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LA REPORT 416-A

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CHEMICAL AND SPECTROCHEMICAL ANALYSIS OF URANIUM AND PLUTONIUM MATERIALS (u)

MANUAL OF PROCEDURES

PUBLICLY RELEASABLE

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MANUAL OF PROCEDURES

(SUPPLEMENT)

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LA - 416 REVISIONS AND CORRECTIONS.



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ABSTRACT

By treatment of the solution to be tested with aqua regia, the cyanide is removed and the gold is oxidized. The color intensity of the yellow chlorauric ion serves as a measure of the gold concentration in the solution. Measurements are made against a known standard using a colorimeter. The method is subject to interference by iron or any other impurity which gives color to the solution under the conditions of the test.



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Applicability

This procedure has been applied only to solutions containing 15- 25 grams of gold per liter. Stronger or weaker solutions may be analysed provided the sample taken gives about 15 to 25 mg of gold in the final volume of 25 ml, this being the optimum concentration for comparison in the colorimeter.

Accuracy

The accuracy of the procedure was established by comparing results with those obtained by gravimetric gold assay of the same solutions.

The percentage error can easily be held to less than 5 o/o if the concentration of the unknown solution be nearly equal to or greater than that of the standard, and the concentration is in the range 15 to 25 mg of gold per 25 ml final volume.

Reagents


1. HCl, concentrated, c.p.)
 2. HNO₃, concentrated, c.p.)
 3. AuCN, c.p.
 4. KCN, c.p.
- } 3 vol. HCl + 1 vol. HNO₃ = aqua regia.

Apparatus

1. Pipet, 1 ml.
2. Beakers, 50 ml.
3. Ribbed watch glasses, 3 inch-dia.
4. Graduates, 5 ml. and 25 ml.
5. Volumetric flasks, 25 ml. and 100 ml.
6. Steam bath.
7. Wash bottle.
8. Colorimeter.

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Preparation of standard auric solution:

Weigh to the nearest 0.5 mg about 70 mg of AuCN and dissolve it in a few ml of water containing about 200 to 300 mg of KCN. Add to the solution 20 ml of aqua regia and evaporate under cover of a ribbed watch glass to complete dryness on the steam bath (HOOD!). Repeat three times the evaporation to dryness with aqua regia, using 20 ml each time. Dissolve the residue in 6.5 ml of aqua regia. Transfer the solution to a 100-ml volumetric flask rinsing the cover glass and beaker with distilled water and transferring the washings to the flask. Aerate the solution to remove colored oxides of nitrogen by shaking vigorously and make the solution up to the mark with distilled water. This solution contains 0.625 mg of gold per ml or 15.6 mg of gold per 25 ml. (This is roughly equivalent to the concentration of gold when 1 ml of plating bath is treated and diluted to 25 ml -- assuming a plating bath solution concentration of 15.6 grams per liter.) The solution is stable for several weeks at least.

Procedure

Accurately pipet 1 ml of plating bath solution into a 50-ml beaker. Add 5 ml of aqua regia, cover the beaker with a ribbed watch glass, and evaporate the solution to complete dryness on the steam bath (HOOD!). Repeat the evaporation with aqua regia three times, using 5 ml each time. Dissolve the residue in 1.6 ml of aqua regia. Transfer the solution to a 25-ml volumetric flask, rinsing the cover glass and beaker with distilled water and transferring the washings to the flask. Shake the flask to remove oxides of nitrogen from the solution and make up to the mark with distilled water. Compare with the standard gold solution on the colorimeter. Set the standard solution at 20.0mm depth.



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Precautions

1. Failure to aerate the oxidized gold solution will lead to high results caused by colored oxides of nitrogen.
2. Best results are obtained when the unknown is nearly equal to or stronger than the standard. Low results are obtained when the unknown is as much as 7 o/o weaker than the standard. Good results have been obtained with unknowns 60 o/o stronger than the standard.
3. The usual precautions concerning eye fatigue when using the colorimeter must be observed. The average of several readings should be taken.

Calculations and expression of results

From Beer's Law,

$$C_1L_1 = C_2L_2, \quad \text{or} \quad C_2 = C_1L_1/L_2$$

where C_1 is the concentration of the known solution, L_1 is the depth through which the known solution is viewed, C_2 is the concentration of the unknown solution and L_2 is the depth through which the unknown solution is viewed. When the two halves of the field are of the same brightness the above relation holds. A scale at the base of the colorimeter gives values of L_1/L_2 when L_1 is 15 or 20. Since the standard solution is equivalent to 15.6 grams of gold per liter, the concentration of the plating bath solution in terms of grams of Au per liter equals

$$15.6 \times L_1 / L_2.$$

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MICROVOLUMETRIC ASSAY OF PLUTONIUM

(Revised Procedure)

Abstract

Plutoniumas sulfate in 2N H_2SO_4 is reduced to + 3 valence with zinc amalgam under a CO_2 atmosphere and is titrated potentiometrically to + 4 valence with ceric sulfate.

Applicability

The method has been used primarily for mixtures of + 4 and + 6 nitrate in 1N HNO_3 , particularly for Hanford material both as received and after purification. The method permits direct determination of Pu in a soluble sample provided the cations of Ti, V, Fe, Mo, W and U are present in amounts not greater than 0.02 to 0.03 per cent. If any one of these ions is present in appreciable amount it must either be removed or determined separately and subtracted (using the proper equivalent weight factor) from the quantitative combination.

The procedure here given treats Pu nitrate solutions which require a correction for iron only.

Method of sampling

Aliquots are taken by weight or volume as required; three aliquots containing from 1 to 10 mg of Pu are taken for assay and two aliquots are used for determination of iron.

Regardless of precautions taken in storing the sample in solution, the concentration increases because of decomposition of water by alpha particles. The magnitude of this effect is related to the concentration of Pu in the solution. It was calculated for one sample to be about 1.1 per cent per week, but was found, in combination with other effects, to be somewhat greater. This effect prevents a gas-tight seal of samples containing as much as 200 mg Pu per ml. For this reason aliquots are taken within a few hours from the time the sample is received.

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Reagents

1. H_2SO_4 , concentrated.
2. H_2SO_4 , 1 N
3. Cerio sulfate, about 0.02 N in 1N H_2SO_4 (?)
4. Saturated zinc amalgam.
5. Solid CO_2

Apparatus

1. Detachable syringe pipet controls for transferring all fu solutions and for filling and emptying the burets.
2. Transfer weight-pipets with waxed tips (Fig. 1).
3. Volumetric pipets, waxed tip, calibrated to contain 20 to 100 λ (Fig. 1).

These pipets are very simply constructed from pyrex glass tubing or small test tubes. The constriction at the meniscus is fine enough so that a variation of 1 mm does not correspond to more than 0.1 per cent of the pipet volume.

4. Platinum crucibles, 8 ml.
5. Evaporation chamber (Fig. 2).
6. Infra-red lamp and Variac.
7. CO_2 generator. A satisfactory generator consists of a dewar flask of one liter volume or larger whose heat conduction is sufficient to supply 1 to 2 ml of CO_2 gas per second when the flask is half filled with solid CO_2 . Heat conduction may be increased by inserting a copper rod through the stopper. The flask should be completely wrapped or taped for the protection of the operator. A combination safety-trap and CO_2 pressure indicator is attached to a side-arm of the CO_2 supply line. It consists of an open-end section of the line immersed to a depth of 8 to 8 inches in water. The operating pressure is maintained at about 6 inches of water by an appropriate selection of diameter and length of the capillary leads

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1. Standardize with Bureau of Standards (253)

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in the apparatus (Fig.4).

8. Combination reduction-titration cups (Figs. 3,4,5, and 6).
9. Variable-speed electric stirring motor, Variac, and waxed glass stirrers.
10. Weight-burets, 0.5 to 3.0 ml capacity (Fig. 1). The tip is waxed outside so that it will not be wet by water solutions. This minimizes loss in weight caused by evaporation and also, for small-bore tips, prevents drainage except when it is forced with a syringe or when the tip is immersed in a solution. The control constriction is waxed inside so that it will not fill with solution and thus prevent gravity drainage when the tip is immersed. If the same buret is used for the end point as for the rest of the titration its delivery rate with the tip immersed should not exceed 2 mg of solution per second.
11. Vacuum residue bottle. The liquid lead is a tapered 2-mm glass tube attached to the bottle by an adequate length of rubber tubing. The vacuum lead contains a cotton-filled drying tube.
12. Beckman pH meter with calomel and platinum electrodes.

