[redacted] UNCLASSIFIED

[redacted]

LA REPORT 416

[redacted]

October 1, 1945

This document contains 182 pages

CHEMICAL AND SPECTROCHEMICAL ANALYSIS OF URANIUM AND PLUTONIUM MATERIALS

MANUAL OF PROCEDURES

Contributing Authors

E. C. Anderson
Myrtle C. Bachelder
L. M. Berry
H. E. Boaz
J. J. Chap
J. G. Conway
R. J. Gettens
R. C. Hirt
W. H. Langham
C. F. Metz
J. P. Miller
N. H. Nachtrieb
L. P. Pepkowitz
H. A. Potratz
O. R. Simi
R. W. Spence
W. H. Throckmorton
S. Wexler
B. S. Wildi
Elizabeth D. Wilson

[redacted]

[redacted] UNCLASSIFIED

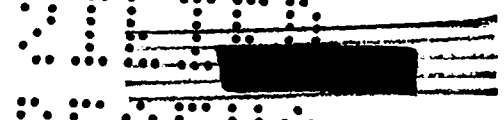
[redacted]

MANUAL OF PROCEDURES

TABLE OF CONTENTS

I

PREPARATION OF PLUTONIUM SAMPLES FOR ANALYSIS



PREPARATION OF PLUTONIUM SAMPLES FOR ANALYSIS

A. General Health-Safety Rules

It should be well understood that for health safety purposes extreme care should be taken in handling plutonium metal and its compounds. Every precaution must be taken to avoid ingesting or inhaling them, even in most minute quantities. When handling plutonium in the small amounts required for analytical procedures, the operator should follow carefully the instructions given in "Health Safety Rules for Chemistry and Metallurgy Division", (revision of 8/16/44).* These cover protective clothing, respirators, use of dry boxes, accidents, laboratory and personal cleanliness. Special precautions to be observed in certain analytical procedures are included in the sections below:

B. Sampling of Plutonium Metal and Compounds

All operations requiring cutting, sawing, or breaking off of metal or requiring transfer of powders must be done in an approved dry box. During these operations, the operator is protected with respirator, cotton overalls, head cover and rubber gloves. Since the insides of the dry box gloves are often contaminated, the operator should wear rubber surgeons gloves and tuck sleeves of the coveralls into the cuffs of the rubber gloves while working in the dry box.

The method of cutting plutonium metal depends on whether it is α or δ phase metal:

1) α-phase plutonium is very brittle and large pieces can usually be shattered into smaller sizes by means of a diamond mortar. The smaller pieces can then be cut to the desired size with a pair of diagonal cutting pliers,

* See also J. F. Tribby, "Memorandum to CM Division Group Leaders: Procedure on handling of contaminated objects" (May 18, 1945)

but care must be taken to prevent loss of small pieces during the operation.

2) δ-phase metal is very soft. Large pieces can best be broken up by first flattening them in the diamond mortar to a thickness of a few millimeters, so they can be broken in two with two pairs of blunt-nosed pliers. When the pieces are small, they can be cut with diagonal cutting pliers.

C. Electrolytic Polishing of Plutonium

The purpose of electrolytic polishing is to remove any surface film of impurities which may adhere to the samples (e.g. slag or oxide). The apparatus for the polishing operation, together with an analytical balance on which the polished samples are weighed, is set up under a good hood. The sample which has been transferred from the dry box to the hood in a closed screw cap vial or weighing bottle, is removed from its container and is placed in a tungsten wire basket, surrounded by a cylindrical platinum cathode, and immersed in a 50:50 mixture of ethylene glycol and syrupy phosphoric acid (Figure 1.). Current is supplied by a 6V storage battery. During the operation of cleaning, the main danger comes from the spray carried out of the electrolyte by the evolved gases. The sides of the glass container should extend 3 cm. or more above the surface of the electrolyte. A respirator or face shield must be worn at all times. The sample is electrolyzed until it is bright and silvery (about 2-4 minutes for samples that weigh less than 150 mg.). If the electrolysis is continued too long, the sample may again turn black. The positive terminal (Pt cylinder) is disconnected and the terminal clamp is raised to lift the basket out of the electrolyte. The piece of metal can then be removed. The sample is immediately immersed in concentrated HNO_3 to rinse off the electrolyte. It is then washed in water and finally in acetone, allowed to dry on a piece of hardened filter paper, and transferred to a tared watch glass if it is to be weighed under the hood, or to a tared screw cap vial or weighing bottle if it is to be weighed outside the hood. In the case of δ-phase samples, it is found that rapid

surface oxidation occurs when the sample is washed with water. If the sample is intended for O_2 analysis, this nullifies the effect of polishing. This can be avoided by omitting the water wash, and using acetone both to rinse off the HNO_3 and to dry the sample.

In transferring the sample every possible precaution must be observed to avoid dropping it. The α form of plutonium is very brittle and small chips may easily be broken off unless great care is used in handling. The metal should be held in the forceps as short a time as possible. If it is to be transferred to a balance for weighing under the hood, it should be placed on a watch glass during transit and should never be carried in the forceps even if the distance to the balance case is only a few inches. A sample, when it is to be removed from the hood (or dry box), must be placed in a closed container.

D. Methods for Dissolving Plutonium Metal

Plutonium metal dissolves in HCl, HI, HBr, $HClO_4$ and Br_4 with vigorous evolution of gas. It dissolves slowly in H_2SO_4 but is practically insoluble in HNO_3 and H_3PO_4. Metal samples are most frequently dissolved in HCl. Danger from spattering during solution in acid increases with sample size; precautions required when handling large samples are considerably greater than when handling small ones. These precautions, necessary to avoid loss of material from spray and spatter in dissolving operations, have become, to an extent, standardized.

Apparatus and reagents:

1 ml. pyrex volumetric flask (test tube shape) for small samples.

Solution vessel for larger samples (Figure 2).

Misco pipets, 50λ.

Constant-boiling HCl, distilled and stored in quartz.

Procedure for small samples (50 mg. or less):

Working under a well-ventilated hood transfer the metal sample from its

container to a 1 ml. volumetric flask and add 2-3 λ or more of constant-boiling HCl per milligram of metal. If the sample is of the order of 50 mg. and requires 100-150 λ of acid do not add the acid at once but divide and add in two or three portions. If the acid is run slowly down the side of the flask the stopper may be inserted before spattering starts. Wait until the action has subsided or stopped before adding more acid. If the sample is to be diluted with water wait until evolution of gas has ceased before adding the water; this is to avoid formation of a black precipitate of plutonium dioxide.

Procedure for large samples (greater than 50 mg.):

Place the sample in the special solution vessel (Figure 2) and add the acid with either the attached pipet or the Misco pipet. After evolution of gas has ceased and solution is complete, transfer the solution to the desired container with a syringe pipet or other suction apparatus. DO NOT POUR THE SOLUTION!

E. Methods for Dissolving Plutonium Tetrafluoride

Because this compound is a fine powder all transfers to solution vessel or other container must be made in a dry box by an operator properly protected with gloves, coveralls and respirator. Before removing the sample from the dry box in a beaker or other container which cannot be tightly stoppered, it is necessary to wet the sample down with acid or water to prevent air currents from blowing it into the laboratory. In addition, it is good practice to cover the beaker with a piece of Parafilm before removing it from the dry box.

Several methods of solution are available; the choice depends upon what is to be done with the dissolved sample.

1. Hot concentrated sulfuric acid. This dissolves plutonium tetrafluoride within a few hours but the resulting stable complex is undesirable for some analytical procedures.

2. Hot concentrated nitric or hydrochloric acid. Heating with these acids in an open container may require up to several days for complete solution.

3. Hydriodic acid or oxalic acid followed by concentrated HNO_3. When the tetrafluoride is boiled with these reagents in this order the solution period is less than one hour.

4. Hot acid in sealed tube. This is a most satisfactory method for dissolving plutonium fluoride and other difficultly soluble compounds. The procedure is as follows: Prepare a heavy wall pyrex tube (5 mm. i.d. and 11 mm. o.d.) about 8 inches long by sealing off one end, taking care to avoid bubbles in the seal. Transfer the sample into the tube and add 0.5 ml. of either concentrated hydrochloric or nitric acid. Cool the lower end of the tube with liquid nitrogen or dry ice until the contents are frozen; seal off the open end and place the tube in a metal bomb and heat in an oven at 100° C. Solution in HCl is complete in a few minutes but in HNO_3 an hour or two is required. To remove the sample after solution, again freeze the contents, crack the sealed end of the tube with a file and hot rod and transfer the solution with a syringe pipet.

F. Dissolving Plutonium Oxide

The same precautions are to be observed as in handling plutonium tetrafluoride. Hot concentrated sulfuric acid will dissolve black oxide but may or may not dissolve the yellow oxide. The sealed tube technique employing HNO_3 or HCl is satisfactory if the temperature is maintained at about 200° C.

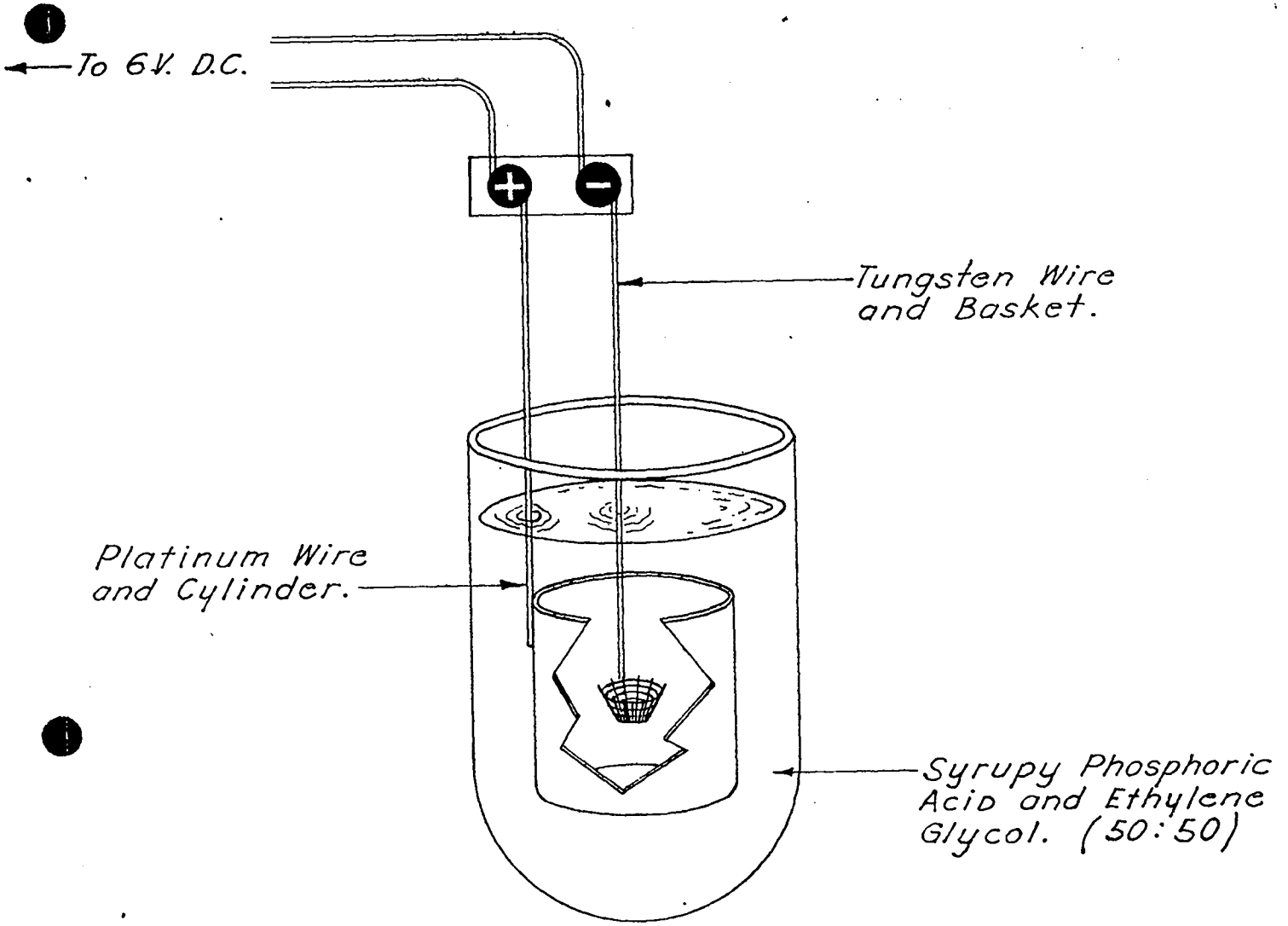


FIGURE: 1 ELECTRO-POLISHING APPARATUS

SCALE: APPROX. FULL SIZE

PREPARATION OF PLUTONIUM SAMPLES FOR ANALYSIS

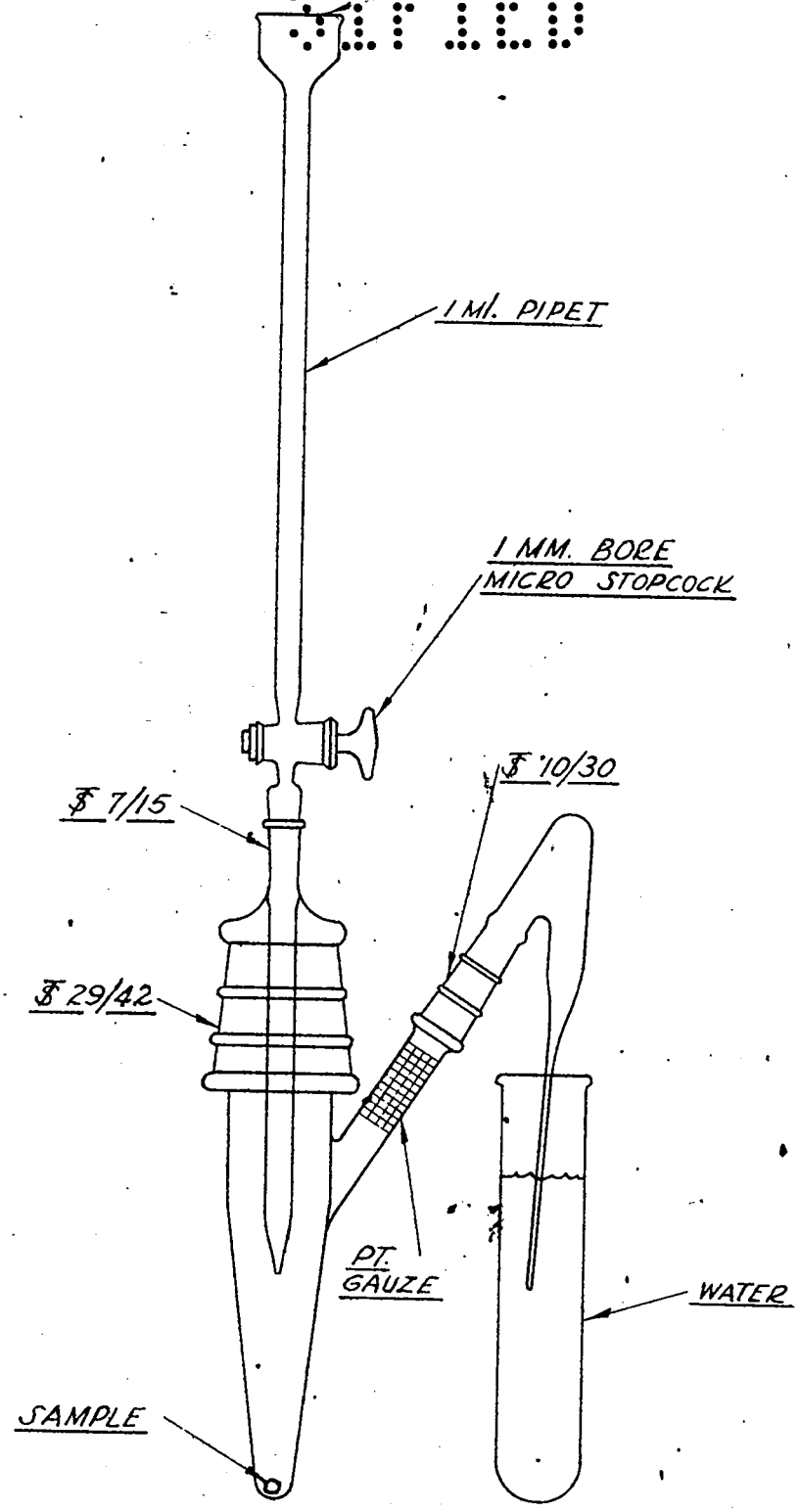


FIGURE: 2 – SOLUTION VESSEL

SCALE: APPROX. HALF SIZE

PREPARATION OF PLUTONIUM SAMPLES FOR ANALYSIS

II

SPECTROCHEMICAL PROCEDURES

II A-1

SPECIAL HEALTH SAFETY PRECAUTIONS TO BE OBSERVED IN SPECTROCHEMICAL ANALYSIS OF PLUTONIUM METAL AND ITS COMPOUNDS

Plutonium metal and its compounds are handled in the spectrochemical laboratory in three essentially different procedures, and the safety precautions to be observed are discussed below under the topics: "Pyro-electric Method", "Direct Spark Method" and "Cupferron Method".

1. Pyro-electric Method

Material received for analysis by this method is in the form of oxide, metal, or nitrate solutions. The conversion of metal into oxide, the compound required by the method, is carried out in a dry box which also serves to house the arc source, a balance, and all tools necessary for the preparation of the sample for arcing. Figure 1 is a view into the left side of the dry box in which the operations of sample oxidation, weighing, grinding, and electrode-loading are carried out. Samples are admitted into this chamber through a double-door vestibule at the left of the box; at least one of the doors must always be closed. The operator, wearing a tightly fitting dust respirator, inserts his gloved hands into tightly fitting gauntlets in the front of the box.

Metal specimens are transferred from their vials to small platinum crucibles in a micro-furnace and ignited at 700-800° C. until conversion to the black oxide is complete. Nitrate solutions, on the other hand, cannot be evaporated in the dry box, which has no exhaust facilities. They are evaporated to dryness in platinum crucibles under an infra-red lamp in a well-ventilated hood and then transferred to the dry box in a nest of alternately inverted beakers. There the conversion to oxide is completed in the micro-furnace.

2 mg. quantities of gallium oxide and 73 mg. of uranium oxide (U_3O_8) are weighed into vials on an analytical balance and introduced into the dry box.

25 mg. quantities of plutonium oxide are weighed out on a torsion or assay balance in the dry box and there ground with the gallium oxide-uranium oxide mixture. The well-ground mixtures are placed in electrode craters in the dry box and transferred in electrode holder blocks to the arc chamber through the door of the separating partition. Great care should be exercised to minimize spillage during the weighing, grinding and transfer operations.

Samples are arced in the conventional pyro-electric manner, the operator continuing to wear a dust respirator (Figure 2). Each electrode is returned to its position in the electrode holder block after arcing and, at the conclusion of a series, the block is returned to the left compartment of the dry box. There each electrode pair is placed in a vial for transport to recovery. The operator should present himself for a "nose count" as soon as possible after arcing a series of samples.

Occasional accidents will occur in which an electrode may be dropped and its contents spilled upon the floor of the dry box; small losses may occur during weighing and grinding. These mishaps are inevitable in routine operation, although every effort should be made to minimize their number. It is therefore necessary to have the interior of the dry box decontaminated at frequent intervals. At such times a decontamination squad, equipped with dust respirators, rubber gloves, and laboratory coveralls should remove a window from the dry box and gather up the spilled material with brushes and moistened cheese cloth. A warning red light on the outside of the room door should be turned on to indicate that entry into the room is prohibited during such times. Following clean-up of the box interior and replacement of the window, the floor and exterior of the dry box should be monitored with a portable alpha-counter ("Pluto"). As a final precaution, the room should be left uninhabited for several hours following decontamination to allow any active dust to settle.

2. Direct Spark Method

Materials received for analysis by this method consist of metal, tetrafluoride, or nitrate solutions. See pp I-3 - I-5 (this Manual), for precautions to be observed in dissolving plutonium metal and tetrafluoride.

Beyond the dissolving operations, safety precautions are to be observed at two stages: (a) evaporation of solutions on electrodes and (b) sparking of electrodes.

(a) Concerning the first -- the evaporations should be carried out under infra-red lamps in a well ventilated hood by an operator wearing rubber gloves, a dust respirator or plastic face shield, and a laboratory garment which covers the arms and trunk completely. The rate of evaporation should be regulated by a Variac in series with the lamps so that spattering never takes place. All equipment used for the evaporation should rest in a stainless steel tray in the hood, so that in event of spillage the contamination area is confined. The hood and equipment should be monitored regularly to detect the rise of contamination and decontamination carried out when counts of $100/dm^2/min.$ are exceeded.

(b) Precautions to be observed in the sparking of electrodes are two-fold: electrical and chemical. The operator should realize that the danger of receiving a fatal shock is ever-present around the spark source and chamber. The case of the spark source and chamber and the bed of the spectrograph have been grounded, but the operator should inspect the ground connections to see that they are intact before operating. Evidence of frayed cables or loose contacts on the high voltage leads should be repaired immediately or called to the attention of the supervisor for repair. Evidence of anything abnormal in the behavior of the

equipment (Odor of burning insulations, stray sparks or corona discharges at connection points, and irregular sounding spark discharges) should be called to the attention of the supervisor for repair. The floor upon which the operator stands should be clean and dry. Under no conditions should the operator stand in water left from mopping the floor. As a final precaution the operator should avoid unnecessary body contact with the case of the spark source, chamber, or spectrograph during operation.

Regarding safeguard from the radio-chemical standpoint, the operator should wear rubber gloves, a dust respirator, and a full length laboratory smock while sparking electrodes. Electrodes bearing any quantity of radioactive material whatsoever should be sparked inside the chamber provided (Figure 3). Its door must be tightly closed except when electrodes are being inserted or removed. Electrodes must be handled only with pliers or forceps reserved for active materials. Electrodes which have been sparked may still bear some activity, and should not be mixed with uncontaminated electrodes. They should be placed in a beaker, and the contamination removed by dissolving in 1:1 nitric acid, the solution being saved for recovery. Electrodes, decontaminated in this way, may be re-used.

Regular checks of the activity of the floor, tables and optical bench should be made with a portable alpha counter and decontamination carried out when indicated. The spark chamber and all tools used in connection with the sparking of active materials must be regarded as contaminated and should be touched only with gloved hands.

Hands should be checked for contamination following use of the equipment and thoroughly scrubbed with soap and water if any is

detected. Nose counts should be taken after active electrodes are sparked.

3. Cupferron Method

Material received for analysis by this method is in the form of nitrate or chloride solutions. Metal or tetrafluoride samples will have been dissolved elsewhere, and by the procedure described in pp I-3 - I-5 of this Manual. The operator must wear rubber gloves and a full-fitting laboratory coat while carrying out the chemical separations in a well-ventilated hood (Figure 4). Care should be taken in the evaporation of solutions that no spray be given off. Frequent monitoring of the glass floor of the hood should be made to detect the activity resulting from accidental spillage.

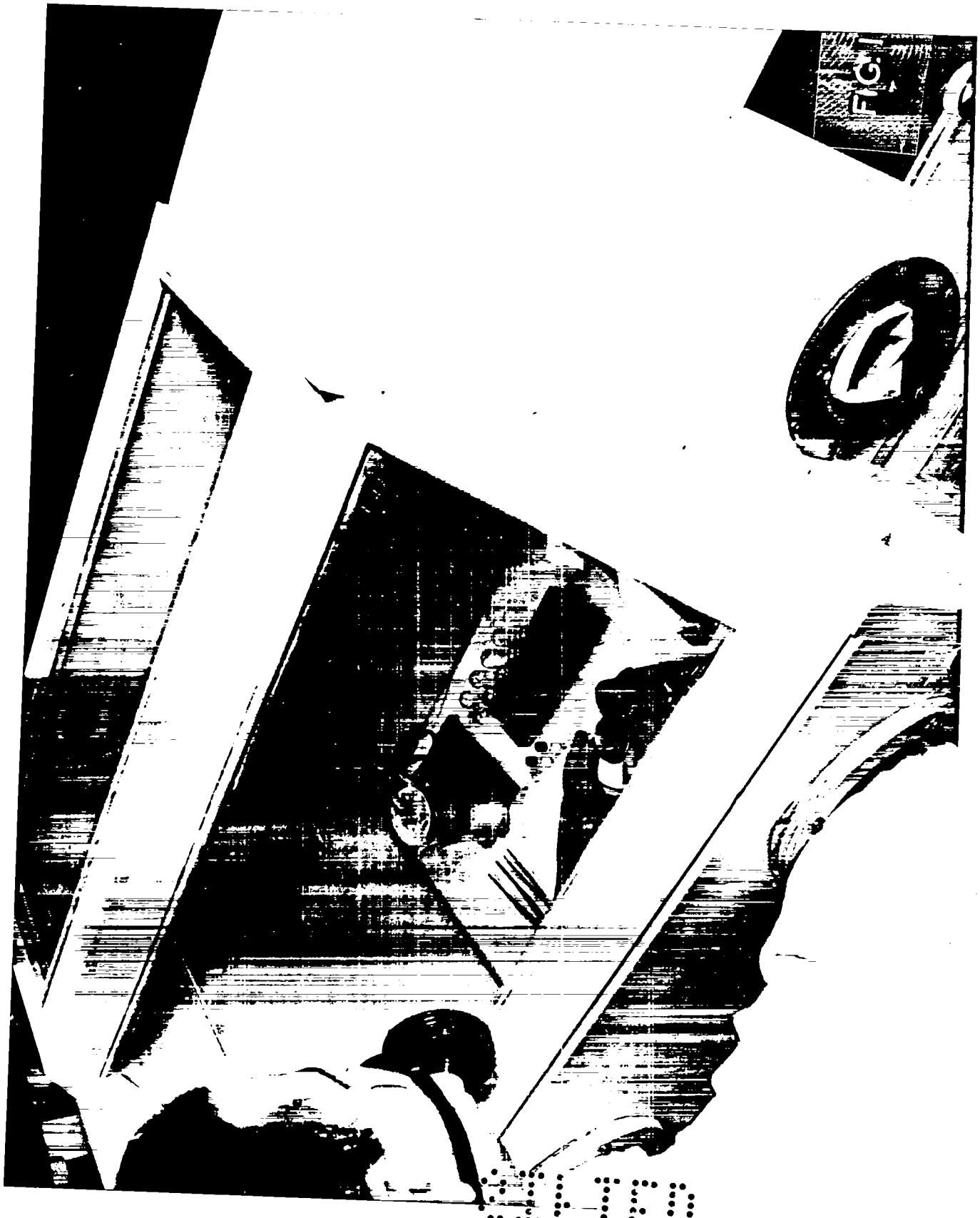
For precautions to be observed in sparking electrodes see (b) under "Direct Spark Method" above.

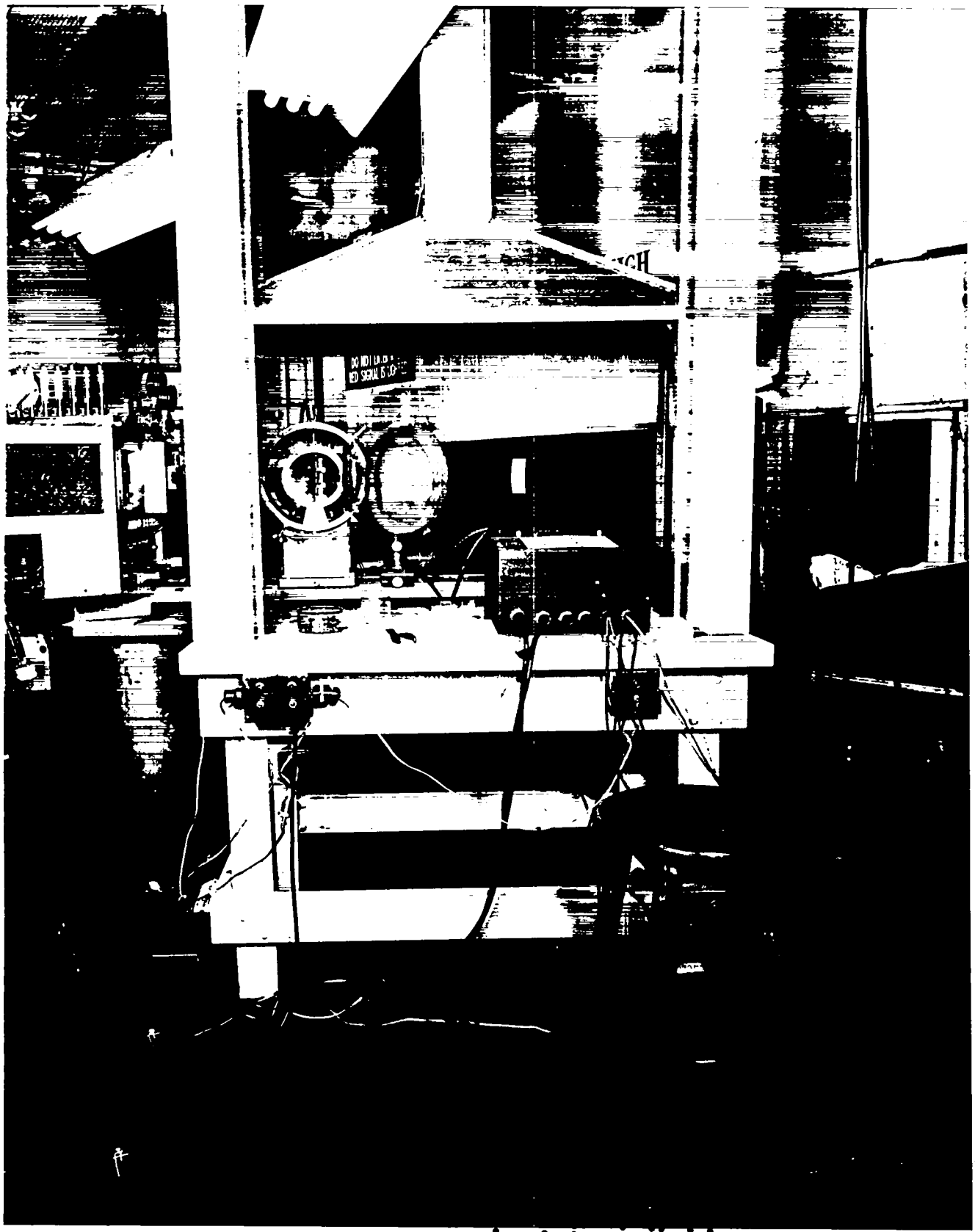
* * * * * * * * * * * * * * *

All individuals carrying out analytical operations on plutonium materials should present themselves daily for a nose count. Weekly urine specimens must be submitted to detect at the earliest time evidence of pathological damage.

Figures

1. View into interior of a dry box showing operator grinding a sample in preparation for analysis.
2. View showing operator preparing to arc a sample in the dry box.
3. Lateral view into hood showing double compartment spark chamber (with doors open).
4. Specially ventilated hood for carrying out chemical separations of plutonium and its compounds. The safety glass front comes between the face of the operator and his work.





