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CHEMISTRY DIVISION

THE SPECTROCHEMICAL ANALYSIS OF RADIOACTIVE SOLUTIONS

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Abstract

A description is given of a chamber designed to permit electrodes for spectrochemical analysis to be loaded outside the spectrographic laboratory, excited with spark or other intermittent excitation, and disposed of with a minimum risk to personnel. If strippable films are used to protect the most heavily exposed surfaces, residual radiation levels of ~ 2 mr/hr at contact on the chamber parts can easily be attained for samples customarily encountered.

1. Introduction

In analyzing and type of material spectrochemically, one naturally attempts to attain the maximum accuracy, precision, sensitivity and speed. In analyzing radioactive materials, however, the main consideration is safety, and the following factors must be considered first:

(a) Protection of operators from α, β and γ radiation (shielding).

(b) Protection of operators from contact with radioactive materials.

(1) Minimization of number of handling and transfer operations prior to excitation of sample.

(2) Prevention of air contamination, especially during excitation of sample.

(3) Safe and rapid disposal of used electrodes.

(4) Safe, rapid, and complete decontamination of auxiliary apparatus.

The general interests of safety and efficiency are usually served best by standardizing techniques as much as possible. When the samples are radioactive, safety and efficiency also affect the choice of excitation technique and sample form.

1. Choice of Excitation Technique

Since the discharges used in spectrochemical analysis are disruptive, they must be conducted within an enclosed chamber in order to provide shielding and prevent contamination of the air. It must be possible to decontaminate such a chamber quickly and safely, both in order to safeguard personnel and to have the chamber available for re-use as soon as possible.

The effectiveness and dispatch with which a surface can be decontaminated tends to vary inversely with its area. The minimum permissible internal area of a chamber is dictated largely by the size and power rating of the discharge taking place within it. If the discharge continuously liberates large amounts of heat and vapor, as is the case with the D. C. arc, the chamber must have a volume large enough to prevent overheating. This is a matter both of convenience of handling and of possible spectral line interferences from chamber materials which might be volatilized into the discharge if the chamber walls were too close to the arc. The use of spark techniques, however, lowers the temperature within the chamber, and makes it possible to adopt two measures which greatly simplify the decontamination problem:

1. The size of the chamber cavity may be greatly reduced, thus decreasing the contaminated area.

2. The area exposed to contamination may be coated before exposure with a strippable film. After exposure, this film may be removed, and the contamination eliminated. This technique can be used only with spark excitation, since the film materials available cannot withstand the temperatures prevailing in an arc chamber.

Almost all of the radioactive materials analyzed in the authors' laboratory occur in solution form. Since this laboratory's non-radioactive

solutions are usually analyzed by either the copper spark method (1), or the porous cup method (2), it appeared that the most serviceable protection chamber would be one built expressly for spark excitation of solutions by either of these methods.

A chamber has been developed which has the following characteristics:

1. It permits the sample to be carried to the laboratory, excited, and disposed of without exposure of operators to dangerous levels of radiation or air-borne contamination.

2. It can be decontaminated in 2 - 3 minutes, with negligible risk to the operator.

The chamber consists essentially of two cassette assemblies and a chamber block. The cassette assemblies contain the electrodes, and can be closed in such a way as to protect the operator against radiation or contaminated dust coming from the sample.

2. Assembly and Operation of Chamber

When the copper spark method is to be used, the order of operations is as follows (See Figure 1): A 1/4" diam. copper rod, machined as described in (1), is inserted part way into a closely fitting stainless steel tube. A long U-shaped cut has been made in the wall of the tube, and the metal tongue thus formed bent into the form of a wave (~) of very low amplitude. The resulting spring action prevents the electrode from slipping out of the tube. A copper electrode in its tube is shown in Figure 1, part D.