Procedure

HEED HEALTH SAFETY RULES OUTLINED IN SECTION I. (LA-416).

1. For weight aliquots weigh by difference the required amount of sample using a clean dry transfer pipet. Transfer the aliquots to 8-ml platinum crucibles. For volume aliquots use clean dry pipets calibrated "to contain". After discharging the volume aliquot into the crucible, rinse the pipet once with 1N H_2SO_4 and twice with water, adding all rinses to the crucible. Dry the pipet on a vacuum manifold and reserve for future use. Add carefully around the side of the crucible 150 λ of conc. H_2SO_4 and enough water to give a volume not less than 0.5 ml. Place these crucibles in the evaporation chamber.

With a steady stream of air passing through the chamber, heat the samples with an infra-red lamp at a temperature somewhat below the boiling point of the solution. When most of the water is driven off and the rose-colored $+ 4$ sulfate has precipitated, increase the temperature until the H_2SO_4 fumes. Turn off the lamp and allow the samples

to cool. When cool add carefully around the crucible rim enough water to redissolve the
 * 4 sulfate precipitate; 0.4 to 0.5 ml. should be enough. Repeat the fuming and dilution.

2. If the reduction-titration cups have not been used for some time clean them thoroughly. Dry the stopcocks and grease them lightly.

With stopcock A open add 1 ml of dilute H_2SO_4 to the amalgam reservoir. Charge the reservoir with enough saturated zinc amalgam to bring the level of the amalgam to the CO_2 side arm⁽²⁾. Open stopcock B and force the dilute acid out of the capillary into the cup. It might be necessary to lower the amalgam with the syringe control. With the CO_2 flowing⁽³⁾ raise the amalgam to a height of about 0.5 cm. in the cup. Close stopcock A. Place the syphon stopper in the position shown (Fig.4) and slowly draw the dissolved sample from the platinum crucible into the cup. In order to minimize spray, draw the last portion over very slowly or allow the syphon lead to remain filled. Rinse the crucible and lead with 2 ml of 1N H_2SO_4 in three portions. Remove the syphon stopper and place the plastic lid (Fig.5) on the cup. Raise the amalgam to a height of about 1.0 cm in the cup. Insert the CO_2 lead through the lid. Adjust the stirrer with the flattened portion half immersed in the amalgam. Stir at a moderate rate for one-half hour or longer.

3. Turn on the pH meter and set the range switch to "+ MV".

4. Fill the buret with more ceric solution than is required to oxidize the sample. Weigh the filled buret to the nearest 0.1 mg. Stop the stirrer. Lower the amalgam to the level of the CO_2 side arm. Open stopcock B to a minimum flow rate. Adjust the pressure in the amalgam reservoir with the syringe control so that the CO_2 passage is alternately locked and opened by the oscillating amalgam column. When the reduced solution has been raised into the cup and the capillary between the cup and side arm is completely filled with CO_2 , close stopcock B. The pressure in the reservoir should be sufficient to just lock the CO_2 passage. Close stopcock A. If any amalgam has been retained in the solution, the above operation must be repeated until the separation is accomplished.

2. An excess of zinc may be added to this reservoir in order to maintain the saturated amalgam.

3. The CO_2 capillary should be fine enough to permit the regulation of the gas flow to a slow rate so that spray of plutonium solution is minimized.

4. A separate residue bottle is kept for second rinses and solutions of this kind, thus eliminating excessive dilution of recoverable residue.

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5. Remove the lid and CO_2 lead. Rinse the electrodes and lower them into the reduced solution (Fig. 6). Titrate with stirring to within a few per cent of the end point -- between 600 and 650 millivolts. Continue the stirring for at least ten minutes or until a reasonably steady potential is attained. As much as 95 per cent of the ceric solution may be force drained with a syringe control. The last 5 per cent or more should be added in small portions by touching the buret tip to the surface of the solution. The end point potential is between 750 and 780 millivolts cell potential but should be determined by each operator from a titration curve. Interpolation of the end point is possible to 0.1 per cent from any potential between 700 and 820 millivolts provided a satisfactory curve has been obtained. With some practice only an initial and a final weight are required.

6. When the titration is completed transfer the solution to the vacuum residue bottle. Rinse the cup and capillary. While the apparatus is not in use store it with stopcock B closed, the cup filled with distilled H_2O or dilute H_2SO_4 , the plastic lid on the cup, and 0.5 ml of dilute H_2SO_4 over the amalgam in the reservoir.

Blank Procedure

Determine the reagent blank in the presence of plutonium in the following way. Take aliquots ranging from 0.01 to 0.10 mg of plutonium and several aliquots of about 5 mg. These are all taken from the same stock solution or accurate dilutions of the stock solution, and are treated according to Procedure outlined above. Since their ratios to each other are accurately known and since the blank is a very small fraction of the 5-mg samples and an appreciable fraction of the smaller ones, the value obtained in the 5-mg sample may be assumed correct for the purpose of calculating the amount in the smaller samples. The difference between this calculated amount and the observed

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amount in the small samples is the reagent blank correction. It should not exceed 10% of plutonium and should be reproducible to 2 or 3%.

Precautions

1. See Method of sampling concerning errors resulting from storage of the sample.
2. Although the plutonium is quantitatively reduced in less than one-half hour the minimum time should be determined not only by this consideration but by the length of time required to free the system from O_2 . This is necessary in order to obtain a low and constant blank.
3. Pu^{+3} is slowly air oxidized to Pu^{+4} . The error is negligible if the titration is performed without interruption according to Procedure 4 and 5.
4. At temperatures below $20^\circ C$ the reaction is rather slow. In any case the end point must be determined or interpolated from steady (not rising) potential readings.
5. If a falling end-point is observed examine the capillary below the titration cup. Evolution of hydrogen gas from the dilute acid film in contact with the amalgam may be enough to raise the amalgam into the capillary. Effective contact of the amalgam with partially oxidized sample will of course make the result worthless.
6. If the potential rises above 820 mv, back titrate with ferrous reagent. This reagent may be standardized by adding an excess of the ceric solution at a satisfactory end point and back-titrating with the ferrous solution.
7. Erratic balance behavior and significant errors in weight have been observed when one attempts to deliver small amounts of solution accurately from relatively large burets handled with rubber gloves. The effect disappears when the burets are held with clean, dry fingers or cotton gloves and for this reason the rubber glove is removed for initial and final weighings.

Correction for iron

The procedure for determination of iron is described in III D of this manual. The requirement that the weight concentration of iron when multiplied by 4.28 (the equivalent weight ratio) be uncertain by not more than 0.1 per cent of the total

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plutonium concentration is satisfied by this method.

Precision and Accuracy

Average deviations from the mean of 0.1 per cent are usual, of < 0.05 per cent accidental, and of > 0.2 per cent rather unusual. Accuracy is demonstrated to a certain extent by results of plutonium metal and tetrafluoride. The former assayed 99.9 per cent plutonium with a standard deviation 0.17 per cent on 14 aliquots of one portion and 0.19 per cent on 6 aliquots of another portion. No results were rejected in calculating the standard deviation. The tetrafluoride assayed 100.07 per cent pure with a standard deviation of 0.07 per cent.