[redacted]

SPECTROCHEMICAL DETERMINATION OF INTERMEDIATE AND HEAVY-ELEMENT IMPURITIES IN PLUTONIUM METAL AND COMPOUNDS BY THE DIRECT COPPER SPARK METHOD

Abstract

A hydrochloric acid solution containing fifty micrograms of plutonium is evaporated on copper electrodes and the spark spectrum photographed in the range, 2500 A° - 5000 A°. The quantity of impurities present is estimated by comparison of the densities of their spectrum lines with the corresponding lines of standard spectra photographed on the same plates.

Limits of Sensitivity (based upon analysis of 50 micrograms of metal)

Element	ppm first order
Be	10
Mg	100
Al	200
Ca	100
Ti	1000
V	---
Cr	200
Mn	200
Fe	400
Co	---
Ni	---
Zn	4000
Zr	1000
Mo	---
Cd	1000
Sn	2000
La	2000
Ce	1000
Bi	200
Th	4000

Reagents

1. Constant-boiling HCl, distilled from and stored in quartz vessels.
2. Nitric acid, distilled from and stored in quartz vessels.
3. Water, distilled from and stored in quartz vessels.

Apparatus and Materials

1. 1 ml. glass-stoppered pyrex volumetric flasks.

[redacted]

2. Misco syringe and 50 micro-liter pipet tips.
3. 1 ml. platinum crucible.
4. Electrode evaporator.*
5. ¼" dia. x 1½" long copper electrodes. Ends should be freshly faced on lathe and sides machined lightly to a distance of ½" back from end.
6. Spark discharge chamber (Figures 1 and 2).
7. 4" x 10" 103-0 photographic plates.
8. Wadsworth fully automatic stigmatic grating spectrograph, 21' grating, 15,000 lines per inch. (Jarrell-Ash Co.)
9. Dietert spark unit.
10. Dietert rocking developing machine.
11. Bausch and Lomb viewing box.

Procedure

HEED HEALTH SAFETY RULES OUTLINED IN SECTIONS I AND II A.

1. If metallic, weigh out a 500 microgram sample and dissolve in the smallest possible quantity of constant-boiling HCl. Dilute to volume with quartz-distilled water in a 1 ml. glass-stoppered pyrex volumetric flask. Examine the solution critically for undissolved material; if a residue remains, shake the solution until it is uniformly dispersed throughout and rapidly withdraw a 50 micro-liter aliquot. Transfer the aliquot to the top of a copper electrode and evaporate it to dryness in an electrode evaporator. Prepare two such electrodes.
2. If the sample is an HCl-soluble salt, weigh out a quantity equivalent to 500 micrograms of metal and dissolve. Proceed as above.
3. If the sample is insoluble in HCl but soluble on digestion in HNO_3 (e.g.

* For illustration of infra-red electrode evaporator see Figure 3, "Spectrochemical Determination of Impurities in Plutonium Metal and Compounds by the Copper Spark-Cupferron Extraction Method."

plutonium tetrafluoride), weigh out a quantity equivalent to 500 micrograms of metal in a 1 ml. platinum crucible. Add the smallest possible quantity of quartz-distilled HNO_3 that will dissolve the sample on digestion under an infra-red lamp; evaporate the resulting nitrate solution just to dryness. Add 50 micro-liters of constant-boiling HCl and dilute to 1 ml. with quartz-distilled water in a 1 ml. glass-stoppered volumetric flask. Proceed as above (1).

4. Prepare a series of copper electrode pairs bearing the following total weights of the elements of interest: 1.0, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.002, 0.001 micrograms and reagent blank. This is most conveniently done by starting with a stock solution containing 1 mg. per ml. of the following elements in 1:1 HCl: Be, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Zr, Mo, Cd, Sn, La, Ce, Bi, and Th. Dilute a 5 ml. portion of this stock solution to 50 ml. in a glass-stoppered graduated cylinder with quartz-distilled water; this solution contains 100 micrograms per ml. Transfer a 5 ml. aliquot of this solution to another 50 ml. cylinder marked No. 1 and dilute to volume. Prepare succeeding standard solutions in accordance with the following table:

Cylinder No.	Dilute ( ) ml. of Cyl.	(No.) to 50 ml.	Micrograms/ml.
1	-	-	10
2	25	1	5
3	20	2	2
4	25	3	1
5	25	4	0.5
6	20	5	0.2
7	25	6	0.1
8	25	7	0.05
9	20	8	0.02
10	25	9	0.01

Use 100 micro-liters of each standard solution per electrode pair to prepare electrodes bearing a total of 1.0, 0.5, etc. to 0.001 micrograms of each

element. Evaporate the solutions on the copper electrodes in the same manner as for samples, using the infra-red electrode evaporator or the nichrome coil evaporator. Prepare each standard solution fresh each day to avoid losses in strength due to hydrolysis or adsorption.

5. Set the Dietert spark unit to give the following conditions: power in-put, 2 KVA; inductance, 8; in-put voltage, 230; rotary gap, 10; primary voltage, 95 - 100.

Set the timer relay for an exposure of 60 seconds. Close the slit of the Wadsworth spectrograph to 25 microns. Insert a pair of copper electrod into the holders in the discharge chamber and align them laterally and vertically at a separation of 2 mm. by projecting their shadow-image on the alignment screen on the optical axis behind the chamber. Strike a spark between the electrodes, and open the spectrograph shutter. Remove the camera from the back of the instrument and observe the spectrum in the visible region with a hand lens through the camera port. This is a check on the electrode alignment, and should reveal the full slit height lines as uniformly bright along their length. Set the Hartmann diaphragm to give lines 2 mm. tall and load the camera with 2 103-O plates. Set the camera to photograph the range, 2500 Å - 5000 Å.

6. Insert the 1.0 microgram standard copper electrodes in the holder in the discharge chamber, close the door of the latter, and pass nitrogen through the chamber for one minute. Stop the flow of nitrogen, open the spectrograph shutter and strike the discharge. Rack the plate up 3 mm. and repeat the operation for succeeding standards. Spark the sample or samples about mid-way between the first and last standard.

7. Develop the plates in total darkness for 5 minutes at 18.0° C. in Eastman D-19 using rocking development. Fix in F-5 for 10 minutes after immersion

in an acetic acid short stop for about 10 seconds. Wash plates in a vertical stream of water for 10 minutes, rinse in distilled water, and dry out of contract with dust after removal of most of the water with a moist viscose sponge.

8. Examine the plates on a viewing box or in the modified Judd-Lewis plate comparator, comparing the line densities of the sample spectra with those of the standards photographed on the same plate. Subtract the quantity of each element appearing in the reagent blank from the quantity of that element appearing in the sample.

Calculation

$$ppm = \frac{\text{Wt. of Element (micrograms)}}{\text{Wt. of Sample in aliquot (grams)}}$$

References

The development of the method described is covered in the following project reports:

CK-670
CK-877
CK-928
CK-993
CK-1229
CK-1326
CC-872
LAMS-72
LAMS-127
LAMS-122
LAMS-109
LAMS-97
LAMS-86

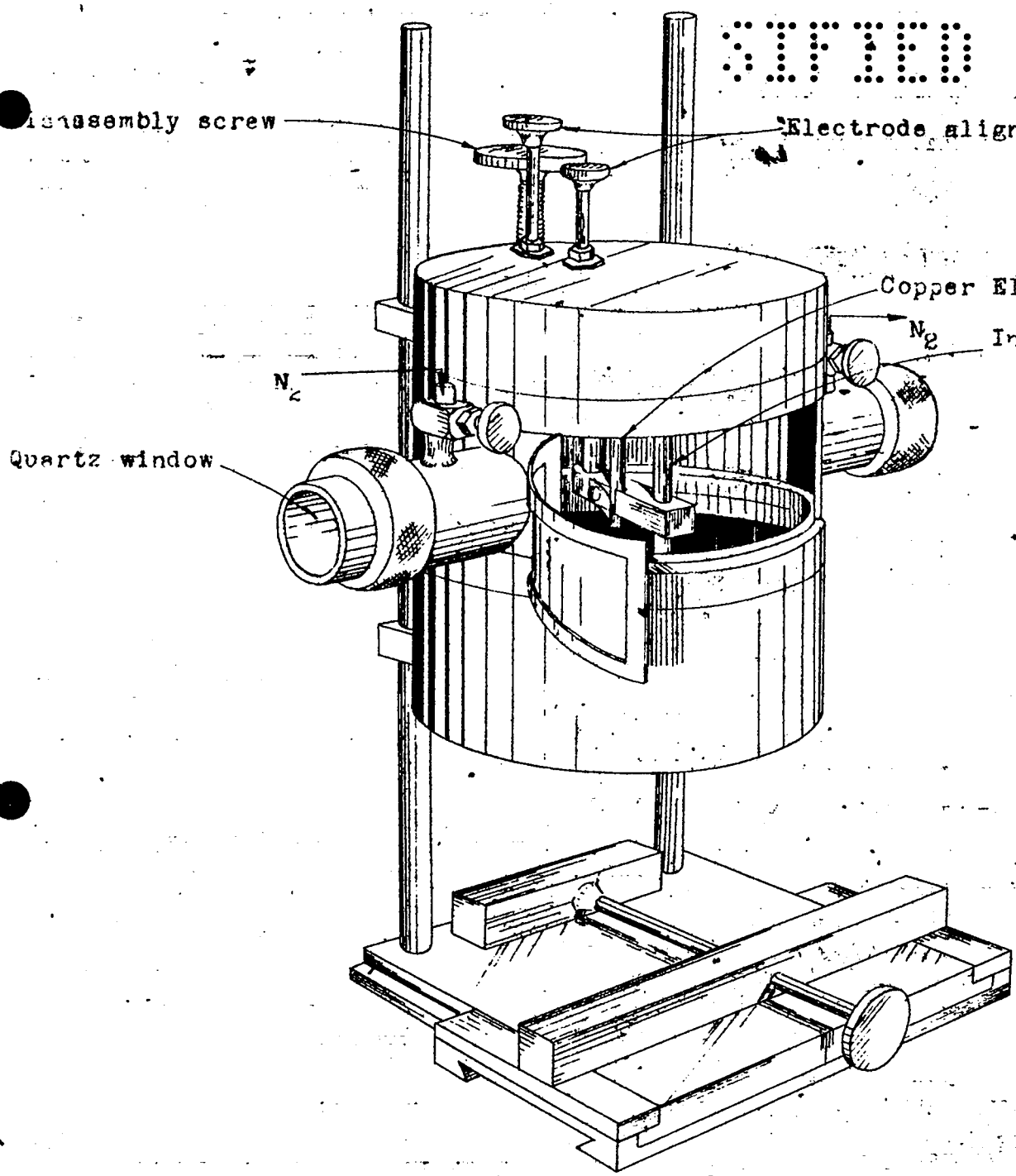


Figure 1. Spark Discharge Chamber

Spectrochemical Determination of Intermediate and Heavy-Element Impurities in Plutonium Metal and Compounds by the Direct Copper Spark Method.

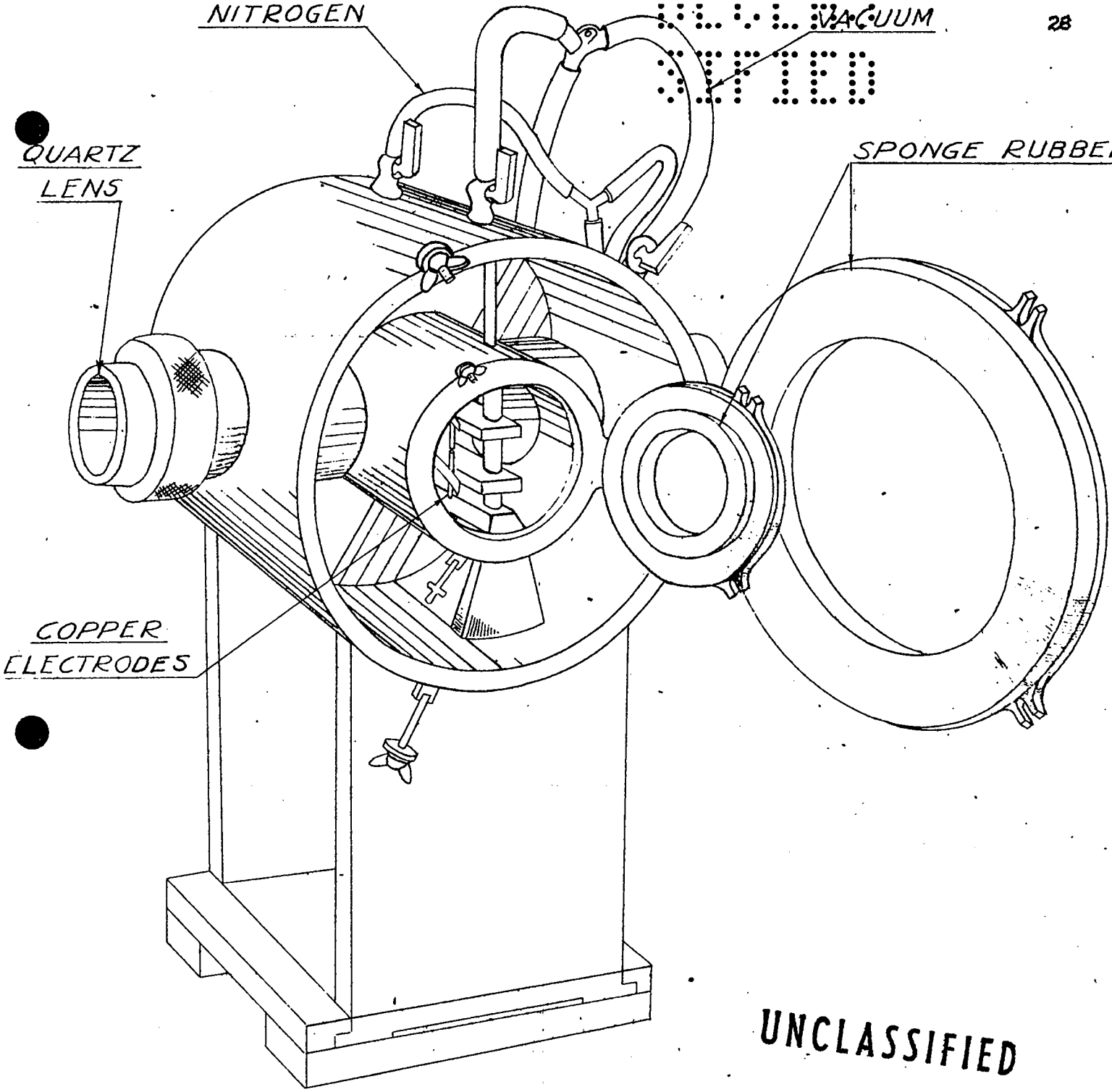


FIGURE 2 SPARK DISCHARGE CHAMBER – IMPROVED DESIGN

SPECTROCHEMICAL DETERMINATION OF INTERMEDIATE AND HEAVY-ELEMENT IMPURITIES IN PLUTONIUM METAL AND COMPOUNDS BY THE DIRECT COPPER SPARK METHOD

II C-1

SPECTROCHEMICAL DETERMINATION OF IMPURITIES IN PLUTONIUM METAL AND COMPOUNDS BY THE COPPER SPARK-CUPFERRON EXTRACTION METHOD

Abstract

Tri- or tetra-valent plutonium is separated from Li, Be, Na, Mg, Al, K, Ca, Mn, Co, Ni, Zn, Sr, Cd, Sn, Ba, La, Ce, Hg and Pb by extraction of plutonium cupferride with chloroform. The aqueous phase is evaporated on copper electrodes, and the latter sparked to produce the impurity spectrum. Comparison of the densities of the impurity lines with standard spectra permits estimates of the amounts of impurities present.

Limits of Sensitivity

(Based upon analysis of 5 mg. of metal).

Element	ppm first order	ppm second order
Li	1.0	---
Be	0.1	0.4
Na	5	---
Mg	2	20.0
Al	2	20.0
K	20	---
Ca	2	20.0
Mn	2	---
Co	10	---
Ni	4	---
Zn	40	---
Sr	1	---
Cd	20	---
Sn	20	---
Ba	1	---
La	2	---
Ce	20	---
Hg	40	---
Pb	20	---

Reagents

1. Constant-boiling HCl, distilled from and stored in quartz vessels.
2. Diluted quartz-distilled HCl, prepared by diluting 12 ml. of c.b. HCl to 100 ml. with quartz-distilled water.

3. Purified cupferron* (Ammonium salt of N-nitroso phenylhydroxylamine.)

4. Chloroform (Baker's Analyzed).

5. Ether (Mallinckrodt).

6. Quartz-distilled water.

Apparatus and Materials

1. Electrolytic reduction cell (Figure 1).

2. 1 ml. glass-stoppered pyrex volumetric flasks.

3. 10 ml. glass-stoppered pyrex graduated cylinder.

4. 1 ml. platinum crucible.

5. Misco syringe and quartz pipet tips (1 ml. capacity).

6. Cylindrical micro-furnace.**

7. Infra-red evaporating apparatus (Figure 2).

8. Electrode evaporator (Figure 3).

9. $\frac{1}{4}$" dia. x $1\frac{1}{2}$" long copper electrodes. Ends should be freshly faced on lathe and sides machined lightly to a distance of $\frac{1}{2}$" back from end.

10. 4" x 10" 103F and NH_3-sensitized 1-N photographic plates.

11. Spark discharge chamber.***

12. Wadsworth fully automatic stigmatic grating spectrograph, 21' grating, 15,000 lines per inch (Jarrell-Ash Company).

13. Dietert Spark unit.

14. Dietert rocking developing machine.

---

* To purify cupferron with respect to the light elements, dissolve the ammonium salt in quartz-distilled water and add an excess of quartz-distilled HCl to produce the free hydroxylamine. Extract the organic compound from the water phase by means of ether and discard the acid. Re-extract the organic compound as the ammonium salt by use of quartz- or platinum-distilled ammonium hydroxide. Precipitate the ammonium salt by adding acetone and collect the crystals in a Gooch-Munroe platinum crucible. Dry the compound thoroughly in a vacuum desiccator and store in a bottle containing a bag of pure ammonium carbonate.

** See figure in "Spectrochemical Determination of Light-element Impurities in Plutonium Metal and Compounds by the Copper Spark-Gallic Acid-Aniline Method".

*** See figure in "Spectrochemical Determination of Intermediate and Heavy-element Impurities in Plutonium and Compounds by the Direct Copper Spark Method".

15. Bausch and Lomb viewing box.

Procedure

HUED HEALTH SAFETY RULES OUTLINED IN SECTIONS I AND IIA

1. If metallic, dissolve the sample in the smallest possible quantity of constant boiling HCl and dilute to volume with quartz-distilled water in a 1 ml. glass-stoppered pyrex volumetric flask. Examine the solution critically for un-dissolved material; if a residue is present, centrifuge it to the bottom of the flask.* If the sample is in solution as +6 nitrate, reduce it to the +4 state at 1.8 volts and 15 milliamperes for 1 hour in the electrolytic cell.
2. If the sample is a salt, dissolve an amount equivalent to about 50 mg. of metal in water, HCl, or HNO_3, as necessary, and dilute it to volume in a volumetric flask of adequate capacity. It may be necessary to digest the sample with these solvents or with HF in a platinum crucible under an infra-red lamp. Some oxides may resist all efforts to dissolve them, and their analysis should not be attempted by this method.
3. Withdraw an aliquot equivalent to about 5 mg. of metal and dilute to 1 ml. with diluted HCl (vide supra) in a 1 ml. glass-stoppered pyrex volumetric flask.
4. Prepare an ether solution of the free acid of cupferron as follows: Dissolve 0.5 g. of the ammonium salt in 6 ml. of water in a 10 ml. graduated cylinder equipped with a glass stopper. Add about 15 drops of constant-boiling HCl or until the free acid is precipitated to produce a permanent turbidity. Add 1 ml. of ether and extract the free acid into the ether by shaking the cylinder.

* If a residue appears at this point which resists all efforts to bring it into solution with HCl, proceed with the analysis of the soluble portion... Transfer the insoluble residue to a 1 ml. platinum crucible and attempt to dissolve it with 0.1 ml. of HF (distilled from platinum). If the residue dissolves in HF, analyze it as a separate sample according to the procedure given above. If the residue fails to dissolve in any of the mineral acids, slurry it up with a few drops of water and transfer to a copper electrode for qualitative identification

5. Add 6 drops of the above ether solution to the diluted sample aliquot and shake vigorously to coagulate the plutonium cupferride. Add 0.1 ml. of chloroform and gently invert the flask several times to dissolve the cupferride. The aqueous phase should be colorless, although it may be somewhat turbid.

6. Draw off the aqueous phase as carefully as possible, using a quartz-tipped syringe pipet, and transfer it to a 1 ml. platinum crucible. Disregard the small volume of aqueous phase (about 5 per cent) which cannot be easily separated from the chloroform layer.

7. Evaporate the aqueous phase to dryness in the infra-red drying chamber, passing nitrogen through the petri dish to carry away the vapors. No considerable amount of undecomposed organic matter should remain at this point. Dissolve any residue which may appear by adding 0.1 ml. of purified 16 N nitric acid and evaporate just to dryness in a micro-furnace.

8. Dissolve the residue in 0.1 ml. of quartz-distilled 1 N HCl. Withdraw the solution, using a graduated 0.2 ml. micro-pipet.

9. Rinse the crucible with .06 ml. of quartz-distilled 6 N HCl and withdraw the solution into the pipet containing the first portion.

10. Divide the solution equally among four copper electrode faces, each electrode bearing approximately 40 micro-liters of solution. Dry the solutions on the electrodes in the glass-covered brass electrode holder, using an infra-red lamp as the source of heat.

11. Prepare a series of copper electrodes bearing known quantities of Li, Be, Na, Mg, K, Al and Ca (and such additional elements from the list as may be desired) in the range of interest (e.g. 0.001, 0.005, 0.01, 0.05 micrograms of each element).

12. Align the electrodes as carefully as possible in the discharge chamber, gauging the 2 mm. electrode separation and the lateral and vertical

positioning by projecting a shadow-image of the electrodes on a screen behind the chamber on the optical path.

13. Spark the electrodes for 50 seconds, using the Dietert spark unit, set for the following conditions: Rotary gap setting at 10; Power, 2KVA; Inductance setting at 8; Input voltage, 230; Output primary voltage, 95-100. Set the slit of the Wadsworth spectrograph for 50 microns. Always check the alignment of the electrodes before starting a run by visual examination of the spectrum of a pair of copper blanks.

Photograph the first order spectrum* of the following lines on two 103-O plates:

Cd: 2288.0 Å
Hg: 2536.5
Mn: 2576.1
Mg: 2795.5
Sn: 2840.0
Pb: 2833.1
Be: 3130.4
Zn: 3282.3
Co: 3453.5
Ni: 3493.0
Zr: 3438.2
Ca: 3933.7
Al: 3961.5
La: 3949.1
Ce: 4012.4
Sr: 4077.7
Cr: 4254.3
Ba: 4554.0

Photograph the following lines on a 103-F plate placed in the right side of the camera cassette (as viewed from the back of the instrument):

Na: 5890 Å
Li: 6707.8

---

* Should only the light elements: Mg, Be, Ca, Al, Li, Na, and K be desired, use only a 1-N plate and a 103-F plate. The second order spectrum of Mg, Be, Ca, and Al will appear on these plates along with the lines of the alkali metals.

Photograph the K: 7664.9 line on an ammonia-sensitized 1-N* plate placed in the left side of the camera cassette (as viewed from the back of the instrument).

14. Develop both 103F and 1-N plates in total darkness for 3 minutes at 18.0° C. in Eastman D-19, using rocking development. Fix in F-5 for 10 minutes after immersion in an acetic acid short stop for about 10 seconds. Wash plates in a vertical stream of water for 10 minutes, rinse in distilled water and dry out of contact with dust after removal of most of the water with a moist viscose sponge.

15. Examine the spectra on a viewing box, comparing the line densities of the sample spectra with those of the standards photographed on the same plate. Subtract the quantity appearing in the spectrum of the procedure blank from that appearing in the sample spectra for each element of interest.

Calculation

$$\text{ppm} = \frac{\text{Wt. of element (micrograms)}}{\text{Wt. of sample in aliquot (grams)}}$$

References

The development of the method described is covered in the following project reports:

CK-1229
CK-1326
CK-1064
CK-993
CK-928
CK-877
CK-801
CK-738
LAMS-72

* To sensitize the plate immerse it in a 4 per cent ammonia solution (by volume) for one minute at a temperature not exceeding 10° C. Transfer the plate to a tray containing methanol at 10° C. for one minute. Dry the plate as rapidly as possible in a stream of cold air. Plates sensitized in this manner are extremely susceptible to fogging, and the operations must be carried out in absolute darkness. The keeping qualities of sensitized plates are poor; they may be kept in a refrigerator, but should be used within 48 hours.

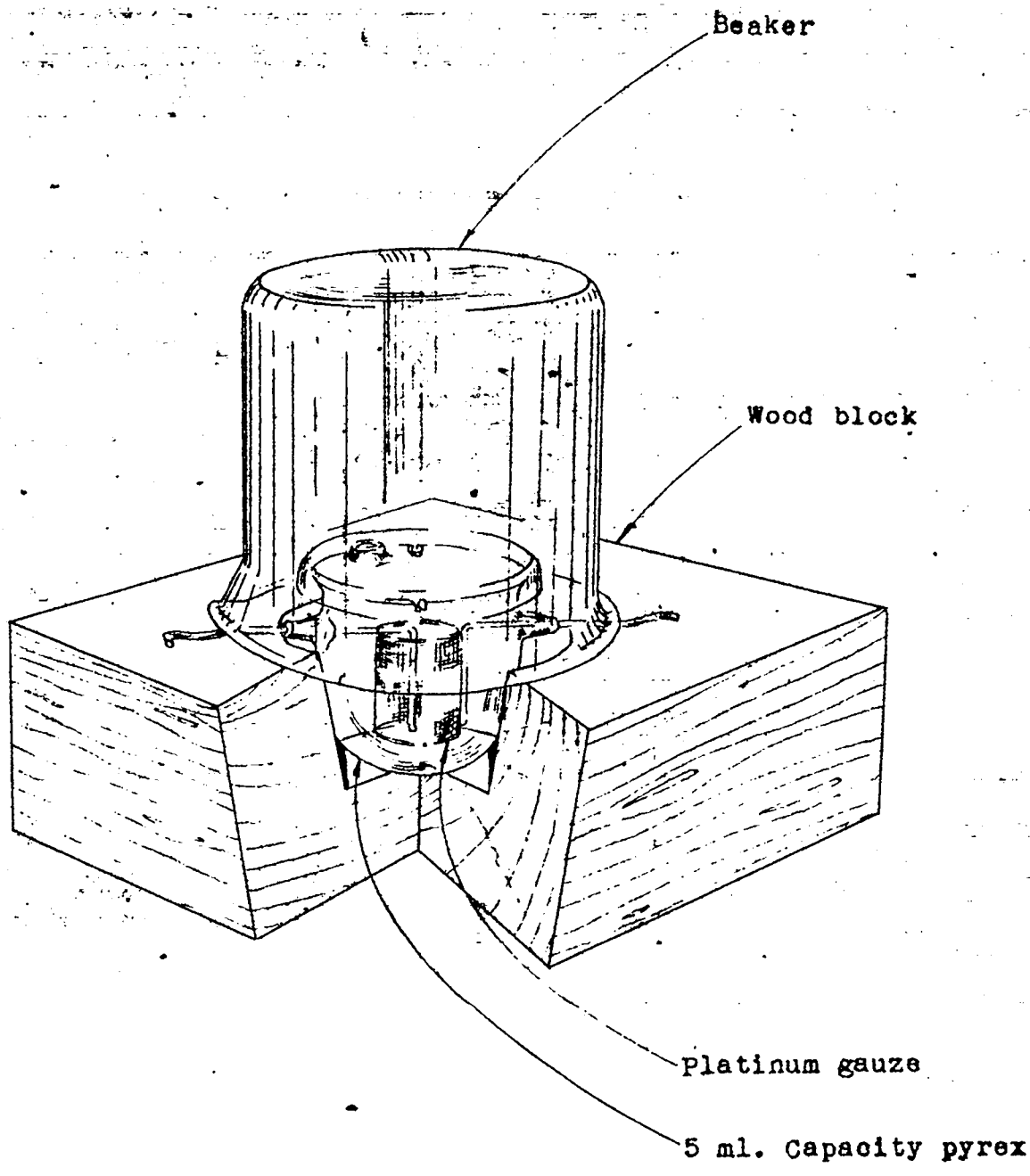


Figure 1. Micro-electro-reduction Cell

Spectrochemical Determination of Impurities in Plutonium Metal and Compounds by the Copper Spark-Cupferron Extraction Method.