The loaded tube is then inserted into a stainless steel-lined hole in the fluorethene rotor (Figure 1, part E) and pushed through until the end of the copper electrode emerges into the hemi-cylindrical cavity hollowed out in the end-surface of the rotor. This entire assembly is then inserted into the stainless steel cassette (Figure 1, part F), and secured by inserting the

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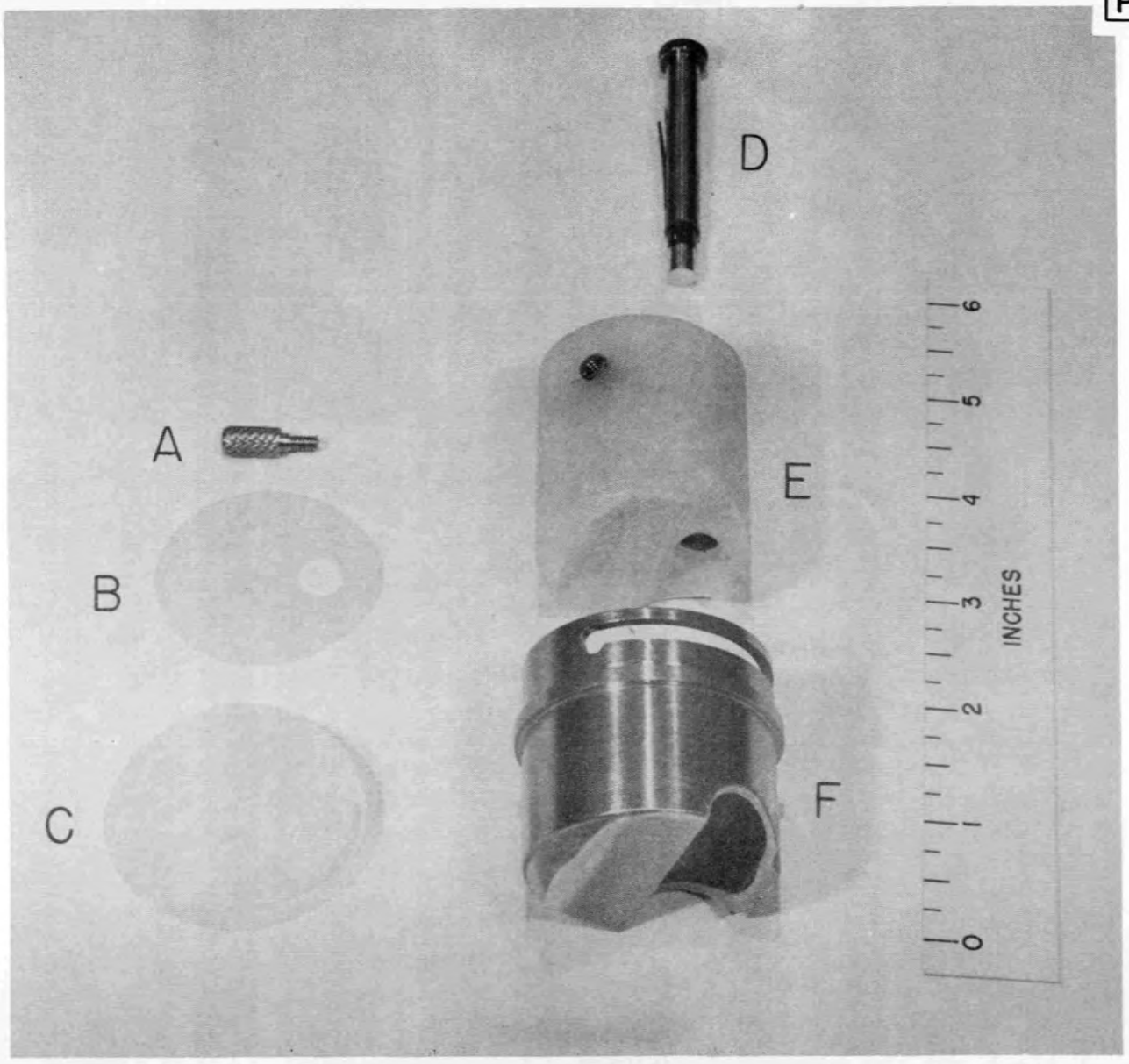

FIG. 1

threaded turning pin (Figure 1, part A) through the slot in the cassette and screwing it into the tapped hole shown on the outside curve surface of the rotor. The completed assembly is shown in Figure 2.

The cassette is then closed by turning the rotor until the pin reaches the end of its slot. Figure 2A shows the cassette assembly when closed.

Two such assemblies are prepared and sent to the laboratory submitting the sample. They are then opened and placed on a suitable support, opened as shown in Figure 2. The radioactive solution is deposited on the end of the electrodes by a remote-control pipette, and dried to a residue by means of an infra-red lamp. If Cocoon protective coatings are used (See Section 4A), care should be taken to avoid overheating. A sheet of metal or cardboard, containing a 3/8" hole, may be placed over the cassette assembly in such a way that the end of the electrode is the only portion of the assembly exposed to the rays of the lamp.