Calculations

$$\text{Apparent mg. Pu/g. solution} = \frac{(\text{wt. of ceric solution in g.}) \cdot T}{(\text{wt. of aliquot in g.})}$$

T = mg Pu per gram of ceric solution

$$\text{Corrected mg. Pu/g. solution} = (\text{apparent value}) - (4.28 \text{ mg. Fe/g. solution})$$

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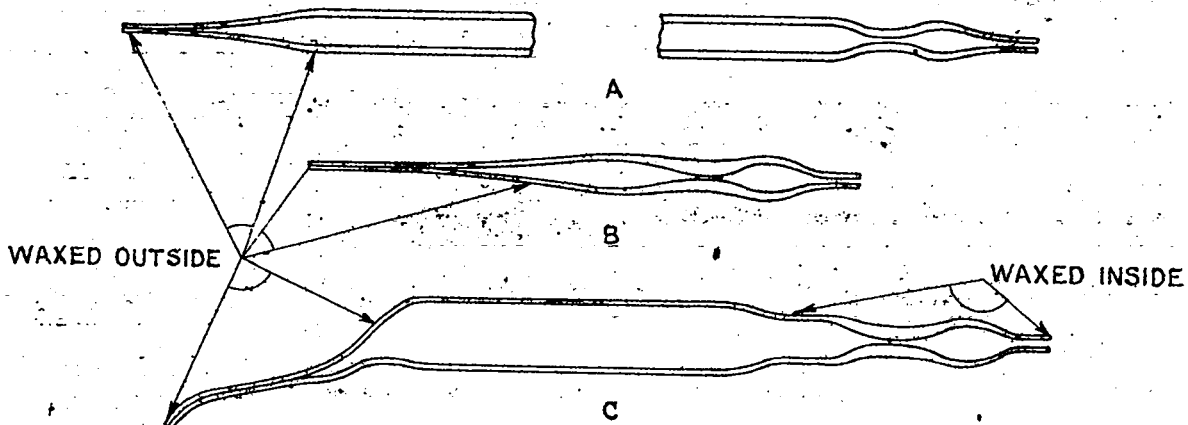


FIGURE 1

- A. TRANSFER PIPET
- B. VOLUMETRIC PIPET
- C. WEIGHT BURET

SCALE: 1"=1"

