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UNITED STATES ATOMIC ENERGY COMMISSION

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By  
 E. Staple  
 E. D. Marshall  
 F. Nelson  
 W. Simon

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K-25 Plant  
 Carbide and Carbon Chemicals Corporation  
 Oak Ridge, Tennessee

Technical Information Extension, Oak Ridge, Tennessee



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A METHOD FOR THE DETERMINATION OF BORON IN TF6

E. Staple, Edward D. Marshall, Frederick Nelson, and Wilbur Simon

I. Development of Boron-Curcumin Color:

In view of the immediate need for a calibration curve for boron, work was first done on the evaporation procedure for developing the boron-curcumin color.

A. Effect of Evaporation with Calcium Hydroxide Suspension:

Color was developed in samples containing varying amounts of boron as follows:

1. The boron-containing solution was evaporated to dryness with 5 ml. of 0.1 N calcium hydroxide suspension.
2. The residue was dissolved in a hot oxalic-hydrochloric acid mixture (one part concentrated hydrochloric acid to 4 parts aqueous 20 per cent oxalic acid).
3. Three ml. of 0.1 per cent curcumin solution (in ethanol) was added and the mixture was evaporated on a water bath at 55° C.  $\pm$  3° C. The samples were kept on the water bath for one hour; after about a half an hour the samples appeared dry.

2/18/46

4. The red boron complex was taken up in ethanol, filtered into a 25 ml. flask, and measured colorimetrically on a Beckman spectrophotometer.

The results obtained on several blanks and on boron containing solutions are given in Table I.

TABLE I  
Effect of Evaporation with Calcium Oxide Suspension

<u>Micrograms of boron added</u>	<u>Micrograms of boron found*</u>
0.0	0.65
0.0	0.60
0.0	0.70
0.0	0.55
0.0	0.80
1.0	0.65
2.0	2.90
3.0	2.98
3.0	3.05

\* Values given here were determined from a calibration curve obtained later.

Table I shows that blank determinations were high and erratic. The discrepancy is probably due to the fact that the calcium oxide used contained boron and was difficult to keep in suspension. Consequently equal amounts of calcium hydroxide could not be measured accurately in each determination.

B. Effect of Evaporation with Sodium Carbonate Solution:

A 0.1 N solution of sodium carbonate was substituted for the suspension of calcium hydroxide, and the color developed as before in blanks and in boron-containing solution.

Table II shows that boron contamination was much less and that results were fairly consistent. The discrepancies noted are probably due to the difficulty in measuring the hot oxalic-hydrochloric acid mixture and in keeping the oxalic acid in solution.

3787

4

TABLE XI

Effect of Evaporation with Sodium Carbonate Solution

<u>Micrograms of boron added</u>	<u>Micrograms of boron found*</u>
0.0	0.14
0.0	0.10
0.0	0.15
0.0	0.18
0.0	0.20
2.0	1.80
2.0	2.15
2.0	2.30
2.0	2.20

\* Values given here were determined from a calibration curve obtained later.

C. Effect of using Alcoholic Oxalic-Hydrochloric Acid Mixture in Color Development.

To facilitate accurate measurement of the oxalic-hydrochloric mixture, the following solution was prepared:

200 ml. of distilled water  
 200 ml. of ethanol  
 50 ml. of concentrated hydrochloric acid  
 40 grams of oxalic acid

Two ml. of the above solution are equivalent to one ml. of the aqueous solution used before. It is stable and the oxalic acid remains in solution at room temperature. Table III shows the effect of using the alcoholic oxalic-hydrochloric acid solution. The results obtained are consistent, and recovery of added boron was found to be complete within ten per cent. The amount of boron found in the blank determinations was low and was sufficiently constant to permit the subtraction of an average blank from a determination impairing the accuracy.

L.H. 17

**TABLE III**  
**Effect of Alcoholic Oxalic-Hydrochloric Acid**  
**Mixture on Color Development**

<u>Micrograms of boron added</u>	<u>Micrograms of boron found*</u>
0.0	0.13
0.0	0.15
0.0	0.10
0.0	0.14
0.0	0.12
0.0	0.13
2.0	2.10
2.0	2.15
2.0	2.02
2.0	2.10
2.0	2.16
5.0	5.09
5.0	5.14
5.0	5.09

\*Values given here were obtained from a calibration curve obtained later.