When the liquid has evaporated, the cassettes are closed again, carried to the spectrographic laboratory, and inserted into either end of the vertical hole passing through the stainless steel chamber block. They are correctly oriented and held in place by their rims and a suitable pair of indexing and retaining screws. The block is provided with windows consisting of glass or fused quartz discs held in suitable recesses by spring clips. It is supported on the optical bench as shown in Figure 4.

Once the cassettes are in place, the chamber cavity is created by rotating the rotors within the cassettes by means of the turning pins. Figure 3 shows the appearance of the chamber after this has been done. It will be noticed that the two cassette assemblies come together at the center

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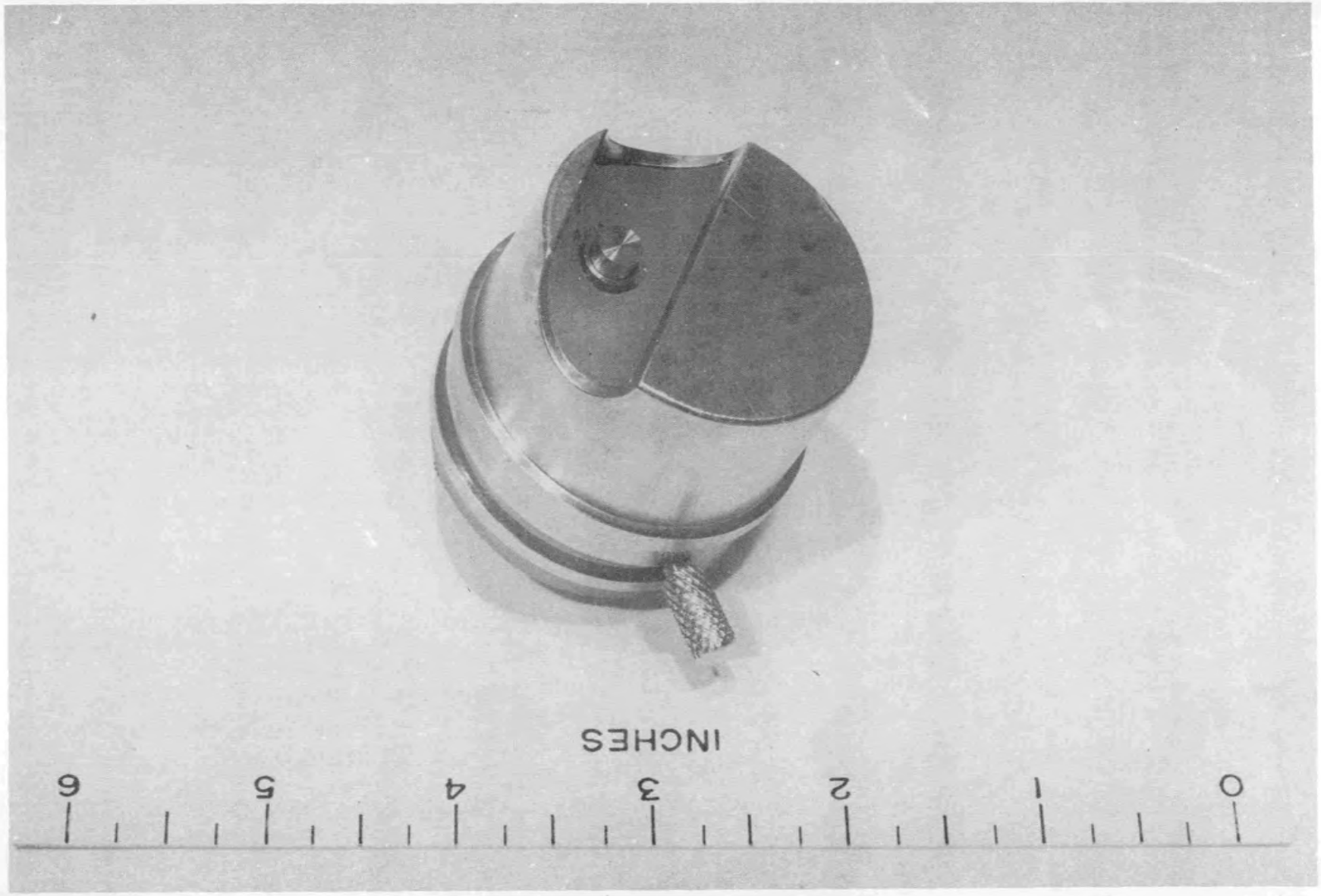