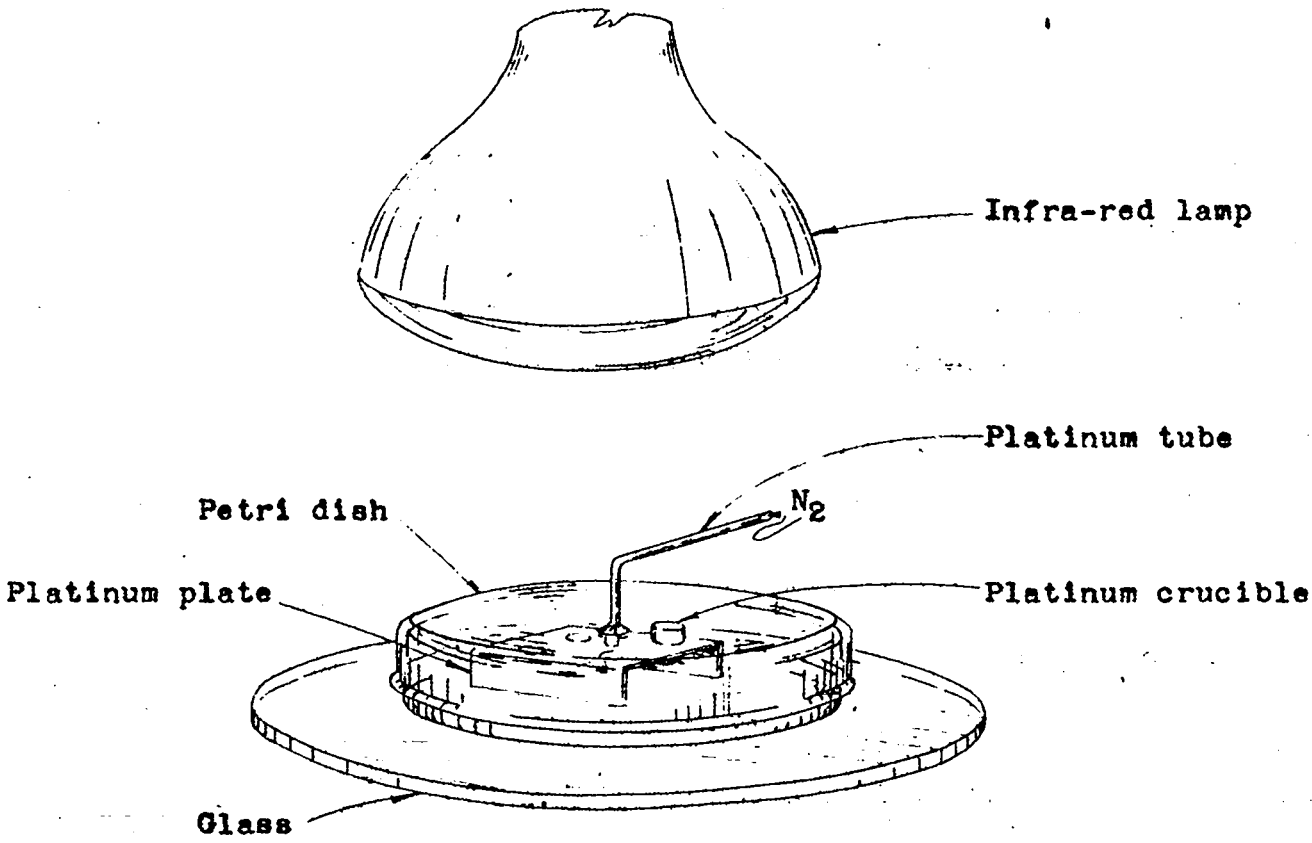


Figure 2. Infra-Red Evaporator

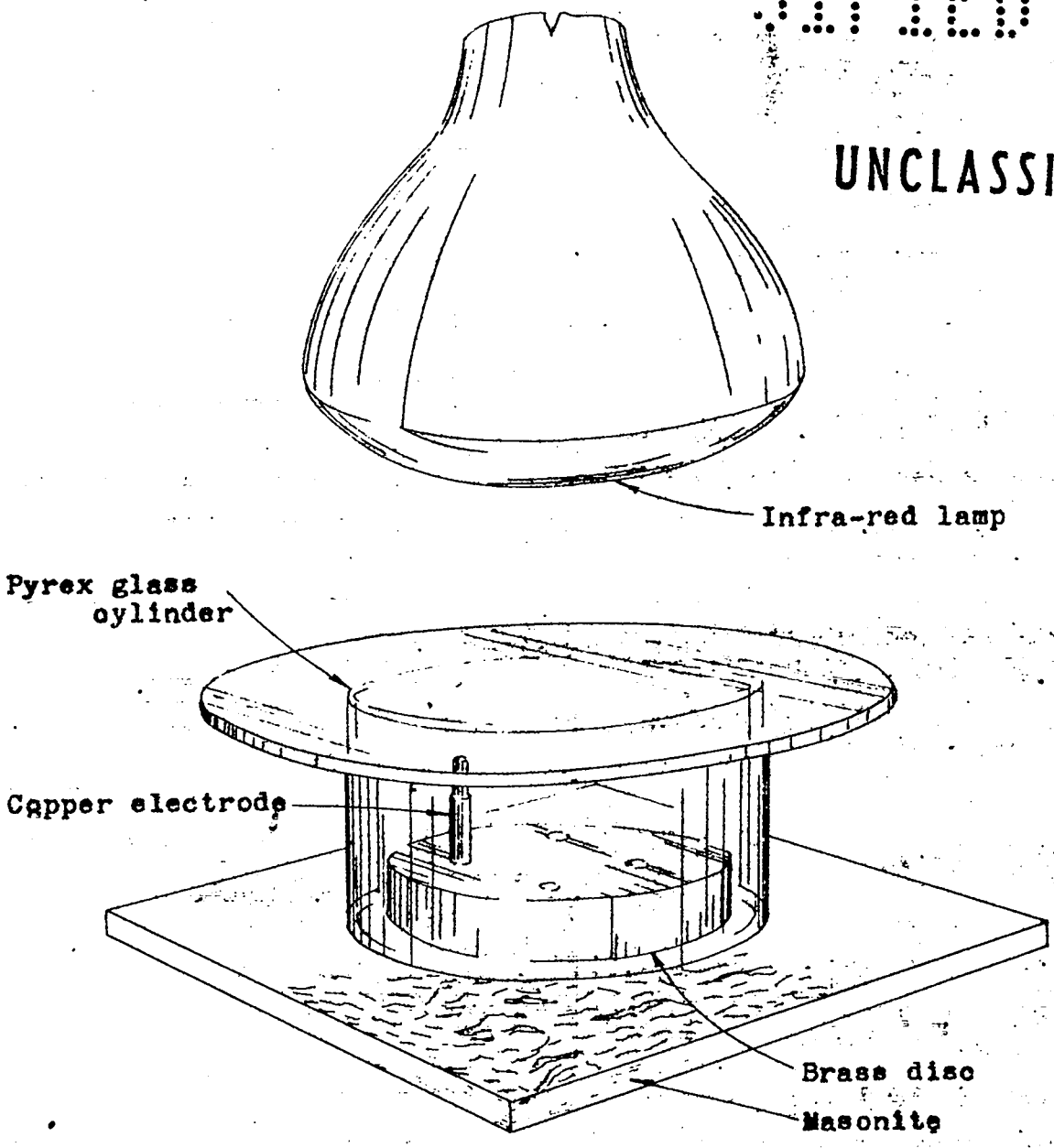


Figure 3. Electrode Evaporator

SPECTROCHEMICAL DETERMINATION OF LIGHT-ELEMENT IMPURITIES IN PLUTONIUM METAL AND COMPOUNDS BY THE COPPER SPARK-GALLIC ACID-ANILINE METHOD

Abstract

Tri- or tetra-valent plutonium nitrate or chloride is separated from Li, Be, Na, Mg, Al, K, and Ca by formation of an insoluble compound with gallic acid and aniline which is selectively wetted by aniline. The aqueous phase, containing the light-element impurities, is evaporated on copper electrodes, which are then sparked to produce the impurity spectrum. Comparison of the densities of the impurity lines with standard spectra permits estimates of the amounts of impurities present.

Limits of Sensitivity

(Based upon analysis of 5 mg. of metal)

Element	ppm first order	ppm second order
Li	1.0	
Be	0.1	0.4
Na	5.	
Mg	1.	3.
Al	3.	20.
Ca	1.	10.
K	20.	

Reagents

1. Constant-boiling HCl, distilled from and stored in quartz vessels.
2. Diluted quartz-distilled HCl, prepared by diluting 1 ml. of c.b. HCl to 5 ml. with quartz-distilled water.
3. Purified gallic acid solution (7.5 mg. per ml.)*
4. Aniline, distilled from quartz and stored in red pyrex vessels.
5. Quartz-distilled water.

* To purify gallic acid, clarify a solution of it using Norite. Re-crystallize three times from water, carefully filtering the solution to remove suspended material between re-crystallizations. Prepare a solution containing 7.5 mg. per ml. and store in a quartz reagent bottle.

6. Quartz-distilled HNO_3.

7. Platinum-distilled HF.

Apparatus and Materials

1. Electrolytic reduction cell.*

2. 1 ml. quartz centrifuge cones.

3. 10 and 50 micro-liter quartz pipets.

4. 1 ml. platinum crucible.

5. Infra-red evaporating apparatus.**

6. Electrode evaporator.***

7. Cylindrical micro-furnace. (Figure 1).

8. 4" x 10" 103F and NH_3-sensitized I-N photographic plates.

9. $\frac{1}{4}$" dia. x $1\frac{1}{2}$" long copper electrodes. Ends should be freshly faced on lathe and sides machined lightly to a distance of $\frac{1}{2}$" back from end.

10. Spark discharge chamber.****

11. Wadsworth fully automatic stigmatic grating spectrograph, 21' grating, 15,000 lines per inch (Jarrell-Ash Co.).

12. Dietert spark unit.

13. Dietert rocking developing machine.

14. Bausch and Lomb viewing box.

15. International clinical centrifuge.

Procedure

HEED HEALTH SAFETY RULES OUTLINED IN SECTIONS I AND IIA

1. If metallic, dissolve the sample (~ 50 mg., if available) in the smallest

* For illustration of the electrolytic reduction cell see "Spectrochemical Determination of Impurities in Plutonium Metal and Compounds by the Copper Spark-Cupferron Extraction Method."
** For illustration of infra-red evaporating apparatus see procedure referred to above.
*** For illustration of electrode evaporator see procedure referred to above.
**** For illustration of spark discharge chamber see "Spectrochemical Determination of Intermediate and Heavy-element Impurities in Plutonium Metal and Compounds by the Direct Copper Spark Method."

possible quantity of constant-boiling HCl and dilute to volume with quartz-distilled water in a 1 ml. glass-stoppered pyrex volumetric flask. Examine the solution critically for un-dissolved material: if a residue is present, centrifuge it to the bottom of the flask. Withdraw most of the supernatant solution with a pipet and wash the residue into a 1 ml. platinum crucible. Digest the residue with a small quantity of platinum-distilled HF, and when the solution is clear, fume it down several times with quartz-distilled HCl or HNO_3 to dispel the fluoride. Combine the solution of the residue and the solution first obtained and adjust to a convenient definite volume.

2. If the sample is a compound, dissolve an amount equivalent to about 50 mg. of metal in water, HCl or HNO_3, as necessary, and dilute it to volume in a volumetric flask of adequate capacity. It may be necessary to digest the sample with these solvents or with HF in a platinum crucible under an infra-red lamp. Some oxides may resist all efforts to dissolve them, and their analysis should not be attempted by this method.
3. If the sample is received in solution, have its concentration determined by assay methods and dilute it to give a concentration of about 50 mg. per ml. In any case, if the valence state is +6, reduce it to the +4 state at 1.8 volts (~15 milliamperes for one hour in the electro-reduction cell.
4. Withdraw an aliquot equivalent to about 10 mg. of metal and transfer it to a 1 ml. platinum crucible. Evaporate the solution just to dryness to expel excess acids. Be careful to avoid overheating in the latter stages of evaporation to prevent formation of an insoluble residue. Dissolve the salt residue (Preferably +4 nitrate) in about 150 micro-liters of quartz-distilled water and transfer the solution to a 1 ml. quartz centrifuge cone. Add about 50 micro-liters of gallic acid solution (5 mg. per ml.) and about 15 micro-liters of aniline. A precipitate should form. Stir it

with a length of platinum wire which has been cleaned by ignition. Centrifuge the precipitate to the bottom of the cone. Test for completeness of precipitation by adding another 50 micro-liters of gallic acid solution. If a precipitate again forms, add another 15 micro-liters of aniline, stir, and centrifuge. Continue testing for completeness of precipitation in this manner, omitting, however, further additions of aniline. If care has not been taken to remove the excess acid it will not be possible to remove the plutonium completely from solution. A final pH of 2 is considered to be satisfactory, and the amount of plutonium remaining in the aqueous phase will then be less than 50 micrograms.

5. Carefully withdraw the aqueous layer from the cone by means of a quartz pipet; the volume should be between 300 and 500 micro-liters. Transfer the solution to a 1 ml. platinum crucible and evaporate it to dryness under an infra-red lamp. Burn off the residue of gallic acid in a cylindrical micro-furnace. Dissolve the residue in 50 micro-liters of HCl (1 part of c.b. acid diluted with 4 parts of water). Rinse the crucible by transferring it back and forth with a quartz pipet.
6. Divide the solution into two equal fractions and evaporate each fraction on a pair of copper electrodes in the infra-red electrode evaporator. (This requires four copper electrodes, each bearing about one fourth of the sample impurities; if desired, the solution may be divided between only two electrodes, using clean blank copper electrodes to oppose the coated ones in the spark).
7. Prepare a series of copper electrodes bearing known quantities of Li, Be, Na, Mg, K, Al, and Ca in the range of interest (e.g., 0.001, 0.005, 0.01, and 0.05 micrograms of each element).
8. Set the Dietert spark unit to give the following conditions: power in-put, 2 KVA; inductance, 8; in-put voltage, 230; rotary gap, 10; primary voltage,

95-100. Set the timer relay for an exposure of 60 seconds. Close the slit of the Wadsworth spectrograph to 50 microns. Insert a pair of copper electrodes into the holders in the discharge chamber and align them laterally and vertically at a separation of 2 mm. by projecting their shadow-image on the alignment screen on the optical axis behind the chamber. Strike a spark between the electrodes and open the spectrograph shutter. Remove the camera from the back of the instrument and observe the full-height spectrum in the visible region with a hand lens through the camera port. This is a check on the electrode alignment and should reveal the tall lines as uniformly bright along their length. Set the Hartmann diaphragm to give lines 2 mm. tall and load the camera. Put a 103-F plate in the right hand side of the camera and an NH_3-sensitized I-N plate in the left hand side. Set the camera to photograph the range, 5500 Å - 8000 Å.

9. Insert the standard electrode pairs and sample electrode pairs in the discharge chamber in turn, passing nitrogen through the chamber for one minute. Stop the flow of nitrogen, open the spectrograph shutter and strike the discharge. Rack the plate up 3 mm. after each 60 second exposure. Spark the sample or samples about mid-way between the first and last standard.

10. Develop the plates in total darkness for 3 minutes at 18.0° C. in Eastman D-19, using rocking development. Fix in F-5 for 10 minutes after immersion in an acetic acid short stop for about 10 seconds. Wash plates in a vertical stream of water for 10 minutes, rinse in distilled water, and dry out of contact with dust after removal of most of the water with a moist viscose sponge.

11. Examine the plates on a viewing box or in the modified Judd-Lewis plate

comparator. Use the following lines:

Mg:	2795.5 Å	2nd order
Be:	3131	2nd order
Na:	5890.0	
Na:	5896.0	
Li:	6103.6	
Li:	6707.8	
Al:	3944.0	2nd order
Al:	3961.5	2nd order
Ca:	3933.7	2nd order
Ca:	3968.5	2nd order
K:	7664.9	
K:	7699.0	

Compare the line densities of the sample spectra with those of the standards photographed on the same plate. Subtract the quantity of each element appearing in the reagent blank from the quantity of that element appearing in the sample.

Calculations

$$\text{ppm} = \frac{\text{Wt. of element (micrograms)}}{\text{Wt. of sample in aliquot (grams)}}$$

References

The development of the method described is covered in the following project reports:

CC-937
CK-1148
CK-1374
LAMS-72
LAMS-86
LAMS-97
LAMS-109
LAMS-122

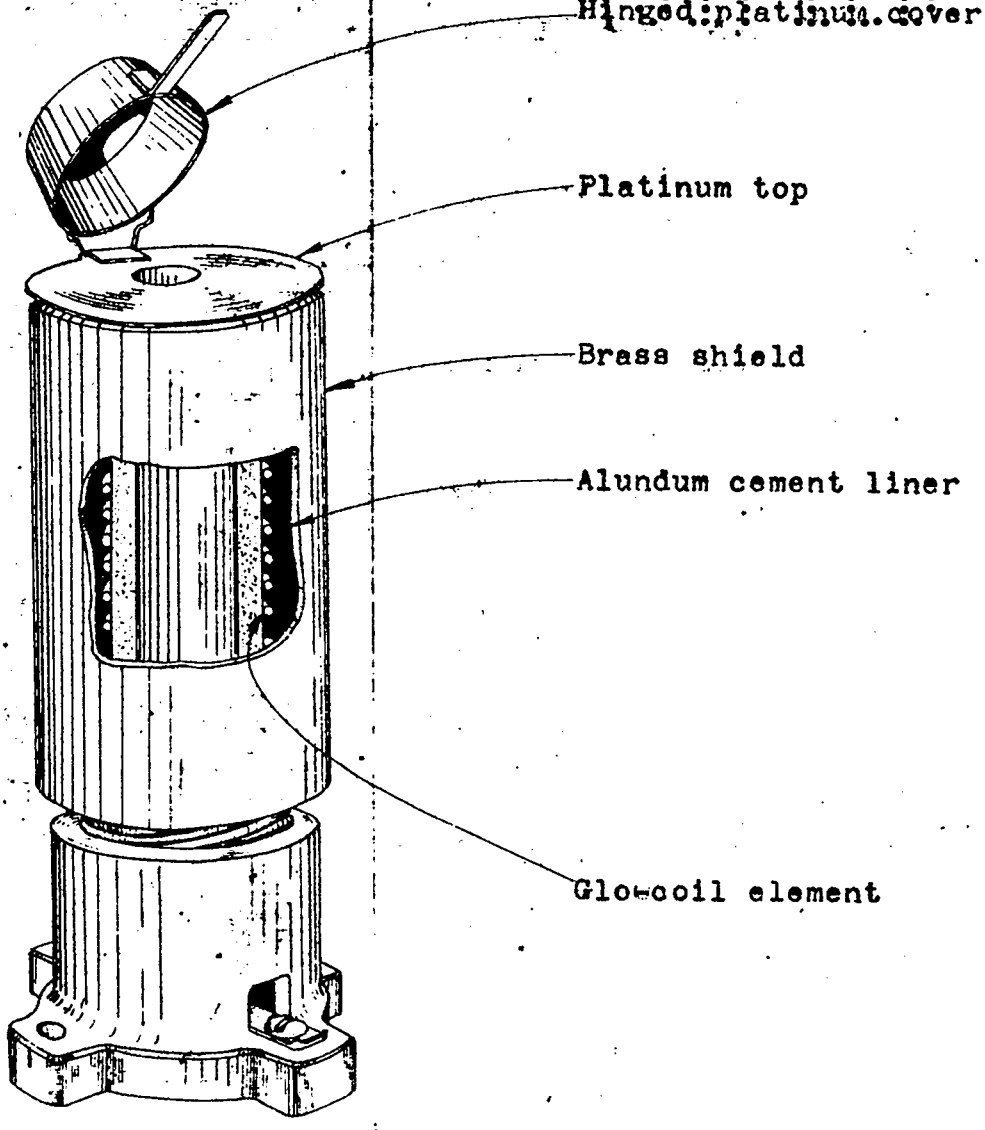


Figure 1. Cylindrical Micro-furnace

Spectrochemical Determination of Light-Element Impurities in Plutonium Metal and Compounds by the Copper Spark-Gallic Acid-Aniline Method

[redacted]

SPECTROCHEMICAL ESTIMATION OF FLUORINE IN URANIUM AND CALCIUM METALS

Abstract

Fluorine is liberated from the sample as HF by H_2SO_4 or $HClO_4$. The HF is distilled and then converted to NaF by absorption in NaOH. The NaF is arced in the presence of excess SrO and the amount of fluorine is estimated by comparing the intensity of the SrF band heads at 5771.9, 5774.8, and 5779.5 Å with the intensity of the same band heads from a suitably prepared standard.

Applicability

The method has been used primarily for uranium metal* but is applicable, presumably, to other materials which are soluble in non-volatile acids without loss of F. The limit of sensitivity is 0.5 γ F.

Method of Sampling

A representative section of the interior of the piece of uranium is cut to size that will fit the electrolytic cell. A section measuring about 4 x 4 x 20 mm. and weighing about 6 grams is suitable for the cell illustrated (Figure 2). Smaller sections may be used.

Reagents

1. 71 per cent HNO_3.
2. 96 per cent H_2SO_4, F free (See Blank Procedure).
3. 30 per cent H_2SO_4, " " " " "
4. 70 per cent $HClO_4$, " " " " "
5. 30 per cent H_2O_2, Superoxol, Merck, "F free".
6. 0.1 N NaOH, F free.
7. SrO, F free

* Applicability of this procedure to the estimation of fluorine in plutonium metal and alloys is under investigation.

[redacted]

8. NaF stock solution containing 1 mg. F/ml.

9. Nitrazine paper, Squibb.

Apparatus and Materials

1. Electrolytic cell (Figure 2) with storage battery, voltmeter, ammeter, and variable resistance, or a unit containing a variable D.C. source with necessary controls and meters.
2. Platinum distillation cell and metal heating block (Figure 1).
3. Hot plate and Variac.
4. 2-liter syphon bottle to maintain reduced pressure on absorption side of distillation cell. It is provided with a stopcock or clamp to adjust flow rate.
5. Safety trap to keep pressure within the required limits (Figure 1).
6. 10 ml. platinum evaporating dish.
7. Platinum crucibles, 3-5 ml. capacity.
8. 1/8" diameter steel drill and bakelite guide for forming craters on electrodes (Figure 3).
9. 1/8" diameter spectrographic graphite rod and 1/4" diameter graphite rod.
10. Ten 1/4" i.d. heating coils mounted on an insulating board -- Variac control (Figure 4).
11. Electrode holder.
12. λ pipet control and pipets of capacity 10, 20, 50, and 100 λ.
13. 4" x 10" 103a-T or 103a-D Eastman-Kodak spectrographic plates.
14. Eastman D-19 developer, F-5 fixer, acetic acid short stop.

Procedure I (for uranium)

1. File small notches near one end of the uranium sample so that it can be fastened firmly with good electrical contact to the center electrode (Figure 2). If the sample has a smooth metallic surface, pickle it in conc. HNO_3 long enough to remove the oxide coating. If it contains cavities or has a

[redacted]

rough surface, pickle it somewhat longer until slag is dissolved and the surface has a metallic appearance. Rinse well with distilled water, allow to dry on filter paper, and weigh to the nearest 10 mg.

2. Attach sample firmly to the center electrode (Figure 2). Connect this electrode to the positive terminal and the platinum gauze electrode to the negative terminal. Electrolyze at 0.2 - 0.6 amperes into 2.5 ml. of 30 per cent H_2SO_4 until 0.5 grams of uranium has been oxidized from the metal sample. If a duplicate is being run and the approximate F content is known, electrolyze enough to give 1 - 5 γ F. With a current of 0.4 amp., 0.5 grams will be electrolyzed in about one-half hour. The $U(SO_4)_2$ precipitate in this case will fill the cell to about one-third the original depth of 30 per cent H_2SO_4. Remove the cooling bath and lower the solution tube. Remove the uranium metal from the center electrode, transfer any appreciable adhering precipitate to the solution, rinse the metal (discarding rinsings), dry on filter paper and weigh.

3. Add 400 λ of 30 per cent H_2O_2 to the solution in the tube. Immerse the gauze electrode in the solution until all adhering precipitate is dissolved. Drain the solution from the electrode into the tube. Discard rinsings. Mix the solution and precipitate by occasional swirling until all the precipitate is dissolved.

4. Add 50 λ of 0.1 NaOH to the pyrex cup C (Figure 1). Place a small piece (1/8" x 1/4") of nitrazine indicator paper in the cup. Add enough water so that the surface just touches the platinum gauze retainer. Assemble the cup.

5. Add the solution prepared in step 3 to chamber A. Add 1.5 ml. of 96 per cent H_2SO_4. Assemble the gas line to the syphon and open the valve on the latter so that 1 or 2 bubbles/sec. pass through the base in C. Screw down tightly the caps on chambers A and B (B need not be opened between distillations)

[redacted]

and assemble the pressure side of the gas line. Before applying pressure, test the line for leaks by running the syphon at about 6 ml./min. (2 or 3 drops/sec.) and observe if air bubbles pass through the safety trap at a steady rate comparable with the rate of flow through C. If they do not, there is probably a leak at one of the caps of the distillation cell. If no gas bubbles through C, either the lead is stopped or there is a leak in the line to the syphon. With the needle valves closed and with air flowing at the proper rate (1 or 2 bubbles/sec.) into the safety trap, gradually turn on the nitrogen at the tank to about 1 lb./sq. in. Open the small needle valves, E, until only an occasional air bubble passes through the tube into the safety trap. With these conditions a pressure about 1 cm. of water below atmospheric pressure will be maintained within the distillation cell. Also the N_2 (with maximum allowable pressure determined by the height of the tube in the safety trap) will prevent gases or solution of samples from backing up into the pressure lines.

6. Raise the temperature of the heating block (See Precaution 1) from 100° C. to 160° C. over a period of 1 hour during which much of the water and some of the HF distills over. The rise in temperature is best controlled by setting the thermostat on the hot plate to a desired maximum and adjusting the rate of temperature rise by making the proper voltage setting on the Variac. Maintain the heating block at 160° C. for 1½ hours and the gas flow at 6 ml./min. (Precaution 2). If the base should be neutralized (blue to yellow) at any time during distillation, add another 50λ portion (Precaution 3). Increase nitrogen pressure slightly before opening cup C so that absorbing solution will not be drawn back into chamber B. Also see that any base solution in platinum lead is forced into C after distillation is complete.

7. Transfer the basic solution containing the distillate to a small platinum crucible or dish and concentrate it to a volume of 50 λ . If the F content is unpredictable, concentrate one-tenth and nine-tenths of the solution separately and arc these aliquots on separate electrodes.
8. Rinse the distillation cell for the next determination by drawing tap water and finally distilled water through it in the reverse direction. Use a trap if this is done either with the mouth or the vacuum line.
9. Form craters in the electrodes by inserting 1/8" diameter spectrographic graphite rod into one end of the bakelite sleeve and a 1/8" steel drill into the other end (Figure 3). A few hand turns of the drill with light pressure will form a crater. Break off 3/4" cratered lengths.
10. Make graphite electrode bases from 1/4" diameter rod (Figure 3). This can be done on a lathe. Use a size drill which will permit a neat fit for the cratered lengths. These bases can be used repeatedly.
11. Make upper electrodes as shown in Figure 3.
12. Place as many electrodes in the heater (Figure 4) as are required for distillations and standards. Weigh 1 mg. of finely divided SrO into each crater. With some practice, careful visual estimation after light tapping of the side of the electrode is adequately quantitative. With a λ pipet add enough water to moisten the SrO. Turn on the Variac at low voltage and evaporate slowly and carefully so that the SrO is not lost. Continue evaporating small portions of water from the SrO until an even coat of oxide (free from large bubbles and fragile crusts) covers the entire crater.
13. Prepare two standard NaF solutions from the stock solution. Dilute respectively 1 ml. and 2 ml. of reagent No. 6 to 10 ml. Prepare fresh standard solutions every 3 days until a solution of a particular concentration has stood in its containing vessel for several weeks. Thereafter, fresh

standards need not be prepared.

14. Make standard electrodes carrying 1 γ, 2 γ, 4 γ, and 8 γ F. For the 1 γ standard, evaporate 10 λ of the solution containing 0.1 mg./ml. on a SrO coated crater as prepared in step 12. Proceed similarly with the other standards and distillate concentrates. Evaporation must not be so rapid as to cause loss of SrO and NaF by spattering. Add the solution in small portions to the edge of the oxide coating. It will spread rapidly over the crater and not creep back along the outside of the pipet. If necessary draw out the tip of the pipet.

15. In total darkness load the right side of the Wadsworth camera with a 4" x 10" 103a-T (or 103a-D) plate, emulsion side down (i.e. facing the grating). With necessary precautions against fogging of the plate, attach the camera to the camera carriage of the Wadsworth, draw down the plate shield and clamp it in position.

16. Turn on the Dietert D.C. source. Set the amperage at a minimum (about 3 amp. with this arc) by turning the hand-crank to the counter-clockwise stop. Set the automatic timer at 60 sec. Set the polarity switch at positive for lower electrode. Adjust the slit height to 2 mm. and the slit width to 30 μ (3 on the micrometer scale). Raise the camera carriage to a reading of 30 mm. and position the wavelength to 5000 - 6300 Å on the short wavelength half. Place in front of the slit a filter which transmits wavelengths of 5000 Å and greater. Set the front edge of the base of the cage at 40.7 cm. on the scale and clamp the 90 mm. spherical quartz lens with its base against that of the cage so that an enlarged (3-fold) image of the arc will be focused on the slit.

17. Clamp a cratered electrode (containing SrO only) in the lower holder and a pointed one in the upper holder (Figure 5). Close the cage door. With an

electrode separation of about 5 mm. strike the arc with a graphite rod mounted in an insulating handle. Raise the upper electrode to a separation of 10 mm. and adjust the electrodes (laterally and vertically) so that the slit is in the upper side of the arc image (Figure 5). Mark the position of the electrode image on the screen behind the cage. Turn off the arc.

18. Replace the SrO blank electrode with a standard or sample and adjust the crater to the same position using the shadow cast on the screen by the small lamp in front of the lens. Open the shutter, strike the arc as in 17 and raise the upper electrode to 10 mm. separation. As the electrodes burn away maintain them at this position. If the SrO should volatilize completely in less than 60 sec. close the shutter and turn off the arc. After each exposure close the shutter and raise the camera carriage 3 mm.

19. Develop the plate in total darkness for 4 minutes at 18° C. in Eastman D-19 using rocking development. Immerse the plate for 10 sec. in an acetic acid short stop. Fix it in F-5 for 10 minutes or until the silver halide is completely dissolved. Wash the plate in running water for 10-20 minutes and rinse it with distilled water. Remove excess water from the plate with a sponge and dry it out of contact with dust.

20. Compare (visually on a plate viewer with the aid of a lens) the samples with the standards. The band heads at 5771.9, 5774.8 and 5779.5 Å are used. With uniform excitation conditions and equal amounts of SrO the backgrounds should be the same for each exposure. Under normal conditions estimation of fluorine by comparison can be made to 40 per cent or better. If the background is not the same for each exposure, make an allowance for the variation.

Procedure II (for calcium)

The conditions stated under Applicability must be met for any particular sample. For Ca metal the following modifications are made:

1. Place the Ca metal (about 1 gram) in a 10 ml. platinum evaporating dish and cover it with a watch glass. Add water dropwise through the lip until the sample is completely oxidized. Neutralize with 70 per cent $HClO_4$ just to the yellow color of the nitrazine indicator. $Ca(OH)_2$ dissolves completely. Add 0.1 N NaOH dropwise -- one drop beyond the appearance of the blue color of the indicator. Evaporate the solution to about half this volume or until the salt crystallizes out when allowed to cool.
2. Add 100 λ 0.1 N NaOH to cup C and follow Procedure I, 4.
3. Transfer the warm concentrated solution of step 1 to chamber A. Rinse the evaporating dish with 2 ml. 70 per cent $HClO_4$ and transfer rinsings to chamber A. Assemble and test the gas line as in Procedure I, 5.
4. Follow Procedure I, 6 with these exceptions. Use a distillation temperature of 170° C. instead of 160° C. If the base in cup C is not neutralized during distillation, follow Procedure I, 7-20.
5. If the base is neutralized (Precaution 3), add 1 ml. of 0.1 N NaOH to cup C and continue distillation. The volatile acid is most probably HCl.
6. To test for Cl^- acidify a small portion of distillate with $HClO_4$ and add $AgClO_4$. Return the test solution to the distillate and proceed as follows: If Cl^- is present neutralize the entire distillate with $HClO_4$ and add 0.5 ml. of 1 N $HClO_4$ in excess. Transfer to a centrifuge cone of twice the volume. Add 0.1 N $AgClO_4$ in 100 λ portions, mixing and centrifuging after each addition until further addition of $AgClO_4$ no longer precipitates AgCl.
7. Follow Procedure I, 4.

8. Empty and rinse the distillation cell. Decant the clear solution of step 6 and transfer it to Chamber A. Add 2 ml. 96 per cent H_2SO_4. Assemble and test gas line as in Procedure I, 5. Follow Procedure I, 6 - 20.

Blank Procedure

Establish the absence of F (to limit of sensitivity) in all the reagents by performing the entire procedure without a sample. A small (< 1 γ F) but reproducible blank may be tolerated in which case this value is subtracted from the plate estimation of F.

