is a chemically deposited silver

mirror on the soft glass envelope. Tritium betas are counted at a level of 50 volts above the starting potential; this voltage has been found to be on the plateau portion of the curve.

The tubes are counted with a decimal scaler (LASL Model 700) built by the Electronics Group of the Physics Division at LASL. The scaler has a 10-microsecond resolving time and a six-place mechanical register which will handle 72,000 counts per minute with a counting loss of less than one percent. Two scalers are used: one to count the background tube and one to count the sample tube. The scalers are equipped with a control panel and a Graylab Universal Timer so that they may be operated simultaneously for a preset time.

3. Reagents

Metallic Calcium - No. 10 mesh. The calcium used is a specially purified calcium obtained from another group at LASL.

Ethylene - 99.5%, Commercial grade

Argon - Commercial grade

Liquid Nitrogen

Apiezon M Stopcock Grease

Dow-Corning High Vacuum Grease - A silicone lubricant

Dow-Corning Antifoam A - A silicone defoamer

Tritium Standard - The stock standard is water containing tritium oxide obtained from Austin Brues of Argonne National Laboratory. The original stock standard was labeled 0.1 μc/ml.

Working Tritium Standard - 200 ml of stock tritium standard is diluted with distilled water to 1 liter. The standard solution contains 20 μc/liter of tritium.

4. Range, Precision and Tolerance

This method can be used for concentrations of tritium ranging from 1 to 250 μc/liter of sample. In this concentration range the precision is approximately ± 5 percent. Samples with higher concentrations may be determined after appropriate dilution. The method is well-adapted for routine work since an experienced operator can do about 50 determinations per day. The urine tolerance level used at LASL is 250 μc of tritium per liter of sample.

5. Procedure

5.1 Preparing the Apparatus for Use.

1. Grease the stopcocks and joints on the vacuum line periodically (usually every few months) with Dow-Corning High Vacuum Grease.

2. Place approximately 3 grams of metallic calcium in the bottom of the glass generator (Fig. III). Ring the generator internally with Dow-Corning Antifoam A and fit the top of the generator to the bottom with Apiezon M stopcock grease. Grease the male joint on the manifold with Apiezon M stopcock grease and place the generator on the vacuum line. Open stopcock a between the generator and the vacuum line.

3. Fill the two spherical traps with liquid nitrogen. Place the tubular liquid nitrogen trap (A) on the line and place it in a 1000-ml wide-mouthed Dewar vessel. Fill the Dewar with liquid nitrogen.

4. Place the glass counting tube on the vacuum line.

5. Close the line (stopcock No. 1) to the atmosphere and start the mechanical pump (Cenco Hyvac pump, 1/3 horsepower). Pump the system for 15 minutes or until the system is evacuated. The pressure should register approximately 0.05 mm (or less) of mercury on the Pirani Gauge.

6. Open the valves on the ethylene and argon cylinders until the pressure is between 1 and 2 pounds per square inch. Close the right side of the system and add ethylene and argon until a pressure of 10 cm of mercury is attained on the manometer. This is done to flush the gas lines. Open the line to the pump and to the counting tube and continue pumping the system until the pressure is again approximately 0.05 mm of mercury.

7. Turn on the master switch on both scalers and let the instruments warm for 30 minutes. At the end of 30 minutes turn on the high voltage on both scalers and let them warm for 5 minutes. Turn on the a-c switch on the control panel.

8. Fill the background counting tube with inert hydrogen (generated from distilled water), argon, and ethylene as described in 5.2, "Analyzing the Sample." Place in the lead shield (Fig. V) and connect to the high voltage of the background scaling circuit.

5.2 Analyzing the Sample

1. Fill the thistle tube on the generator with the urine or water sample. This normally requires from 10 to 15 ml of liquid, but samples may be run on 5 ml of liquid if extreme care is used. Close the line to the vacuum pump and slowly drop the liquid on the calcium metal until a pressure of 16-17 cm of mercury is attained. Shut off the left side of the vacuum line and open to the atmosphere. Bleed off the excess gas in the right side of the vacuum line with stopcock No. 3 (ground for micro-control) until the pressure on the manometer is 15 cm of mercury. Close the stopcock between the counting tube and the vacuum line.

