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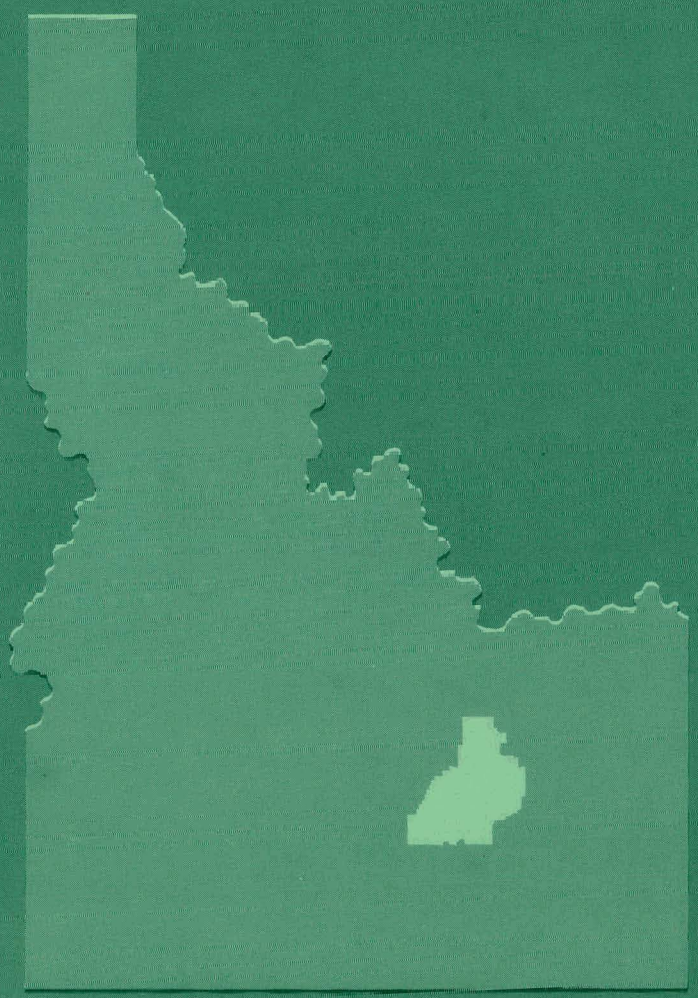
REMOTE DISSOLUTION AND ANALYTICAL PROGRAM FOR IRRADIATED THORIUM

G. A. Huff et al

July 14, 1961



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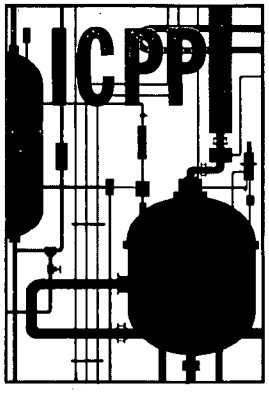

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R. D. Fletcher, and M. E. Jacobson

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Atomic Energy Division
Contract AT(10-1)-205
Idaho Operations Office
U. S. ATOMIC ENERGY COMMISSION

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A B S T R A C T

A remote dissolution and analytical program for irradiated thorium is given. The aluminum jacket on the slug was dissolved with 6M nitric acid and 0.005M mercuric nitrate. After a water wash the thorium dissolution was accomplished with concentrated nitric acid made 0.04M in hydrofluoric acid. Weighing, dissolving, and sampling was done remotely in the multicurie cell at the Idaho Chemical Processing Plant. Handling techniques for weighing and dissolving the slugs are described. Transferring and sampling apparatus as well as sampling techniques for the dissolved material are discussed. Analytical data obtained are tabulated. Abstracts of analytical methods for uranium concentration and isotope ratio, aluminum, thorium, cesium, and cerium are given.

Work done under Contract AT(10-1)-205 to the U. S. Atomic Energy Commission.

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INTRODUCTION

The Analytical Section was requested by the Reactor Physics Research Group to analyze six irradiated thorium slugs for uranium concentration and isotope ratio, aluminum, thorium, cesium-137, and Zr-95. It was determined from cooling time of the slugs that Zr-95 would not be present in sufficient quantity to detect; therefore, cerium-144 was substituted in its place. It is the purpose of this report to describe the remote dissolution, sample preparation, and the analytical methods used to determine the various constituents requested.

The multicurie cell described by Fletcher and Slansky[2] was used to dissolve and prepare the slugs for analysis. The cell provides five feet of shielding composed of barytes concrete and viewing windows of 3.2 density laminated glass. Manipulations within the cell are made with a pair of Argonne Model 8 master slave manipulators.