Precautions

1. Adequate heating of distillation cell is essential. The leads between chambers A, B and C must be maintained at such a temperature that water will not condense in them; otherwise distillation will not be smooth and recovery may not be complete. If contact between heating block and cell is not satisfactory, a wax or oil bath may be used.
2. Establishment of quantative recovery of known amounts of F must be done by any one operator. If conditions as given in Procedure I, 6 are not sufficient they will have to be altered accordingly. This applies equally to all modifications.
3. Neutralization of the base is caused either by acid spray from chambers A and B or by distillation of volatile acids; it is the latter, if the sample has an unexpectedly high F^- content, or has Cl^-, NO_3^- etc. in excess of .05 milliequivalents (See Procedure II).

Calculations

$$\text{ppm F} = \frac{\text{F present (in micrograms)}}{\text{wt. of sample (in grams)}}$$

Literature References

The development of this method is unreported. The following references contain discussions and references pertinent to the method.

1. Petrey, A. W., Ind. Eng.Chem., Anal. Ed. 6, 343 (1934)

2. Ahrens, L.H., S. African J. Sci. 39, 98 (1943).

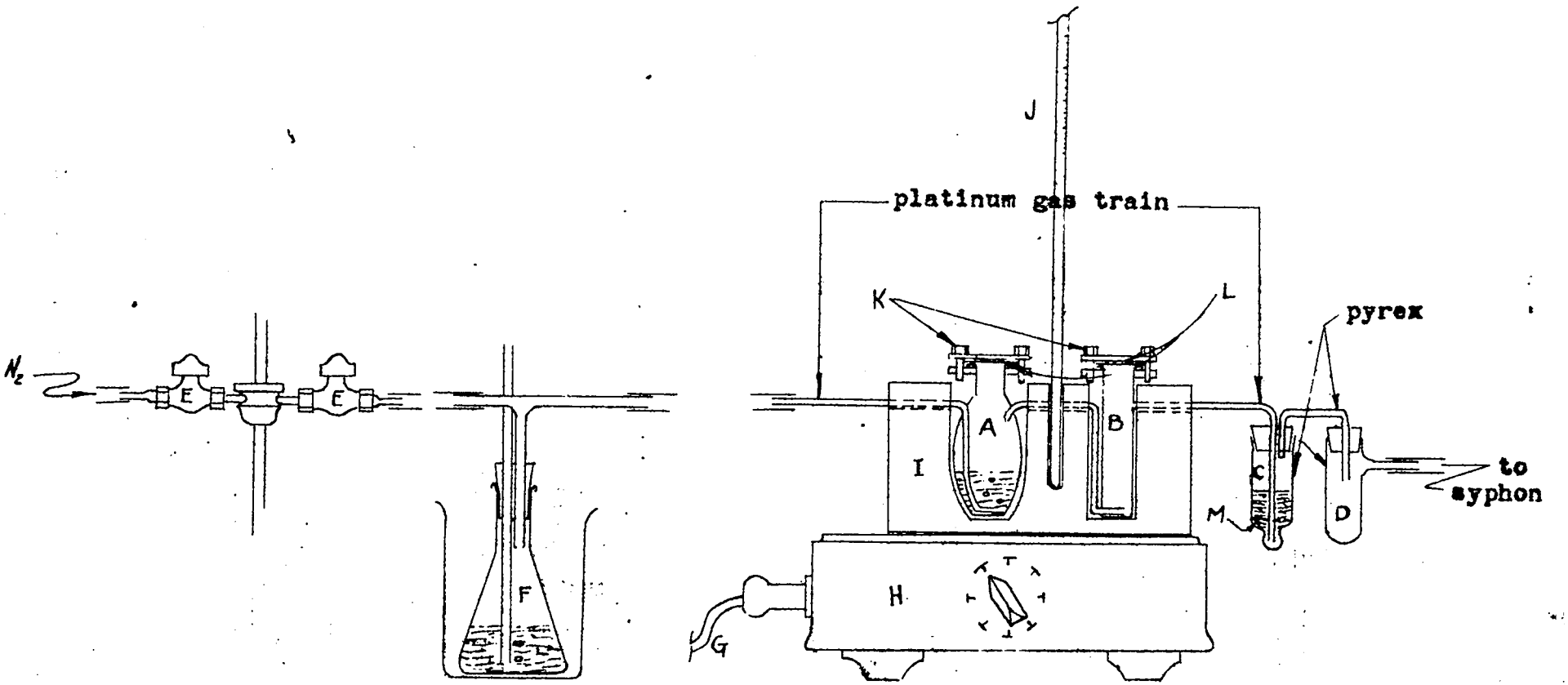
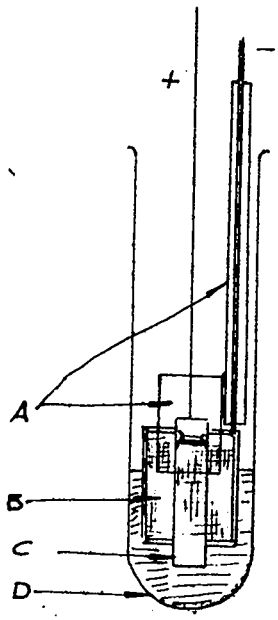


Figure 1. Distillation Apparatus (One-half actual size)

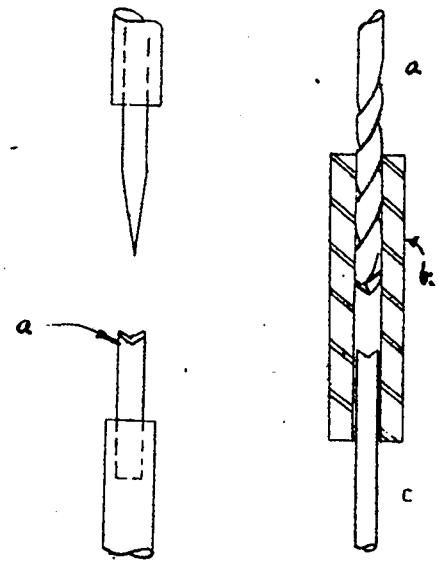
A. distillation chamber
B. spray trap
C. absorption cup
D. water trap
E. needle valves
F. safety trap
G. A.C. from variac
H. hot plate
I. metal heating block drilled for cell chambers and thermometer, and grooved for gas line
J. thermometer
K. steel ring clamps
L. flat platinum caps
M. platinum gauze bubble retainer

APPROVED FOR PUBLIC RELEASE



A. glass tubing insulation
B. circular platinum gauze cathode
C. sample as anode
D. solution tube

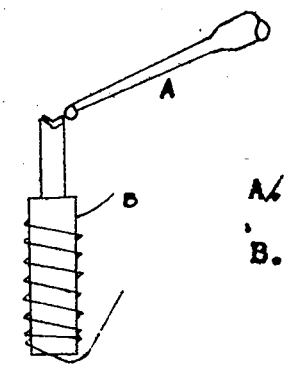
Figure 2.
Electrolytic Cell



A. electrode assembly
a. SrO coated crater containing sample

B. crater forming apparatus
a. steel drill
b. bakelite guide
c. 1/8"dia. graphite

Figure 3.



A. pipette
B. A.C. from Variac

A. position of slit
B. molten SrO

Figure 4.
Detail Of A Heating Coil

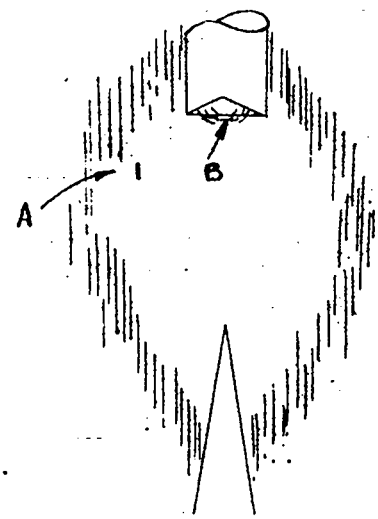


Figure 5.
Arc Image (inverted)

(all drawings actual size)

II F-1

SPECTROCHEMICAL DETERMINATION OF IMPURITIES IN URANIUM METAL AND COMPOUNDS BY THE GALLIUM OXIDE-PYROELECTRIC METHOD

Abstract

The uranium metal or compound is converted to U_3O_8 by ignition in air. A 100 milligram sample of the resulting oxide containing 2 per cent of gallium oxide is arced from the crater of a graphite electrode in a direct current arc. The complex spectrum of uranium does not appear. The quantity of impurities present is estimated by comparison of the densities of their spectrum lines with the corresponding lines of standard spectra.

Sensitivity, Precision and Applicability

Following is a list of elements determinable in U_3O_8 according to the pyroelectric method, together with their sensitivities of detection. Sensitivities are reported in parts per million on the basis of 98 mg. of U_3O_8 analyzed. In general the precision is good to 20 per cent of the amount reported.

It should be emphasized that the limits of sensitivity listed relate to impurities present in oxide. Impurities in metal or salt samples may be determined only if such impurities are not lost in burning the metal or salt to oxide. Boron and silicon in fluoride and mercury in metal are, for example, not determinable by this procedure.

Element*	Sensitivity (ppm)
Li	0.2
Be	0.05
B	0.05
Na	5

* Sc, Ge, Se, Rb, Sr, Y, Te, Cs, Ba, Ru, Rh, [redacted], Re, Os, Ir, Pt, Tl not investigated.

Element	Sensitivity (ppm)
Mg	1
Al	5
Si	2
P	50
K	40
Ca	20
Ti	*
V	20
Cr	5
Mn	1
Fe	*
Co	1
Ni	1
Cu	0.5
Zn	20
As	5
Zr	*
Cb	*
Mo	1
Pd	1
Ag	0.05
Cd	0.05
In	0.2
Sn	1
Sb	5
Rare Earths	*
Ta	*
Au	0.05
Hg	1
Pb	1
Bi	0.2
Th	*

Reagents

1. Purified gallium sesquioxide, Ga_2O_3.**

---

* Unsatisfactory by pyroelectric method.

** To purify gallium sesquioxide or to prepare pure gallium sesquioxide from gallium metal proceed as follows: Dissolve 10 g. of gallium metal (or its equivalent weight of oxide) in HCl, heating to effect solution. Dilute the solution to 50 ml. and adjust the acidity to 7.3 N. Shake the solution in a separatory funnel with a small amount of mercury to reduce the ferric iron and render it non-extractable. Add 50 ml. of di-isopropyl ether and shake thoroughly. Re-extract the aqueous phase with a second ether portion and combine the two fractions. Add 50 ml. of quartz distilled water and shake thoroughly to re-extract the gallium from the ether. Add an equivalent quantity of ammonium oxalate to precipitate the gallium. Collect the gallium oxalate in a platinum Gooch-Munroe crucible and ignite to gallium sesquioxide at 1000° C.

2. Purified uranium oxide, U_3O_8.*

3. LiF, BeO, B_2O_3, NaCl, MgO, Al_2O_3, SiO_2, $Ca_3(PO_4)_2$, KCl, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3, Co_2O_3, Ni_3O_4, CuO, ZnO, As_2O_3, MoO_3, Ag_2O, CdO, In_2O_3, SnO, Sb_2O_3, Au_2O_3, $PdCl_2$, HgO, PbO, Bi_2O_3, c.p. reagent grades.

Apparatus and Materials

1. Tungsten carbide mortar and pestle.

2. Pin vise and needle.

3. Platinum crucibles (18 ml. capacity).

4. A.R.L. graphite electrode cutter.

5. Special spectroscopic graphite electrodes, available from National Carbon Co.

6. Watch-glasses (4 cm.) with off-center holes (Figure 1).

7. Mini-mill, available from Fisher Scientific Co.

8. 2" x 2" 45° quartz prism in adjustable mounting (Figure 2).

9. 35 mm. SA1 film.

10. 4" x 10" 103-F and NH_3- sensitized I-N photographic plates.

11. Bakelite electrode holders (Figure 3).

Procedure

1. Prepare 5 grams of a U_3O_8 standard containing 1000 ppm of each of the metals in the following salts and oxides: LiF, BeO, B_2O_3, NaCl, MgO, Al_2O_3, SiO_2, $Ca_3(PO_4)_2$, KCl, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3, Co_2O_3, Ni_3O_4,

* Place several hundred grams of uranyl nitrate hexahydrate (Mallinckrodt) in a 1 liter separatory funnel and add about 500 ml. of anhydrous ether (Merck). Separate the ether layer from the water layer and re-extract the nitrate into quartz-distilled water. Add enough nitric acid to prevent formation of the insoluble orange compound on evaporation. Evaporate the solution to crystals of uranyl nitrate hexahydrate. Remove as much water and nitric acid as is possible without formation of the insoluble salt. Repeat the ether extraction and the above steps twice. Finally, ignite the resulting salt to U_3O_8 in a muffle furnace.

CuO, As_2O_3, ZnO, MoO_3, Ag_2O, CdO, In_2O_3, SnO, Sb_2O_3, Au_2O_3, $PdCl_2$, HgO, PbO, and Bi_2O_3. Grind the above compounds thoroughly into the U_3O_8 in a tungsten carbide mortar, and mill the mixture on the Mini-mill. Prepare a standard containing 500 ppm. of each of the same metals by grinding 2.50 grams of the first standard with 2.50 grams of pure U_3O_8. Mill the mixture as before. In similar fashion, prepare succeeding standards so that the following ppm are available: 1000, 500, 200, 100, 50, 20, 10, 5, 2, 1, 0.5, 0.2, 0.1, 0.05 and blank.

2. If the sample is metallic, convert it to U_3O_8 by ignition in platinum in air. A Meker burner provides adequate heat for the operation. Salts which may be converted to U_3O_8 by ignition in air should be so converted before proceeding with the analysis.

3. Weigh out 8.0 mg. of gallium sesquioxide as accurately as possible on a tared watch glass pierced with an off-center hole. On the same watch glass weigh out 392 mg. of the U_3O_8 blank. Transfer the whole to a tungsten carbide mortar and grind the gallium oxide thoroughly into the uranium oxide.

4. Prepare a number of 1/4" and 1/8" graphite electrodes to the dimensions shown in Figure 4. Pre-burn the electrodes at 13.5 amperes d.c. for 30 seconds to remove surface contamination. Weigh out 100 mg. of the uranium oxide-gallium oxide blank mixture and transfer it to the 8 mm. deep crater of one of the pre-arced electrodes. Similarly, grind all of the other standards with gallium oxide and load electrodes with 100 mg. charges.

5. Tap each electrode on a hard surface to compact the sample at the bottom of the crater. Push a needle, held in a pin vise, through the charge and into the graphite at the bottom of the crater. Tap the electrode again and withdraw the needle with a rotary motion.

6. Adjust the Dietert Arc Unit to give a current of 13.5 amperes on closed circuit with graphite electrodes in place. Place a pointed 1/8" diameter electrode in the upper electrode holder and a graphite post in the lower holder. Place the electrode bearing the uranium oxide-gallium oxide blank on the lower post and align the electrodes laterally and vertically at a separation of 4 mm. by back-projection of their shadow images on the alignment screen. Check the polarity of the arc, making the lower electrode the anode.

7. Place the 2" quartz prism on its table on the 2nd optical bench of the Dietert and the 3" quartz lens in its place in front of the prism. Their positions should be determined previously, so that a beam of light is sent into the Wadsworth spectrograph. Close the slit of the Wadsworth spectrograph to a width of 50 microns and adjust its height to 2 mm. with the Hartmann diaphragm. Place a 103-F plate in the right hand side of the camera cassette and an NH_3-sensitized I-N plate in the left hand side (as viewed from the rear of the instrument). Set the camera to photograph the range, 5300 Å - 7800 Å. Check the Dietert camera to make certain it contains film.

8. Open the slit of the Dietert spectrograph to a width of 20 microns and bring the No. 2 diaphragm in position at the secondary focal point. Open the spectrograph shutters and strike the arc. Continue the exposure during the pre-silent periods, extinguishing the arc when it begins to sputter.

9. Rack up the cameras of both spectrographs and repeat the arcing procedure for the remaining standards. By arcing the weaker standards first the danger of contamination of succeeding samples is reduced. Develop both film and plates for 3 minutes at 18.0° C. in Eastman D-19 using rocking development. Fix the film in F-5 for 3 minutes and the plates for 10

[redacted]

minutes. Rinse in distilled water and dry out of contact with dust after removal of most of the excess water with a moist viscose sponge.

10. Bind the film between frames cut from 1/16 inch Lucite so that it may be used as a master plate in the Dietert densitometer. The plates should be left unbound, for use on the viewing box.

11. Prepare and arc samples in exactly the same way. All samples should be run in duplicate and a standard sample should be arced on each film and plate to reveal abnormalities which may arise in the procedure.

Evaluation and expression of results

To evaluate a film place it in the film jig in the densitometer and insert the master film in the master plate slide. Compare the standard spectrum with the corresponding standard spectrum on the master film. If the line densities agree for all of the elements of interest, proceed to compare the lines of the sample spectra with the corresponding lines on the master plate, noting the concentrations for which the densities are equal. If necessary, interpolate the sample lines' densities into the standard series of spectra. If the standard spectrum fails to agree with the corresponding spectrum on the master plate, look for a density match with one of the other master spectra. Provided the disagreement is no greater than a factor of two and provided the standard spectrum's gallium lines and general background compare with those of the sample spectra, the evaluation may still be made. In this case, employ the factor necessary to make the standard spectrum agree with the corresponding master plate spectrum in reporting results in ppm.

References

The development of the method described is covered in the following project reports: CC-240, CK-928, CK-993, CK-801, LAMS-122, LAMS-127, LAMS-257.

[redacted]

Figure 1. Watch glass with off-center hole

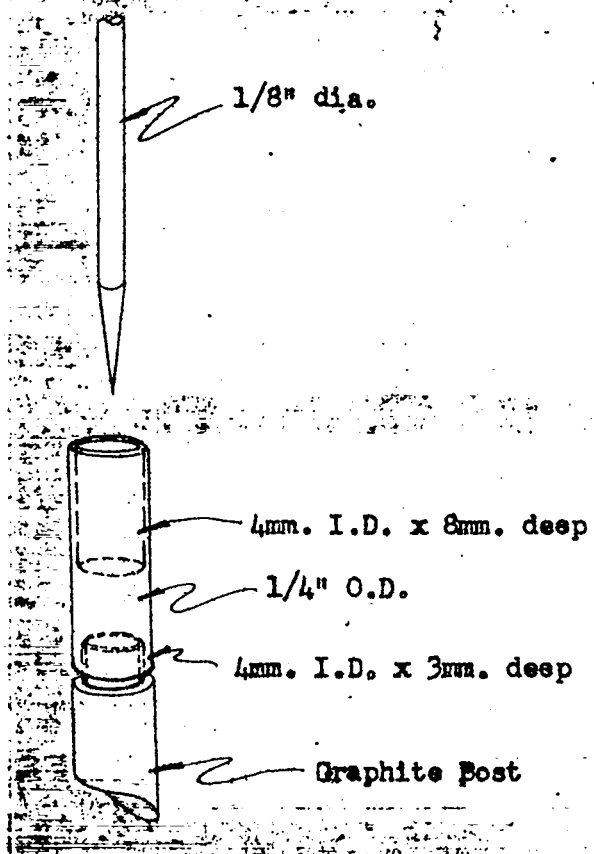


Figure 4. Graphite Electrode Dimensions

Spectrochemical Determination of Impurities in Uranium Metal and Compounds by the Gallium Oxide-Graphite Method.

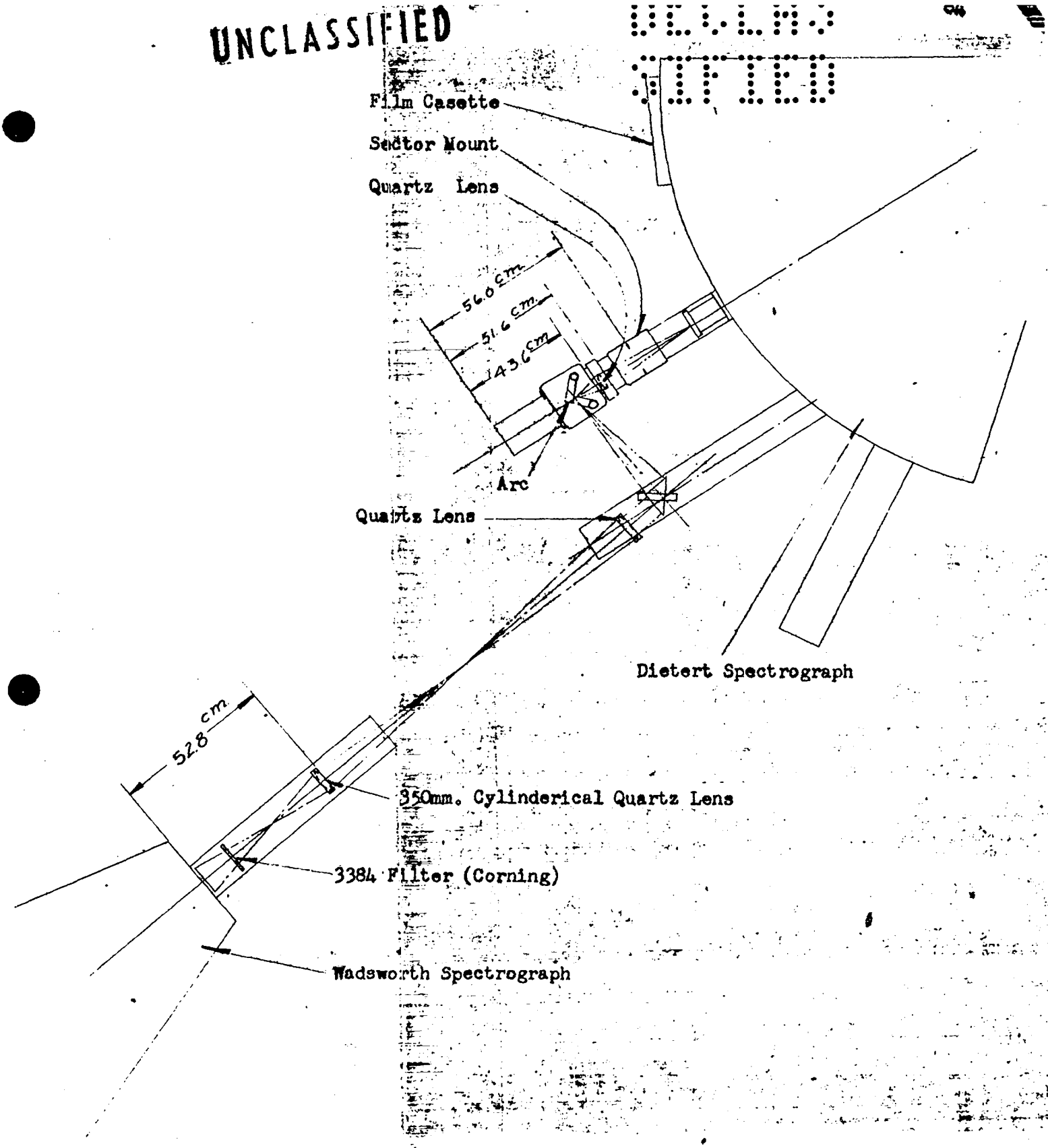


Figure 2. Optical Alignment of Spectrograph

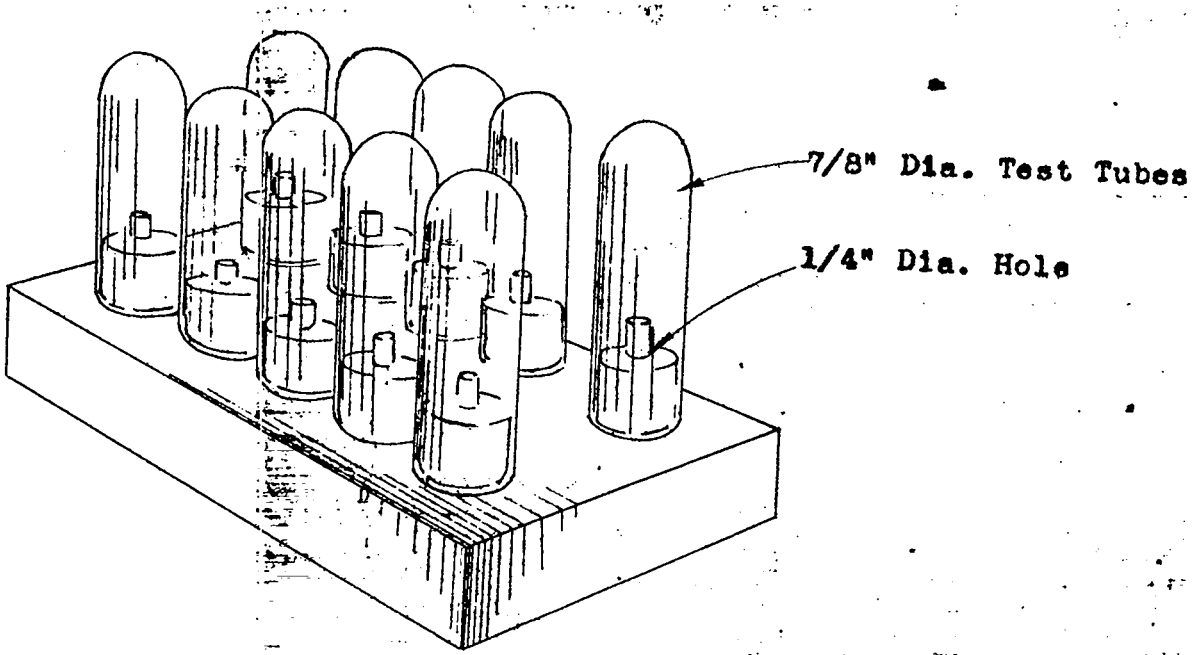


Figure 3. Bakelite Electrode Holder

II G-1

SPECTROCHEMICAL DETERMINATION OF IMPURITIES IN MAGNESIUM OXIDE AND CALCIUM OXIDE

Abstract

5 mg. samples of finely ground MgO or CaO are weighed into 2.5 mm. deep craters of 1/4 inch diameter graphite electrodes and arced at 13.5 amperes for 2½ minutes. A rotating sector, adjusted to transmit 40 per cent of the light is employed to prevent excessive background. Comparison of the densities of the impurity lines with standard spectra permits estimates of the amounts of impurities present.

Sensitivity and Precision

Following is a list of the elements determinable by the method described, together with corresponding sensitivities of detection. The precision is estimated to be ± 50 per cent, average deviation from the mean.

Element	Sensitivity (ppm) MgO	CaO
Be	1	1
B	20	10
Mg	—	? *
Al	20	20
Si	50	50
Ca	10	—
V	—	50
Cr	20	—
Mn	5	10
Fe	10	—
Ni	—	50
Co	—	50
Cu	—	10
Mo	100	50
Ag	—	1
Cd	—	50
In	—	50
Sn	20	10
Sb	—	50
Au	—	10
Pb	20	10
Bi	10	10

* No grade of CaO sufficiently free of Mg was found.

Reagents

1. MgO (best grade available).*
2. CaO (best grade available).*
3. BeO, B_2O_3, Al_2O_3, SiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3, Ni_3O_4, Co_2O_3, CuO, MoO_3, Ag_2O, CdO, In_2O_3, SnO, Sb_2O_3, Au_2O_3, PbO, Bi_2O_3, c.p. grades.

Apparatus

1. Tungsten carbide mortar and pestle.
2. Perforated watch glass (Figure 1, IIF).
3. A.R.L. graphite electrode cutter.
4. Special spectroscopic graphite electrodes, available from National Carbon Co.
5. Mini-mill, available from Fisher Scientific Co.
6. 35 mm. 103 AF film.
7. Bakelite electrode holders (see Fig. 3, II F-3).

Procedure

1. Prepare, by dry grinding and milling, a magnesium oxide (calcium oxide) standard containing 1000 ppm of each of the following impurities: Be, B, Al, Si, Ca(Mg), V, Cr, Mn, Fe, Ni, Co, Cu, Mo, Ag, Cd, In, Sn, Sb, Au, Pb, and Bi. Non-hygroscopic oxides and salts should be used whenever possible. From the 1000 ppm standard, prepare standards of the following concentrations by dilution with pure MgO (CaO): 500, 200, 100, 50, 20, 10, 5, 2, and 1 ppm. Reserve some of the original MgO (CaO) as a blank.
2. Prepare the electrodes 16 mm. long from 1/4 inch diameter special spectroscopic graphite rods (National Carbon Co.) In the ends of each electrode drill craters 2.5 mm. deep. (Both of the craters should have inside diameters of 4 mm.) On the lathe prepare a [illegible] from ordinary 1/4 inch

* The MgO or CaO used should be spectrochemically examined for impurities.

diameter graphite rod to fit tightly into one end of the 2.5 mm. deep craters. (The electrode assembly is similar to that shown in Figure 4, Procedure IIF.)

3. Prepare upper (cathode) electrodes from 1/8 inch diameter special spectroscopic graphite rods, pointing one end to a sharp cone in an adapted pencil sharpener. The electrodes should be about 1½ inches long (Figure 4, II F). Alternatively, cut the upper electrodes to 5/8 inch lengths and fit them into holes drilled in the ends of ordinary 1/4 inch graphite rods; this is done for economy's sake. (A No. 31 drill will make a hole into which the electrodes fit snugly.)
4. Weigh 5 mg. portions of the standards and samples into perforated watch glasses and transfer them to the 2.5 mm. deep craters of the electrodes. Tap the electrodes smartly to accumulate all of the powder at the bottom of the craters.
5. Align the electrodes as carefully as possible on the electrode stand, gauging the 4 mm. electrode separation and lateral and vertical positioning by projecting a shadow-image of the electrodes on a screen behind the stand on the optical axis.
6. Set up a plane mirror, a No. 3384 Corning filter, and a 9 inch f.l. lens on the second optical bench of the Dietert spectrograph so that the spectrum may be photographed simultaneously in both the ultra-violet and visible regions. (See project report LAMS 257 for details.)
7. Adjust the widths of both slits involved to 20 microns and regulate the current output of the D.C. rectifier unit to 13.5 amperes (on short circuit). Arc the electrodes for 2½ minutes before a rotating sector adjusted to transmit 40 per cent of the light. Check the alignment of the electrodes constantly during arcing so that their 4 mm. separation remains

constant.

8. In the same manner photograph the spectra of several standards on the same film, choosing the standards so as to provide lines in the concentration range expected for the impurities of interest.

9. Develop the 103-AF film in total darkness for 3 minutes at 18.0° C. in Eastman D-19, using rocking development. Fix in F-5 for 3 minutes after immersion in an acetic acid short stop for about 10 seconds. Wash the film in a stream of water for about 5 minutes, rinse in distilled water, and dry before a warm air blower after removing most of the water with a viscose sponge.

11. Examine the spectra in the Dietert densitometer-comparator, comparing the line densities of the sample spectra with those of the standards photographed on the same film. Repeat the analysis of any sample whose spectrum shows considerable deviation (weaker or stronger matrix spectrum) from those of the standards.

Expression of results

Express results in ppm as read directly from the standards of equivalent line density, and interpolate if necessary.