II. Distillation of the Boron in  $TF_6$  Samples:

A. Removal of Fluoride from  $TF_6$  Samples:

Distillation of the boron in  $TF_6$  samples was tried at the natural fluoride concentrations of the hydrolyzed samples. It was found that considerable hydrofluoric acid distilled over into the sodium carbonate trap used and that some leaching of boron from the glassware took place as evidenced by abnormally high results. Removal of the fluoride was accomplished by carefully evaporating the aqueous  $TF_6$  solution twice to near dryness with 10 drops of concentrated sulfuric acid.

B. Distillation of the Boron:

Several techniques for distilling boron as methyl borate were tried. Table IV gives the results obtained when carrying out the distillation by the following procedure:

5287

1. An aliquot containing 100-200 mg. of T as the sulfate was placed in a Vycor distilling flask and was neutralized with ammonia to the first permanent precipitate. (When standard boron solution was added, without T, no neutralization was required).
2. The volume was reduced to about 5 ml. by evaporation.
3. Concentrated sulfuric acid was added dropwise until the precipitate redissolved and two drops were added in excess.
4. Ten ml. of methanol were added and a stream of methanol vapor was bubbled through the solution. The methanol vapor was supplied by a boiling methanol bath and was led into the solution in the distilling flask by means of a tube drawn to a capillary.
5. About 200 ml. was distilled into a flask containing 5 ml. of 0.1 N sodium carbonate solution.
6. The distillate was evaporated to dryness and the boron curcumin color was developed in the residue using the color development procedure.

TABLE IV

Recovery of Boron by Distillation in a Current of Methanol Vapor

<u>Micrograms of boron added*</u>	<u>Micrograms of boron recovered (blank not subtracted)</u>
0	0.35 (blank run)
2	0.50
2	1.00
5	2.80
5	3.45
5	1.40
5	1.60

\*Boron was added from a standard boron solution. No T was present in these runs.

The above table indicates that boron recovery is poor.

Several more runs were made following a revised procedure, using direct distillation rather than a stream of methanol to distill the methyl borate. Table V gives the results of several runs made using the following procedure:

317

1. An aliquot containing 100-200 mg. of T as the sulfate was placed in the Vycor distilling flask and neutralized with ammonia to the formation of the first permanent precipitate.
2. The precipitate was just dissolved in 6 N sulfuric acid added dropwise; and three drops of concentrated sulfuric acid were added.
3. About 30 ml. of methanol was added and the sample was distilled at 100° C. (boiling water bath) under slight suction. Air was drawn through the solution in the distilling flask to hasten the distillation.
4. Additional methanol was added from time to time through the air inlet tube to replace the methanol distilled over. The volume of solution in the distilling flask was kept between 20 and 60 ml.
5. About 200 ml. of solution were distilled over into a flask containing 5 ml. of 0.1 N sodium carbonate solution.
6. The solution from (5) was evaporated and the boron-curcumin color developed by the color development procedure.

TABLE V

Recovery of Boron by Direct Distillation

<u>Micrograms of boron added*</u>	<u>Micrograms of boron recovered (total boron less boron in blank and in sample)</u>
1.0	0.8
2.0	1.6
2.0	1.0
2.0	1.8
2.0	1.2
2.0	1.5
3.0	2.5
3.0	1.8
3.0	2.4
5.0	3.4
5.0	4.2
5.0	4.5

\*Boron was added to the hydrolysed T76 aliquot which was then converted to the sulfate by evaporating with sulfuric acid.

The low yields obtained were attributed to incomplete reaction of the boron in the sample.

12/87

To obtain better yields, the distilling flask was fitted with a reflux condenser which extended into the distilling flask to within a few inches of the liquid level and the solution was refluxed for an hour before distilling. The procedure followed was the same as that previously used with the exception of the refluxing. Table VI indicates that more boron was obtained as a result of the refluxing.