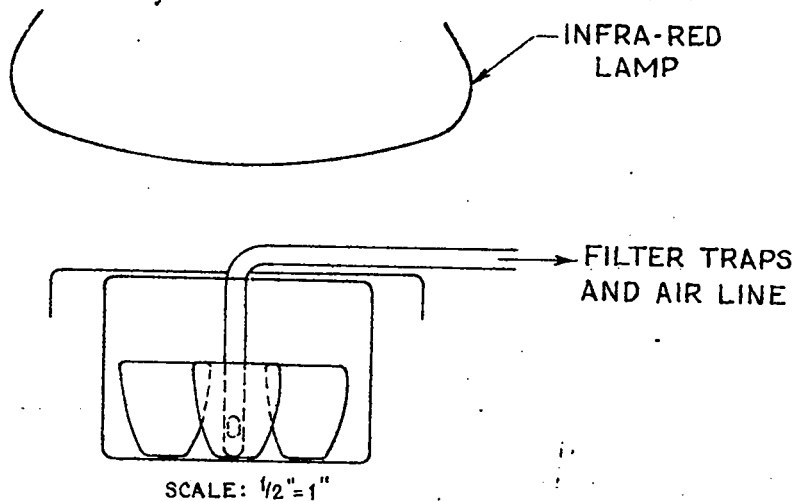


FIGURE 2

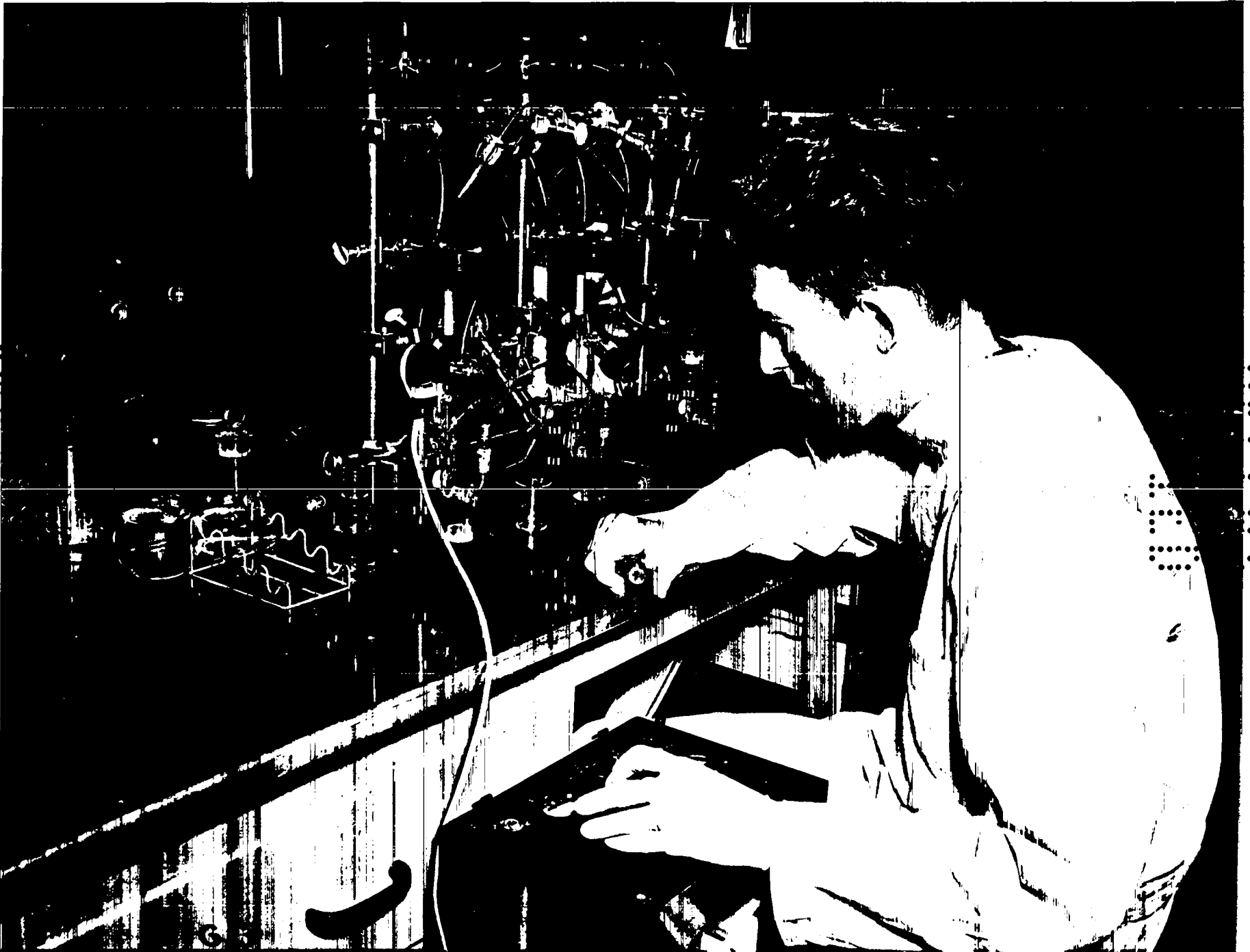
EVAPORATION CHAMBER

VOLUMETRIC ASSAY OF PLUTONIUM

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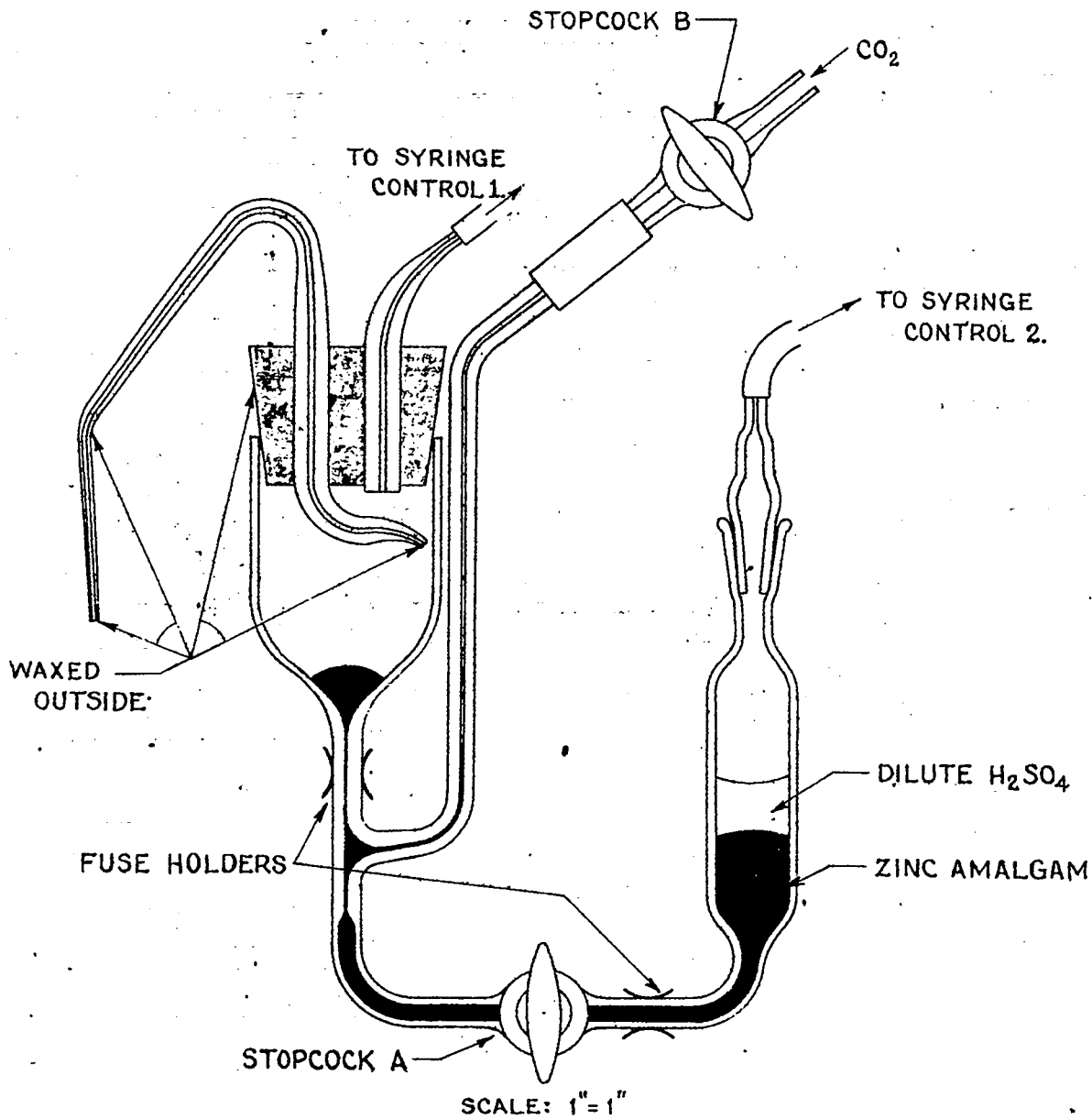


FIGURE 4
REDUCTION-TITRATION CUP
VOLUMETRIC ASSAY OF PLUTONIUM

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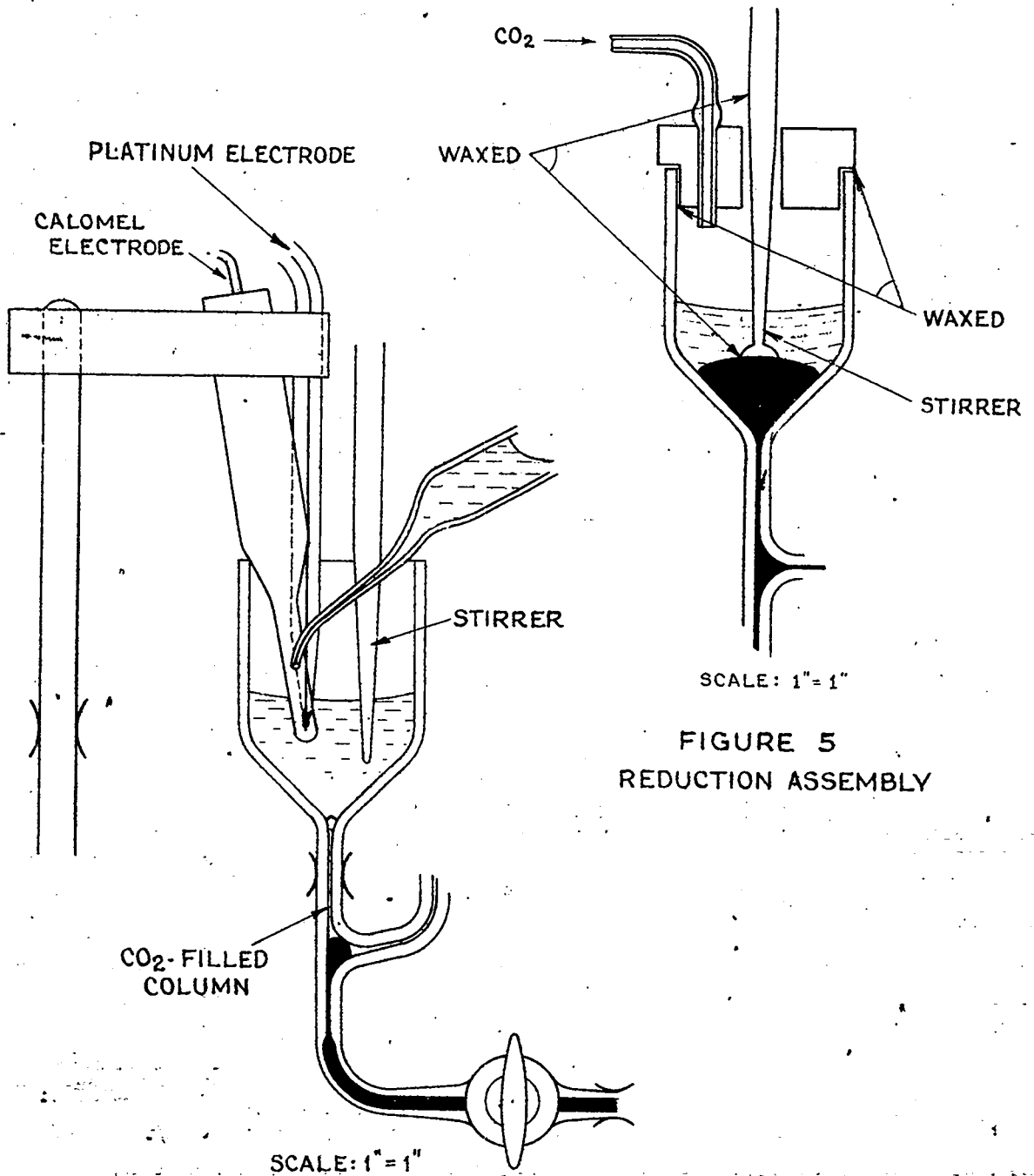


FIGURE 5
REDUCTION ASSEMBLY

FIGURE 6 - TITRATION ASSEMBLY
VOLUMETRIC ASSAY OF PLUTONIUM

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THE DETERMINATION OF CARBON AND HYDROGEN IN CALCIUM METAL

Abstract

The sample is burned at 1000° C in oxygen diluted with helium and the carbon dioxide and water formed by the oxidation of carbon and hydrogen compounds in the sample are quantitatively absorbed on Ascarite and Dehydrite and weighed. Calcium burns at an uncontrollably fast rate in pure oxygen or in air; by properly diluting the oxygen with the inert gas, helium, the rate of combustion can be easily controlled.

Applicability

The method has been used only for calcium metal but it is expected that it would give equally satisfactory results with magnesium and other active metals which are difficult to handle by the conventional procedure.

Method of Sampling

The sample should be in the form of small pieces about 2 to 3 mm across or in thin strips or turnings. Thick pieces are difficult to oxidize completely because of the formation of a protective oxide layer. Exposure of the sample to the air should be kept at a minimum to prevent reaction with carbon dioxide and moisture.

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Size of Sample and Limit of Sensitivity

Samples of the order of one half to one gram are used. The limits of sensitivity on a one-gram sample are approximately 50 ppm of carbon and 20 ppm of hydrogen.