[redacted]

SPECTROCHEMICAL DETERMINATION OF THE RARE EARTH ELEMENTS IN URANIUM METAL AND COMPOUNDS

Abstract

The rare-earth elements are separated from uranium in its compounds by means of an ether extraction of the uranium, precipitation of the rare earths as fluorides, and purification of the latter by way of the hydroxides. The final determination is carried out spectrographically, using a Jarrell-Ash-Wadsworth Spectrograph and an A.R.L.-Dietert Multi-Source Unit.

Sensitivity and Precision

Following is a list of elements which have been determined by the procedure described, together with their sensitivities of detection. In general the precision is about 20 per cent deviation from the correct values; usually, results are low by about this amount.

Element	Micrograms	ppm (10 g. sample)
Dy	0.05	.005
Gd	0.05	.005
Sm	0.50	.050
Nd	0.20	.020
Pr	0.10	.010
La	0.01	.001
Ce	0.10	.010

Reagents

1. Nitric acid, 50 per cent, c.p.
2. Ethyl ether, anhydrous.
3. Hydrofluoric acid, 48 per cent, stored in wax containers.
4. Sulfuric acid, conc., c.p.
5. Hydrochloric acid, conc., c.p.
6. Salicylic acid, reagent quality.
7. Ammonium hydroxide, 28 per cent, c.p.
8. Distilled water, stored in Pyrex containers.

[redacted]

Apparatus and Materials

1. 100 ml. platinum dish.
2. 50 ml. platinum crucible and cover.
3. 5 ml. platinum crucible.
4. Paraffin-coated funnel and 100 ml. beaker.
5. Micro-syringe and assorted microliter pipet tips (5, 10, 25, 50, and 100 microliter capacities).
6. Platinum spatula, small.
7. Whatman No. 42 filter paper, 12 cm.
8. 50 ml. and 100 ml. Pyrex beakers.
9. Electrode evaporator.*
10. Arc stand.**
11. 4" x 10" S.A. No. 1 photographic plates (Eastman).

Procedure

1. Weigh sample (~10 g. of metal or equivalent amount of oxide), and dissolve in 50 per cent HNO_3. If sample is already in nitrate form, dissolve in minimum amount of water, acidified with HNO_3. Place the solution on a steam-bath or hot-plate, and evaporate to dryness. Dissolve the nitrate in ethyl ether (anhydrous). (Use 80 ml. for a 10 gram sample). Draw off the aqueous phase and extract the ether three times with 1 ml. portions of distilled water. The ether layer now contains the bulk of the uranium and is discarded.
2. Combine the water extractions in a large platinum dish and dilute to about 5 ml. with dilute HNO_3. Add 15 ml. 48 per cent HF, stir, and allow to stand overnight.

* Use either the infra-red type electrode evaporator described in "Spectrochemical Determination of Impurities in Plutonium Metal and Compounds by the Copper Spark-Cupferron Extraction Method", or a Variac-controlled heating coil fitted about the base of the electrode.

** Arc stand, the regular open arc stand provided with the Jarrell-Ash-Wadsworth Spectrograph.

3. Filter the liquid from the platinum dish through Whatman No. 42 filter paper on a paraffin-coated funnel into a paraffin-coated beaker. Wash out dish with 5 per cent HF and then with distilled water, using these portions to wash the filter paper and precipitate. The filtrate containing uranium is rejected. Ignite the precipitate and paper in a platinum crucible. At the end of the ignition, add 1 ml. of conc. H_2SO_4 to the ignited residue and carefully heat the crucible to drive off HF.

4. Dissolve the sulfate residue in HCl, and dilute to 50 ml. Add 0.5 gram of salicylic acid, and precipitate the rare-earth hydroxides with 28 per cent NH_4OH. Allow at least three hours (or overnight) for the digestion. Filter the solution through Whatman No. 42 paper, and wash the beaker and filter paper several times with 5 per cent NH_4OH until all yellow color is gone. The filtrate contains Ca, Al, and U.

5. Ignite the precipitate and paper in a platinum crucible, and re-dissolve in a minimum amount of dilute HCl. The solution should be reduced in volume to about 50 microliters. Transfer the solution to a freshly-cut copper electrode* by means of a micro-syringe and pipet-tip. Evaporate by means of an electrode evaporator.**

6. Set the A.R.L.-Dietert Multisource Unit for 40 second exposure, C 60 microfarads, L = 25 microhenries, R = 25 ohms, $I_{primary}$ = 19 amperes at 230 volts. Connect the Multisource to the open arc stand. The arc should be 45 cm. from the slit, with a 90 mm. spherical quartz lens 37 cm. from the slit. Set the slit opening for 35 microns wide and 2 mm. high. Use Eastman Spectrum Analysis No. 1 plates for the region from 2100 Å to 4800 Å. Use the coated electrode as the bottom (negative) electrode.

---

* Copper electrodes 1/4" in diameter and 2" long, faced on a lathe, with the sides lightly machined back for 3/4" to insure fresh surfaces.

**See note * on page II H-2.

7. After exposure develop the plates for three minutes in Eastman D-19 developer. Place in an acetic acid short-stop bath for 10 seconds, and then in Agfa fixing bath for 3 minutes. Wash for 10 minutes and dry in stream of warm air.

8. Photometer the selected lines for the rare-earth elements* on the A.R.L. Dietert Projection-Comparator Densitometer, and apply the percentage-transmissions to a percentage-transmission versus quantity curve plotted from a standard plate, to determine the amount of any particular rare earth present in the sample. For a more rapid determination, compare the plate directly (visually) with the standard plate on the modified Judd-Lewis Comparator.

Calculation and Expression of Results

Express results in ppm, obtained by means of the following equation:

$$\text{ppm} = \frac{\text{wt. of element (micrograms)}}{\text{wt. of sample (grams)}}$$

References

The development of the method described above is covered in the following project reports. Details of procedure not here covered may be found in these reports.

BM-325

LAMS-98

* Selected wave lengths, limits of sensitivity and recovery data are given in project report LAMS-98.

[redacted]

SPECTROCHEMICAL DETERMINATION OF IMPURITIES IN PLUTONIUM METAL AND COMPOUNDS BY THE GALLIUM OXIDE-PYROELECTRIC METHOD

Abstract

The plutonium metal or compound is converted to oxide by ignition in air in a dry box. A 25 milligram sample of the resulting oxide is ground with 2 mg. of gallium oxide and 73 mg. of purest uranium oxide (U_3O_8). The mixture is arced in a dry box from the crater of a graphite electrode in a direct current arc. The complex spectra of uranium and plutonium do not appear. The quantities of impurities present are estimated by comparison of the densities of their spectrum lines with the corresponding lines of standard spectra or by photometry, using internal standards.

Sensitivity, Precision and Applicability

Following is a list of elements determinable in plutonium oxide according to the pyroelectric method, together with corresponding sensitivities of detection. Sensitivities are reported in parts per million on the basis of 25 mg. of oxide analyzed. The precision averages about 6 per cent (average deviation from the mean).

It should be emphasized that the limits of sensitivity listed relate to impurities present in oxide. Impurities in metal or compounds may be determined only if such impurities are not lost during the conversion to oxide. Boron and silicon in plutonium tetrafluoride and mercury in metal are, for example, not determinable by this procedure.

In addition, only those compounds which may be converted to essentially pure oxide (PuO_2) may be analyzed. Residues high in sodium (e.g., from the ignition of sodium plutonyl acetate) are not amenable to pyroelectric analysis.

[redacted]

Element	Sensitivity (ppm)
Be	<6
B	<6
Mg	15
Al	300
Si	50
Ca	60
P	500
V	600
Ge	6
Cr	30
Mn	15
Fe	30
Co	30
Ni	60
Cu	<6
Zn	150
As	150
Pd	300
Ag	<6
In	15
Sn	20
Sb	30
Hg	15
Pb	15

Reagents

1. Purified gallium sesquioxide, Ga_2O_3.*

2. Purified uranium oxide, U_3O_8.**

* To purify gallium sesquioxide or to prepare pure gallium sesquioxide from gallium metal proceed as follows: Dissolve 10 g. of gallium metal (or its equivalent weight of oxide) in HCl, heating to effect solution. Dilute the solution to 50 ml. and adjust the acidity to 7.3 N. Shake the solution in a separatory funnel with a small amount of mercury to reduce the ferric iron and render it non-extractable. Add 50 ml. of di-isopropyl ether and shake thoroughly. Re-extract the aqueous phase with a second ether portion and combine the two fractions. Add 50 ml. of quartz-distilled water and shake thoroughly to re-extract the gallium from the ether. Add an equivalent quantity of ammonium oxalate to precipitate the gallium. Collect the gallium oxalate in a platinum Gooch-Munroe crucible and ignite to gallium sesquioxide at 1000° C.

** Place several hundred grams of uranyl nitrate hexahydrate (Mallinckrodt) in a 1-liter separatory funnel and add 500 ml. of anhydrous diethyl ether (Merck). Shake the funnel until all of the solid has dissolved and distributed itself between the ether and water phases (water from the hydrated salt). Remove and discard the aqueous phase. Re-extract the uranyl nitrate from the ether into the quartz-distilled water and add enough nitric acid to prevent formation of the orange insoluble compound on evaporation. Evaporate the solution to crystals of uranyl nitrate hexahydrate. Avoid removing nitric acid and water in quantities sufficient to produce the insoluble orange compound. Repeat the foregoing steps and finally ignite the resulting salt to U_3O_8 in platinum in a muffle furnace.

3. BeO, B_2O_3, MgO, Al_2O_3, SiO_2, $Ca_3(PO_4)_2$, V_2O_5, GeO_2, Cr_2O_3, MnO_2, Fe_2O_3, Co_2O_3, Ni_3O_4, CuO, ZnO, As_2O_3, $PdCl_2$, Ag_2O, In_2O_3, SnO, Sb_2O_3, HgO, PbO, c.p. reagent grades.

Apparatus and Materials

1. Combination dry box for preparing and arcing samples (Figures 1 and 2, II A).
2. Pin vise and steel needle.
3. Platinum crucibles (1 ml. capacity).
4. A.R.L. graphite electrode cutter.
5. Special spectroscopic graphite electrodes, available from National Carbon Co.
6. Arc stand for dry box (Figure 1).
7. Watch glasses (4 cm.) with off-center holes. (Figure 1, II F).
8. Mini-mill, available from Fisher Scientific Co.
9. 103-aF film.
10. Bakelite electrode holders (Figure 3, II F).
11. Tight-fitting dust respirator.
12. 1st-surface aluminized plane mirror in mounting for optical bench.

Procedure

1. Prepare 5 g. of a U_3O_8 standard containing 1000 ppm of each of the metals in the following salts and oxides: BeO, B_2O_3, MgO, Al_2O_3, SiO_2, $Ca_3(PO_4)_2$, V_2O_5, GeO_2, Cr_2O_3, MnO_2, Fe_2O_3, Co_2O_3, Ni_3O_4, CuO, ZnO, As_2O_3, $PdCl_2$, Ag_2O, In_2O_3, SnO, Sb_2O_3, HgO and PbO. Grind the above compounds thoroughly into enough U_3O_8 to bring the total weight to 5 g. Use a tungsten carbide mortar and pestle for the grinding, and mill the mixture on the Mini-mill. Prepare a standard containing 500 ppm of each of the same metals by grinding 2.50 grams of the first standard with 2.50 grams of pure U_3O_8. Mill the mixture

as before. In similar fashion, prepare succeeding standards so that the following are available (ppm): 1000, 500, 200, 100, 50, 20, 10, 5, 2, 1, and blank. The foregoing operations may all be carried out without fear of danger to the analyst. Succeeding operations must be carried out in the dry box by an operator wearing a full laboratory smock, rubber gloves, and a well-fitting dust respirator. Read "Special Health Safety Precautions to be Observed in Spectrochemical Analysis of Plutonium Metal and its Compounds" (Section II A) under "Pyroelectric Method" before continuing.

2. Grind together 2 mg. of gallium sesquioxide* and 25 mg. of pure plutonium dioxide with 73 mg. of each of the standards prepared above. In this manner the following standards are available (ppm referred to the plutonium contained in the mixture): 3000, 1500, 600, 300, 150, 60, 30, 15, 6, 3, and blank.

3. If the sample is in the form of plutonium metal or alloy, transfer it to a 1 ml. platinum crucible in the dry box and ignite it in a micro-furnace at 700-800° C. until conversion to the oxide is complete. If the sample is a solution (e.g. dissolved nitrate) evaporate it to dryness under an infrared lamp in a well-ventilated hood. Wear a plastic visor during this operation and take every precaution to minimize spray during the evaporation. Transfer the platinum crucible containing the evaporation residue to the dry box in a nest of alternately inverted beakers. Ignite the residue to oxide in a micro-furnace in the dry box.

4. Weigh out 6.0 mg. of Ga_2O_3 as accurately as possible on a tared watch glass

---

* The gallium oxide should have been previously ground with Bi_2O_3, CdO, Au_2O_3, and MoO_3 in amounts to give a mixture containing 8 micrograms of Bi, 8 micrograms of Cd, 0.8 micrograms of Au, and 40 micrograms of Mo in each 2 mg. of gallium oxide.

pierced with an off-center hole. On the same watch-glass weigh out 219 mg. of pure U_3O_8 and 75 mg. of the PuO_2 sample in the dry box. Grind the mixture thoroughly in a tungsten carbide mortar and divide it into three 100 mg. portions. Transfer the mixtures to 8 mm. deep craters of pre-burned graphite electrodes. (See Figure 4, II F for dimensions of electrodes.)

5. Tap each electrode smartly on a hard surface to compact the sample at the bottom of the crater. Push a needle, held in a pin vise, through the charge and into the graphite at the bottom of the crater. Tap the electrode again and withdraw the needle with a rotary motion.

6. Adjust the D.C. rectifier unit to give a current of 13.5 amperes on closed circuit with graphite electrodes in place. Put a pointed 1/8 inch diameter electrode in the upper electrode holder and a graphite post in the lower holder. Place the electrode bearing the standard blank on the lower electrode post and align the electrodes laterally and vertically at a separation of 4 mm. by back-projection of their shadow-images on the alignment screen. Check the polarity of the arc, making the lower electrode the anode.

7. Place the 1st surface aluminized mirror and its table on the optical bench of the spectrograph, making sure that its angle is such as to direct the light falling upon it centrally into the slit of the spectrograph. Insert a quartz lens (f.l. 50 cm.) on the optical bench between the mirror and the slit at a position predetermined to focus an image of the arc upon the grating. Check to insure that the slit of the spectrograph is 20 microns wide, and check the diaphragm to make certain that the No. 5 aperture is in place. Test the tension of the film in the camera to insure that it is neither slack nor under stress, and rack the

[redacted]

camera to the No. 10 position.

8. (From this point on the assistance of a second operator is required. One operator must stand behind the dry box with his gloved hands inserted through the gauntlets for the purpose of removing old electrodes and inserting new ones in position. He must also strike the arc by bridging the electrode gap with a piece of clean graphite rod. The second operator must stand before the dry box and manipulate the electrode controls which issue from the front of the dry box. He must also operate the switches for extinguishing the arc, remove or insert the alignment lamp and shutter as required, and attend to the racking of the camera.)

Ignite the arc and expose from this point until the arc hisses and sputters, after having passed through a silent period. Arc succeeding standards in identical manner, proceeding from the weaker standards to the stronger ones to minimize the danger of contamination from dust produced in the arcing. (A film so run is called a "standard film".) Ordinarily, the operator should plan to run several samples in triplicate and to run one or two standards on the same film for normalizing variations from the standard film.

9. Develop the 103-AF film in total darkness for 3 minutes at 18.0° C. in Eastman D-19, using rocking development. Fix the film for 3 minutes in Eastman F-5 after immersion for about 10 seconds in an acetic acid short stop. Wash the film for 5 minutes, rinse in distilled water, and dry in a current of warm air after removal of most of the excess water with a moist viscose sponge.

10. Bind the "standard film" between frames cut from 1/16 inch Lucite so that it may be used as a master plate in the Bietry densitometer.

[redacted]

Evaluate the spectra on a film according to either of the following procedures:

A. Evaluation by Visual Comparison with the Standard Film

Insert the sample film in the film jig of the densitometer and the master film in the master plate guides of the instrument. Compare the standard spectrum of the sample film with the corresponding standard spectrum of the master film. If the line densities agree for all of the elements of interest, proceed to compare the lines of the sample spectra with the corresponding lines on the master film, noting the concentrations for which the densities are equal. If necessary, interpolate the sample lines' densities into the standard series of spectra. If the standard spectrum fails to agree with the corresponding spectrum on the master film, look for a density match with one of the other standard spectra. Provided the disagreement is no greater than a factor of two, and provided the standard spectrum's gallium lines and general background compare with those of the sample spectra the evaluation may still be made. In this case, employ the factor necessary to make the standard spectrum agree with the corresponding master film spectrum in reporting the concentration of each element in ppm.

B. Evaluation by Photometry, Using an Internal Standard

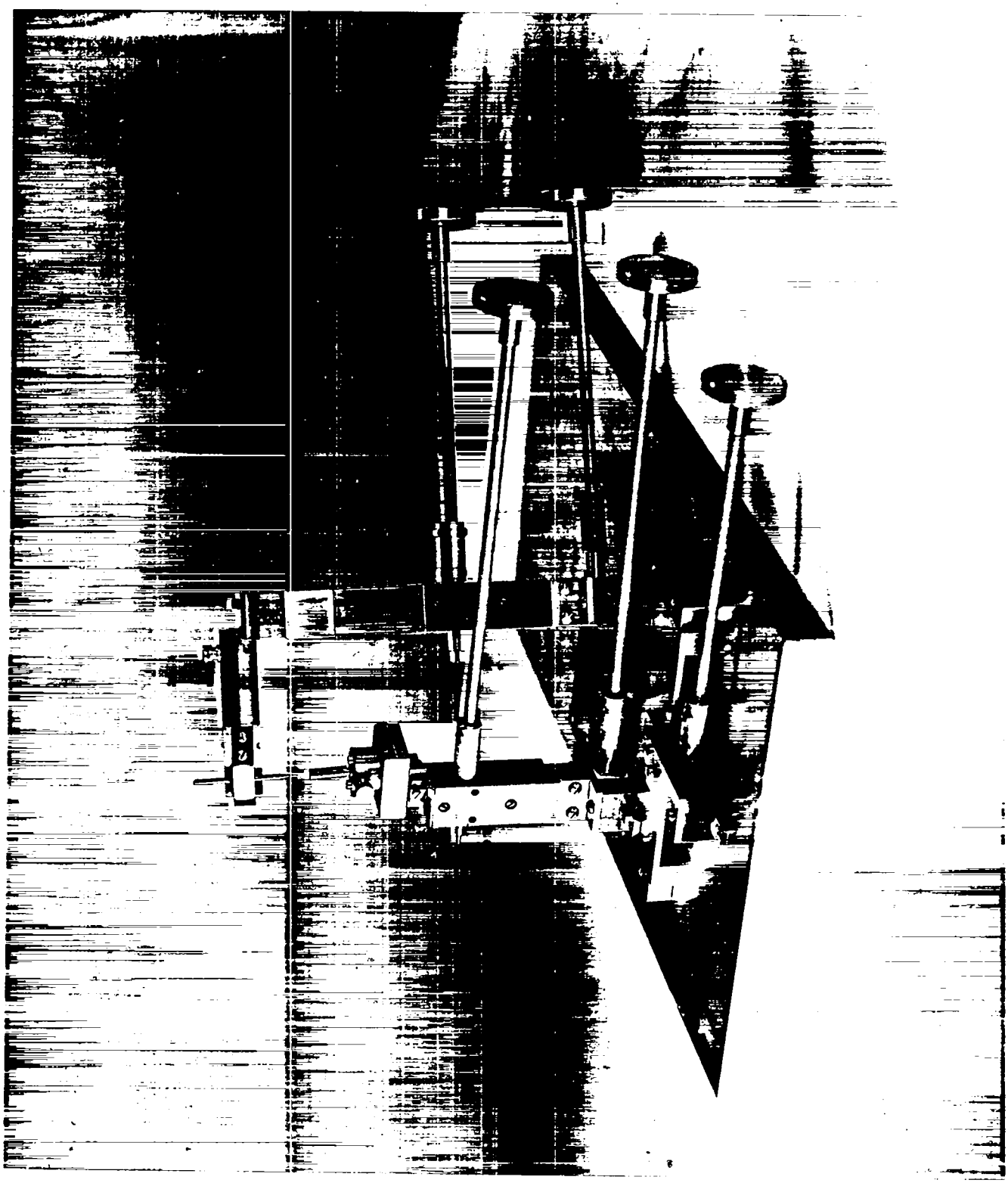
Select, in general, the most sensitive lines of the elements of interest on the master film. Photometer them, together with their adjoining backgrounds, in each of the standard spectra. Select internal standard lines (Bi, Mo, Au, or Cd) which lie within 50 Å of the analysis lines chosen. Photometer the internal standard lines and their neighboring backgrounds. Convert the line and background transmission values into relative line intensity values by reference to a film calibration curve. Subtract the background intensities from the

corresponding line-plus-background intensities. Divide each background-corrected analysis line intensity value by its background-corrected internal standard line intensity value to obtain the so-called "intensity ratio". Plot logarithms of the intensity ratio against logarithms of concentration. Straight line graphs with unit slope should result.

To evaluate sample spectra, obtain the log intensity ratios of interest as described above. Refer these log ratios to the appropriate working curve and read off the concentration of the impurity from the graph. It is well to check the constancy of the working curve from time to time (on each film, if possible) by analyzing a standard sample.

Figure 1.

Arc stand for dry box.



SPECTROCHEMICAL DETERMINATION OF IMPURITIES IN GRAPHITE BY THE GALLIUM OXIDE - PYROELECTRIC METHOD

Abstract

A 50 milligram sample of graphite containing 4 per cent of gallium oxide is arced from the crater of a graphite electrode in a direct current arc. The quantity of impurities present is estimated by comparison of the densities of their spectrum lines with thencorresponding lines of standard spectra.

Sensitivity, Precision and Applicability

Following is a list of elements determinable in graphite according to the pyroelectric method, together with their sensitivities of detection. Sensitivities are reported in parts per million on the basis of 48 mg. of graphite analyzed. The precision obtainable is of the order of ± 20 per cent of the amount reported.

Element	Sensitivity (ppm) (First order)
Ag	<1
As	50
Au	1
B	1
Be	<1
Bi	<1
Ca	10
Cd	<1
Co	<1
Cr	<1
Fe	5
Hg	10
In	<1
Li	5
Mg	5
Mn	<1
Mo	<1
Na	50 (not D lines)
Ni	<1
P	~300
Pb	<1
Pd	<1
Sb	5
Si	5
Sn	1
Tl	1
V	2
Zn	20

Al, Ba, Cb, Ge, Ir, K, Pt, Rh, Ru, Sr, Ta, Th, Ti, U, W, Zr and the rare earths were not investigated.

Reagents

1. Purified gallium sesquioxide. (See footnote p. II F-2 of this manual for method of purification).
2. Ag_2O, As_2O_3, Au_2O_3, B_2O_3, BeO, Bi_2O_3, CaO, CdO, Co_2O_3, Fe_2O_3, HgO, In_2O_3, LiF, MgO, MnO_2, MoO_3, NaCl, Ni_3O_4, $Ca_3(PO_4)_2$, PbO, $PdCl_2$, Sb_2O_3, SiO_2, SnO, Tl_2O, V_2O_5, ZnO, c.p. reagent grades.

Apparatus and Materials

1. Tungsten carbide mortar and pestle.
2. Watch glasses (4 cm. diameter) with off-center holes (See Figure 1, following p. II F-6 of this manual).
3. A.R.L. graphite electrode cutter.
4. 1/4 inch diameter and 1/8 inch diameter special spectroscopic graphite electrodes, available from National Carbon Company.
5. Spectrograph of adequate resolving power and dispersion (e.g. A.R.L.-Dietert 1.5 meter grating spectrograph, 2 inch aperture, 24,000 lines per inch, or Jarrell-Ash-Wadsworth, 6 inch, 21 foot grating spectrograph, 15,000 lines per inch).
6. 35 mm. film (I-N and I-F) or 4" x 10" plates (SA1, 103-0 or 103a-0).
7. Mini-mill, available from Fisher Scientific Company.
8. Rocking developing machine, A.R.L.-Dietert.
9. D. C. arc source, 15 amps, 220 volt (e.g. A.R.L.-Dietert).
10. Bakelite electrode holders (See Figure 3, following p. II F-6 of this manual)
11. Plate viewing box or A.R.L. Densitometer-Comparator.
12. Spectroscopically pure graphite powder (Grade [illegible]-1, National Carbon Co.)

Procedure

1. Prepare 1 gram of a graphite standard containing 1000 ppm of each of the

metals in the following salts and oxides: Ag_2O, As_2O_3, Au_2O_3, B_2O_3, BeO, Bi_2O_3, CaO, CdO, Co_2O_3, Cr_2O_3, Fe_2O_3, HgO, In_2O_3, LiF, MgO, MnO_2, MoO_3, NaCl, Ni_3O_4, $Ca_3(PO_4)_2$, PbO, $PdCl_2$, Sb_2O_3, SiO_2, SnO, Tl_2O, V_2O_5, ZnO, c.p. reagent grades. Use SP-1 graphite for the base material. Grind the above compounds thoroughly into the graphite in a tungsten carbide mortar and mill the mixture on the Mini-mill.

Prepare a standard containing 500 ppm of each of these metals by grinding 500 mg. of the above standard with 500 mg. of pure SP-1 graphite. Mill the mixture as before. In similar fashion prepare succeeding standards so that the following standards (ppm) are available: 1000, 500, 200, 100, 50, 20, 10, 5, 2, 1, and blank.

2. Cut lower electrodes from 1/4 inch diameter special spectroscopic graphite rods to the dimensions shown in Figure 1. Cut upper electrodes from 1/8 inch diameter special spectroscopic graphite rods to the dimensions also shown in Figure 1. Prepare lower electrode support posts and upper electrode holders from 1/4 inch diameter ordinary graphite rod to dimensions shown in Figure 1, following p. II J-4.

   Preburn a number of upper and lower electrodes for 30 seconds at 13.5 amperes to remove superficial contamination.

3. Weigh out 96 mg. samples of graphite to be analyzed and 4 mg. of Ga_2O_3 on watch glasses and transfer the material to a tungsten carbide mortar for thorough grinding. Divide the mixtures into 50 mg. portions and transfer to the craters of previously burned lower electrodes. In similar fashion, prepare a number of electrodes containing standard graphite samples in the range of impurity concentration anticipated.

4. Adjust the slit of the spectrograph to 25 microns. Regulate the arc source to provide a short circuit current of 13.5 amperes. Arc the samples and standards on the same film or plate, exposing the emulsion from the beginning

of arcing to the end of the silent period.

5. Develop films or plates for 3 minutes at 18.0 ±0.5° C. in Eastman D-19 developer. Fix SA1 emulsions for 3 minutes in Eastman acid hypo after brief immersion in an acetic acid short stop, and wash for 3 minutes in running water. (103-O, 103a-O, I-N, and I-F emulsions should be fixed for 10 minutes and washed for 10 minutes). Dry plates or films in a stream of dust-free air.

6. Examine plates or films either on the viewing box with a magnifying glass, or, preferably, in the A.R.L. Dietert Densitometer-Comparator. Compare the sample spectra with the standard spectra, interpolating the visual blacknesses and breadths of the lines of the former into the lines of the series of standard spectra. Express the impurity concentrations directly in parts per million.

In general, the most sensitive arc lines of the elements (raies ultimes) are used in the evaluation of the spectra. A table of such lines is to be found in the M.I.T. Wave-Length Tables.*

* Harrison, George R. (editor), "M.I.T. Wave-Length Tables", p. xviii, Table III, New York, John Wiley and Sons, Inc., 1939.

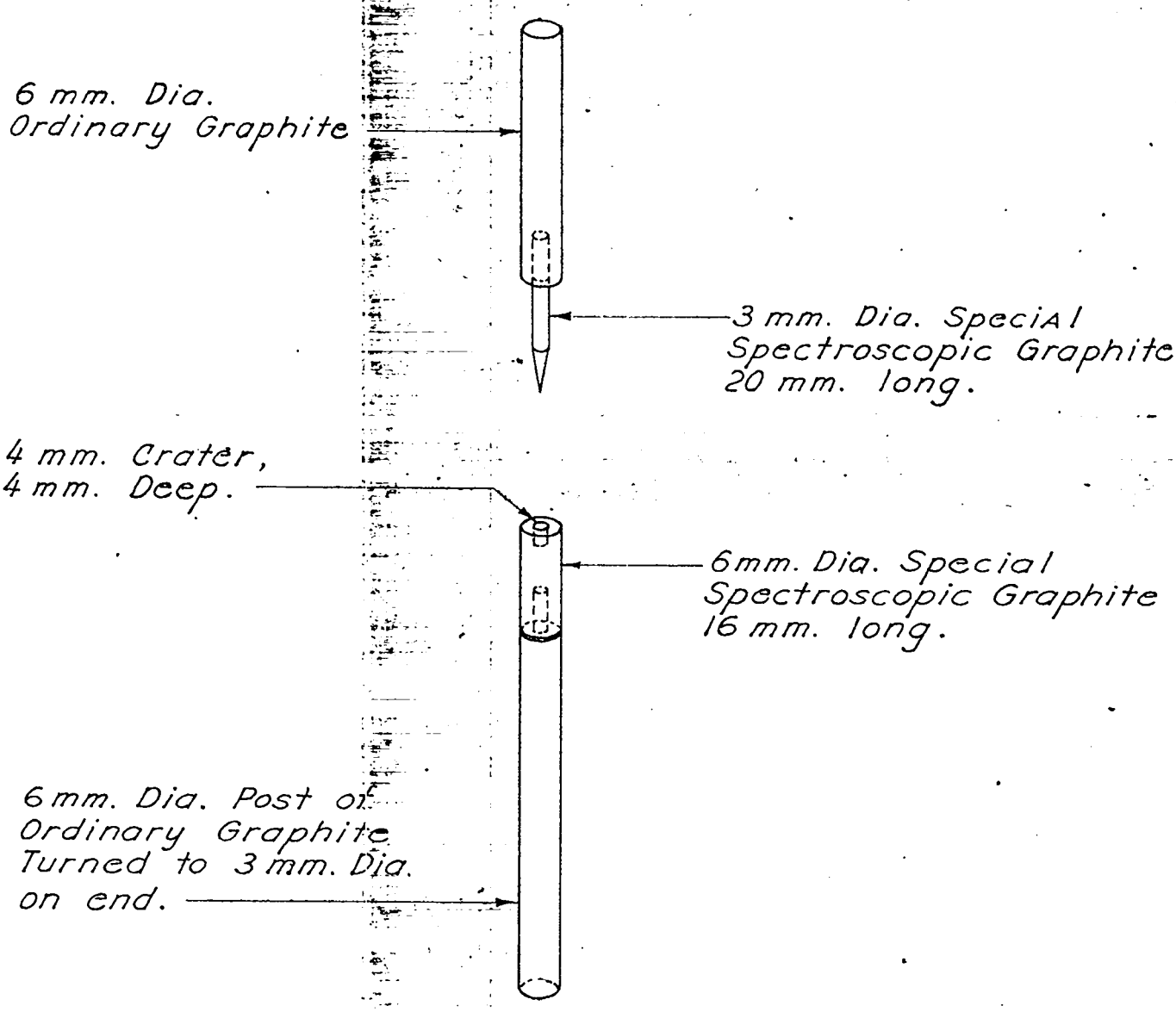


FIGURE 1 - ELECTRODE DIMENSIONS

The Spectrochemical Determination of Impurities in Graphite by the Gallium Oxide - Pyroelectric Method.