TABLE VI

Recovery of Boron by Combined Reflux and Distillation Procedure

<u>Micrograms of boron added*</u>	<u>Micrograms of boron recovered (total boron less boron in blank and in sample)</u>
2.0	2.0
2.0	1.8
2.1	1.8
<hr/> 5.0	<hr/> 5.0

\*Boron was added to the hydrolyzed  $\text{UF}_6$  aliquot which was then evaporated with sulfuric acid to remove fluorides.

III. Method:

A. Reagents and Apparatus:

The following reagents are used in the color development procedure:

1. Oxalic-hydrochloric acid mixture

20 milliliters distilled water

20 milliliters c.p. ethanol

5 milliliters concentrated hydrochloric acid

4 grams oxalic acid

2. Curcumin extract: Dissolve 0.10 grams of crystalline curcumin in 100 ml. of c.p. ethanol.

3. Methanol, c.p.

4. Sodium carbonate solution (0.2 N).

5. Boron free ammonia.

6. Concentrated sulfuric acid.

7. Three inch diameter platinum evaporating dish.

827



9. Water bath ( $55^{\circ}\text{C.} \pm 2^{\circ}\text{C.}$ ),

10. Distilling and reflux apparatus made of boron-free glass.

11. Beckman spectrophotometer.

C. Distillation Procedure: (For distillation apparatus see Fig. II)

1. Add 0.5 ml. concentrated sulfuric acid to the  $\text{TF}_6$  sample in the platinum dish. Evaporate on a steam bath until  $\text{H}_2\text{SO}_4$  crystallizes freely.
  2. Dilute to approximately 25 ml. Take a small aliquot, (1 ml. usually) and analyze colorimetrically for T.
  3. Pipette an aliquot containing 150 to 200 mg. T into reaction flask (H). Add boron-free ammonia water until the first permanent precipitate forms. Dissolve the precipitate by adding concentrated sulfuric acid dropwise; then add two drops more.
  4. Put 5 ml. of 0.2 N sodium carbonate in soft glass receiving bottle (K) but do not stopper tightly. (The sodium carbonate solution is stored in lucite ware).
- 9287

5. Add 25-30 ml. of c.p. methanol to the solution in the reaction flask; and attach reflux condenser (D) immediately. Reflux vigorously for an hour.
6. At the end of the refluxing time, stopper the receiving bottle tightly, and adjust the aspirator to about 2 inches of mercury vacuum. Remove the reflux unit (Figure 2), quickly wash it with methanol, and replace it with the boron free glass tube (V) drawn to a capillary. Readjust the aspirator so as to give from 2-4 bubbles per second through the T solution.
7. Distil 200 ml. into a receiving bottle by keeping the water bath at 93-98° C. (incipient boiling). Add 10-15 ml. of methanol periodically. Do not let the volume in the reaction flask (H) get below 15 ml.
8. Evaporate the distillate to dryness on a steam bath to avoid spattering. Use a 3 inch porcelain evaporating dish. The analysis may be safely interrupted and samples may be stored at this point.

D. Procedure for Development of the Boron-Curcumin Color:

1. Dissolve the residue obtained in evaporating the distillate in 2 ml. of the oxalic-hydrochloric acid mixture, rotating the dish to bring the residue entirely into solution.
  2. Add 3 ml. of 0.10 per cent curcumin solution.
  3. Float the evaporating dish on a constant temperature water bath (55° C.  $\pm$  2° C.) for exactly one hour to develop the color.
  4. Extract the red boron color with c.p. methanol and filter through No. 41 Whatman filter paper into a 25 ml. volumetric flask. Dilute to volume.
  5. Measure the transmission on a Beckman spectrophotometer using a 1 cm. cell and a wavelength of 540 millimicrons, using ethanol as the standard.
  6. Determine the amount of boron by comparison with a calibration curve determined by developing the boron-curcumin color of known amounts of boron. Use a boric acid solution containing one microgram of boron per ml. for determining the calibration curve and evaporate the aliquots to dryness with 5 ml. of 0.2 N sodium carbonate. (See Figure V for calibration curve).
- 10/2/47

7. Check the purity of the reagents by running a blank, carrying it through the distillation procedure and the color development procedure.
8. Subtract the average of several blank determinations from each sample determination to correct for boron contamination.