Reagents

1. Ascarite (soda-asbestos).
2. Dehydrite (Arthur H. Thomas, anhydrous $Mg(ClO_4)_2$).
3. H_2SO_4 , concentrated, c.p.
4. Tank oxygen, 99.5 per cent minimum purity.
5. Tank helium, 98 per cent minimum purity.
6. Copper oxide, wire form.
7. Copper gauze.

Apparatus

1. Multiple-unit organic combustion furnace (see Fig. 7).
2. Single-unit combustion furnace (see Fig. 7).
3. Fused-quartz combustion tube, 25-mm OD x 100 cm.
4. Fused-quartz combustion tube, 20-mm OD x 50 cm.
5. Porcelain combustion boats, size 6A (Coors).
6. 2 U-tubes containing Dehydrite.
7. 4 U-tubes containing Ascarite and Dehydrite.
8. 2 absorption towers containing Ascarite and Dehydrite.
9. 3 bubblers containing concentrated H_2SO_4 .

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10. Thermocouple and pyrometer.
11. Boat hook.
12. Radioactive source (1 mg of radium).
13. Gum rubber tubing, 7-mm ID.
14. Two adjustable pinch clamps.
15. Glass wool.
16. Copper wire, 0.1-inch diameter.

Assembly of the combustion train

The complete assembly is shown in Fig. 7. The tube fillings for the combustion furnace and the preheater furnace are identical and are shown in Detail A. Also shown in Detail A is the method by which the tip of the combustion tube and the side arm of the Dehydrite absorption tube are kept warm to prevent condensation of water vapor. The filling of the absorption tubes is shown in Fig. 2, Detail B, p. 182, of the manual (LA-416).

The oxygen is sufficiently pure to use without pre-heating. The helium always contains more or less organic matter. This is removed by passing the gas through a preheater and through carbon dioxide and water absorbers before it is led into the combustion furnace.

Procedure

1. Test the train for leaks by permitting oxygen to flow through the main system with pinch clamp P¹ closed. If there are no leaks the rate of bubbling in the acid bubblers A and C will be the same. Then test the preheater

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system by opening pinch clamp P', closing pinch clamp P, and allowing helium to flow through the system as the rates of bubbling in acid bubblers B and C are observed.

2. With the furnaces maintained at the correct temperatures, i.e., approximately 1000°C for the small unit and approximately 600°C for both the large unit and preheater, adjust the rates of flow of oxygen and helium to about 1 to 2 bubbles per second each and burn out the tubes 3 to 4 hours.

3. Turn off the helium and close pinch clamp P'. After about 30 minutes connect the weighed absorption tubes and tare as shown in Fig. 7. (Handle the tubes with clean dry cotton gloves.) Allow the tubes to remain on the train 30 minutes.

4. Remove the tubes from the train and weigh each against the tare tube as described under (8) on p. 179 of the manual (LA-416). Repeat the procedure until the weight change of each tube is not more than 0.1 mg per 30-minute period. The train is then ready for use.

5. Adjust the temperature of the preheater furnace to about 600°C. Open the valve on the helium tank to give a rate of flow of about 10 bubbles per second and reduce rate by means of pinch clamp P' to about 3 bubbles per second.

6. Adjust the valve on the oxygen tank to give a rate of flow of about 5 bubbles per second and reduce rate by means of pinch clamp P to about 1 bubble per second.

7. Weigh to the nearest mg. between 0.5 and 1.0 gram of sample into a pre-ignited No. 6A porcelain boat.

8. Connect the absorption tube and tare to the train as shown in Fig. 7.

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There should be glass-to-glass contact between the Dehydrite tube and the end of the combustion tube; otherwise moisture may condense on the rubber connection between the two glass ends.

9. Remove the stopper from the front end of the combustion tube. Insert the boat containing the sample into the open tube end and with the boat hook quickly push the boat past the hot small furnace into the unheated portion of the tube between the two furnaces. Replace the stopper into the end of the tube.

10. Advance the small furnace until the front end of the boat is just covered. As the calcium becomes hot it will ignite and burn smoothly in the diluted oxygen. If the rate of combustion tends to become too rapid it is lessened by reducing the rate of flow of oxygen and increasing the rate of flow of helium by means of the above-mentioned pinch clamps. By cutting off the oxygen altogether, the combustion can be completely stopped. A little practice is required and since samples differ somewhat in behavior continuous control is necessary during the burning operation. When the calcium directly under the furnace is burned advance the furnace again slightly and burn another small portion. Continue in this way until the entire sample is burned. Then discontinue the helium flow completely and heat the sample in a moderate flow of oxygen for 45 minutes. This heating is necessary to burn the sample completely and to flush all of the helium out of the train.

11. Remove the absorption tubes and tare and weigh as described under step 8, p. 179 of the manual (IA-416).

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Blank Procedure

A blank determination is necessary in order to make sure that the helium is being properly purified by the preheater and absorption system and to ascertain the blank correction to be applied to the entire determination -- this is seldom zero and usually is about 0.1 to 0.2 mg. It is sufficient to determine the blank only occasionally -- for instance, whenever the apparatus has been idle for some time or when a new tank of helium or oxygen is to be used. To determine the blank proceed exactly as for an actual sample run, using approximately the same rates of flow of helium and oxygen and the same time as for the sample determination.

Precautions

1. Avoid undue exposure of the sample to the air to prevent its reaction with carbon dioxide and moisture.
2. After the sample appears to be burned in the diluted oxygen continue the combustion for not less than 45 minutes in pure oxygen. Failure to do this will give rise to two errors, the first due to incomplete combustion of the sample, and the second due to incomplete removal of helium from the absorption tubes.
3. Observe the precautions mentioned on p. 180 of the manual (LA-416) concerning static charges.

Calculation and expression of results

The carbon content is usually reported as parts per million and is

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calculated as follows:

$$\text{Wt. (g.) C} \approx \frac{\text{Wt. (g.) increase Ascarite tube (sample) minus wt. (g.) increase Ascarite tube (blank)} \times 0.273}{1}$$

$$\text{ppm C} \approx \frac{\text{Wt. (g.) C} \times 10^6}{\text{Wt. of sample (g.)}}$$