II K-1

SPECTROCHEMICAL DETERMINATION OF GALLIUM IN PLUTONIUM METAL AND COMPOUNDS BY THE ISOPROPYL ETHER EXTRACTION METHOD

Abstract

Gallium is extracted as a chlorogallic acid complex from hydrochloric acid solutions by means of isopropyl ether. The complex is re-extracted into a small quantity of pure water, which is evaporated on copper electrodes together with an internal standard solution. The residue is excited in a condensed spark discharge and the quantity of gallium evaluated by photometry of the resulting photographed spectrum.

Reagents

1. Concentrated hydrochloric acid.
2. Re-distilled isopropyl ether.
3. Distilled water.

Apparatus and Materials

1. Glass-stoppered pyrex graduated cylinder, 10 ml.
2. Glass-stoppered volumetric flask, 10 ml.
3. Copper electrodes, $\frac{1}{4}$" dia. x $1\frac{1}{2}$" long.
4. Electrode evaporator (see Figure 3, Section II C).
5. Micro-syringe and pipet tips (50 microliter capacity).
6. Type 103-0 Eastman photographic plates, 4" x 10".
7. Spark discharge chamber (see Figures 1 and 2, Section II B).
8. Wadsworth fully automatic stigmatic grating spectrograph, 21' grating, 15,000 lines per inch (Jarrell-Ash Co.).
9. Dietert spark unit.
10. Dietert rocking developing machine.
11. Dietert Comparator-Densitometer.

Procedure

HEED HEALTH SAFETY RULES OUTLINED IN SECTIONS I AND II A.

1. Dissolve a sample of gallium-plutonium alloy, weighing about 50 milligrams, in hydrochloric acid in a 10 ml. glass-stoppered volumetric flask. Adjust the acidity to 7.25 N and make the solution up to 5 ml. volume with acid of this concentration. (Note that allowance should be made for the consumption of hydrochloric acid in the dissolving operation. See "Microgravimetric Determination of Gallium in Plutonium-Gallium Alloys", Section V B).
2. Add 5 ml. of isopropyl ether to the solution and shake vigorously for 20 minutes. Allow the phases to separate and transfer a 1 ml. aliquot of the ether phase to a 10 ml. glass-stoppered volumetric flask. Add 5 ml. of distilled water to the volumetric flask and shake vigorously for 20 minutes to re-extract the gallium into the water. Make the water phase volume up to 10 ml.
3. Withdraw, by means of a micro-pipet, a 50 micro-liter aliquot of the water phase and divide it about equally between the tips of two copper electrodes. Evaporate the solutions just to dryness on the copper electrodes by means of an electrode evaporator.
4. Divide a 50 micro-liter portion of an internal standard solution (containing 80 micrograms of molybdenum per milliliter) between the same electrodes. Evaporate these solutions to dryness as described above.
5. In similar fashion, prepare copper electrodes bearing 1.0 and 0.28 micrograms of gallium and 4 micrograms of molybdenum (duplicate pairs) by evaporation of appropriate volumes of a standard gallium chloride solution.

6. Insert the electrodes, by pairs, in the holders of the spark discharge chamber, gauging their 2 mm. separation and lateral and vertical alignment by back-projection of their shadow image on a graduated screen behind the chamber.

7. Place a 4" x 10", 103-0 plate in the left side of the camera cassette (as viewed from the back of the spectrograph). Set the spectrograph to photograph the region, 2300 - 4700 Å. Excite the electrodes for 50 seconds in a condensed spark discharge (25,000 volts, 0.32 m H, 0.021 μF) and photograph their spectra through a slit whose width is 25 microns.

8. Prepare a "standard plate" bearing the spectra of gallium in the following quantities: 1.0, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, and 0.00 micrograms. Each spectrum should contain the lines of molybdenum at 4.0 micrograms. Employ the techniques described above for electrode preparation and excitation. (The "standard" plates need be prepared only once or twice, since data obtained from them are used to construct working curves.)

9. Develop plates for 3 minutes at 18.0° C. in Eastman D-19. Following brief immersion of the plates in an acetic acid short stop, fix them for 10 minutes in acid hypo. Wash the plates in a stream of water for 10 minutes, rinse in distilled water, and finally dry them in a stream of warm air.

10. Photometer the Ga: 4033 Å and Mo: 4232 Å lines in all sample and standard spectra. Convert the line and background transmissions into relative intensities by reference to an H & D curve (one plate from each box should be calibrated). Subtract the background relative intensities from the line plus background intensities to obtain the net line

intensities. Compute the log ratios of the analysis and internal standard line intensities (Ga/Mo). Plot the log intensity ratios for the standard plates against the log of the gallium quantity. (This should yield a straight line of unit slope.) Refer the log intensity ratios for samples to this working curve to obtain the quantity of gallium obtained in the extractions. Use the intensity ratios of the standards which were photographed on the same plates as the samples to check the validity of the working curve, correcting the latter as may be necessary for any given plate. Finally, calculate the quantity of gallium present in the original samples. Express results in parts per million:

$$\text{ppm} = \frac{\text{Wt. of element (micrograms)}}{\text{Wt. of sample (grams)}}$$

Literature Reference

Project report LA-417

III

COLORIMETRIC PROCEDURES

III A-1

SPECTROPHOTOMETRIC UNITS

Spectrophotometric analysis is based on the property of certain substances of absorbing light of a given wave length more or less selectively. There are several ways of expressing quantatively the amount of absorption.

1. Transmittance

If a beam of light of intensity I_1 enters a medium and a beam of intensity I_2 emerges from the other side of the medium, then the per cent transmittance of the medium is defined as $\frac{I_2}{I_1} \times 100$. Since the light suffers reflection in going from one medium to another (about four per cent of the light is reflected when a perpendicular beam goes from air to glass or vice-versa), it will be seen that per cent transmittance includes reflection losses as well as absorption losses. (A perfectly clear glass having no absorption would have about 92 per cent transmittance.) This unit is most useful for the measurement of light filters, but is useless for chemical analytical purposes because the reflected light has no analytical significance.

2. Transmission

If a beam of light falls on two cuvets a and b (Figure I), cuvet b containing the solution to be measured and cuvet a containing only the "solvent" (i.e., everything in b except the chromophoric substance to be determined) and if a beam of intensity I_o emerges from a and a beam of intensity I emerges from b, then the per cent transmission of the solute in b is defined as

$$T \frac{I}{I_o} \times 100.$$

It will be noted that if the solvent is properly chosen (i.e., if it has the same refractive index as the solution for the wave

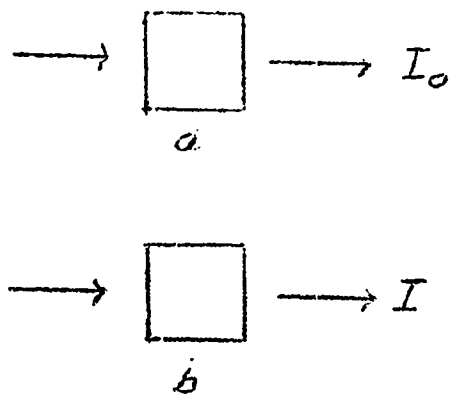


Figure 1

length of light under consideration), the reflection losses are equal in a and b and therefore cancel out.

3. Extinction or Optical Density

According to the Beer-Lambert law, a ray of monochromatic light traversing an absorbing medium decreases in intensity according to the exponential function:

$$(1)\quad I = I_o e^{-\mu l}$$

where I_o is the initial intensity of the beam and I is the intensity after traversing a length l in a medium whose absorption coefficient is μ.

Equation (1) may also be expressed logarithmically:

$$(2)\quad \log_{10}\left(\frac{I_o}{I}\right) = Kl$$

in which $K = \mu \log_{10} e$. The constant K is called the extinction coefficient. If the medium under consideration is a solution of the absorbing material, then K is a function of the concentration of the solution, and if no alteration of the solute occurs with changes in concentration, K will be directly proportional to the concentration. That is to say

$$(3)\quad K = kc$$

The constant k is called the specific extinction of the solute in the particular solvent used, if the concentration, c, is expressed in g/l (mg/ml). The dimensions of k are cm^2/mg.

From (2) and (3) we obtain

$$(4)\quad \log_{10}\left(\frac{I_o}{I}\right) = kcl$$

It is a great advantage in analytical spectrophotometry to define a new unit, called the "extinction" (sometimes called "optical density") by the equation:

$$(5)\quad E = \log_{10}\left(\frac{I_o}{I}\right) = kcl$$

The advantage of this unit is that it is a linear function of the analytically

significant variable, the concentration, and hence cumbersome graphical methods for finding an unknown concentration can be discarded and the calculations performed swiftly and easily with a slide rule.

In the case of a standardized routine analytical procedure, it is convenient to combine several of the factors in (5) since they are kept constant. Substituting m/v for c in equation (5) we write

$$(6)\quad E = \frac{k\, m\, l}{v}$$

in which v is the (standardized) volume of the solution whose absorption is measured, l is the (standardized) light path, and m is the total amount of the substance being determined in the (standardized) volume of solution. (e.g., the total amount of Fe^{++} which has reacted with a standard amount of o-phenanthroline in the standardized volume.)

Since l and v are constant, equation (6) becomes

$$(7)\quad E = k' m \quad \text{or}$$

$$(8)\quad m = E \cdot \frac{1}{k'}$$

It is proposed that the factor, $f = \frac{1}{k'} = \frac{v}{kl}$, be called the "extinction factor by analogy with the gravimetric factor. If f is determined for a standardized spectrophotometric procedure, then the amount of the material being determined in the original sample is found simply by multiplying the observed extinction by f.

Most spectrophotometers read in both per cent transmission and in extinction. It will be noted from equation (5) that when T = 100 per cent, E = 0; when T = 10 per cent, E = 1; when T = 1 per cent, E = 2; etc.

The use of E rather than T has a distinct advantage in qualitative spectrophotometric analysis. Equation (5) may be written for two different concentrations c_1 and c_2 $(c_2 = q\, c)$

$$(9)\quad \log E_1 = \log k\, l + \log c_1$$

$$(10)\quad \log E_2 = \log kl + \log c_1 + \log q$$

It will be noted that (10) differs from (9) only by the presence of a constant term (log q). That is, if E is plotted against wave length on semi-logarithmic paper for two solutions differing only in concentration, the two curves will be identical except for vertical displacement. The fact that such a plot gives a curve whose shape is independent of concentration is a great aid in determining possible differences between solutions.

A convenient summary of terms and abbreviations used in analytical spectrophotometry will be found in Gibb.* Chapter II of this text is recommended as a reference for a discussion of the Beer-Lambert Law and a description of many commercial spectrophotometers.

* Gibb, T. R. P. "Optical Methods of Chemical Analysis", Table 7, p. 75 New York, McGraw Hill Book Co., 1942

III B-1

COLORIMETRIC DETERMINATION OF PHOSPHORUS IN URANIUM AND PLUTONIUM METALS

Abstract

The method is essentially that of Berenblum and Chain[1] with slight modifications as given in the project reports [2,3]. The phosphorus is converted to ortho-phosphate by dissolving the sample in an oxidizing acid. The phosphate is then treated with ammonium molybdate and the resulting phosphomolybdic acid complex is extracted into n-butyl alcohol. The alcoholic phase is shaken with stannous chloride solution to give molybdenum blue which is measured spectrophotometrically. Silicate interference is eliminated by extracting the phosphomolybdic acid complex from 1 N H_2SO_4 solution.

Applicability

The method is applicable to both uranium and plutonium metals and to their compounds.

Size of Sample, Limit of Sensitivity and Range

Sample size, 10 -100 mg. Limit of sensitivity, about 0.2δ P, (20 ppm on 10 mg. sample). Range, 0.2 - 12δ P.

Reagents

1. Conc. HCl (P and As free).
2. Conc. HNO_3 (P and As free).
3. 10 N H_2SO_4 (approx.) prepared by diluting As free H_2SO_4.
4. 1 N H_2SO_4 prepared by diluting the 10 N H_2SO_4.
5. Stock solution of $SnCl_2$, made by dissolving 10 g. of c.p. salt in 25 ml. conc. HCl. This solution should be stored in a brown bottle and kept in the dark; it should be made up fresh every 10 days.
6. Dilute $SnCl_2$ prepared by diluting 1 ml. of the stock solution to 200 ml. with 1 N H_2SO_4. This solution should be made up fresh daily.
7. Ammonium molybdate solution (5 per cent) prepared from Bakers special

reagent for micro analysis, P content not over 0.0002 per cent PO_4. This solution should be stored in a paraffin-coated, glass-stoppered bottle to prevent picking up of silica.

8. n-Butyl alcohol, redistilled.

9. 95 per cent ethyl alcohol, undenatured.

10. Stock standard phosphate solution, 100 γ P per ml. prepared by dissolving 0.4389 g. KH_2PO_4 in 1 l. of distilled H_2O.

Apparatus

1. 8 ml. quartz crucibles.

2. Special separatory funnels 30 - 60 ml. (Figure).

3. 5 ml. mixing cylinders.

4. Beckman Spectrophotometer.

Procedure

IF PLUTONIUM METAL AND ITS COMPOUNDS ARE TO BE ANALYZED, HEED HEALTH SAFETY RULES OUTLINED IN SECTION I.

1. To the sample of metal (10 - 100 mg.) in a 8 ml. quartz crucible add 0.5 ml. of conc. HNO_3 and cover to prevent loss of spray. In case of plutonium metal conc. HCl is added dropwise after the addition of HNO_3 until solution of the metal begins. When the reaction subsides more HCl may be added.*

2. After the metal has dissolved take the solution to dryness under an infrared lamp.

3. Take up the residue (with heating) in 0.5 ml. of 10 N H_2SO_4.

* Plutonium metal is difficultly soluble in aqua regia and tends to become passive. The addition of HCl will cause the reaction to begin again. After solution, however, a small amount of black oxide residue remains. In phosphorus analysis this residue is ignored because it is doubtful if it contains an appreciable amount of phosphorus after the H_2SO_4 treatment which follows. If desired, the black residue may be dissolved by heating to fuming with H_2SO_4.

4. Transfer the solution to the specially designed separatory funnel (Figure) using three 1 ml. portions of distilled water.
5. Add 1.5 ml. of 5 per cent ammonium molybdate and mix. Let stand for 5 - 10 minutes.
6. Add 5 ml. of n-butyl alcohol and agitate for 2 minutes by passing a current of nitrogen through the side arm of the separatory funnel. The nitrogen should be passed through a scrubbing bottle containing a small amount of 1 N H_2SO_4 and a layer of n-butyl alcohol. The gas issuing from the funnel is passed through a cotton plug or another wash bottle to trap any spray (Figure).
7. Let stand 5 minutes to permit the two phases to separate; draw off the aqueous phase and save for metal recovery.
8. Wash the n-butyl alcohol layer twice with 4 ml. portions of 1 N H_2SO_4. The washing is carried out by passing nitrogen through the separatory funnel for about 30 seconds.
9. Draw off the wash liquid each time and add to the original aqueous phase for recovery of metal.
10. Add 5 ml. of dilute $SnCl_2$ solution and agitate by passing nitrogen through the solution for about 1 minute.
11. Draw off and discard the aqueous phase. Transfer the n-butyl alcohol containing the molybdenum to a 5 ml. glass-stoppered mixing cylinder, washing the funnel with about 1 ml. 95 per cent ethyl alcohol.
12. Dilute the alcoholic solution to exactly 5 ml. with 95 per cent ethyl alcohol.
13. Using 0.5 ml. 10 N H_2SO_4 prepare a reagent blank by exactly the same procedure used in the analysis of a sample (steps 4 through 12 above).
14. Compare the sample with the reagent blank using the Beckman spectrophotometer and a wavelength setting of 730 mμ.
15. Read the amount of phosphorus contained in the sample from a standard trans-

mittance curve prepared by measuring the transmittance of known amounts of P as KH_2PO_4 or calculate it from the extinction equation given under "Calculations and expression of results".

Precautions

1. Frequent checks should be made on the reagents to insure a good blank. A good blank of all reagents should give an optical density no greater than 0.20 when compared with pure n-butyl alcohol.
2. It is essential that HNO_3 be added first in the dissolving of the metal to prevent possible loss of P as PH_3.
3. Because of the great tendency for ammonium molybdate solutions to pick up silica, it is essential that this solution be kept in a paraffin coated bottle. This is the most probable source of a high blank.
4. To prevent silica interference it is important that the solution to be extracted be made at least 1 N with H_2SO_4 before adding the ammonium molybdate. Because of the suppressed ionization of silicic acid in 1 N H_2SO_4 the n-butyl alcohol soluble silicomolybdic acid complex is not formed; once formed, however, it is extractable even from 1 N H_2SO_4.
5. If the $SnCl_2$ solution is old a turbidity can be centrifuged down before transferring to the spectrophotometer cuvets.
6. Arsenic interference is not completely eliminated by extracting from 1 N H_2SO_4 [3].

Calculations and expression of results

The phosphorus content of the sample may be calculated from the extinction equation

$$c = \frac{E}{0.112}$$

where c represents the micrograms of P per 5 ml. of n-butyl alcohol and E is the extinction (optical density) observed when the length of the light path is

1 cm.

Results are expressed in ppm which are given by the following formula:

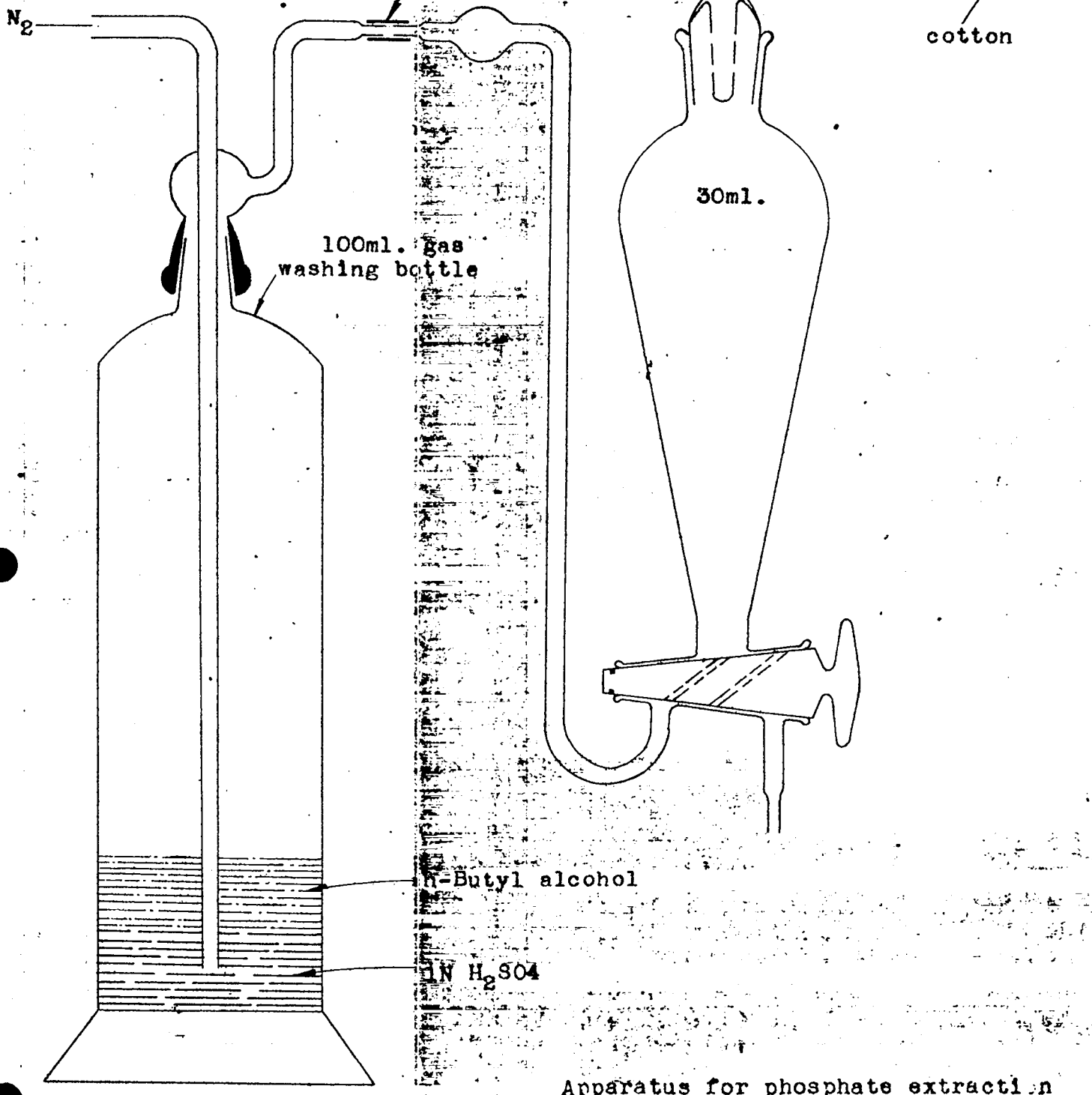
$$\text{ppm P} = \frac{\gamma \text{ P in sample}}{\text{wt. sample in grams}}$$

Literature References

(1) Berenblum and Chain, Biochem. J., 32, 295 (1938).

(2) Project report CK-1229

(3) Project report CK-1326



Apparatus for phosphate extraction

Colorimetric Determination of Phosphorus in Uranium and Plutonium Metals

III C-1

COLORIMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF ACID-SOLUBLE SULFIDE SULFUR

Abstract

Sulfide sulfur in the sample is converted to H_2S by treatment with HCl and is distilled into a solution of $ZnAc_2$. The distillate is treated with p-amino-dimethylaniline and $FeCl_3$ which converts the H_2S to methylene blue. The latter is then determined spectrophotometrically.

Applicability

The method has been applied to uranium and to plutonium metals and is presumably applicable to any materials which dissolve in non-oxidizing acids with the release of their sulfide sulfur as H_2S.

Size of sample and Limit of Sensitivity

The size of sample is determined by the sensitivity required. Since the limit of detection of the method is approximately 1γ, the limits of sensitivity are:

Sample size	Limit of sensitivity
10 mg.	100 ppm
100 mg.	10 ppm
1 gram	1 ppm

Reagents

(a) Separation of H_2S

1. 2 N HCl for dissolving sample.
2. 2 per cent $ZnAc_2$ solution for trapping H_2S.

(b) Color development

1. Standard Na_2S solution for determining specific extinction — Dissolve 0.746 grams $Na_2S \cdot 9H_2O$ in H_2O and dilute to 100 ml. 1 ml. ⇔ 1 mg. $S^=$. (If care is taken to select large, well-formed crystals of $Na_2S \cdot 9H_2O$ which are not discolored and are not wet, this solution may be taken

as a primary standard and need not be assayed.*

2. Caro-Fischer reagent — Dissolve 25 mg. p-aminodimethylaniline (Eastman practical grade) in 7 ml. conc. HCl. Add 2.0 ml. 0.1 M $FeCl_3$ solution and dilute to 20 ml. This solution must be prepared fresh daily and is hence best made up in small quantities.

Apparatus

(a) Separation of H_2S

Same as for volumetric method.**

(b) Determination

1. 25 ml. volumetric flasks.
2. 2 and 4 ml. pipets.
3. Assorted micropipets — 5, 10, 20, 25 λ.
4. Constant temperature water bath.
5. Spectrophotometer (e.g. Coleman Model No. 11).

Procedure

IF PLUTONIUM AND ITS COMPOUNDS ARE TO BE ANALYZED HEED HEALTH SAFETY RULES OUTLINED IN SECTION I

(a) Separation of H_2S

Same as for volumetric S method. (See "Volumetric Determination of Microgram Quantities of Acid Soluble Sulfide Sulfur") Use 4 ml. 2 per cent $ZnAc_2$ solution to trap the H_2S.

(b) Determination of H_2S

1. Transfer the $ZnAc_2$ solution to a 25 ml. volumetric flask and dilute to about 20 ml. with distilled water. Place the flask in the constant temperature bath at 25° C. (± 0.5° C.) and allow it to reach thermal equilibrium.

* A few assays have indicated that such a solution is not more than 1 per cent below the calculated value.

** See "Volumetric Determination of Microgram Quantities of Acid-Soluble Sulfide Sulfur", Procedure IV A.

2. Add 2.0 ml. freshly prepared Caro-Fischer solution and mix well. Return the flask to the bath for about 5 minutes.
3. Dilute to volume with distilled water and allow to remain in the constant temperature bath for 20 - 30 minutes more.
4. Determine the extinction spectrophotometrically at 660 mμ using as the reference a similarly prepared solution containing 4 ml. 2 per cent $ZnAc_2$ and 2.0 ml. Caro-Fischer solution diluted to 25 ml. The reference should be prepared fresh daily, preferably at the same time as the samples.

Blank Procedure

It is unnecessary to run blanks on the distillation. The reference solution is equivalent to a blank on the other reagents.

Precautions

(a) Separation

Same as for volumetric procedure.*

(b) Determination

Since the Lauth reaction (conversion of H_2S to methylene blue) is not quantitative, all conditions must be carefully controlled so that the yield may be reproducible:

1. Temperature control is very important and the reaction must always be carried out at the same temperature at which the specific extinction was determined. Not more than 0.5° C. variation should be permitted.
2. The Caro-Fischer solution must be freshly prepared.
3. The extinction of the solution slowly increases on standing, especially if large amounts of $S^=$ are present. The increase after 20 minutes, however, is very slight, usually less than 1 per cent from 20 minutes to

* See "Volumetric Determination of Microgram Quantities of Acid-Soluble Sulfide Sulfur", Procedure IV A.

2 hours.

4. A more dilute Na_2S standard solution should not be used since it would not be stable. The 1 mg./ml. solution should show no significant changes over a period of several weeks if it is kept well stoppered.
5. A single determination of the specific extinction should be sufficient so long as all conditions are kept unchanged. It is desirable occasionally, however, to check the value by running a standard.

Calculation and expression of results

From the series of standards prepared from the standard Na_2S solution (omitting the distillation) calculate the extinction factor f*, which is the quantity of $S^=$ in micrograms required to produce unit change in extinction for the standardized procedure. f can best be evaluated by the least squares equation:

$$f = \frac{\Sigma x^2 - \frac{(\Sigma x)^2}{n}}{\Sigma xy - \frac{\Sigma x \Sigma y}{n}}$$

where

x = micrograms of $S^=$ in the standardized volume of 25 ml.

y = E = extinction

n = number of observations.

The summation is taken over the entire series of standards run. 5, 10, 15, 20 and 25 γ S is a convenient series, since it is easily obtainable with the standard Na_2S solution and commercial micro-pipets. The precision of the colorimetric determination may be evaluated from the five standards by calculating an f for each concentration and comparing it with the least-squares f. This is best expressed as the standard deviation, σ.

$$\sigma = \sqrt{\frac{\Sigma(\Delta f)^2}{n-1}}$$

* See "Spectrophotometric Units", Section III A.

where Δf is the difference between an individual f and the least-squares f,

n = the number of standards.

$\frac{\sigma}{f} \times 100$ = the standard deviation expressed as per cent error.

In addition spiked samples should be distilled to check on the recovery obtained.

The amount of $S^=$ present in the sample is simply

$\gamma S^= = E \cdot f$

when the above method of calculation is used.

Results are best expressed in parts per million.

$$\text{ppm } S^= = \frac{\gamma S^= \text{found}}{\text{weight of sample in grams}}$$

Literature references

L. H. Almy, J. Am. Chem. Soc. 47, 1381 (1925).

A. Suslova, Lab. Prakt. (U.S.S.R.) 16, No. 6, 19-20 (1941).
(in Chemical Abstracts 36, 5110).

O. Spengler, K. Zablinsky and A. Wolf, Z. Wirtschaftsgruppe Zuckerind. 90, 106 (1940) (in Chemical Abstracts 35, 4988).

R. Pomeroy, J. Am. Water Works Assoc. 33, 943 (1941).

R. Pomeroy, Water Works and Sewerage, 83, 279 (1936).

I. St. Lorant, Z. Physiol. Chem. 185, 245 (1929).

W. Mecklenberg and F. Rosenkranzer, Z. Anorg. Chem. 86, 143 (1914).

Project Reports

CC-2078
CK-928
CK-993
CK-1229
CK-1714

COLORIMETRIC DETERMINATION OF IRON IN PLUTONIUM MATERIALS

Abstract

The iron is reduced to the ferrous state with hydroxylamine and determined spectrophotometrically in the presence of trivalent plutonium as the ferrous-orthophenanthroline complex.

Applicability

The method permits the determination of iron down to 100 ppm in relatively pure plutonium metal, plutonium-gallium alloys and plutonium nitrate process solutions.

Method of Sampling

Samples received as solutions are aliquoted by weight or by volume. When samples are in the form of small metal buttons, the entire button is dissolved in constant-boiling HCl and a suitable-sized aliquot of the solution is taken.

Range and Limit of Sensitivity

Although the optimum amount of iron per determination lies between 10 and 40 micrograms, amounts from 1 to 100 micrograms can be determined with some sacrifice in accuracy. The aliquot size should be governed by these limits.

Reagents

1. Constant-boiling HCl, Fe free.
2. HCl, 1 N.
3. Acetic acid-sodium acetate buffer solution. This is prepared by dissolving 84 g. of reagent grade sodium acetate trihydrate in distilled water, adding 20 ml. of glacial acetic acid and diluting to one liter.
4. 20 per cent hydroxylamine hydrochloride solution. This is prepared by dissolving Eastman's white label reagent in distilled water.

5. 0.5 per cent o-phenanthroline. The reagent is prepared by dissolving recrystallized o-phenanthroline in distilled water. A small amount of 95 per cent ethyl alcohol may be used to facilitate solution. This reagent should be colorless.
6. 10 per cent ammonium hydroxide, Fe free.

Apparatus

1. Volumetric pipets, 10 - 200λ capacity, and 1 ml. capacity.
2. Weight pipets, 200λ capacity (see Procedure IV C, Figure 1a).
3. Syringe pipet controls.
4. Volumetric flasks, 10 ml.
5. Beckman quartz spectrophotometer.
6. Cuvets, 1 cm. light path.