FIG. 2

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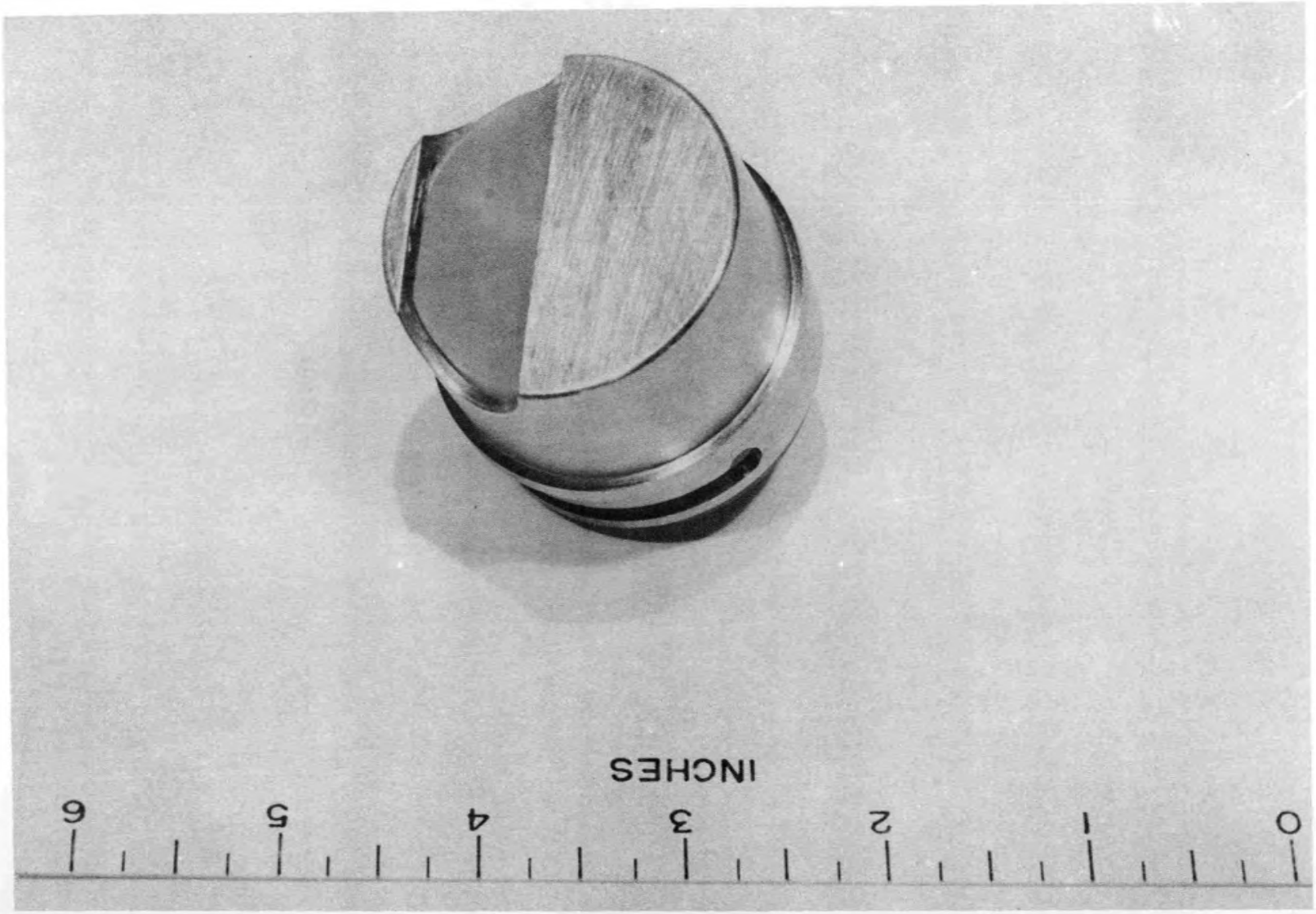