2. Evacuate the right side of the vacuum line and add ethylene to the counting tube, to a pressure of 2 cm of mercury. Similarly add argon to a pressure of 5 cm of mercury.

3. Remove the counting tube from the vacuum line. Place in the lead counting shield and connect to the high voltage of the sample scaling circuit.

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4. Turn the high voltage up slowly on both circuits until the counter starts. Check the starting voltage several times. Add 50 volts to both scalers with the preset addition switches on the scalers.

5. Count the sample and the background tubes for two minutes. Count the sample until the observed single counts (two-minute counts), obtained by subtracting the background count from the sample count, do not differ by more than one standard deviation from the average net count.

6. Calculation of results.

$$\frac{\text{Average net sample count per minute - counting tube background}}{\text{tube standardization factor}} = \mu c \text{ of tritium per liter of solution}$$

The procedure for obtaining the "counting tube background" and the "tube standardization factor" are given under 5.4, "Preparation of Counting Tubes."

5.3 Procedure for Shutting Down the Apparatus

1. Evacuate all counting tubes.

2. Open the vacuum line to atmospheric pressure and turn off the mechanical pump. Close the valves on the ethylene and argon cylinders. Remove the tubular liquid nitrogen trap and the caps on the spherical traps from the line. Clean and dry them when they have thawed.

3. Turn off both scalers.

4. Rinse the calcium from the generators with water and soak for several hours in kerosene. Scrub with Alconox, rinse well and dry in an oven.

5.4 Preparation of Counting Tubes

The counting tubes (Fig. IV) are made with a volume of 200 ml, of lime glass with a 1-mil tungsten centerwire, according to specifications at LASL. The centerwire has a hook at each end, one of which is fastened to a small stainless steel spring. At each end of the tube is a 20-mil platinum lead (fused with the glass) which extends at least 1 inch beyond the end of the tube and approximately 1 inch inside the tube. The inner ends of the leads are hooked. One lead is hooked to the stainless steel spring and the other to the centerwire. The metal-to-metal connections are secured with silver solder. The outside of the tube is coated with a silver mirror which serves as the cathode.

1. Wrought copper tube caps (3/8" ID) are procured from stock. A small hole is drilled in the end of a cap and the cap is partially filled with Armstrong's cement and placed over the end of the glass tube with the centerwire through the hole. When the cement is thoroughly set and the cap firmly fixed on the tube, the protruding wire is clipped off and sealed to the cap with a drop of solder.

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2. Clean the tube by washing with a weak solution of Alconox. Rinse thoroughly with distilled water to remove all the detergent and rinse twice with ethyl alcohol. (If the tube background is too high the tube may be decontaminated by rinsing with 15 ml of 10% nitric acid. Do not let the tube stand with the acid for more than 15 minutes since the acid will attack the silver solder. Rinse thoroughly with distilled water.) Dry the tube by placing on the vacuum line and pumping for several hours. Wash and polish the outside of the tube.

3. Silver the tube on the outside with Brashear's Silvering Solution.[4] Cover the ends of the tube with masking tape and dip them in paraffin to keep them from being silvered. Give each tube two coats of silver.

4. After the tubes have been plated and the paraffin has been cleaned off, place a strip of copper foil (20 mil, 3/8" x 3-1/2") in contact with the silver mirror. Two and one-half inches of the foil should be in contact with the mirror. Fasten the strip in place with Scotch electrical tape and wrap the entire mirror with the tape to protect the plate. Allow one inch of the copper strip to extend beyond the wrapping to serve as contact for the ground lead from the scaler.

5.5 Counting Tube Background. Fill each tube with inert hydrogen generated from distilled water and count as given under 5.2, "Analyzing the Sample." The difference between the counts per minute of the background tube and the counts per minute of the new counting tube is known as the counting tube background. The tube background is expressed in counts per minute. The background tube should be chosen so that its counting rate is lower than that of the sample tubes. The tube background changes with use and should be rechecked every week or two, or after being filled with samples with extremely high tritium concentrations. If the tube background is more than 30 c/m the tube should be recleaned until the background drops to 30 c/m or less.