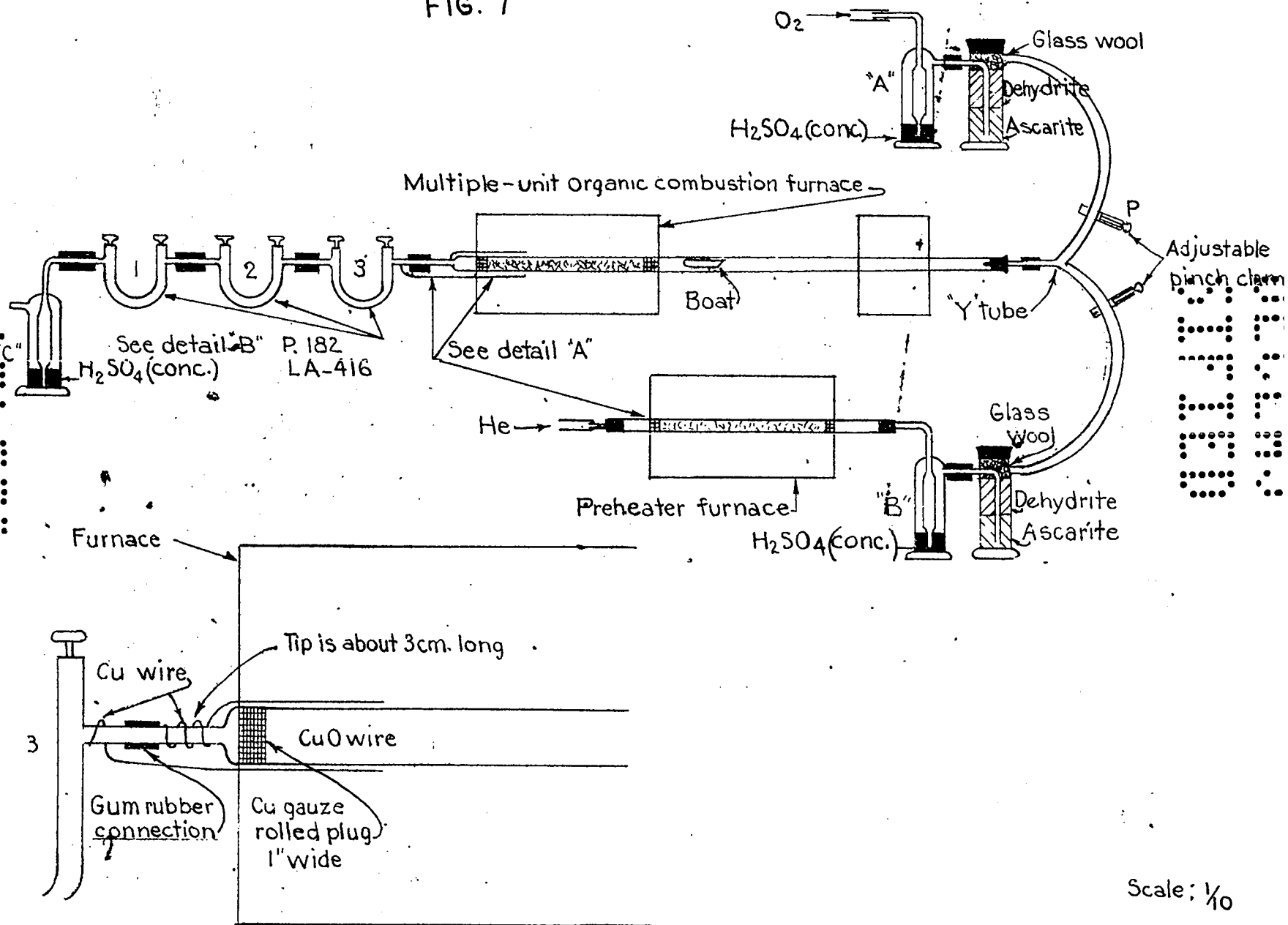
The hydrogen content is usually reported as per cent and is calculated as follows;

$$\text{Wt. (g.) H} \approx \frac{\text{Wt. (g.) increase Dehydrite tube (sample) minus wt. (g.) increase Dehydrite tube (blank)} \times 0.1119}{1}$$

$$\text{Per cent H} \approx \frac{\text{wt. (g.) H} \times 100}{\text{wt. sample (g.)}}$$

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FIG. 7



DETERMINATION OF CARBON & HYDROGEN IN CALCIUM METAL

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ELECTROLYTIC DETERMINATION OF COBALT IN TUNGSTEN-CARBIDE-COBALT ALLOYS

Abstract

The alloy is dissolved in a mixture of hydrofluoric acid and nitric acid. The volatile acids are removed by fuming with sulfuric acid and the residue is dissolved in ammonium hydroxide. Ammonium chloride and sodium bisulfite are added to the solution which is cooled to 10° C and electrolyzed for 45 minutes using a rotating cathode.

Range of applicability, size of sample, accuracy

The method has been used with satisfactory results in the analysis of alloys containing from 1 per cent to 9 per cent cobalt. The weight of sample taken should be sufficient to furnish 60 to 80 mg of cobalt. When more than 90 mg of cobalt is electrolyzed low results are obtained.

The spent electrolyte contains a small amount of cobalt. Except in the most accurate work, however, this amount of undeposited cobalt as well as the small amount of extraneous material (sulfur and tungsten) deposited on the cathode can be neglected since the two quantities are approximately equal.

Reagents

1. HF, concentrated, c.p.
2. HNO₃, concentrated, c.p.
3. H₂SO₄, concentrated, c.p.
4. NH₄OH, concentrated, c.p.

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5. NH_4Cl , c.p.
6. NaHSO_3 , c.p.
7. Ethanol, 95%.

Apparatus

1. Diamond mortar and pestle made of hardened steel.
2. Analytical balance.
3. Platinum beakers, 70 ml. (A crucible will do; it serves better if a lip is made by cold hammering.)
4. Platinum covers, ribbed (Ordinary crucible covers are easily ribbed by cold hammering.)
5. Electrolytic beakers, 200 ml.
6. Steam bath.
7. Hot plate.
8. Ice bath.
9. Thermometer.
10. Platinum gauze electrodes;

Cathode -- gauze cylinder (with blades), length 50 mm., dia. 25 mm., overall length 125 mm.

Anode -- gauze cylinder, length 30 mm., dia. 13 mm.
11. Drying oven.
12. Desiccator.
13. Electrolysis apparatus equipped for stirring (the Electro Analyzer made by the Fisher Scientific Company is well suited when equipped with a variable rheostat to control rate of stirring.).

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Procedure

1. If material has been pressed crush into small pieces in a hardened steel mortar.
2. On a tared watch glass weigh to the nearest 0.1 mg a sample containing not more than 80 mg of cobalt and transfer with the aid of a small brush to a 70-ml platinum beaker.
3. Add to the sample 3 ml of concentrated hydrofluoric acid followed by 5 ml of concentrated nitric acid. Cover the beaker with a ribbed platinum cover and heat until dissolution of the sample is complete. Evaporate the solution to dryness. Add 2 ml of sulfuric acid (1:1) and evaporate to strong fumes of sulfuric acid. Cool, dilute with 1 ml of water, and evaporate to dryness to effect removal of hydrofluoric acid and nitric acid.
4. Cool the residue to room temperature. Dissolve it in concentrated NH_4OH and transfer the solution to a 200-ml electrolytic beaker. Loosen any residue adhering to the platinum beaker by scrubbing with a policeman and using concentrated ammonium hydroxide for rinsing. Use a total volume of about 50 ml of ammonium hydroxide. Add 5 grams of ammonium chloride and 0.5 grams of sodium bisulfite and warm the covered solution on the steam bath until the residue is completely dissolved. Ignore any graphitic carbon and iron which may be present.
5. Remove the solution from the steam bath, add an additional 25 ml of concentrated ammonium hydroxide and cool to 10° C. Electrolyze 45

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minutes using a cathode rotating at about 120 rpm and a current of 0.2 amperes. Without interrupting the current lower the beaker as the cathode is rinsed with a stream of water from a wash bottle. Disconnect the cathode and wash thoroughly with water and then with alcohol to remove the water. Dry the cathode by waving it in air to evaporate the ethanol and then place it in the oven at 105° C for two or three minutes. Cool in a desiccator and weigh. Dissolve the deposit in concentrated nitric acid, wash the cathode in water and alcohol and dry and weigh as before. The difference in weight is equal to the amount of cobalt in the sample.

Calculation and expression of results

The per cent cobalt in the sample is calculated as follows:

$$\frac{\text{Weight cobalt deposited}}{\text{Weight sample taken}} \times 100 = \text{per cent cobalt}$$

References

Brophy, Ind. Eng. Chem., Anal. Ed. 3, 363 (1931)

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FLUORIMETRIC ESTIMATION OF MICROGRAM AMOUNTS OF URANIUM

Abstract

The strong greenish fluorescence of uranyl ion in ultraviolet light is used as a measure of its concentration in solution. Cooling to the temperature of dry ice-methanol mixture enhances the fluorescence. The uranium is contained in either concentrated phosphoric or sulfuric acid since they form a clear glass at this temperature. The amount of uranium present is estimated by visual comparison of the intensity of the fluorescence of the sample with that of known standards.

Applicability

The method has been used routinely for the determination of microgram amounts of uranium in plutonium nitrate solutions, and with the modifications to be described, in gunk solutions, ores and some miscellaneous materials.

Size of sample and limit of sensitivity

Sufficient sample is taken to give not less than 1 microgram of uranium, 10 micrograms being the optimum amount. The limit of sensitivity is about 1 microgram of uranium per ml of solution.

Reagents

1. Phosphoric acid, 85%, c.p. Organic matter is removed by boiling the acid with 30% hydrogen peroxide until it exhibits no fluorescence under test conditions.