FIG. 2a

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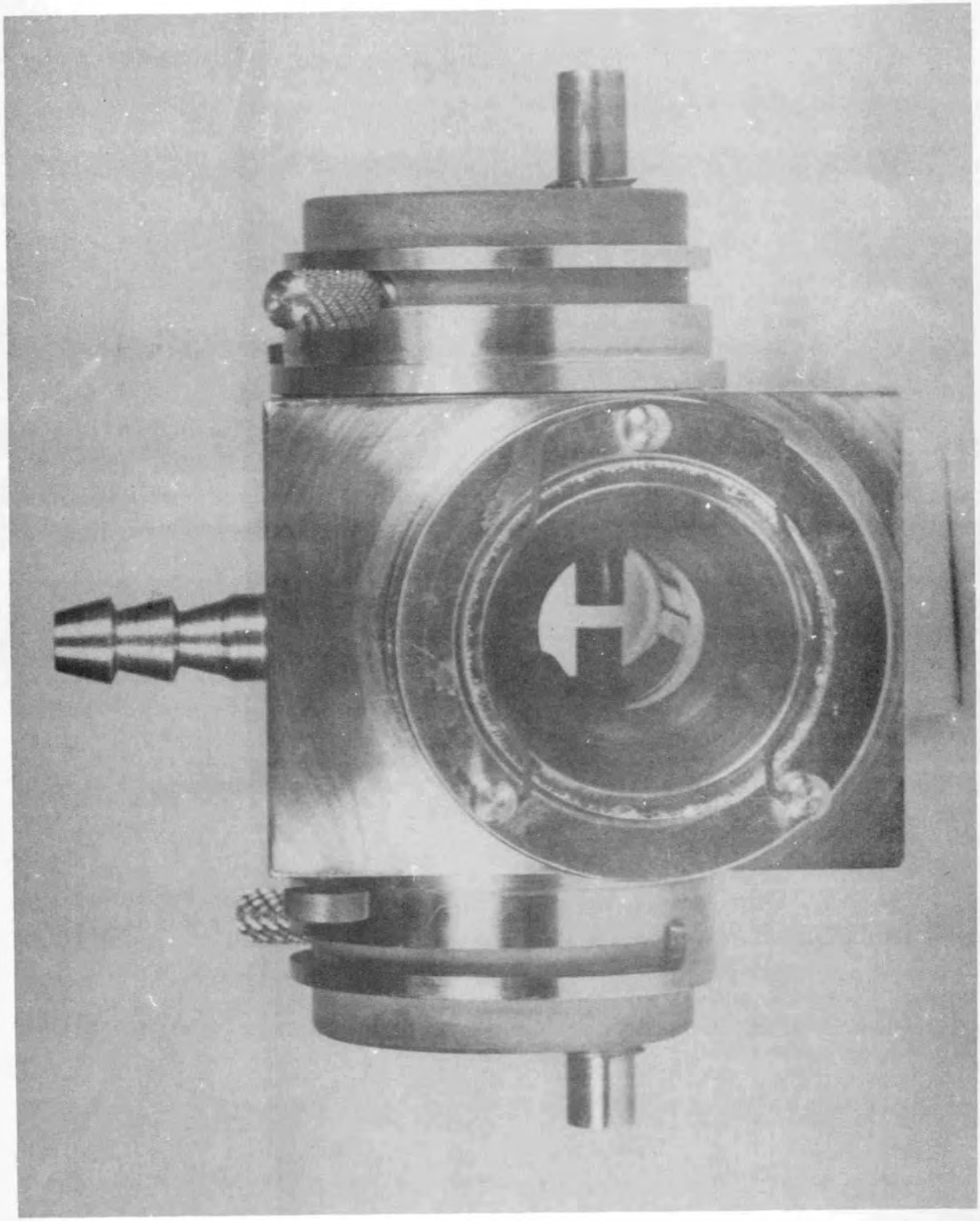