Calculations:

1.  $\text{Mg. T in sample} \times \frac{352}{238} = \text{mg. TF}_6 \text{ in sample}$
2.  $\frac{\text{Mg. boron in sample}}{\text{Mg. TF}_6 \text{ in sample}} \times 100 = \text{per cent boron in TF}_6$

11287

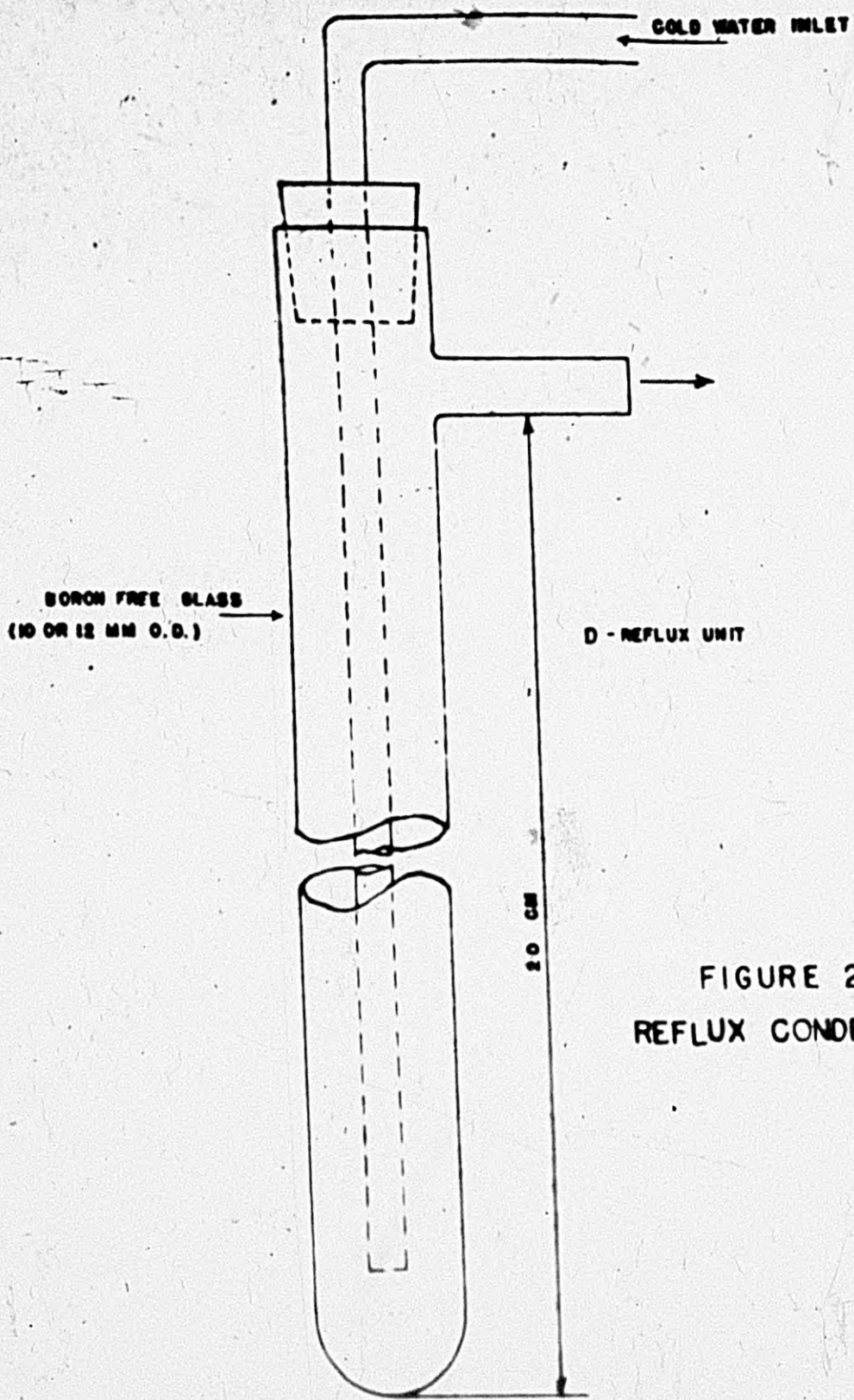


FIGURE 2  
REFLUX CONDENSER

13287

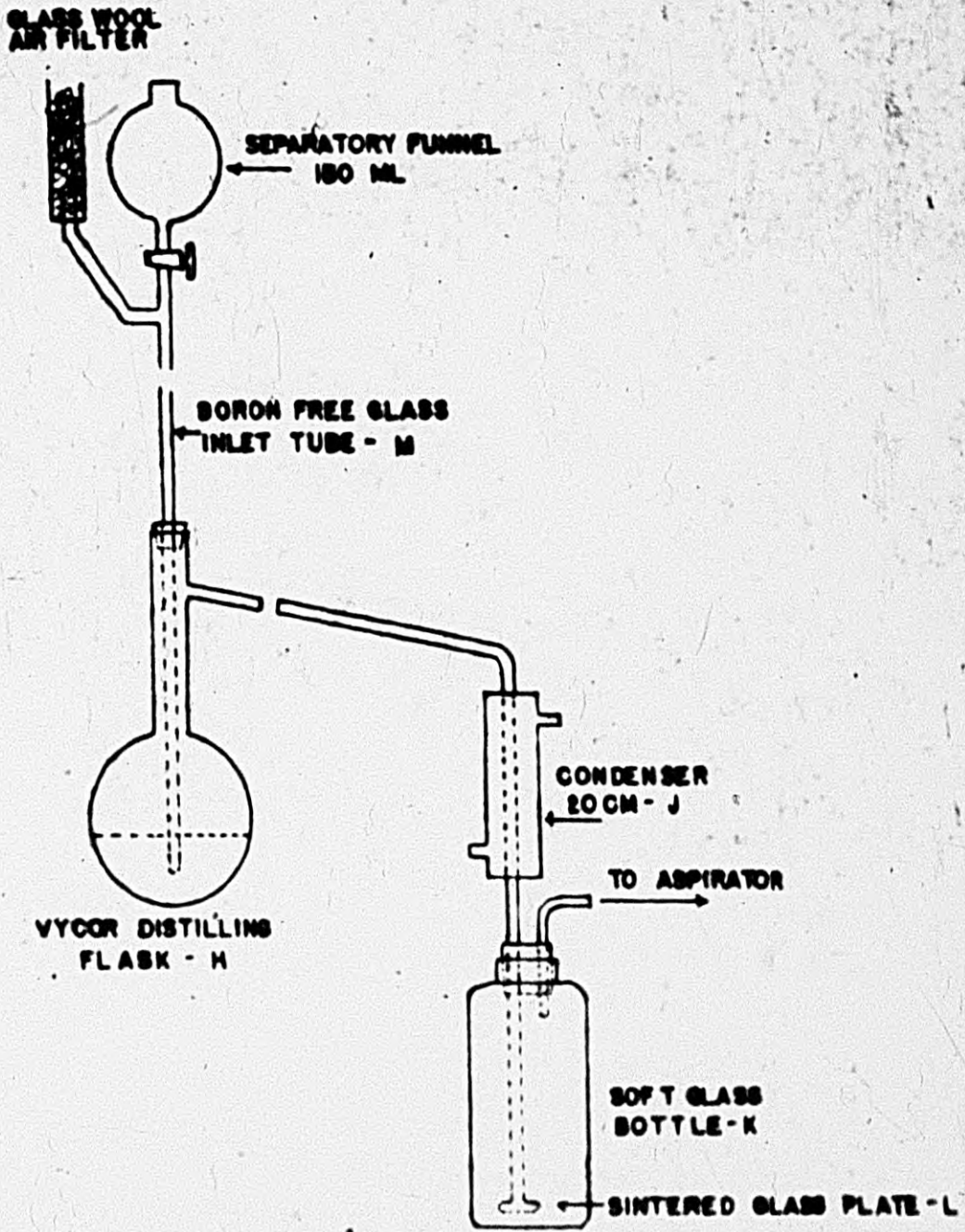
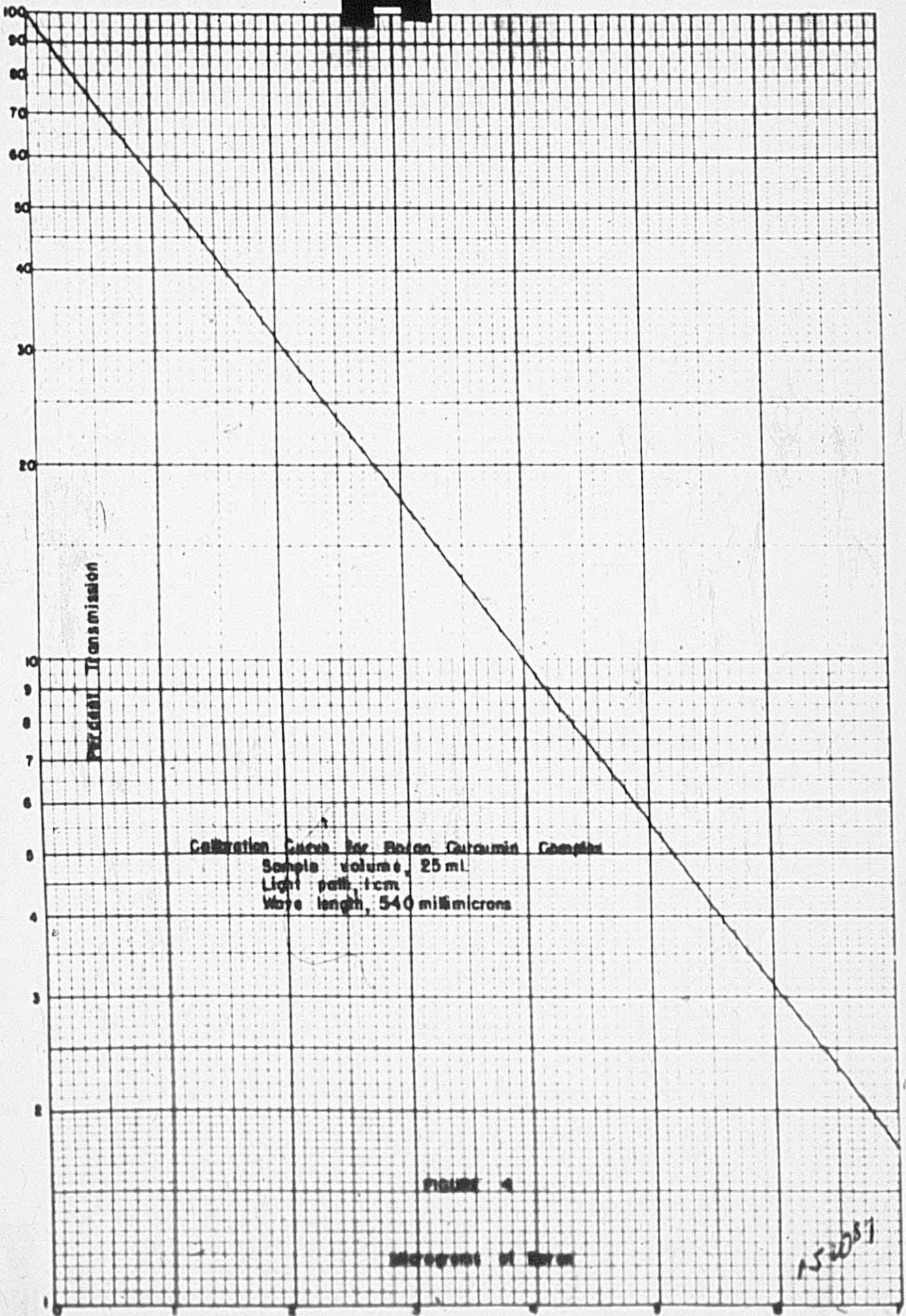


FIGURE 3  
DISTILLATION APPARATUS

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EDUCATIONAL EXHIBITION CO.  
 PROVIDENCE, R. I. U.S.A.  
 NO. 4 25 x 38 1/2 SEMI-LOGARITHMIC PAPER  
 2 1/2 INCH CELLS 2 1/2 INCH PER INCH - 70 DIV.

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