REMOTE HANDLING PROCEDURE

Description of Elements and Dissolution Procedure

The slugs were 6.5 inches x 1.43 inches O.D. thorium cylinders clad with 0.034 inches of aluminum, each weighing about 1730 grams. These slugs had been irradiated from 1 to 24 cycles in the Materials Testing Reactor and were estimated to contain from 1 to 7 grams of uranium-233. The slugs together measured 100 mreps/hr. through 2 feet of water and 1 foot of air. As reported by Paige[7] et al. the aluminum jackets of the slugs were dissolved in a solution of 6M nitric acid and 0.005M mercuric nitrate. The slugs were rinsed free of aluminum and the thorium was dissolved with concentrated nitric acid made 0.04M in hydrofluoric acid.

Description of Apparatus -Dissolution, Dilution, and Sampling

The apparatus used for dissolution, dilution, mixing, and sampling is shown in Figures 1, 2, and 3. Figure 1 shows the face of the multicurie cell with supporting apparatus. Reagents were gravity fed from reservoirs on a platform behind the cell through reagent lines (A). Reagent addition was controlled by valves (B). Samples were drawn with a syringe. Tubing (C) for the sampling system consist of air lines for the bottle lift and a line to the syringe. Variacs were used to control temperature of hot plates in the cell. Cooling water for the condensers was controlled from a valve (D), and was returned through the cell wall at port (E). The water was then discharged to a drain (F). A mechanical vacuum pump was used to obtain vacuum for the transfer system within the cell.

An aluminum basket was devised to contain each slug for remotely lowering into the dissolvers. Each basket was constructed from 2.1 grams of 99% pure aluminum wire. The slugs and wire basket are shown in Figure 2. Also shown in Figure 2 is the Torsion balance which was used to weigh each slug. After the weighings were complete, the balance and weights were covered to protect them from further contamination.

Dissolution, dilution, mixing, and sampling was accomplished with the apparatus shown in Figure 3. The three dissolvers (G) were 12.5 liter Pyrex flasks fitted with Teflon stoppers and water condensers. The condensers were attached to the plant off-gas system. The off-gas could be varied from 2-20 inches of water. In addition to the dissolvers, six more 12.5 liter flasks (H) were used as dilution and/or holding vessels. Stainless steel pans were used as secondary containers for all 12.5 liter flasks. Small hot plates were used to supply heat for the dissolvers. A transfer system (I) was devised using controlled vacuum to transfer solutions from vessel to vessel. This system was fed through a trap (J) in order to prevent radioactive solution being transferred outside the cell.

The first three aluminum jacket dissolutions were made using 18 inches of water off-gas. This off-gas reduced the volume of dissolver solution too rapidly, so ensuing dissolutions were made with the off-gas reduced to 3 inches. The aluminum jackets were dissolved using 965 watts heat and incrementally adding 6M HNO_3 - 0.005M Hg (100, 150, 250, 500, 1000, 1000 ml.) until a total of 3 liters had been added. Each additional increment was added after the initial vigorous reaction, which gave off copious brown fumes, had subsided. About 15 minutes were required for this reaction to subside. The jacket dissolution was complete in 3-4 hours leaving a dark colored cylinder. The aluminum solutions were transferred to holding flasks with several water rinses. The removal of the aluminum from the dissolver was necessary because HF acid was used in the thorium dissolution step.

The thorium was dissolved in 5 liters of concentrated HNO_3 - 0.04M HF. This acid was added in approximately 1 liter increments over a period of 5 hours at 965 watts heat. The heat was then turned up to 1250 watts and left over night. An additional 1 liter of acid was then added to complete the dissolution. The thorium dissolution time was about 30 hours. These dissolutions were then transferred to the vessels containing the aluminum solutions. In the thorium solution transfer, a slurry in the bottom of the dissolver vessel was encountered which proved difficult to transfer. Numerous 100-200 ml. water rinses achieved this transfer. The solution in the dilution vessel was then diluted to volume, mixed with mechanical stirrer (K), and allowed to stand over night to cool. The solution was again diluted to volume, stirred for 15 minutes with a mechanical stirrer, and the temperature noted. All significant solids dissolved on dilution and stirring.

The second set of three slugs were handled in the same manner as the first with one modification. The aluminum solution was transferred to a holding vessel and held until the thorium dissolution was complete. It was then transferred back to the dissolver. This eliminated transferring the thorium solution and its slurry.