FIG. 3

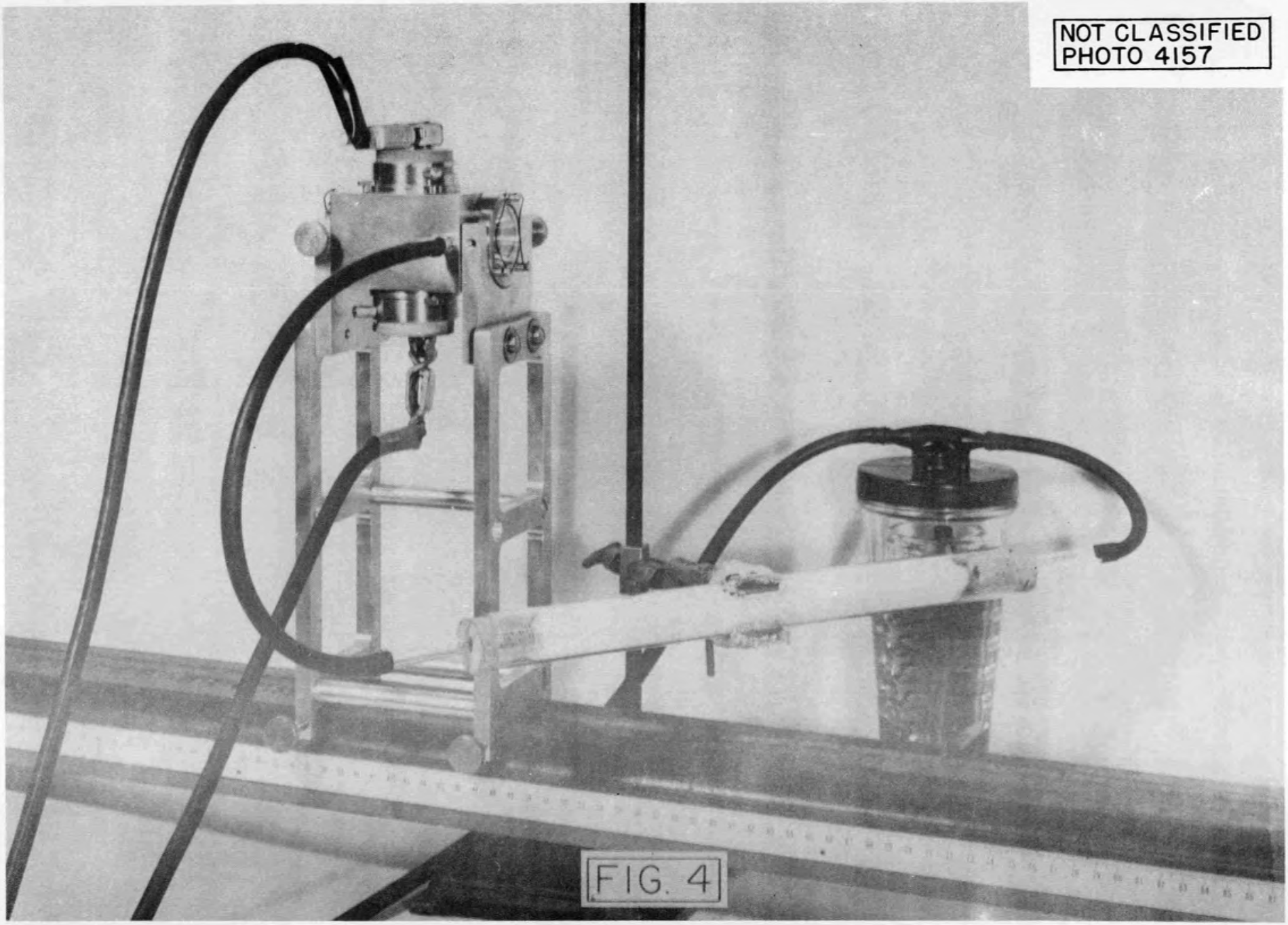

FIG. 4

of the block, completely filling it except for the cylindrical cavity surrounding the electrode gap. The surface of this cavity, most of which is on the rotors, is the only surface directly exposed to contamination.

The steel sleeves lining the hole in the rotor through which the electrodes tube is thrust project 5 - 10 mm. from the outside end-surface of the rotors; excitation is provided by clamping the electrical leads to this projecting portion (See Figure 4). The insulation furnished by the body of the rotor has proven sufficient to permit the use of an ARL spark source (peak voltage ~35 kv). The spark gap is given its final adjustment with the aid of a projected shadow-image, and the exposure made. The electrical leads are then disconnected, and the rotors turned to the closed position, thus covering the greatest part of the contaminated area. The entire chamber, still containing the cassettes, is then removed from the supporting yoke and carried to the laboratory for disposal of electrodes and decontamination.