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2. Sulfuric acid, concentrated, c.p. Organic matter is removed as for phosphoric acid.
3. Hydrogen peroxide, 30%, c.p.
4. Perchloric acid, 70%, c.p.
5. Uranyl sulfate, c.p. (For preparation of standards).
6. Methanol, absolute, U. S. P.

Apparatus (see Figures)

1. Volumetric flasks, pyrex, glass stoppered, 1 ml.
2. Drying oven.
3. Hot plate.
4. Aluminum heating block.
5. Pocket spectroscope.
6. Small Dewar flask.
7. Ultraviolet source. Westinghouse Type A-H6 Lamp (Hg vapor) used with quartz water jacket.
8. Mirrored concave reflector, 6 in. dia.
9. Metal-case housing for lamp.
10. Solenoid controlled water cooling system.
11. Quartz lens, plano-convex, 70 mm dia., about 10 in. focal length.
12. Lens support.
13. Copper sulfate solution filter -- 3-inch thick.
14. Corning glass filter #986.
15. Cardboard tube, 3-inch dia. x 12 inches, to prevent light scattering.

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-32- FILEDPreparation of standards

1. Prepare a stock uranyl solution by dissolving 0.0864 grams of $UO_2SO_4 \cdot 2 \frac{1}{2} H_2O$ in water and diluting to 1000 ml. This solution contains 50 micrograms of uranium per ml.
2. Into clean 1-ml volumetric flasks transfer by means of micro-pipets aliquots of the stock solution to give two sets each of the following amounts of uranium; 1, 3, 5, 7, 5, 10, 15 and 20 micrograms.
3. Add to each of the above flasks 0.5 ml of phosphoric acid ("organic free") and 2 drops of hydrogen peroxide (30%). Place the flasks in the aluminum heating block and heat at about $150^{\circ}C$ until evolution of oxygen is complete. Cool and repeat treatment with two more drops of H_2O_2 . Cool and fill to the mark with "organic free" phosphoric acid. Heat about an hour at about $185^{\circ}C$ to remove excess water, cool and stopper the flasks.
4. Turn on the ultraviolet light and turn off all room light. It is essential that the room be dark. Cool the flask to be examined for 3 to 4 minutes in the dry ice-methanol bath. When sufficiently cooled the solution will solidify to give a clear hard glass with a rather pointed cone shaped meniscus.
5. Look through the pocket spectroscope at an ordinary fluorescent light with the spectroscope held so that the red end of the spectrum is on the left. Adjust the slit width so that the sharp yellowish-green band appears to be about 1 mm wide.
6. Remove the flask from the bath and hold at the focal point of the

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ultra-violet light. Examine the fluorescent light emitted by the uranium by looking through the spectroscope held within 1 cm of the flask. ⁵⁾

7. Prepare and study the various standards as above. Preparation of duplicate sets of standards is a good practice when learning the technique since it will help eliminate errors due to faulty preparation. Considerable practice is required and the personal factor is large. Two experienced analysts, however, will usually not be in disagreement by more than 1 microgram over the range 1 to 15 micrograms.

5)

The spectrum of the uranyl ion shows a set of five or six narrow bands, beginning at about 4900 Å and extending toward the red. The second band at about 5100 Å is the most intense, the succeeding bands decreasing steadily in intensity (see literature reference 3 on page). Visual examination with the pocket spectroscope usually reveals no more than four bands. Those on the right (the violet end of the spectrum) are of a wave length that do not affect the eye as much as those on the left. With less than 2 micrograms of uranium only the two bands on the left may be visible. Therefore, both the number and intensity of the bands are an aid in determining the amount of uranium present.

If organic matter has not been completely removed by the peroxide treatments there will be a uniform green fluorescence over the entire field. This may be strong enough to obscure the uranium bands or merely enough to cause uncertainty of the intensity of the bands due to the green background. In any case it must be completely eliminated for an accurate evaluation of the intensity of the uranium bands. A drop of 70% perchloric acid may be added to help oxidize the organic material.

Nitrate ion is said to quench the fluorescence of the uranyl ion but is effectively removed by the above treatment. The effect of a large number of other ions on the fluorescence of uranyl ion in aqueous solutions has been investigated by Finecke and Harms (literature reference 1) and Sill and Peterson (literature reference 2).

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Procedure for plutonium nitrate solutions

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1. Into a clean 1-ml volumetric flask pipet sufficient sample to contain about 10 micrograms of uranium.
2. Evaporate the solution to dryness at 105°C in an oven.
3. Allow the flask to cool and add 2 drops of "organic free" phosphoric acid and 0.5 ml of 30% hydrogen peroxide. Heat in the oven at 105° C until the peroxide is removed.
4. Repeat the addition and evaporation of peroxide.
5. Fill to the mark with "organic free" phosphoric acid and compare the intensity of the fluorescence produced in ultra-violet light with the standards as described above.

Procedure for ores, etc.

1. Bring the material into solution by an appropriate method -- acid attack or fusion as may be required. Run the analysis in triplicate, spiking one of the samples with a few micrograms of uranium to determine the per cent recovery in the procedure.
2. With high silica ores it is best to remove the silica by dehydration and filtration in the usual way since large amounts of insoluble material would be troublesome in the extraction procedure to follow.
3. After removal of the silica, evaporate the solution to remove excess acids and make the solution 3 M in nitric acid. Extract the uranium by shaking

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the solution in a separatory funnel with an equal volume of ether for 15 minutes. Repeat the extraction two more times, discard the aqueous phase, and evaporate the ether phases to dryness on the steam bath.

4. Take up the residue in a little dilute phosphoric acid and transfer to a 1-ml volumetric flask. Remove the water by evaporation in an oven at 105° C, cool, add 0.5 ml of 30% hydrogen peroxide and repeat the evaporation. Repeat the peroxide treatment and finally heat with a drop of perchloric acid to remove the traces of organic matter. Fill to the mark with "organic free" phosphoric acid and determine the uranium as described above.

Precautions

1. The volumetric flasks used must be free of any uranium contamination and should be tested under ultra-violet light before use.
2. The solution must be free of organic matter and nitrates.
3. The solution must be cold when examined as the intensity of the fluorescence decreases rapidly as the solution is allowed to warm.
4. Excess water must be removed by heating as described above. Otherwise the solution will crystallize and some of the emitted light will be absorbed and scattered by the crystals.
5. The room must be dark, and a few minutes should be allowed for accommodation of the eyes to the darkness before examination of the sample.
6. With use, the ultra-violet lamp will weaken and samples will appear to contain less uranium than when examined when the lamp is new. This results in a loss in sensitivity. Furthermore, it makes unwise the practice of memory

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comparison omitting the use of the standards. With experience, this can be done without any appreciable loss in accuracy; but the standards should be examined frequently to assure that the lamp has not weakened considerably.

Calculations and expression of results

1. Plutonium nitrate solutions

The uranium is reported as ppm based on plutonium and is calculated as follows:

$$\frac{\text{micrograms uranium in aliquot} \times 10^3}{\text{mg. Pu/ml. of solution} \times \text{volume of aliquot (ml.)}} = \text{ppm uranium}$$

3. Ores, etc.

The uranium is reported as ppm and is calculated as follows:

$$\frac{\text{micrograms of uranium}}{\text{weight sample (g.)}} = \text{ppm uranium}$$