All six final dilutions were sampled from top and bottom. Samples were taken with a suction type sampler (L). The sampler's tip was fitted with two hypodermic needles of different lengths that punch through the neoprene cap on the sample bottle. The long tip was connected to a tube which was lowered into the solution to be sampled. The other tip was connected with tubing through a trap to a 50 ml. hand syringe on the outside of the cell. The sampler was cleaned after each sample with water and dried with acetone. Homogeneity in the dilution flasks was checked by uranium analysis on top and bottom samples from the first three dissolutions. Homogeneity was checked on the second three dissolutions by analyzing top and bottom samples from each container for acidity and specific gravity. The data shown in Table I indicates homogeneity of each dilution and good sampling technique from each container.

TABLE I. HOMOGENEITY TEST DATA

	Container I	Container II	Container III
	Uranium, mg./ml.	Uranium, mg./ml.	Uranium, mg./ml.
Top	0.025	0.12	0.20
Bottom	0.025	0.11	0.20

	Container IV		Container V		Container VI	
	Acid, N	Sp.Gr.*	Acid, N	Sp.Gr.*	Acid, N	Sp.Gr.*
Top	5.04	1.406	6.68	1.449	5.38	1.415
Bottom	5.08	1.406	6.72	1.449	5.40	1.415

*Sp.Gr. measured at 25°C.

ANALYTICAL METHODS

Uranium Concentration and Isotope Ratio

Uranium concentration and isotopic ratios were determined by the isotopic dilution mass spectrometric method. This technique was proposed by Inghram[4] and further developed for uranium by Duffy and Tingey[1] and Goris and Tingey.[3] This method requires a uranium spike and a preliminary liquid-liquid solvent extraction separation in order to obtain a sample which can be handled in the mass laboratory. In order to select the type of spike to be used, the material was checked for isotopic ratio. It was determined that uranium-238 was not present in sufficient quantities to interfere, consequently, normal uranium was chosen for the spike material. Paige[8] et al. demonstrated that moderate amounts of thorium could be tolerated; therefore, a single hexone extraction followed by aluminum nitrate scrubs was used. The uranium was precipitated from the hexone as the peroxide and washed with water. After preparation the samples were transferred to the mass laboratory.

Thorium and Aluminum

The method used to determine thorium and aluminum was developed by Yamamura.[9] The method requires measuring thorium and total thorium-aluminum. Perchloric acid fuming is required to volatilize traces of fluoride introduced during slug dissolution. Thorium is separated from aluminum by hexone extraction using saturated lithium nitrate as a salting agent. Thorium is water stripped from the hexone. Thorium or thorium-aluminum total is determined by adding a measured excess of EDTA to the sample and titrating this excess with thorium to an alizarine red S end point. Aluminum is obtained by difference.

Cesium-137 and Cerium-144

Nuclides of cesium and cerium were chemically separated. These separations were scanned on the multi-channel analyzer and disintegration ratios were calculated. Yield determinations were made in each separation. The method of cesium-137 separation was adapted to these samples by Olson[6]. It involves a precipitation of cesium perchlorate. The precipitate is dissolved and iron scavenged for additional decontamination. The cesium is again precipitated as the perchlorate for counting.

The method used to determine cerium-144 was developed by Marsh[5]. It involves an oxidation of cerium(III) to (IV) with divalent silver. The cerium is extracted into nitroethane as the tetrapropylammonium nitrate complex. Cerium is then stripped from the organic with peroxide. Additional decontamination is achieved by precipitating cerium as the oxalate.

The data obtained from this work are shown in Tables II and III.

TABLE II. MATERIAL BALANCE SUMMARY

Slug	Aluminum, gms.	Thorium, gms.	Uranium, gms.	Uranium-233, %	Uranium-234, %	Uranium-235, %	Initial Weight of Slug, gms.	Material Balance, gms.
1 Top	72.86	1663.5	0.31	95.0	----	5	1736.1	1736.7
Btm	71.50	1660.5	0.31	95.0	----	5		1732.3
2 Top	70.60	1632.1	1.50	99.42	0.56	0.01	1731.3	1704.2
Btm	73.30	1632.1	1.38	99.46	0.54	----		1706.8
3 Top	73.77	1658.3	2.51	99.33	0.58	0.04	1737.3	1734.6
Btm	69.37	1655.4	2.51	99.28	0.68	0.03		1727.3
4 Top	72.83	1648.4	3.65	99.08	0.91	0.01	1729.0	1724.9
Btm	72.50	1639.7	3.77	99.08	0.91	0.01		1716.0
5 Top	72.74	1654.9	4.27	98.61	1.34	0.05	1736.4	1731.9
Btm	72.74	1649.1	4.27	98.56	1.38	0.06		1726.1
6 Top	72.79	1650.3	5.65	98.07	1.84	0.09	1735.7	1728.7
Btm	72.45	1647.4	5.65	98.07	1.84	0.09		1725.5