To dispose of the electrodes, each cassette assembly is removed, still closed, from the chamber block. It is then inverted over a disposable container, such as a wide-mouthed bottle, opened, and the contaminated electrode pushed out of its tube from behind, into the bottle. The cassette assembly is then closed, and the bottle capped and discarded. After both electrodes have been disposed of, the cassette assemblies and the chamber block are ready for decontamination (See Section 4).

If the porous graphite cup technique is to be used, the porous cup electrode (PCE) is first dipped open side down into a dilute solution of Zapon until most of the side surface, but none of the end, or sparking surface, has been coated ((2), Figure 1B). This prevents corrosion of the

electrode tube by any acid solutions which may be inserted into the PCE. (Alternatively, parts coming in contact with corrosive solutions may be made of tantalum or platinum.) The PCE is then inserted into an electrode tube open end first, until the sparking surface projects about 1/4" from the end of the tube. This is used as the upper electrode. A 1/4" diam. graphite rod is used as the lower electrode. The chamber is assembled as above, and the sample solution inserted into the porous cup from outside the chamber. ((2), Figure 1A.) Subsequent disposal and decontamination are accomplished as with the copper spark techniques. Chambers now in use provide at least 2,300 mg/cm^2 of shielding in all directions, so that once the cassette assemblies have been closed, after evaporation of the residue, the operator is completely protected from α and β radiation. Protection against γ radiation, however, is comparatively slight, even after the cassettes have been inserted into the chamber block (see Table I.).

Table I*

Transmission of Radiation through Shielding

Type of Radiation	% Transmitted	
	Through cassette walls (3 mm. of stainless steel)	Through chamber block walls (10 mm. of stainless steel)
α	None	None
β (up to 4 mev.)	None	None
γ (0.5 mev.)	83	54
γ (1.0 mev.)	87	64
γ (2.0 mev.)	90	72

*Data for this table kindly supplied by Dr. F. Western.

3. Avoidance of Air Contamination

The breathing in of radioactive solid particles may be particularly dangerous because of the extremely high level of radiation in the immediate neighborhood of such a particle (4). It is therefore urgent that the vapors

created by the excitation of radioactive samples be kept under control.

In order to prevent the escape of radioactive vapors into the room, a partial vacuum is maintained in the chamber. No attempt is made to have the chamber vacuum-tight; clearances of 0.2 - 0.3 mm. are purposely left between chamber-block and cassette, cassette and rotor, etc. The air which thus leaks into the chamber is drawn off through a small outlet drilled through the body of the block near the rear (glass) window. (See Figure 3.). The current of the air seeping into the chamber makes the escape of radioactive vapors into the room virtually impossible. Air samples taken during the sparking of residues which read ~ 5 r/hr at a distance of 3" when unshielded have shown no activity above background*. Before entering the vacuum line, the air emerging from the outlet passes through ten inches of cotton wadding and a gas washer whose gas inlet tube is fitted with a coarse fritted glass disc. The scrubbing liquid is chosen to correspond to the chemical nature of the radioactive species. Tests of the gas stream before and after scrubbing show that this step removes 90 - 99.8% of the activity remaining in the air stream after passage through the cotton. Tests have shown no radioactivity to be present in the condensate or oil from the vacuum pump*.

4. Decontamination of Chamber

(a) Technique

It has always proven possible to reduce surface activity of the chamber parts to a negligible level (~ 2 mr/hr for ($\beta + \gamma$) activity or ~ 30 decompositions/min. for α activity at a distance of 1") by some combination of chemical treatment and abrasion. The chemical methods of decontamination

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*Measurements made by P. E. Brown and co-workers.

have involved disassembly of the chamber below the surface of a chemical bath whose ingredients were chosen, if possible, to form a complex with the radioactive chemical species. The baths were renewed until activity was down to the level mentioned.

Chemical decontamination methods have several disadvantages, however:

(1) Their effect on β- and γ-active substances, especially on porous surfaces, tends to follow a law of diminishing returns. Surfaces contaminated with radioactive isotopes of elements amenable to chemical treatment, such as the alkalis, alkaline earths, common metals, etc., may require several hours for decontamination; the last traces of the more stubborn elements, such as W, Cb, etc., may yield to nothing short of sandpaper.

(2) Their effect on some α-active substances, such as Pu and Am, is both slow and incomplete. Prolonged abrasion of the surface is always necessary, thus increasing the danger to the operator.