Literature References

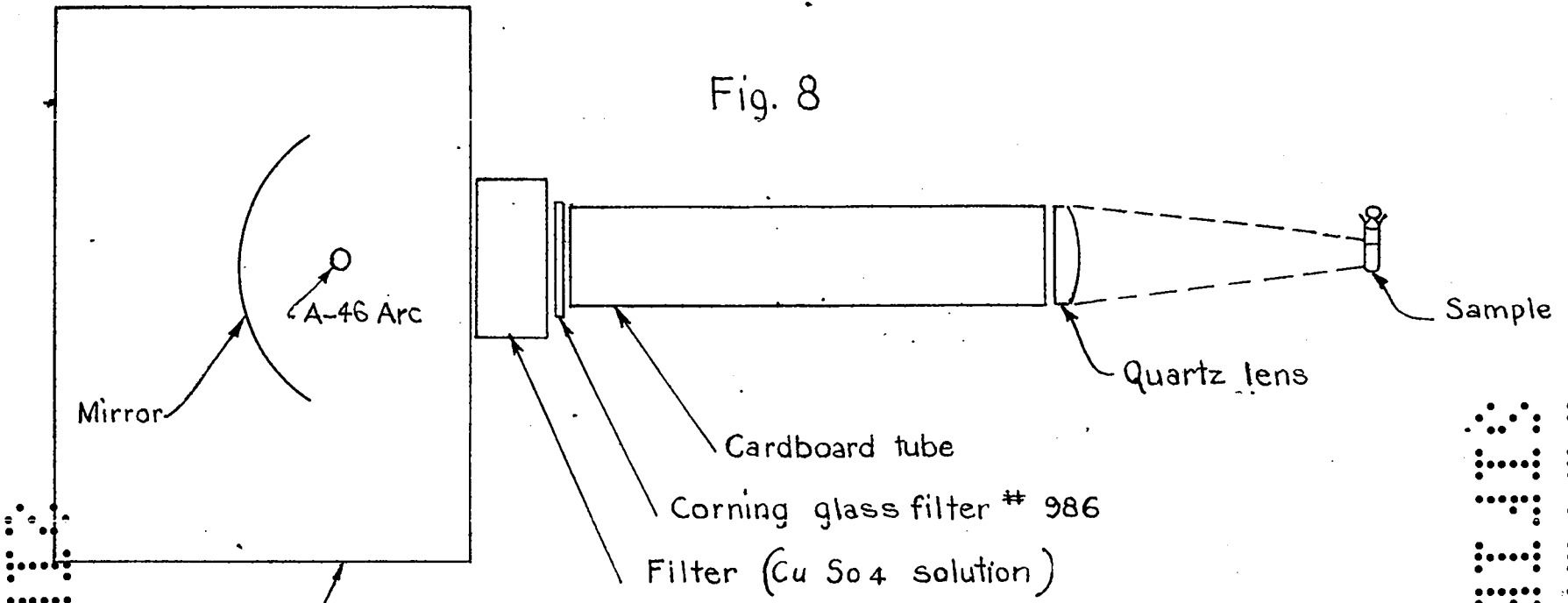
1. Eineke, E., and Harms, J., Z. Anal. Chem. ; 99, 123-128, (1934)
2. Sill, C. W., and Peterson, H. E., Bureau of Mines Information Circular 7337, August 1945
3. Project Report IA-15

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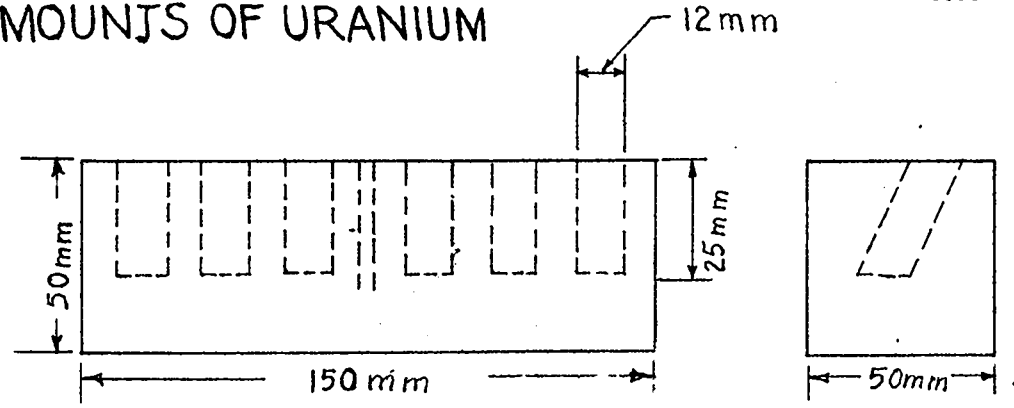
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Fig. 8



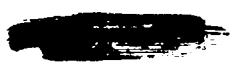
FLUORIMETRIC ESTIMATION OF MICROGRAM AMOUNTS OF URANIUM

Fig. 9



Aluminum heating Block

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LA - 416 REVISIONS AND CORRECTIONS

Procedure II B

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References Add LA - 386 (Terminal Report)

Procedure II C

p 31

Step 3. Withdraw an aliquot equivalent to about 5 mg. of metal, add 200 microliters of 6 N HCl, dilute to 1 ml. in a 1-ml. glass stoppered.....

Step 4. Dissolve 1.0 g. of the ammonium salt in 10 ml. of water... Add about 30 drops of constant boiling.....

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Step 5. Add 7 drops of the above ether solution per 5 mg. of plutonium to the diluted aliquot and

Step 7. (last sentence) Dissolve any residue which may appear by addingand evaporate just to dryness in the infra red drying chamber.

Step 8. (last sentence) Withdraw the solution, using a 0.05 ml. micro pipet and coat it on a pair of copper electrodes.

Step 9. Rinse the crucible with 0.05 ml. of quartz distilled 6 N HCl and add the solution to the copper electrodes.

Step 10. Delete the first sentence.

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References Add LA - 387 (Terminal Report)

Procedure II D

pp 38-43

The procedure as outlined does not give consistent results on beryllium and aluminum. It is believed that the acidity must be very carefully controlled to prevent the co-separation of these elements with plutonium in Step 4. A revised procedure will be issued at a later date.

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Procedure II E

p 47

- Step 2. (second sentence) With the electrolytic cell immersed in a beaker of cold water, electrolyze at 0.2 to 0.6 amps.....
- Step 5. (third sentence) Assemble the gas line to the syphon and open the stop cock on the latter.....

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- Step 14 (last sentence) If necessary draw out the tip of the pipet or wax it lightly with a high melting wax.

p 53

Precaution 3. Neutralize....., NO_3^- etc. in excess of 0.005 milliequivalents.....

Procedure II F

p 61

- Step 8. (third sentence) Continue the exposure during the presilent and silent periods.....
- Step 9. (insert after third sentence) Place the film in 0.5 per cent acetic acid short stop for 10 seconds.

An alternative procedure by means of which the complete spectrum (2250-7100 Å) of a sample may be obtained in a single exposure (on 103 a-F film) using only one spectrograph is described in Project Report LA-257.

Procedure II I

p 74

Paragraph 2. (last sentence) The precision averages about 9 per cent (average deviation from the mean) by the internal standard method.

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Footnote. If beryllium is not to be determined and if spectra are to be evaluated by the internal standard procedure (part 10 B below), the gallium oxide should be first ground with Bi_2O_3 , BeO , Au_2O_3 and MoO_3 in amounts to give a mixture containing 8 micrograms of bismuth, 0.8 micrograms of beryllium, 0.8 micrograms of gold and 40 micrograms of molybdenum in each 2 mg. of gallium oxide.

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Paragraph B (third sentence) Select internal standard lines (Bi, Mo, Au or Be) which lie reasonably close to the analysis lines chosen.

(insert after third sentence) Also try to select for comparison the particular internal standard element which volatilizes at about the same temperature as the element being determined.

An alternative procedure, used in analyzing samples in which gallium is to be determined, substitutes silver chloride for gallium oxide. Standard and sample oxide mixtures are made up to contain 4 per cent silver chloride in place of 2 per cent gallium oxide. The limit of sensitivity for gallium by this procedure is about 6 ppm. Sensitivities for other impurities are essentially the same as those given on page 75.

Procedure III D

p 110

Reagents

6. NH₃ solution, 1.5 N. This is prepared by diluting 50 ml. of analytical reagent 30 per cent NH₃ to 500 ml.

Procedure

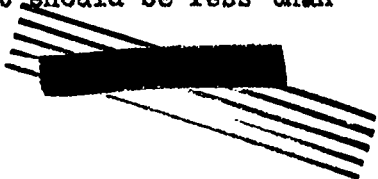
Step 4. Add 1 ml. of 1.5 N NH₃ and again mix thoroughly.

Procedure III E

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Reagents

2. Nitric acid, The boron content should be less than 0.1 micrograms per ml.



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