Procedure

HEED HEALTH SAFETY RULES OUTLINED IN SECTION I

1. Transfer the aliquot to the bottom of a dry 10 ml. volumetric flask, being careful to get none of the solution in the necksof the flask. For samples containing less than 300 ppm of iron, take two aliquots for plutonium blanks and two aliquots for determinations. For samples containing more than 300 ppm of iron one plutonium blank is sufficient. One plutonium blank is sufficient in any case if a fixed absolute accuracy throughout the range is all that is required.
2. Add 200λ of hydroxylamine hydrochloride solution and allow to stand for one hour or longer.
3. Add 1 ml. of acetic acid-sodium acetate buffer and mix thoroughly.
4. Add 1 ml. of 10 per cent ammonium hydroxide and again mix thoroughly.
5. Add 200λ of 0.5 per cent o-phenanthroline to the samples in which iron is to be determined (not to the plutonium blanks), mix thoroughly, and

allow to stand for 30 minutes. Dilute with distilled water to 10.0 ml. and mix thoroughly.

6. Let the solution stand for 30 minutes and then transfer about 3 ml. of the solution to a clean, dry Beckman cuvet.

7. If equal volume aliquots were taken, use the plutonium blank as a reference. If unequal weight aliquots were taken, use distilled water as a reference (see Precaution 3). Read the extinction at 515 mμ. For unequal weight aliquots correct the observed extinction of the sample for the extinction caused by plutonium. Calculate this from the plutonium blank.

8. Determine the extinction factor by carrying known amounts of iron through the procedure. Distilled water is used as a reference in reading the extinction (see Precaution 3). The concentration of HNO_3 should be approximately the same in the extinction factor determination as in the sample determinations (see Precaution 4). The extinction factor is expressed as micrograms of iron per extinction unit. This factor was determined by one operator as 49.9γ iron per extinction unit in the absence of HNO_3; 51.0γ iron per extinction unit in the presence of 0.005 M HNO_3. The extinction factor for Pu at 515 mμ was found to be approximately 150 mg. Pu per extinction unit.

Precautions

1. Dilution of the sample while still in the +4 valence may cause hydrolysis. The resulting oxide will go into solution slowly when hydroxylamine hydrochloride is added.

2. $SO_4^=$ appreciably decreases the rate of reduction of plutonium to +3 valence. It is presumed to have little effect on the quantitative reduction of the iron. Samples containing sulfate are usually allowed to reduce

[redacted]

for 12 to 24 hours.

3. It is convenient to use distilled water or the plutonium blank as a reference. The use of either is valid only if the iron content of the reagents is negligible and if the extinction of the o-phenanthroline reagent itself is negligible. If the extinction of a reagent blank exceeds 0.010 it should be subtracted from the observed extinction or used as the reference. Each operator should run a reagent blank on any particular set of reagents used.

4. HNO_3 present in amounts to give a final concentration of 0.005 M in the 10 ml. volume appears to decrease the extinction by about 2 per cent. In 0.5 M HNO_3, the decrease is of the order of 90 percent. If the HNO_3 concentration should exceed 0.01 M (in the final 10 ml. volume) it is removed between steps 2 and 3 by adding a small excess of H_2SO_4 to the aliquot and taking it to dryness in a platinum crucible under an infra-red lamp (see Procedure IV C, Figure 2).

Calculations

Express the result as micrograms of iron per gram of plutonium.

Micrograms of iron = extinction x extinction factor.

[redacted]

[redacted]

COLORIMETRIC DETERMINATION OF SUB-MICROGRAM QUANTITIES OF BORON IN CALCIUM METAL

Abstract

Calcium metal is oxidized with water and the hydroxide dissolved in a slight excess of nitric acid. The boron, in the presence of sodium nitrate, is distilled as methyl borate from a specially designed quartz still. The distillate is trapped in calcium hydroxide solution and the boron is estimated by the colorimetric curcumin procedure.

Applicability

The method has been applied to relatively pure calcium metal and calcium oxide. It should be equally useful for other metals and similar compounds. Since both calcium borate and calcium boride are soluble in nitric acid, it is assumed the method can be used to determine boron if present in either of these forms. Satisfactory recoveries have been obtained with samples containing up to 0.5 γ boron corresponding to 5 ppm in a 100 mg. sample. The upper limits of recovery, however, have not been determined.

Range and Limits of Sensitivity

The procedure here described permits the determination of boron in the range 0.05 to 0.5 micrograms which corresponds to a concentration of 0.5 to 5 ppm in a 100 milligram sample, with an accuracy of 12 percent. Accordingly, the lower limit of sensitivity is 0.05 γ of boron in the final volume of 3 ml. to which the solution is diluted for spectrophotometric determination.

Sampling

Small chips are removed from the calcium metal piece and ground in a Wiley mill to fineness -20 mesh to +80 mesh. A 100 milligram sample is taken for analysis.

Reagents

[redacted]

Store all reagents (except where noted) in quartz containers.

1. Distilled water, from a double Barnstead still. If free boric acid is present in the water supply, it will be necessary to distill from NaOH through a quartz still.

2. Nitric acid, concentrated, c.p. The boron content should be less than 1 microgram per ml. Distillation from quartz may be necessary.

3. Calcium hydroxide, 0.1 N suspension, prepared from boron-free calcium metal* and distilled water.

4. Sodium nitrate, reagent grade crystals.

5. Methyl alcohol, absolute. Distill from sodium hydroxide in a quartz still equipped with an efficient spray trap. The alcohol should contain not more than 0.0005 micrograms of boron per ml.

6. Hydrochloric acid 6N. Dilute c.p. concentrated acid with an equal volume of distilled water.

7. Curcumin, 0.1 per cent in ethyl alcohol, using c.p. material, like Eastman's best grade.

8. Ethyl alcohol, 95 per cent. Distill from NaOH through a quartz still.

9. Oxalic acid, 15 per cent solution in distilled water. Use c.p. crystals.

10. Standard boric acid solution, 1 ml. containing 1 microgram of boron. To make stock solution, dissolve 35.7 mg. c.p. H_3BO_3 crystals and dilute to 250 ml. with distilled water. 10 ml. of this stock solution diluted to 250 ml. contains 1 microgram of boron per ml.

11. Sodium hydroxide, 3 N. Sodium from a solution of c.p. sodium chloride in distilled water is electrolyzed into a mercury cathode forming sodium amalgam. The sodium amalgam is drawn off into a quartz beaker, distilled water added

* Boron-free calcium metal was obtained from the Electrometallurgical Corporation, Niagara Falls. It was specially prepared by electrolyzing calcium from a boron-free molten bath and distilling the metal in vacuo in an iron retort.

[redacted]

and allowed to stand overnight. 10 ampere hours of current will yield sufficient sodium for approximately 100 ml. 3 N solution. The NaOH solution is decanted into a weighed platinum bottle. The normality is determined by titrating portions with a standard acid. The weight of the remaining NaOH solution is determined by weighing the bottle and contents, then subtracting the weight of the bottle. The volume of the NaOH solution is determined by this weight and from standard density tables. Dilution to a concentration of 3 N is made by adding the calculated volume of distilled water. For a check, a final titration is made with standard acid. The NaOH solution is stored in the platinum bottle. This method of preparation produces sodium hydroxide with extremely low boron content.

Apparatus

1. Four quartz stills (Figure 1).
2. Spectrophotometer, Beckman Quartz, using absorption cells of 1.00 cm. light path.
3. Steam bath, with openings for four or more vessels, equipped with quartz manifold and distributing apparatus for evaporating in an atmosphere free from carbon dioxide (Figure 2).
4. Drying oven, 10 x 12 x 12 inches, electrically heated and thermostatically controlled. Insert a glass tube through a vent in the top, terminating the tube near the floor of the oven. The air stream is filtered through cotton and dispersed by blowing through the tube into a 10 cm. evaporating dish placed on the floor of the oven.
5. Two flasks, volumetric, 250 ml., quartz, g.s.
6. Four flasks, volumetric, 10 ml., pyrex, g.s.
7. Four flasks, Erlenmeyer, 250 ml., quartz.
8. Two pipets, 5 ml., graduated in 0.1 ml.

[redacted]

9. Five pipets, 1 ml., graduated in 0.01 ml.

10. Filter dome equipped with medium porosity sintered glass filter.

11. Soft glass dropping bottle, 60 ml.

12. Four platinum evaporating dishes, 40 ml. (Quartz beakers may be substituted).

13. Four beakers, quartz, 50 ml.

Procedure

1. Preparation of standard curve.

(It is recommended that quadruplicate determinations be made for each point on the standard curve.) Add 2.5 ml. 0.1 N $Ca(CH)_2$ suspension to each of several 40 ml. platinum dishes.* Add 0, 0.1, 0.2, 0.3, 0.4, etc., up to 0.8 microgram of boron (0.8 ml. standard boric acid solution) to successive dishes. Place on the steam bath, lower the quartz funnel in place (Figure 2), adjust the flow of nitrogen so that it ripples the surface of the liquid, and evaporate to dryness. Watch carefully and remove immediately after dryness is reached and allow to cool. To each dish add 0.25 ml. 6 N HCl and carefully dissolve all precipitate. Next add 0.5 ml. 0.1 per cent alcoholic curcumin and then 0.5 ml. 15 per cent oxalic acid. Swirl to mix thoroughly. Place in the drying oven with forced ventilation, at a temperature of 55° C. ±3° and observe time of drying. Leave in oven 30 minutes in excess of time of drying. Remove and allow to cool. Extract the contents of each dish with 1 ml. 95 per cent ethyl alcohol. Filter through a medium sintered glass filter catching the clear filtrate in a 3 ml. volumetric flask. Repeat with successive small portions of alcohol until all color is quantitatively removed. Dilute with additional alcohol to a final volume of 3 ml., shake, transfer to a cuvet and stopper. Read the extinction E (sometimes referred to as the optical density) at 540 mμ in the spectrophotometer using

* 50 ml. quartz beakers may be substituted although platinum dishes are easier to handle, especially in dissolving the precipitate with HCl.

95 per cent ethyl alcohol as reference. Plot extinction against micrograms of boron present. Repeat in quadruplicate for each level of boron. Figure 3 shows a typical standard curve.

2. Analysis of sample.

Pipet 2.5 ml. of a 0.1 N $Ca(OH)_2$ suspension into a clean 50 ml. quartz beaker. Set the quartz condenser tip in place. Place the beaker in the CO_2 trap and adjust so the condenser tip is beneath the surface of the base (see Figure 1).

Weigh 0.1 gram of calcium metal into flask B, keeping the flask in a horizontal position. Add 0.5 ml. distilled water, keeping the flask under the tap until action ceases. Add 200 mg. $NaNO_3$ crystals and then carefully acidify the solution by adding 0.4 ml. concentrated HNO_3, keeping the flask cool under the tap. Swirl gently to dissolve all calcium hydroxide. (Keep the flask horizontal during the above operations.) This amountoof HNO_3 is sufficient for an excess of 0.1 ml.* Next add 8 ml. purified methyl alcohol and immediately connect flask B to the condenser.

Pour 50 ml. purified methyl alcohol into flask A and connect to still. Place pinch clamp in position. Heat flask A, gently at first, to prevent bumping. Increase heat gradually until alcohol vapors continuously pass through flask B. Then turn on Flask B heater and adjust the Variac to maintain the initial volume in the flask during the entire distillation. Distill approximately 45 ml. methyl alcohol into the receiver, and then lower the receiver until the condenser tip is above the surface of the distillate. Continue distilling until one or two ml. of methyl alcohol have washed the condenser tip. Remove the pinch clamp and turn off both heaters.

Place the receiver on the steam bath and lower the quartz funnel into

* This condition of acidity is important because too much HNO_3 seems to interfere in the subsequent distillation of methyl borate.

place. Regulate the flow of nitrogen so that it ripples the surface of the liquid in the beaker, and evaporate to dryness. Remove immediately upon reaching dryness, allow to cool and proceed with the color development as described in (1) above.

It will be noted that evaporation on the steam bath has left a thin film of precipitate on the walls of the beakers. It is essential that all this precipitate be dissolved by the 0.25 ml. 6 N HCl. This is best accomplished by tilting the beakers and rotating slowly. Care and patience will be essential in developing this technique. It is equally important that the same procedure be followed after the addition of the oxalic acid.

Procedure for total reagent blank

Pipet 1.5 ml. 3 N electrolytic NaOH into flask B. Add 200 mg. $NaNO_3$ crystals, 0.4 ml. conc. HNO_3 and 8 ml. purified methyl alcohol. Proceed with distillation and color development as described above. (Since the electrolytic NaOH is boron free, this procedure results in a true reagent blank.)* Determine the reagent blank at frequent intervals to guard against contamination.

Procedure for individual reagent blanks

If the total reagent blank is greater than 0.10 extinction units when using the Beckman spectrophotometer and regular cuvets, further purification is necessary. To determine that part of the total blank contributed by the various reagents proceed as follows:

$Ca(OH)_2$, HCl, Curcumin, Oxalic acid: Measure 2.5 ml. of the 0.1 N $Ca(OH)_2$ suspension into each of 4 platinum evaporating dishes. Evaporate to dryness on the steam bath in an atmosphere of nitrogen. Allow to cool and proceed with the color development as described under "Preparation of Standard Curve". In

* If boron-free calcium metal is at hand, an alternate procedure is as follows: Weigh 0.1000 gram calcium metal into the distillation flask. Dissolve and proceed as described under "Analysis of Sample."

other words, carry out the standard curve procedure omitting the addition of boron.

Methyl Alcohol: Measure 2.5 ml. of the 0.1 N $Ca(OH)_2$ suspension into each of four platinum evaporating dishes. Add 55 ml. methyl alcohol from a pipet to each dish and proceed as above. The value for the extinction obtained here minus the value for the optical density obtained above gives the data for the calculation of the boron content of the methyl alcohol.

Nitric Acid: Pipet 0.10 ml. concentrated nitric acid into each distillation flask, add 8-10 ml. purified methanol and immediately connect to the condenser. Add approximately 50 ml. purified methanol to flask A (Figure 1) and distill, evaporate and develop color as described under "Analysis of Sample". The extinction obtained in this procedure minus the total extinction obtained under "Methyl Alcohol" gives the data for calculating the boron content of the nitric acid.

Sodium Hydroxide: If it is suspected that the sodium hydroxide is not free from boron, proceed as follows: Carry out the procedure for the "Total Reagent Blank", omitting the sodium nitrate. The value for the extinction obtained here minus the total extinction obtained under nitric acid gives the data for calculating the boron content of the sodium hydroxide. Correction for 0.4 ml. nitric acid must be applied since this is a larger volume of acid than was used under "Nitric Acid".

Sodium Nitrate: The "total reagent blank" minus the blank obtained under "nitric acid" gives the data for the calculation of the boron content of the sodium nitrate. Experience has shown the boron content of reagent quality sodium nitrate to be negligible.

Precautions

1. Observe every possible precaution to prevent reagent contamination.

2. Store all reagents, except where noted, in quartz containers. Corning 728 glass is satisfactory for methyl and ethyl alcohols. The electrolytic NaOH must be kept in a platinum bottle.

3. When a new quartz still is to be put in operation, distill through it a considerable quantity of methyl alcohol to remove boron from the surface of the quartz. Experience has shown that a new quartz surface is contaminated with boron which is difficult to remove. It actually requires weeks to decontaminate a new still. Exercise great care in the use of decontaminated stills.

4. Keep all pipets, glassware and still scrupulously clean. Always rinse with distilled water.

5. Do not use pyrex pipets. Quartz pipets are to be preferred although Kimball glass seems to be satisfactory.

6. Maintain drying oven temperatures at 55° C. ± 3°.

7. Keep flask B cool during addition of reagents to prevent loss of boron.

8. Keep the volume of solution in flask B at the initial volume during the entire distillation.

9. Exclude CO_2 from receiver during distillation. This is the purpose of the enclosure with the ascarite tube placed around the receiving vessel (Figure 1).

10. To prevent bumping, do not heat flask A too rapidly.

11. Avoid spattering during evaporation on the steam bath.

12. Exclude other work, especially glass blowing, from the laboratory as much as possible.

Calculations and expression of results

Express results in parts per million unless otherwise requested.

Calculations by a method of least squares gives a slope of 2.29 for the standard curve (Figure 3). This number indicates the increase in extinction

caused by one microgram of boron under the conditions of the experiment.* For ease in calculating results, the reciprocal of the slope which is given the name "extinction factor", is used. In this case, the "extinction factor" is $\frac{1}{2.29}$ or 0.436. The significance, then, of the "extinction factor" is that it represents the amount of boron (in micrograms of B per 3 ml.) required to produce a change of one unit in the extinction.

To calculate the amount of boron in micrograms, multiply the increase in extinction by the extinction factor.

E (increase) = E sample - E reagent blank

Amt. boron (in micrograms) = (E sample - E reagent blank) x Extinction factor.

Expressed as parts per million:

$$B\ (ppm) = \frac{(E\ sample - E\ reagent\ blank) \times Extinction\ factor}{Wt.\ sample\ in\ grams}$$

Reference

Naftel, James A., Ind. Eng. Chem., Anal. Ed., 11, 407 (1939).

* This value for the slope of the standard curve holds for the type of spectrophotometer and cuvets used here. In addition, the conditions existing for the color reaction with curcumin also influence the slope. The value given above should not be taken as real unless actually determined by experiment.

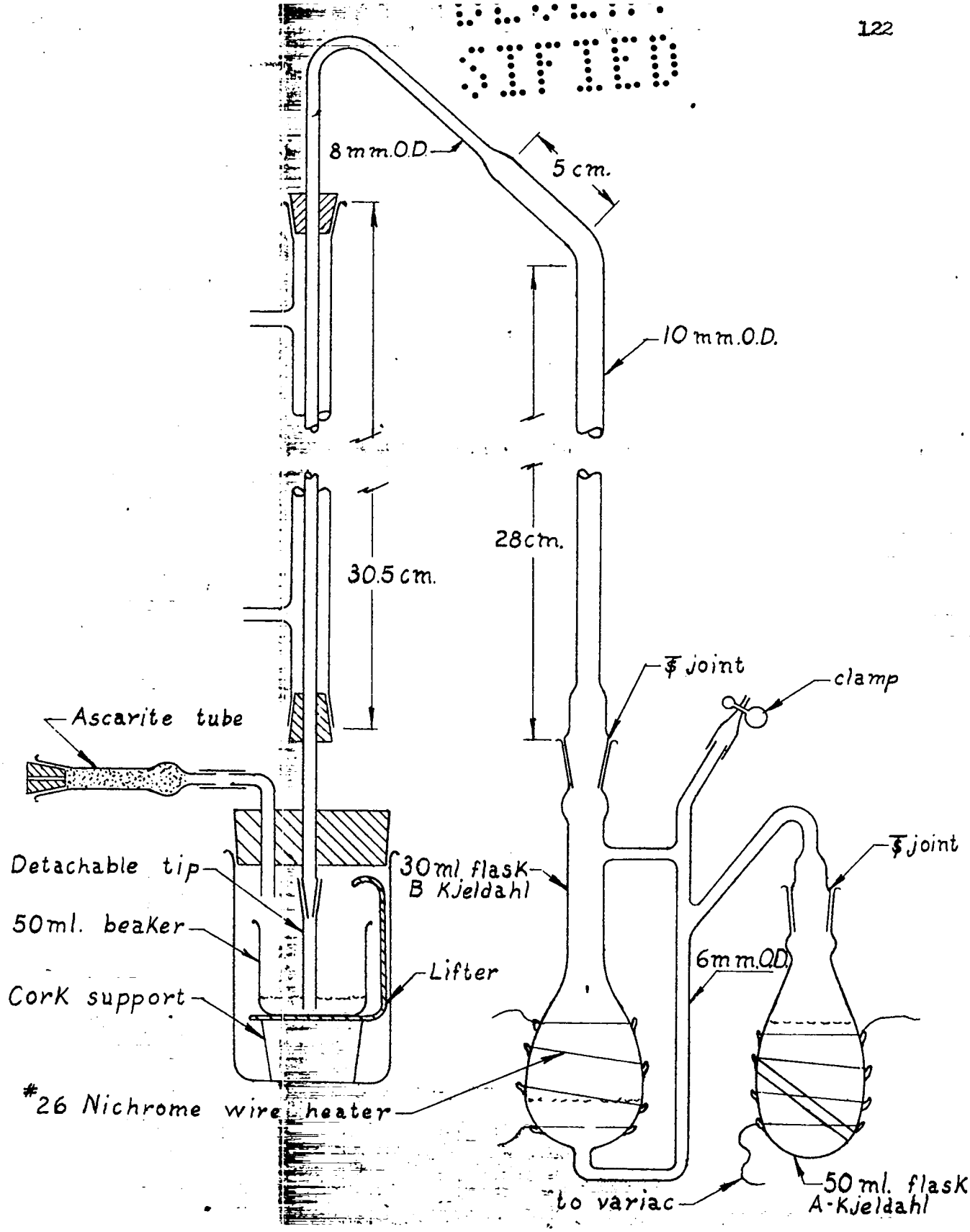


FIGURE 1: Quartz still for boron determination

COLORIMETRIC DETERMINATION OF SUB-MICROGRAM QUANTITIES OF BORON IN CALCIUM METAL

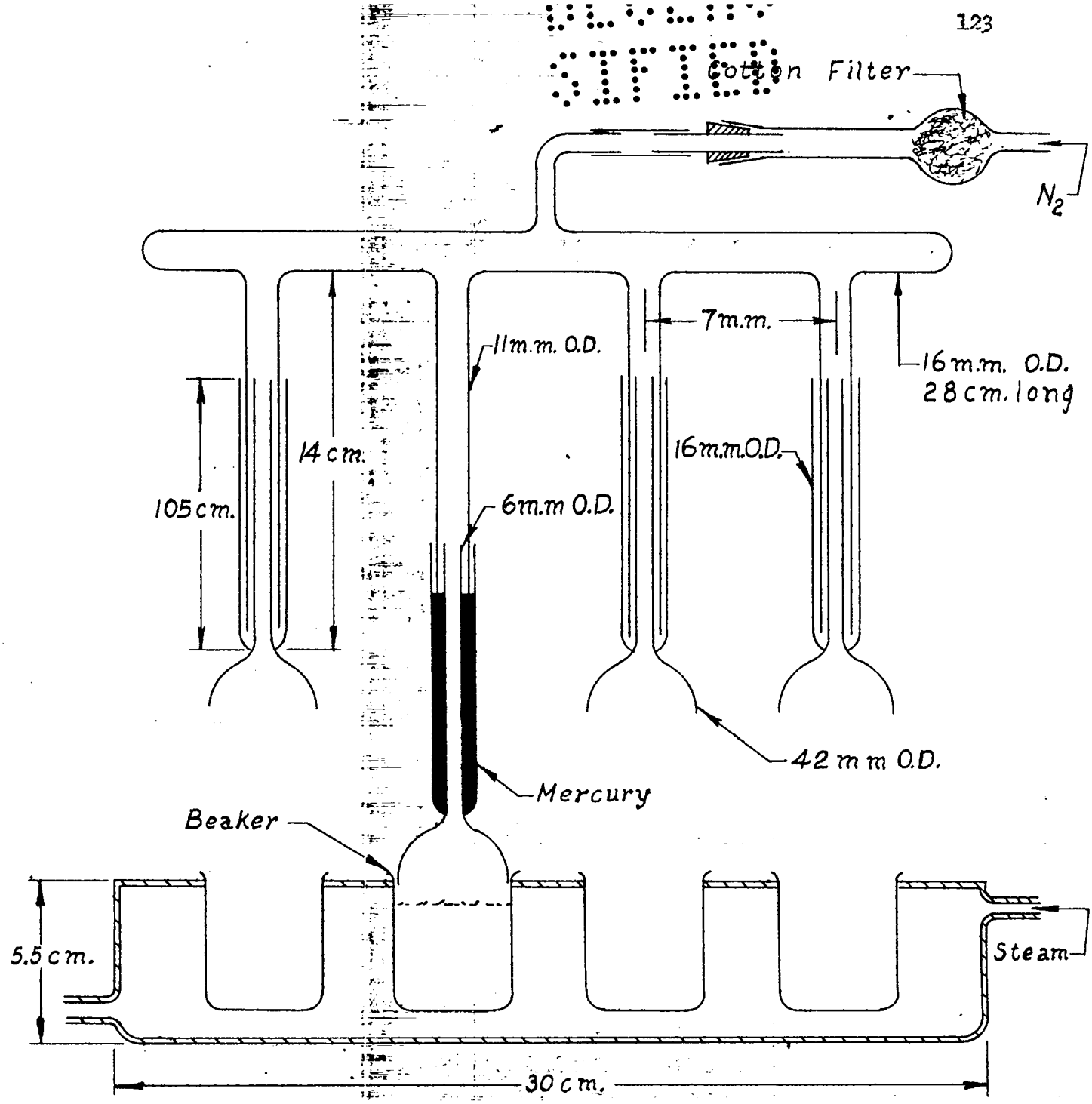


FIGURE 2: Steam bath with device for evaporating in nitrogen atmosphere (made from fused quartz)

COLORIMETRIC DETERMINATION OF SUB-MICROGRAM QUANTITIES OF BORON IN CALCIUM METAL

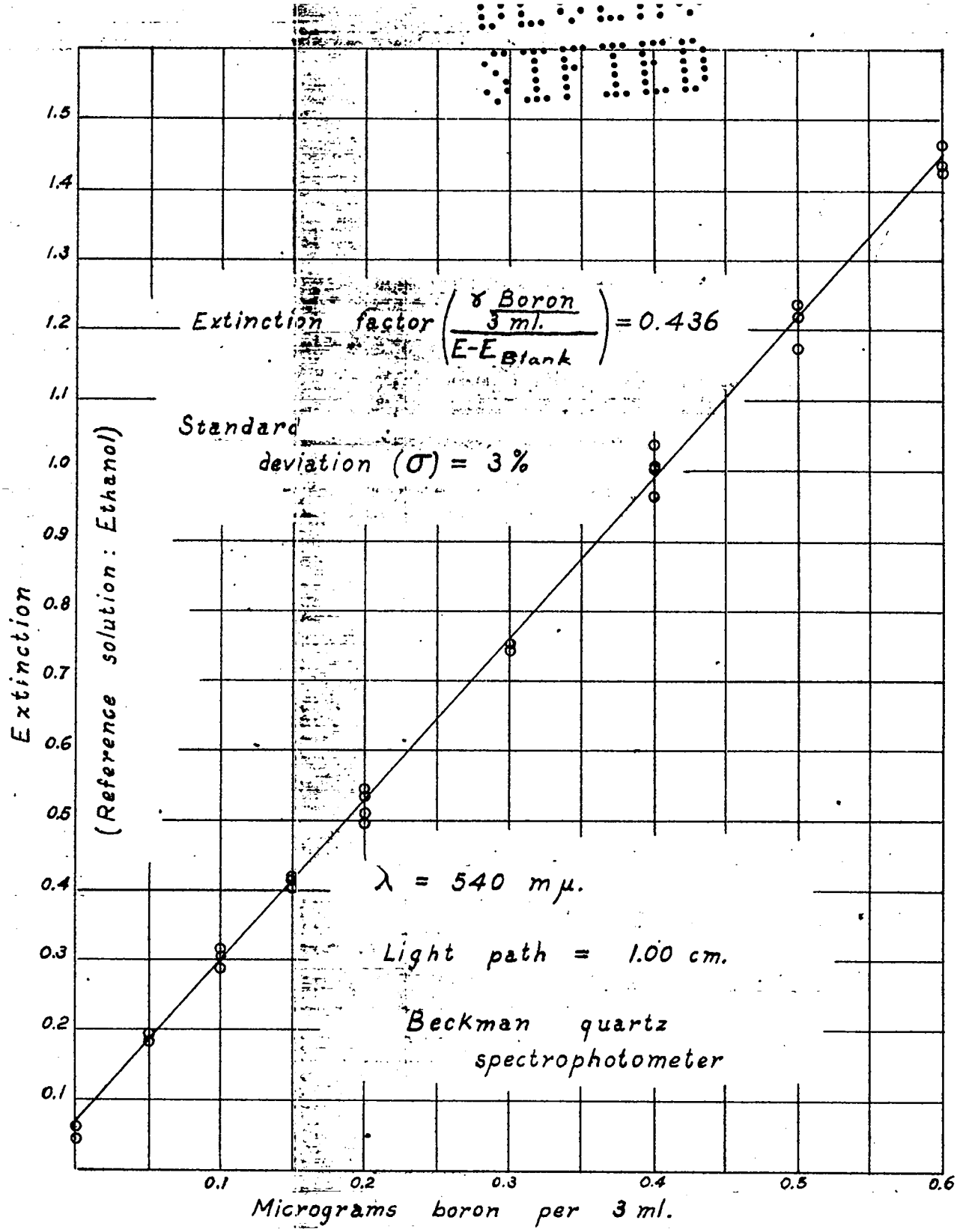


FIGURE 3 - Standard curve for boron analysis

COLORIMETRIC DETERMINATION OF SUB-MICROGRAM QUANTITIES OF BORON IN CALCIUM METAL

III F-1

COLORIMETRIC DETERMINATION OF SUB-MICROGRAM QUANTITIES OF BORON IN URANIUM TETRAFLUORIDE

(Many of the reagents, pieces of apparatus and steps in procedure are similar to those used in "Colorimetric Determination of Sub-Microgram Quantities of Boron in Calcium Metal", pp. III E-1 to III E-9 in this Manual. To avoid undue repetition, material in that section that applies to this procedure will be referred to by page number.)

Abstract

Uranium tetrafluoride is dissolved in 3 N sodium hydroxide and 30 per cent hydrogen peroxide. The fluoride ion is either precipitated as CaF_2 or complexed as FeF_6^{---}. The boron is distilled as methyl borate. The quartz stills described under Procedure, III E, in this Manual are used for distillation. The methyl borate distillate is trapped in calcium hydroxide solution and the boron estimated by the colorimetric curcumin procedure.

Applicability

This method applies to relatively pure uranium tetrafluoride.

Range and Limits of Sensitivity

In a 100 mg. sample, 0.05 to 0.5 micrograms of boron have been determined with an accuracy ±10 per cent in the final volume of 3 ml. to which the solution is diluted for spectrophotometric determination. This corresponds to a concentration range from 0.5 to 5 parts per million.

Sampling

The sample must be finely ground in a boron-free mortar. Coarse particles will not dissolve in the quantities of reagents employed.

Reagents

Store all reagents except where noted in quartz containers.

1. Distilled water, from a double Barnstead still. If free boric acid is present in the water supply, make alkaline with NaOH and distill from a

quartz still.

2. Nitric acid, concentrated, c.p. The boron content should be less than 1 microgram per ml.

3. Calcium hydroxide, 0.1 N suspension, prepared from boron-free calcium metal* and distilled water.

4. Methyl alcohol, absolute. Distill from sodium hydroxide in a quartz still equipped with an efficient spray trap. The alcohol should not contain more than 0.0005 micrograms of boron per ml.

5. Hydrochloric acid, 6 N. Baker's c.p. acid was found sufficiently low in boron.

6. Curcumin, 0.1 per cent in ethyl alcohol. Use c.p. material like Eastman's best grade.

7. Ethyl alcohol, 95 per cent. Re-distill from NaOH in a quartz still equipped with an efficient spray trap.

8. Oxalic acid, crystals, c.p. 15 per cent solution in distilled water.

9. Standard boric acid solution, 1 ml. containing 1 microgram of boron. To make stock solution, dissolve 35.7 mg. c.p. H_3BO_3 crystals and dilute to 250 ml. with distilled water. 10 ml. of this stock solution diluted to 250 ml. contains 1 microgram of boron per ml.