(3) The use of drastic chemical agents is limited by the nature of the material of the chamber. Although the use of fluorothene (polymerized monochlorotrifluoroethylene) in constructing the rotors makes them proof against any combination of chemical reagents (3), the stainless steel parts are particularly susceptible to attack by hydrochloric acid and alkalis.

In view of the difficulties connected with chemical decontamination methods, it appeared that the problem might be solved more effectively by avoiding contamination of the surface in the first place.

Attempts were first made to pre-coat parts to be exposed to contamination with a layer of Carbowax 1540 or Carbowax 4000 (water-soluble polyethylene glycols). After exposure, this coating was removed by immersing the parts in a bath of warm complexing agent and flushing this away with warm water. This procedure considerably decreased the amount of activity deposited on the chamber parts themselves, but some chemical and abrasive treatment was

still necessary for surfaces contaminated with Pu, Am, or large amounts of β- and γ- active substances.

The most successful coating agent found so far has been Cocoon*, a liquid which, when spread on a surface, dries rapidly to give an elastic, strippable film. The coating may be applied either by dipping or by cementing suitably shaped pieces of the dried film to the surface to be protected.

The surfaces coated are usually the internal surface of the rotor and both flat surfaces of the cassette, including the edges which form a part of the cylindrical cavity. When Pu or Am contamination is expected, the conical surfaces between the cylindrical cavity and the windows (seen forshortened in Figure 3) are also coated with the liquid.

The specially shaped pieces used in coating the rotor and the cassette are prepared as follows: Cocoon is sprayed onto a smooth surface to form a layer approximately 0.015 inches (0.3 mm) thick, and allowed to dry for approximately thirty minutes. It is then stripped from the surface. The pieces are next stamped out of this sheet with the aid of suitably shaped cutting dies. Stamped pieces for the rotor and cassette, respectively, are shown in Figure 1, part B and part C.

When needed, the coatings are cemented to the rotors and cassettes with a mixture consisting of one part Cocoon and four parts acetone. This procedure readies the chamber for use much more quickly than would be possible if the coating were applied by dipping, since the exposed coating surfaces do not have to be dried, and no trimming is required. Figure 1, part E and part F show coatings on the rotor and cassette, partly peeled away.

If such coatings are used, clearances between the parts involved

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*Manufactured by the R. M. Hollingshead Company, Camden, N. J.

must, of course, be correspondingly increased.

When the exposure has been completed and the electrodes removed, the chamber is disassembled under the surface of a complexing solution to prevent contamination of the air by radioactive dust. The film is immediately peeled away from the surface with forceps, and discarded. The part is then flushed with fresh water and allowed to dry.

(b) Results

Table II gives the results of recent measurements made on rotors and cassettes with the aid of a "Zeus" ionization meter. All parts were dry when measured, and the instrument geometry was the same for all measurements. All readings are given in mr/hr; the activity in each case was a combination of β and γ.

Table II

Effectiveness of Decontamination with Strippable Coating*

Sample No.	Residual Activity on Part before Coating	Activity on Coating Part after Spectrographic Exposure, before Removal of Coating	Activity on Part after Removal of Coating
1	< 1	400	4.0
2	<1	250	2.5
3	<1	150	2.5
4	<1	100	1.5
5	<1	50	1
6	<	47	< 1
7	<	15	<1
8	<	12.5	<1

*Measurements by Amanda Estepp.

After porous cup exposures of solutions containing ~ 1 mg/ml of Pu (specific activity = 1.8×10^8 decompositions/min/mg), the face of the rotor has been found to have as few as 30 counts per minute of α activity after removal of the coating.

Acknowledgement

The authors wish to thank L. B. Rogers for suggesting the development of a new chamber, and for his advice and encouragement in connection with the development of the present model.

References

(1) Fred, M., Nachtrieb, N. H., and Tomkins, F. S., J. Opt. Soc. Am. 37:279 (1947); Bachelder, M. D., Conway, J. G., Nachtrieb, N. H., and Wildi, A. B. S., MDDC-511 (December 12, 1946) (Declassified).

(2) Feldman, C., AECD-2392; Analyt. Chem. 21, 1041 (1949).

(3) Reysen, W. H., and Vanstrum, P. R., AECD-2032.

(4) Thirring, H., Acta Phys. Austr., II, 379 (1948).