5.6 Counting Tube Standardization Factor. The tube standardization factor gives the number of counts per minute for each microcurie of tritium in a liter of Standard Tritium Solution. The factor is expressed in terms of counts per minute per microcurie of tritium. Fill the tube with tritium generated from the working tritium standard and count as given under 4.2, "Analyzing the Sample."

Calculation:

$$\frac{\text{Average net count per minute - tube background}}{20\ \mu c/\text{liter}} = \text{tube standardization factor in } c/m/\mu c/\text{liter}$$

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2. Wolfang, R. L., and W. F. Libby, Phys. Rev. 85, 437 (1952)
3. Maze, Roland, J. Phys. Radium 7, 164-6 (1946)
4. Strong, John, Procedures in Experimental Physics, pp 152-157, Prentice Hall, New York, 1938

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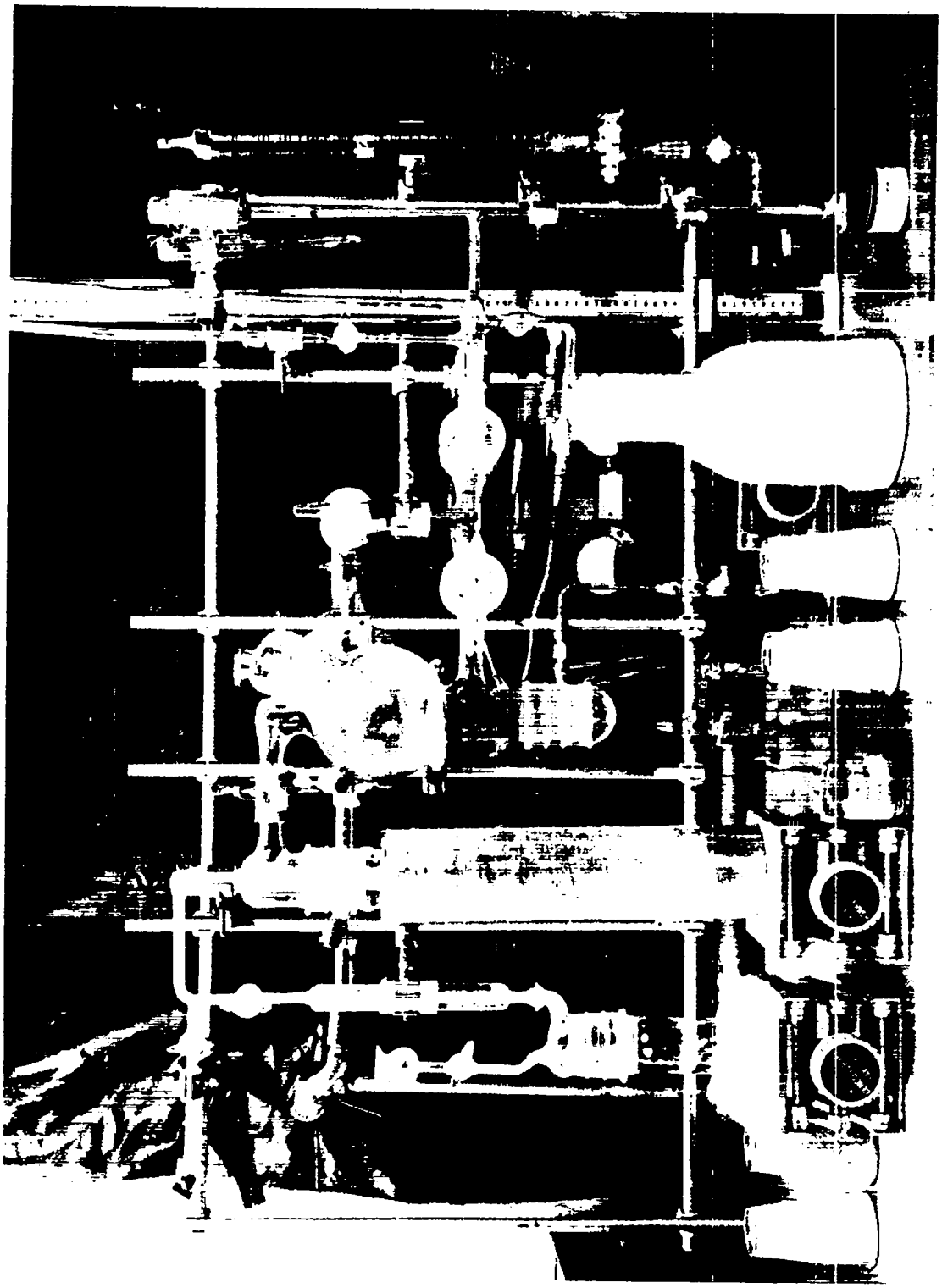