TABLE III. RADIOCHEMICAL DATA

	Cs 137, d/m/ml	Date	Ce 144, d/m/ml	Date
1 T	3.11×10^5	5-16-61	2.69×10^6	5-25-61
B	3.22×10^5	5-16-61	2.69×10^6	5-25-61
2 T	2.41×10^7	5-16-61	9.64×10^7	5-25-61
B	2.29×10^7	5-16-61	9.64×10^7	5-25-61
3 T	7.34×10^7	5-16-61	4.70×10^6	5-25-61
B	7.25×10^7	5-16-61	4.87×10^6	5-25-61
4 T	1.03×10^8	5-24-61	5.01×10^6	5-25-61
B	1.02×10^8	5-24-61	5.09×10^6	5-25-61
5 T	2.64×10^8	5-24-61	8.61×10^8	5-25-61
B	2.58×10^8	5-24-61	8.69×10^8	5-25-61
6 T	4.38×10^8	5-24-61	1.47×10^9	5-25-61
B	4.42×10^8	5-24-61	1.48×10^9	5-25-61

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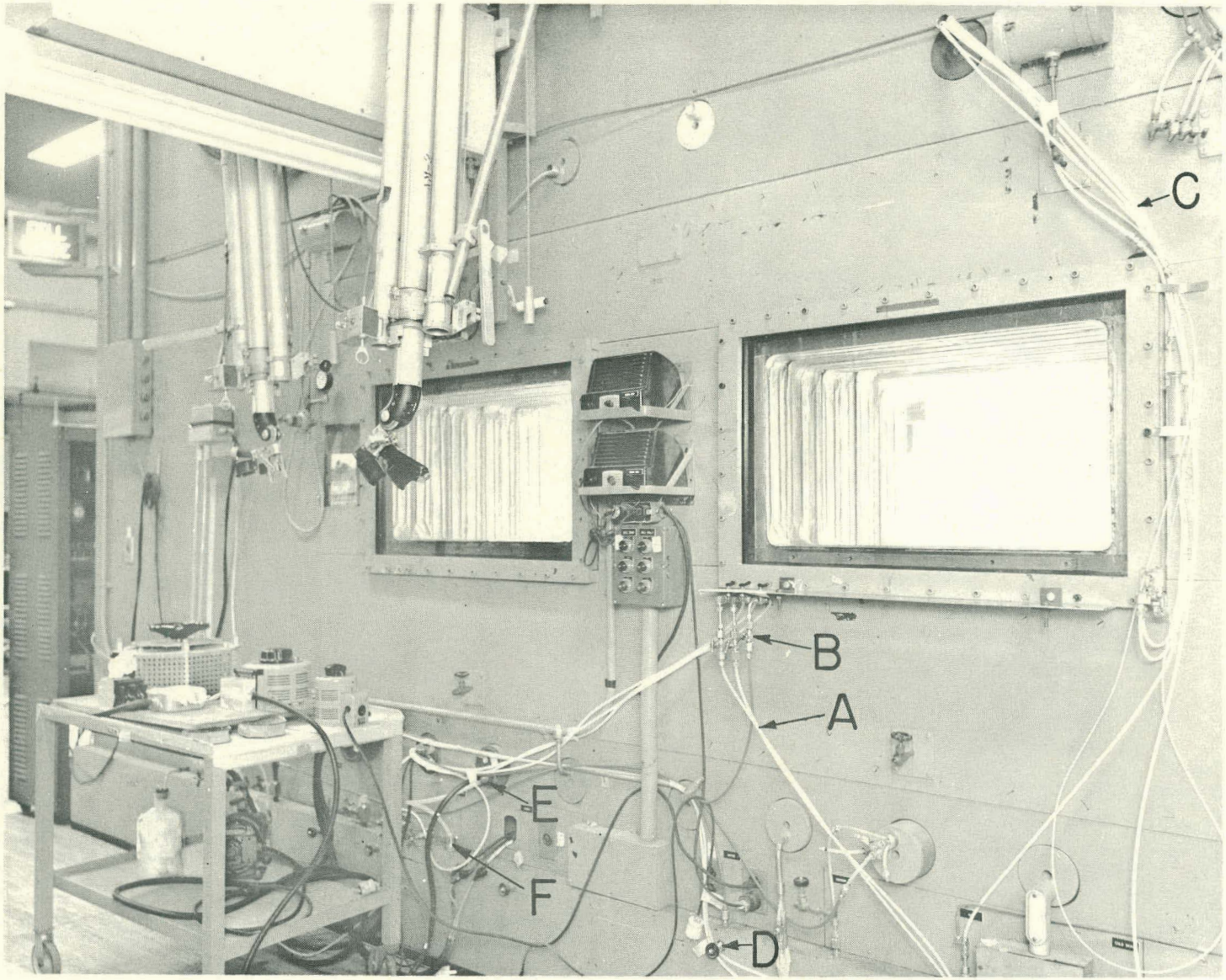