FIGURE 1 - GLASS MANIFOLD FOR FILLING OF TUBES

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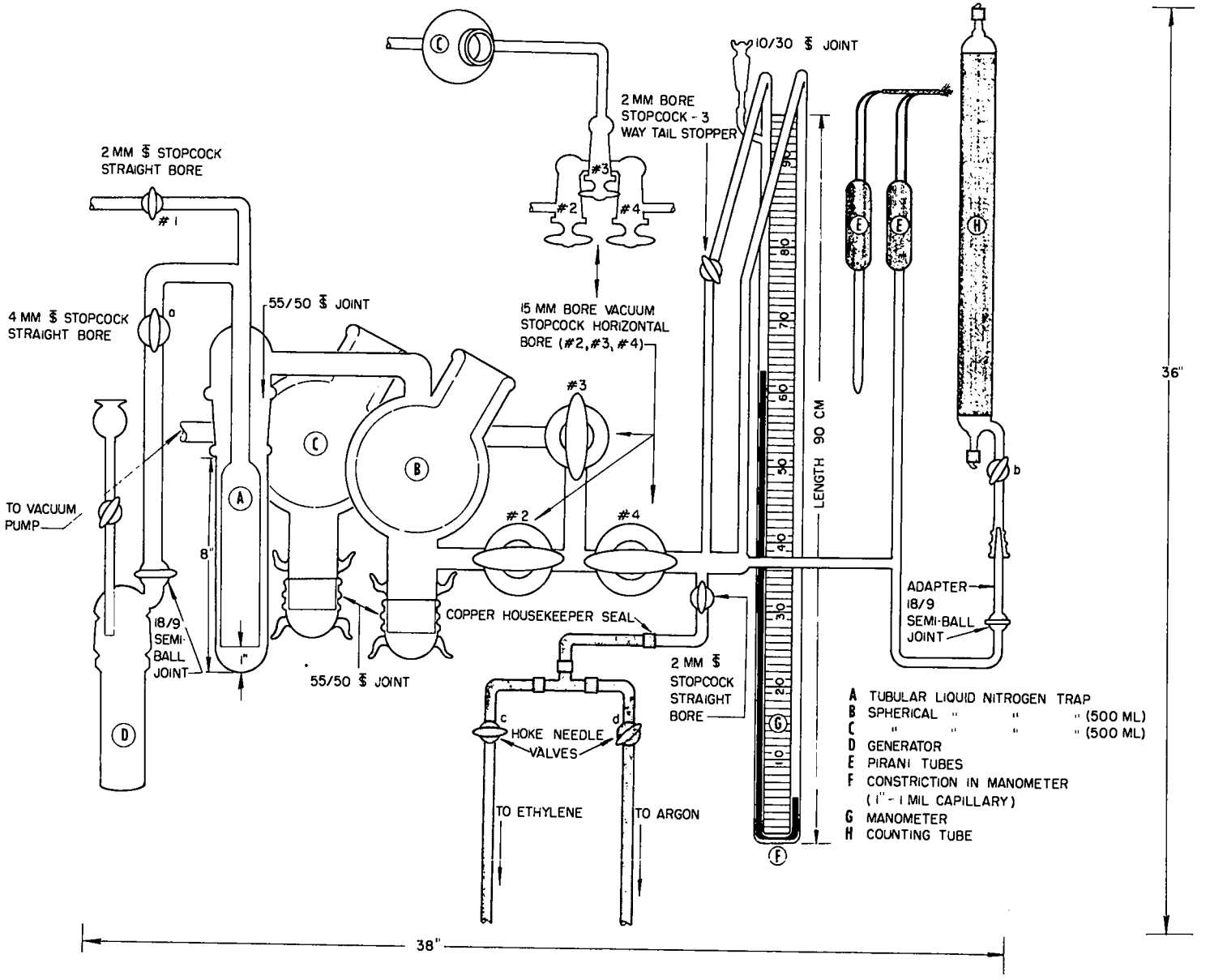

FIGURE II - GLASS MANIFOLD FOR FILLING OF TUBES

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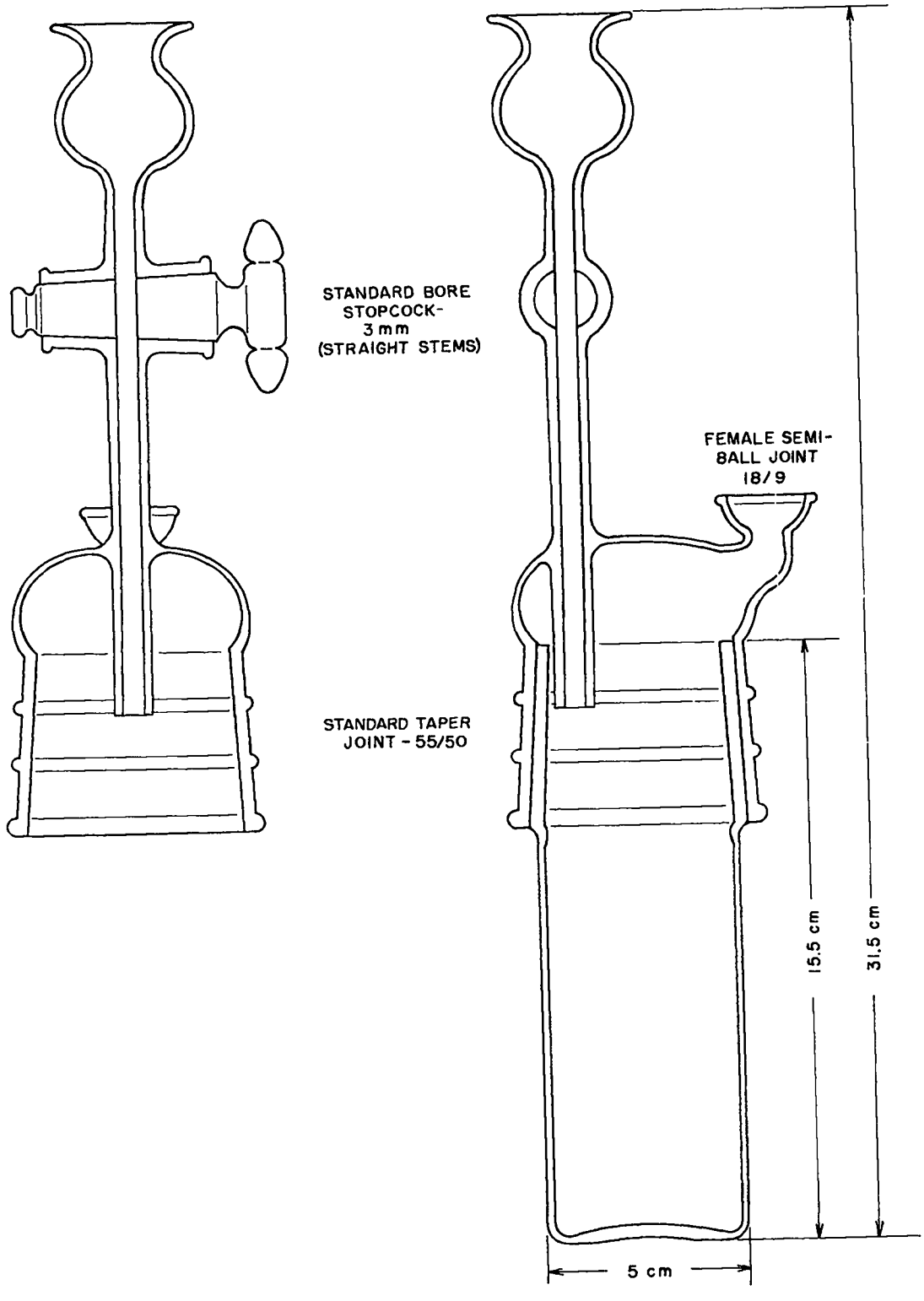