Figure 1. Face of Multicurie Cell and Supporting Apparatus

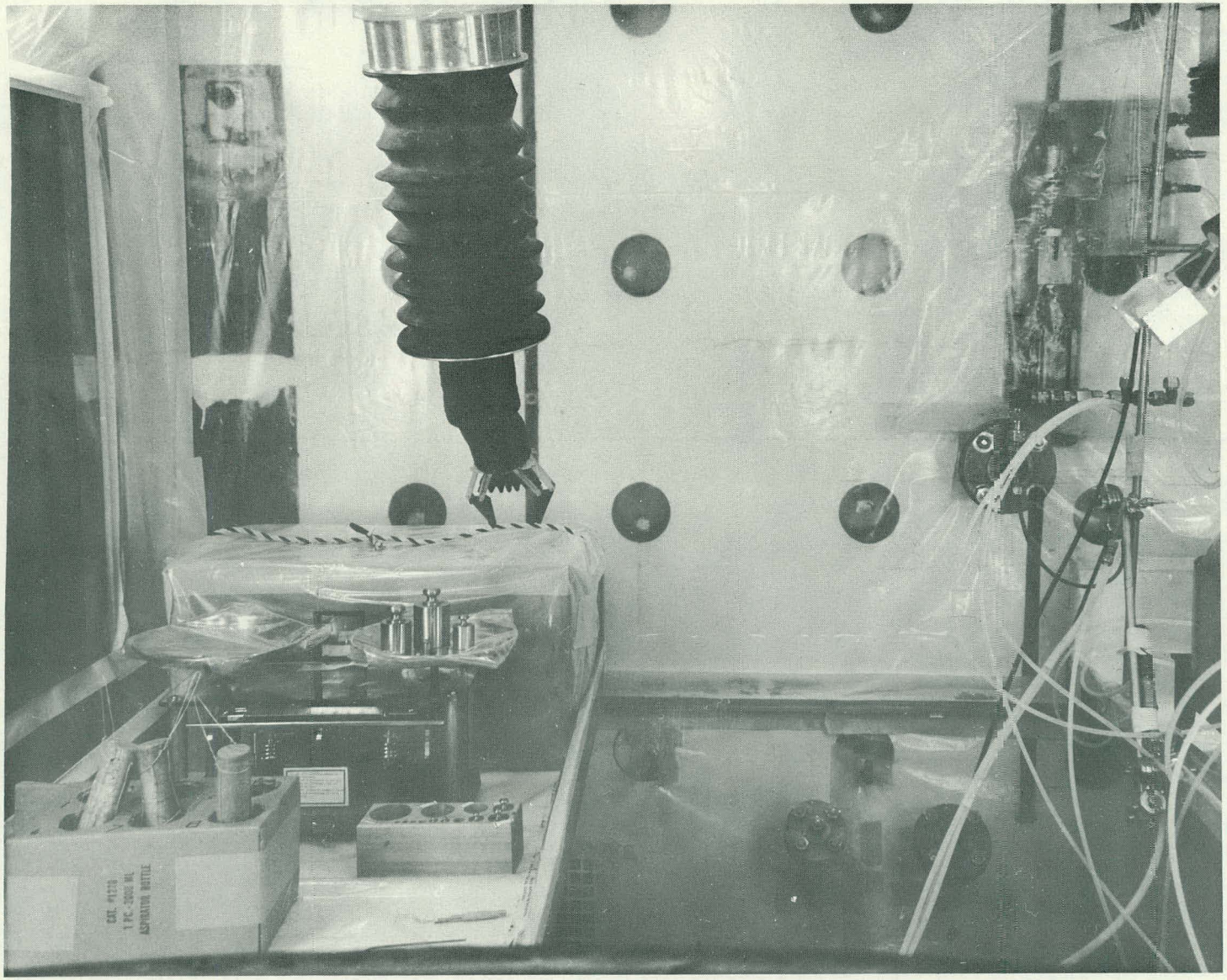

Figure 2. Thorium Slugs and Balance