FIGURE III - COMPLETE GENERATOR FLASK

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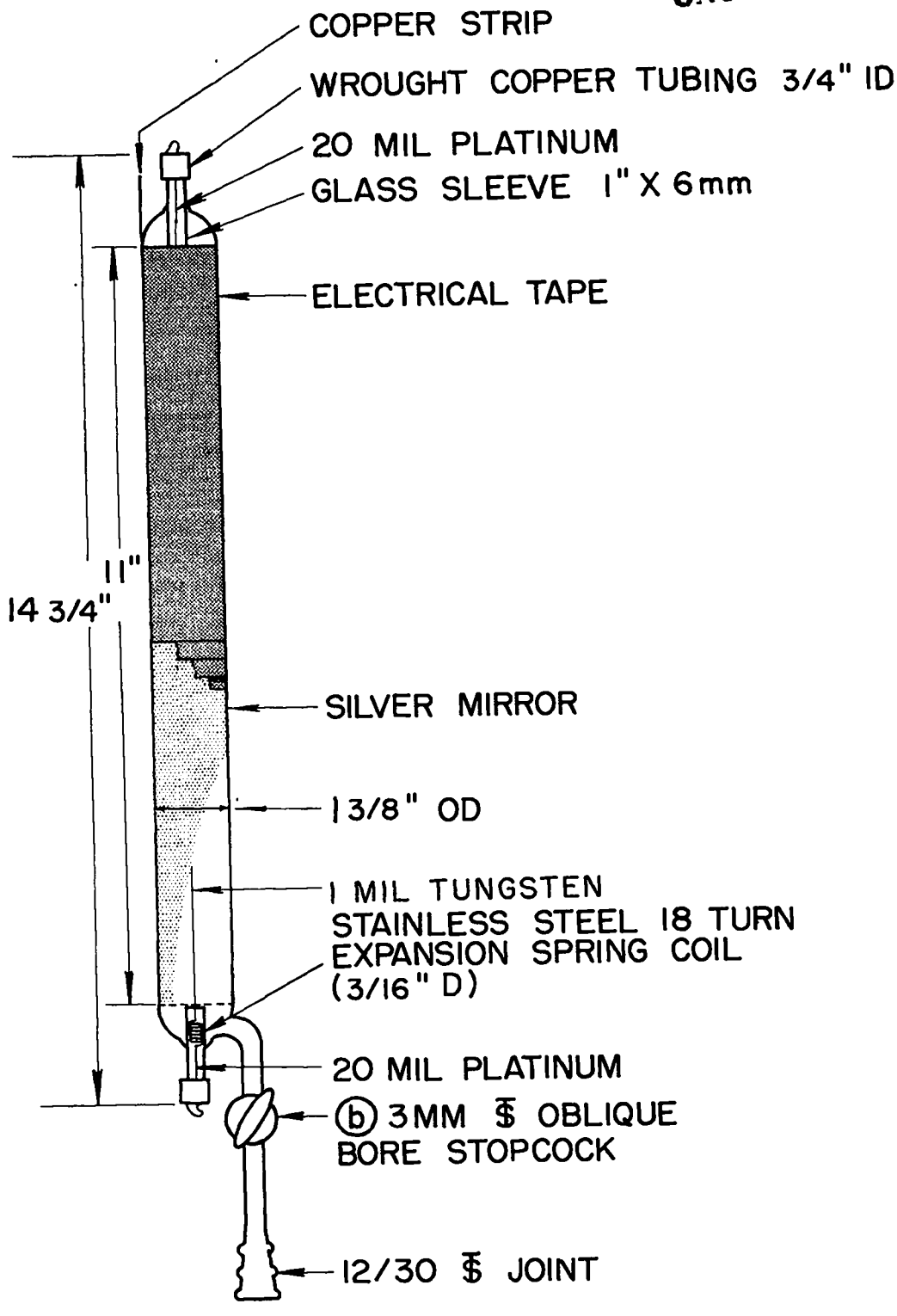

FIGURE IV - TRITIUM COUNTING TUBE

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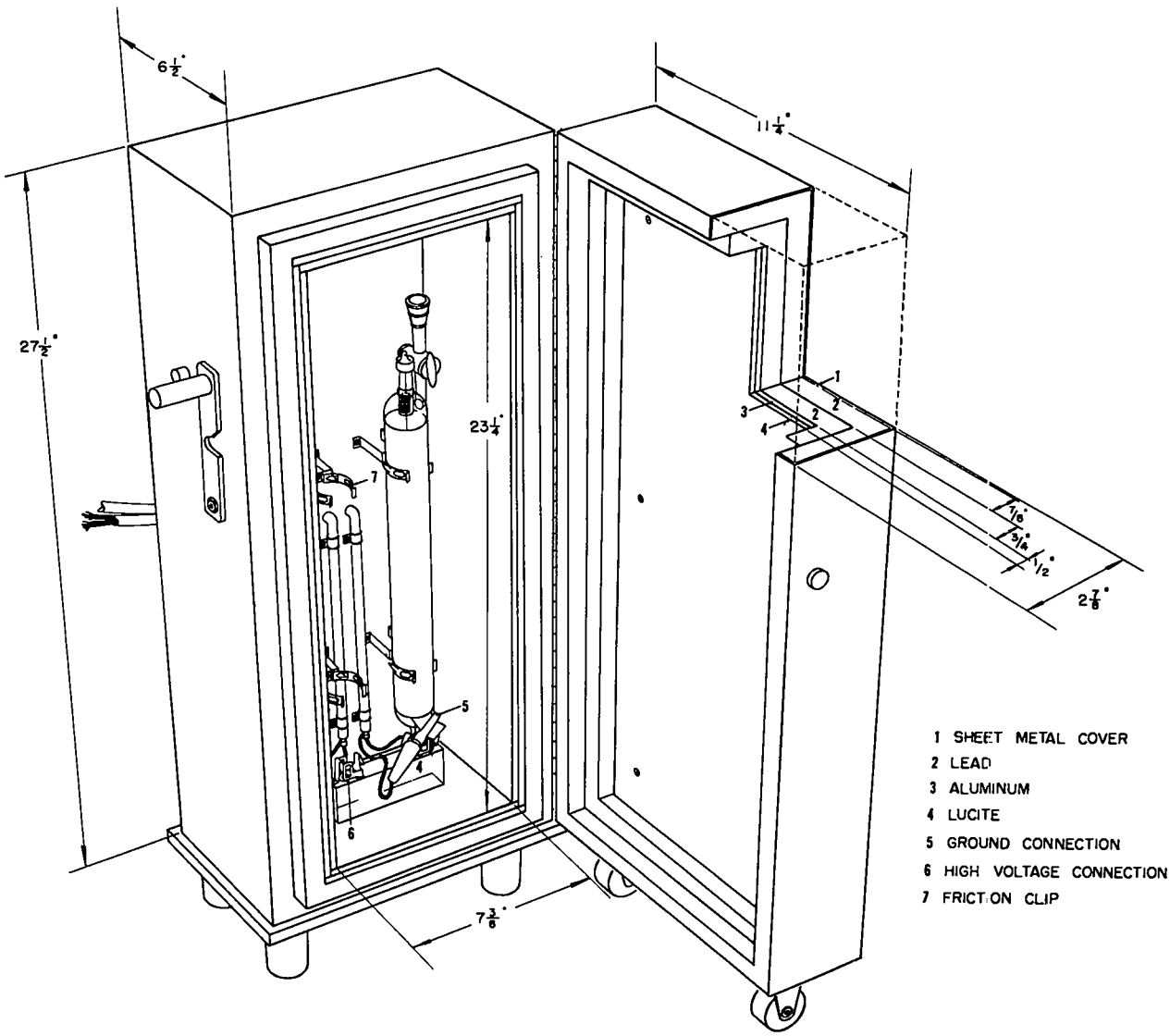

FIGURE V - LEAD COUNTING SHIELD