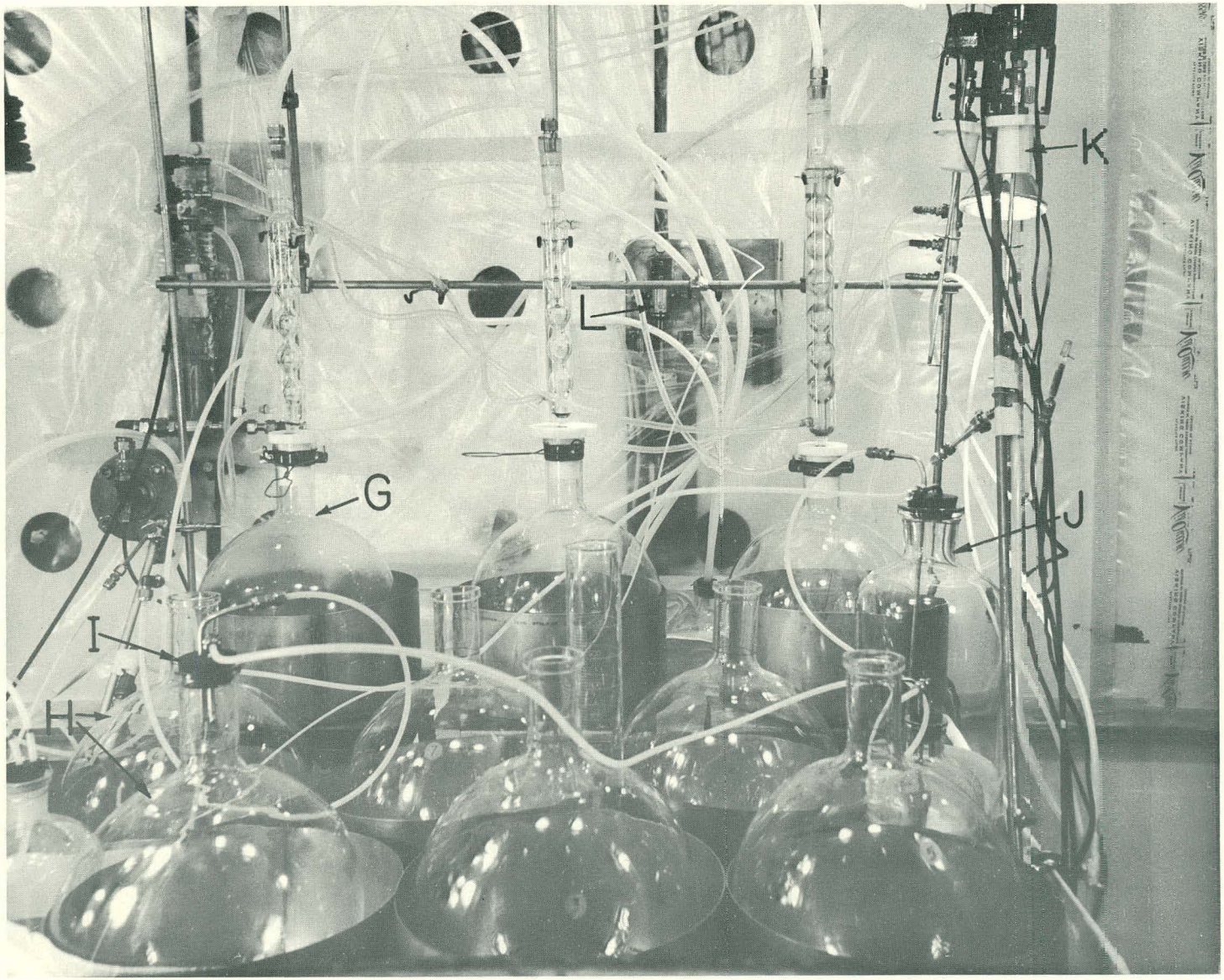

Figure 3. Dissolution, Dilution, and Sampling Apparatus

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