10. Sodium hydroxide, 3 N. Sodium is electrolyzed from c.p. sodium chloride or sodium hydroxide in distilled water into a mercury cathode, forming sodium amalgam. The sodium amalgam is drawn off into a quartz beaker, washed thoroughly, distilled water added and allowed to stand overnight. A large piece of platinum placed in contact with the amalgam will catalyze

---

* Boron-free calcium metal was obtained from the Electro-Metallurgical Corporation, Niagara Falls. It was prepared by electrolysis of the metal from a molten bath free from borates and distilled in vacuo in an iron retort.

the dissolving of the sodium metal. 10 ampere hours of current will yield sufficient sodium for approximately 100 ml. 3N solution. The NaOH solution is decanted into a weighed platinum bottle. The normality is determined by titrating portions with a standard acid. The weight of the remaining NaOH solution is determined by weighing the bottle and contents, then subtracting the weight of the bottle. The volume of the NaOH is determined by this weight and from standard density tables. Dilution to a concentration of 3 N is made by adding the calculated volume of distilled water. For a check, a final titration is made with standard acid. The NaOH solution is stored in the platinum bottle. This method of preparation produces sodium hydroxide with extremely low boron content.

11. Hydrogen peroxide, 30 per cent. Merck's reagent grade.
12. Ferric chloride, Baker's c.p. 10 g. $FeCl_3.6H_2O$ are dissolved in 50 ml. distilled water in a quartz volumetric flask. 25 ml. concentrated HCl are added and the volume made up to 100 ml.
13. Calcium nitrate solution. To 10 g. boron-free calcium metal in a quartz flask, add distilled water dropwise until all the metal has been oxidized. Then add the calculated amount of concentrated nitric acid necessary to convert the calcium hydroxide to calcium nitrate. Dilute to 100 ml. with distilled water.
14. Hydrochloric acid, concentrated, c.p.
15. Hydrochloric acid, 6 N. Dilute the concentrated acid with distilled water.

Apparatus

The apparatus described, pp. III E-3 and III E-4, in this Manual is used here.

Procedure

1. Preparation of standard curve.

Prepare a standard curve in the same manner as described on p. III E-4 in this Manual.

2. Analysis of the sample.

Pipet 2.5 ml. of 0.1 N $Ca(OH)_2$ suspension into a clean 50 ml. quartz beaker. Set the quartz condenser tip in place. Place the beaker in the CO_2 trap and adjust so the condenser tip is beneath the surface of the calcium hydroxide but not touching the bottom of the beaker (see Procedure III E, Figure 1).

Weigh 0.100 gram of finely ground sample and transfer to the distillation flask. Add 1 ml. 3 N NaOH and 0.5 ml. 30 per cent H_2O_2. Shake to mix thoroughly, warm slightly and allow to dissolve. This usually requires five to ten minutes. After solution is complete, heat to boiling for thirty seconds to decompose most of the excess H_2O_2 and to remove some of the water from the solution. Cool the flask under the tap. From this point two methods for preventing the distillation of fluoride ion are available:

Method I. To the cold solution add 0.5 ml. $Ca(NO_3)_2$ solution, 0.20 ml. concentrated HNO_3, then shake to mix. Add 8 - 10 ml. purified methyl alcohol and quickly connect the flask to the condenser. Pour 50 ml. purified methyl alcohol into flask A (see Procedure III E, Figure 1, this Manual) and distill approximately 45 ml. methyl alcohol into the receiving beaker while keeping the volume of solution constant in the distilling flask. This is easily accomplished by proper adjustment of the Variacs.

Method II. To the cooled solution add 1 ml. $FeCl_3$-HCl solution. Shake to mix thoroughly. (If the $FeCl_3$-HCl solution is prepared as directed under "Reagents", one ml. will contain sufficient hydrochloric acid to give the proper acidity). Add 8 - 10 ml. purified methanol and quickly connect the distillation flask to the condenser. Pour 50 ml. purified methyl alcohol into flask A, as in Method I and distill approximately 45 ml. into the receiving beaker, while keeping the level of the liquid constant in the distilling flask.

From this point the procedure is the same for either method. Before the end of the distillation, lower the receiver until the condenser tip is above the surface of the liquid in the beaker. Continue distilling until one or two ml. of methyl alcohol have washed the condenser tip. Remove the pinch clamp and turn off both Variacs.

Immediately place the beaker on the steam bath, lower the quartz funnel into place (see Procedure III E, Figure 2, this Manual) and turn on a sufficient flow of nitrogen to ripple the surface of the liquid and evaporate it to dryness. Remove from the steam bath immediately upon reaching dryness, allow to cool and proceed with the color development as follows:

Add 0.25 ml. 6 N HCl to the beaker. Tilt and rotate the beaker until the acid has dissolved all the residue on the walls. This step is important and requires patience and practice to develop sufficient technique to prevent any loss of contents. Then add 0.50 ml. of 0.1 per cent alcoholic curcumin and then 0.50 ml. 15 per cent oxalic acid. Again tilt and rotate the beaker to bring the reagents into contact with the wall surface of the beaker. Immediately place the beaker in the drying oven at a temperature of 55° C. ± 3°. Note when dryness is reached and continue to heat at the same temperature for an additional 30 minute period. Remove from the oven and allow to cool. Extract the color from the contents of the beaker with 1 ml. of 95 per cent ethyl alcohol. Filter through a medium porosity sintered-glass filter into a 3 ml. volumetric flask. Continue extracting and filtering with small volumes of alcohol until the color has been quantitatively extracted and transferred to the volumetric flask. Dilute to a final volume of 3 ml. with additional alcohol.

Pour into standard Beckman cuvet having a 1.00 cm. light path, stopper and determine the extinction at a wavelength of 540 mμ using 95 per cent ethanol as a reference solution.

Calculation and expression of results

Express results as parts per million unless otherwise requested.

The "extinction factor" obtained from the standard curve in III E, Figure 3, may be used to calculate the amount of boron present in the sample.

To calculate the amount of boron in micrograms, multiply the increase in extinction by the extinction factor (see p. III E-9).

E increase = E sample - E reagent blank

∴ Amt. Boron (in micrograms) = (E sample - E reagent blank) x extinction factor

Expressed as parts per million,

$$\text{Boron (in ppm)} = \frac{(\text{E sample} - \text{E reagent blank}) \times \text{Extinction factor}}{\text{Wt. sample in grams}}$$

Procedure for total reagent blank

Since calculation of the amount of boron present involves a knowledge of the boron content of the reagents used, it is necessary that a "total reagent blank" be determined. This is done as follows: For Method I and Method II carry out the procedure for analysis of the sample omitting the weighed sample. The extinction under the conditions used here should not be over 0.070. If an abnormally high reagent blank is found it is necessary to find the source of contamination and reduce it by purification of the reagent or reagents involved.

Procedure for individual reagent blanks

The blank for the "color development" reagents, $Ca(OH)_2$, HCl, $(COOH)_2$ and curcumin is determined as follows: Pipet 2.5 ml. 0.1 N $Ca(OH)_2$ suspension into a 40 ml. platinum evaporating dish. Evaporate to dryness on the steam bath. Remove the dish and allow to cool. Add 0.25 ml. 6 N HCl and dissolve the residue. Next add 0.50 ml. of 0.1 per cent alcoholic curcumin and finally 0.50 ml. of 15 per cent oxalic acid. Swirl gently to mix and place in the drying oven at 55° C. ±3°. Heat at that temperature for 30 minutes beyond dryness. Remove, allow to cool and quantitatively extract the color and filter into a final volume of 10

ml. Read the extinction as described above. It should not be over 0.04 extinction units.

Methyl alcohol: Pipet 2.5 ml. of 0.1 N $Ca(OH)_2$ suspension into a 75 ml. platinum evaporating dish. Add 50 ml. purified methanol and evaporate to dryness in an atmosphere free from carbon dioxide. Proceed with the color development and estimation of the extinction as described above. The extinction obtained here should be only slightly greater (0.02 units), than that obtained for the "color development" reagents.

Calcium nitrate: Carry out the procedure as described under "Analysis of the sample" omitting the weighed sample and the calcium nitrate. The "Total reagent blank" minus the extinction obtained here gives that portion of the total blank contributed by the calcium nitrate.

Ferric chloride: Carry out the procedure as described under "Analysis of the sample" omitting the weighed sample and the ferric chloride solution. The total reagent blank minus the extinction obtained here gives that portion of the reagent blank contributed by the ferric chloride.

Nitric acid: Carry out the procedure for "Analysis of the sample" omitting the weighed sample and the calcium nitrate. The extinction obtained minus the total extinction obtained under "Methyl alcohol" gives that portion of the reagent blank contributed by the nitric acid.

Hydrochloric acid, concentrated: Add 0.125 ml. concentrated HCl to the distillation flask. Carry out the distillation, evaporation and color development as described under "Analysis of the sample". The extinction obtained minus that obtained for the "color development" reagents plus the methanol gives the extinction contributed by 0.125 ml. concentrated hydrochloric acid. Let this contribution be represented by X. Then 2X plus the extinction obtained for the "color development" reagents plus the methanol gives the total reagent blank resulting from a distillation from 0.25 ml. concentrated HCl. Let this value be

represented by Y. (Actually distillations are not made from such a large quantity of concentrated HCl because of the tendency of the acid to distill with the methanol).

Sodium hydroxide: Add 0.7 ml. 3N electrolytic NaOH and 0.25 ml. concentrated HCl to the distillation flask. Carry out the distillation, evaporation and color development as described under "Analysis of the sample". The extinction obtained here minus "Y" (see above) gives that portion of the total extinction contributed by 0.75 ml. 3 N NaOH.

The preceding paragraphs give in considerable detail methods for determining individual reagent purity. In practice it will usually not be necessary to carry out these individual operations. Experience has shown that sufficiently pure chemicals are obtainable or can be purified to a very low boron content. Nitric acid seems to be an exception. Du Pont's concentrated c.p. acid has been found acceptable although its boron content is higher than that of any other single reagent used in this procedure.

Precautions

All the precautions described on pp III E-7, III E-8 in this Manual apply here.

Reference

"Colorimetric Determination of Sub-Microgram Quantities of Boron in Calcium Metal", Procedure III E in this Manual.

COLORIMETRIC DETERMINATION OF SUB-MICROGRAM QUANTITIES OF BORON IN PLUTONIUM METAL

(The reagents, apparatus and procedure used in this determination are similar to those used in "Colorimetric Determination of Sub-microgram Quantities of Boron in Calcium Metal", pp. III E-1 to III E-9 of the Manual. To avoid undue repetition, material in that section that applies to this procedure will be referred to by page number.)

Abstract

Plutonium metal is dissolved in 6 N HCl. The boron is distilled as methyl borate from a specially designed quartz still. The distillate is trapped in a calcium hydroxide suspension. The boron is estimated by the colorimetric curcumin procedure.

Applicability

The method has been applied to relatively pure plutonium metal and to gallium alloys of the metal containing up to 3.5 atomic per cent gallium.

Range and Limits of Sensitivity

The procedure described here permits the determination of boron in the range 0.05 to 0.5 micrograms, which corresponds to a concentration of 0.5 to 5 ppm in a 100 milligram sample, with an accuracy of ±10 per cent. 0.03 micrograms of boron can be estimated with an accuracy of ±20 per cent in the final volume of 3 ml. to which the sclution is diluted for spectrophotometric determination.

Sampling

The metal is cut into pieces ranging from 50 to 100 milligrams in weight. If surface contamination is suspected it is recommended that the sample be cleaned by electrolytic polishing method described on page I-2 of this manual. The metal is then placed in concentrated nitric acid for a few seconds, washed in distilled water and then in acetone and allowed to dry.

Reagents

See p. III E-2 of this Manual.

Apparatus

The apparatus described on pp. III E-3 and III E-4 in this Manual is used here.

Procedure

HEED HEALTH SAFETY RULES OUTLINED IN SECTION I

1. Preparation of a standard curve.

Prepare a standard curve in the same manner as described on p. III E-4 in this Manual.

2. Analysis of the sample.

Pipet 2.5 ml. of 0.1 N $Ca(OH)_2$ suspension into a clean 50 ml. quartz beaker. Set the quartz condenser tip in place. Place the beaker in the CO_2 trap and adjust so the condenser tip is beneath the surface of the $Ca(OH)_2$ suspension but not touching the bottom of the beaker. (See Figure 1, Procedure III E of this Manual).

Pipet 0.25 ml. 6 N HCl into the distillation flask. Drop the weighed sample (a piece of metal weighing between 50 and 100 milligrams) into the flask and allow it to dissolve; this requires only a few minutes. Then add 8 - 10 ml. purified methanol and immediately connect the flask to the condenser. Distill approximately 45 ml. purified methanol through the distillation flask into the $Ca(OH)_2$ suspension, at the same time keeping the volume in the distillation flask essentially constant. This is done by proper control of the Variacs. Lower the receiving beaker so the quartz tip of the condenser is above the surface of the distillate and continue distilling for 20 or 30 seconds to wash the tip. Immediately place the beaker on the steam bath and lower the inverted funnel. (See Figure 2, Procedure III E). Start the nitrogen flow and carry cut the evapora-

tion in an atmosphere free from carbon dioxide. Remove the beaker immediately upon reaching dryness and allow to cool.

Add 0.25 ml. 6 N HCl to the beaker, incline and rotate to bring the acid into contact with all the precipitate. This operation is important and requires patience and skill to prevent loss of the reagent. Next add 0.50 ml. 0.1 per cent curcumin in 95 per cent alcohol, swirl gently, then add 0.50 ml. 15 per cent oxalic acid. Again incline and rotate the beaker to bring the reagents into contact with all the wall surfaces of the beaker.

Place the beaker in the drying oven at 55° C. ± 3° C. and heat 30 minutes beyond the drying time. At the end of this period remove from the oven and allow to come to room temperature. Extract the color from the contents of the beaker with 1 ml. 95 per cent ethyl alcohol. Filter through a medium porosity sintered-glass filter and catch the clear filtrate in a 3 ml. volumetric flask. Repeat with successive small portions of alcohol until the color is quantitatively removed. Dilute with additional alcohol to a final volume of 3 ml., shake and transfer to a Beckman absorption cell with 1.00 cm. light path and determine the extinction at 540 mμ on the Beckman spectrophotometer.

Calculation and expression of results

Express results in parts per million unless otherwise requested. Information obtained from the standard curve in Figure 3, Procedure III E in this Manual may be used to calculate the boron content of the sample. To calculate the amount of boron in micrograms, multiply the increase in the extinction by the "extinction factor" (see p. III E-9).

E increase = E sample - E reagent blank

Boron (in micrograms) = (E sample - E reagent blank) x Extinction factor

Expressed as parts per million:

$$B\ (ppm) = \frac{(E\ sample - E\ reagent\ blank) \times extinction\ factor}{wt.\ sample\ in\ grams}$$

Procedure for total reagent blank

Since the amount of boron in the sample can only be calculated if the amount of boron in the reagents is known, it is necessary to determine the total reagent blank. To do this, repeat the entire procedure for analysis of the sample, omitting the weighed sample but using the same quantities of reagents as in an actual analysis. Under the conditions described here, the total reagent blank should be between 0.050 and 0.070 extinction units. If this blank is much greater than this value, it is necessary to determine the source of the contamination.

Procedure for individual reagent blanks

The blank for the "color development" reagents, $Ca(OH)_2$, HCl, $(COOH)_2$ and curcumin is determined as follows: Pipet 2.5 ml. 0.1 N $Ca(OH)_2$ suspension into a 40 ml. platinum evaporating dish. Evaporate to dryness on the steam bath. Remove the dish and allow to cool. Add 0.25 ml. 6 N HCl and dissolve the residue. Next add 0.50 ml. 0.1 per cent alcoholic curcumin and finally 0.50 ml. 15 per cent oxalic acid. Swirl gently for thorough mixing and place in the drying oven at $55^{\circ}C. \pm 3^{\circ}$. Heat at that temperature for 30 minutes beyond dryness. Remove, allow to cool and quantitatively extract the color and filter into a final volume of 3 ml. Read the extinction as described above. It should not be over 0.050 extinction units.

Methyl alcohol: Pipet 2.5 ml. 0.1 N $Ca(OH)_2$ suspension into a 75 ml. platinum evaporating dish. Add 55 ml. purified methanol and evaporate to dryness in an atmosphere free from carbon dioxide. Then proceed with color development and estimation of the extinction as described above. The extinction obtained here minus the extinction obtained for the "color development" reagents gives the increase in extinction contributed by the methanol. This increase should be not over 0.02 extinction units.

[redacted]

Hydrochloric acid, 6 N: The extinction found in the total reagent blank minus the total extinction found under "Methyl alcohol" gives that portion of the reagent blank contributed by the hydrochloric acid.

Precautions

All the precautions that were described on pp. III E-7, III E-8 in this Manual apply here.

Reference

"Colorimetric Determination of Sub-Microgram Quantities of Boron in Calcium Metal", Procedure III E of this Manual.

[redacted]

IV

VOLUMETRIC PROCEDURES

VOLUMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF ACID-SOLUBLE SULFIDE SULFUR

Abstract

The sulfur is distilled as hydrogen sulfide from acid solution and absorbed in an excess of calcium hypochlorite. The sulfide is oxidized to sulfate and the excess calcium hypochlorite is determined iodometrically. Stoichiometric relationships, however, are not borne out experimentally. Quantitative results are obtained by determining the titer values of the reagents against known quantities of sulfide.

Applicability

The method has been applied to uranium and plutonium metals and is presumably applicable to all materials which are soluble in 2 N HCl and give up their sulfide sulfur as H_2S under such circumstances. The principal application is to metals.

Size of Sample and Limit of Sensitivity

The sample size is determined by the sensitivity required. The absolute limit of sensitivity is about 1 γ of S. The procedure may also be used for determining milligram quantities of sulfur if 0.1 N solutions are employed.

Reagents

1. $Ca(OCl)_2$: Dissolve 6 - 10 grams calcium hypochlorite, U.S.P., depending on the chlorine content[1] in 250 ml. distilled water, shake well and filter. Dilute the filtrate to one liter and store in an amber bottle in a dark place. Under these conditions the solution is stable. This solution is approximately 0.1 N. For use on the microgram scale dilute to 0.01 N each day before use and redetermine the titer.
2. KI, 0.1 N.
3. $Na_2S_2O_3$, 0.1 N. Dilute to 0.01 N for use.

[redacted]

4. Starch indicator solution saturated with HgI_2.

5. Zinc acetate, 2 per cent.

6. Conc. H_2SO_4.

7. Conc. HCl.

8. Standard Na_2S solution, 1 ml ≈ 1 milligram. Standardize against standard I_2-KI and $Na_2S_2O_3$.

Apparatus

1. Pyrex still (Figure 1).

2. 1 ml. buret calibrated in hundredths.

3. 25 ml. Erlenmeyer flasks.

4. Pipets, 5 ml., 2 ml., 1 ml., 100 λ, 50 λ, 10 λ.

Procedure

IF PLUTONIUM METAL AND ITS COMPOUNDS ARE TO BE ANALYZED, HEED HEALTH SAFETY RULES OUTLINED IN SECTION I.

1. Determination of titer: To 2 ml. of 0.01 N hypochlorite solution in a 25 ml. Erlenmeyer flask, add 100 γ of sulfide sulfur (100 λ of the standard Na_2S solution). Add 2 ml. of 0.1 N KI and 2 drops concentrated H_2SO_4. Let the reaction proceed for 3 - 4 minutes to allow the iodine reaction to go to completion. Titrate the liberated iodine with the 0.01 N thiosulfate adding 2 drops of the starch indicator just before the endpoint. Denote this volume of thiosulfate as a. Similarly determine the volume of thiosulfate necessary to titrate 2 ml. of 0.01 N hypochlorite without any added sulfur. Denote this volume of thiosulfate as A.

   Then $K = \frac{100\ \gamma}{A-a}$ where K is the titer value for the thiosulfate and hypochlorite solutions.

2. Recoveries from the still: (a) Pipet measured amounts of $S^=$ into 2 ml. 2 per cent zinc acetate contained in the still pot B (Figure 1) and assemble

the still. (b) Pipet 1 ml. of 0.01 N hypochlorite into the 25 ml. receiving flask and add a little distilled water so that the tip of the condenser is below the surface of the solution. (c) Add sufficient conc. HCl through A to make the solution in B approximately 1 N and wash the acid down with a little water. (d) Connect the air and adjust to a moderate rate so that the flow is rapid enough to prevent sucking back when the still cools. (e) Heat the solution in B to incipient boiling. (f) Allow the air stream to sweep over the liberated H_2S for 5 minutes. (g) Disconnect the tip C and wash inside and out into the receiving flask with a small quantity of water. (h) Add 2 ml. of 0.1 N KI and 2 drops of conc. H_2SO_4. (i) After 3 - 4 minutes titrate with 0.01 N thiosulfate adding 2 drops of the starch indicator just before the end point.

3. Unknowns: Proceed as in 2 without the addition of the zinc acetate. Introduce the weighed sample into the flask, assemble the still and continue as above. Be sure that the sample is in solution before starting the 5 minute sweep interval. Gentle heating below the boiling point is permissible to insure complete solution. Keep the air stream flowing throughout the entire operation.

Blank Procedure

Determine the blank by running through the distillation procedure without added sulfide. The blank is positive and constant and is apparently caused by the destruction of a small quantity of hypochlorite during the distillation. No blank correction is necessary if the sulfide is added directly to the hypochlorite.

Precautions

1. Do not allow the air stream to pass through too rapidly.
2. Keep distillation time short to cut down the blank; 5 minutes is usually sufficient.

3. Do not heat to boiling.

4. Allow sufficient time for oxidation of iodide by hypochlorite before titrating.

5. Use suitable buret. One of 1 ml. capacity calibrated in hundredths, so that 0.001 ml. can be estimated, is adequate.

Theoretical

The basic reactions involved are:

$$S^{=} + 4OCl^{-} \longrightarrow SO_4^{=} + 4Cl^{-}$$

$$OCl^{-} + 2I^{-} + 2H^{+} \longrightarrow I_2 + H_2O + Cl^{-}$$

$$I_2 + 2S_2O_3^{=} \longrightarrow 2I^{-} + S_4O_6^{=}$$

The reactions used in standardizing the Na_2S solution are:

$$S^{=} + I_2 \longrightarrow S^{o} + 2I^{-}$$

$$I_2\ (\text{excess}) + 2S_2O_3^{=} \longrightarrow 2I^{-} + S_4O_6^{=}$$

Calculations

Calculate micrograms of sulfide sulfur directly from the volume of thiosulfate used. If X ml. are used

$$(A - X)K = \gamma\ S^{=}$$

Express the results in ppm.

$$\text{ppm} = \frac{\gamma\ S^{=}}{\text{sample weight in grams}}$$

References

1. Kolthoff, I.M., and Sandell, E.B., "Textbook of Quantitative Inorganic Analysis", pp. 587-588, 639-640, New York, The MacMillan Co., 1943.

2. Kolthoff, I.M., and Stenger, V.A., Ind. Eng. Chem., Anal. Ed., 7, 79, 1935.

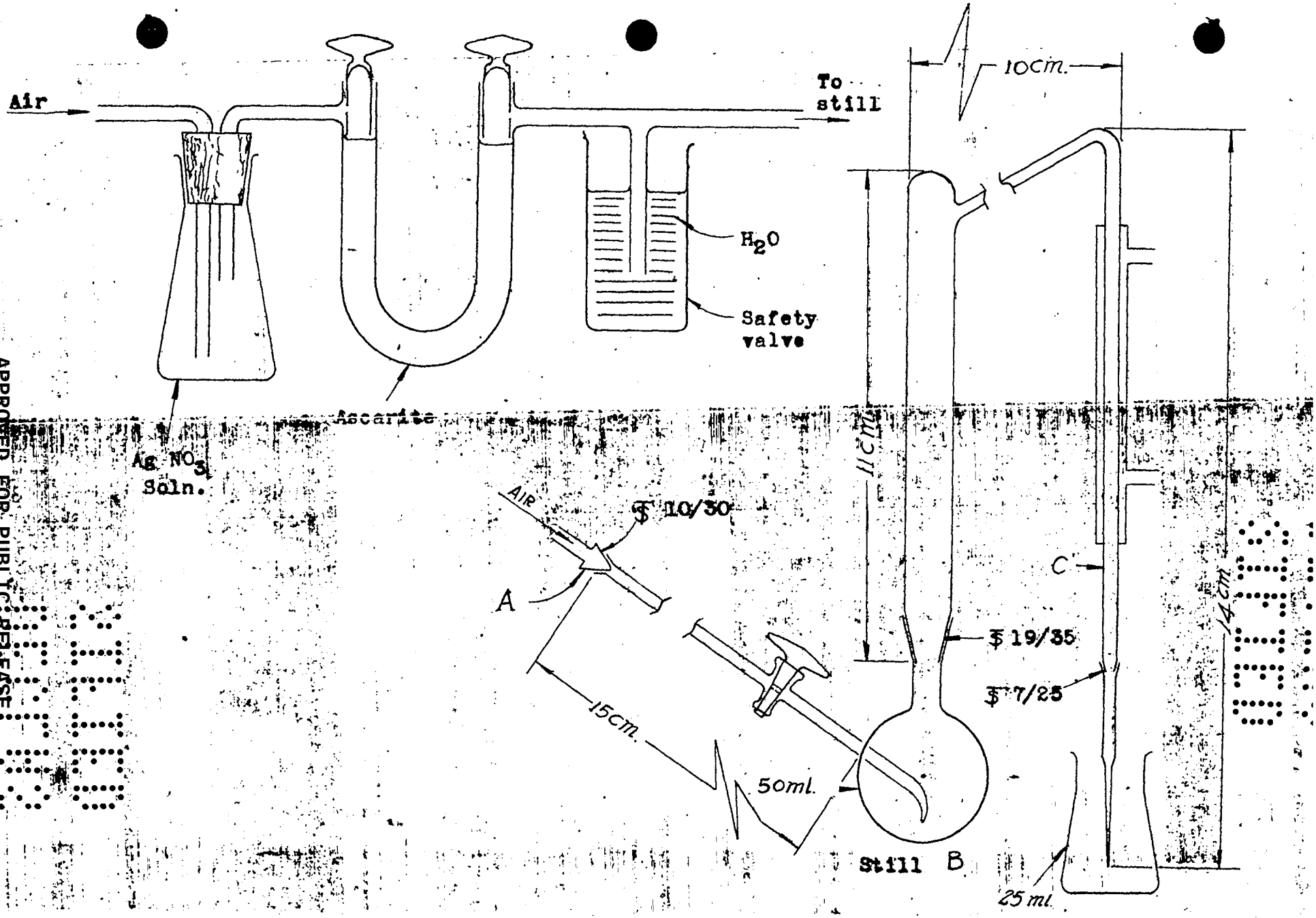


Figure 1. Pyrex Distillation Apparatus

Volumetric Determination of Microgram Quantities of Acid-Soluble Sulfide Sulfur.

APPROVED FOR PUBLIC RELEASE

VOLUMETRIC DETERMINATION OF SULFATE SULFUR IN PLUTONIUM MATERIALS

Abstract

The sulfate is reduced to sulfide by means of a reducing mixture composed of hydriodic acid, hypophosphorous acid and hydrochloric acid. The hydrogen sulfide is trapped in ammoniacal cadmium chloride solution and the sulfide sulfur is then determined iodometrically. The method is based on Luke's procedure for determination of total sulfur in rubber[1].

Applicability

The method has been applied to plutonium nitrate solutions and is presumably applicable to other plutonium solutions and to all plutonium materials that can be put into solution without the loss of sulfur.

Size of Sample and Limit of Sensitivity

Sufficient plutonium solution is taken to give approximately 1 mg. of sulfide sulfur or 3 mg. of sulfate. Good results can be obtained, however, in the range 0.3 mg. to 5 mg. of sulfur.

Reagents

1. Reducing mixture. Mix 160 ml. HI (47 per cent), 160 ml. concentrated HCl and 40 ml. $H(H_2PO_2)$ (30 -32 per cent). Add a few glass beads and boil for 5 minutes. Cool and store in a brown, glass-stoppered bottle.
2. HCl, concentrated.
3. $HClO_4$, 70 per cent.
4. I_2 - KI solution, 0.1 N.
5. $Na_2S_2O_3$, 0.01 N.
6. Standard Na_2S solution, 1 ml. = 1 mg. S .
7. Starch indicator.
8. Ammoniacal $CdCl_2$. Dissolve 10 g. $CdCl_2 \cdot 2H_2O$ in distilled water, add 500 ml. NH_4OH and dilute to 5 liters.

9. Tank nitrogen gas.

Apparatus

1. Distillation equipment (Figure 1).
2. Iodine flasks, 250 ml.
3. 5 ml. buret, calibrated in hundredths.
4. 1 ml. pipet, accurately calibrated.
5. Pipets, 50λ, 100λ.
6. Graduated cylinders, 5, 25, 50, 250 ml.
7. Evaporating equipment (Figure 2).

Standardization of Reagents

1. Standardize the 0.1 N I_2-KI solution against arsenious oxide in the usual way.
2. Standardize the 0.01 N sodium thiosulfate by carrying 1 ml. of the standard sulfide solution through procedure 1 as described below. The resulting titer is then a relative value with respect to the iodine solution and the known amount of sulfide. The blank correction is also eliminated by this procedure.

   If x equals the number of milliequivalents of thiosulfate used to titrate the excess iodine from the 0.1 milliequivalents used with 1 mg. of sulfide carried through the complete procedure, then

   $$x = 0.1 \text{ meq.} - 1/16 \text{ meq.} = 0.0375 \text{ meq.}$$

   The normality of the thiosulfate is:

   $$N = \frac{0.0375}{n}$$

   where n is the number of milliliters of thiosulfate used in the titration.

Procedure

HEED HEALTH SAFETY RULES OUTLINED IN SECTION I.

1. In the absence of nitrate:

Place 50 ml. of the ammoniacal cadmium chloride solution in the 250 ml. iodine flask and place in position with the end of the delivery tube touching the bottom of the flask. Pipet an aliquot of the unknown (containing approximately 1 mg. of S) into the distillation flask, add a few glass beads and 20 ml. of the reducing mixture. Immediately connect the flask to the still. Place the heater in position and bring to a rapid boil. When no more H_2S comes over (approximately 10 minutes), start nitrogen bubbling through the boiling solution at a gentle rate. Pass the nitrogen through for 10 - 15 minutes.

At the end of the distillation, disconnect the delivery tube at the semi-ball joint and wash down the inside with a few milliliters of water. Disconnect the lower part of the delivery tube at the standard taper joint and leave the lower part in the receiver. Remove the heater and stop the gas stream.

Add 10 ml. concentrated HCl to the cadmium sulfide solution in the iodine flask, stopper immediately, swirl to mix and place in an ice bath. When the solution is cold, remove from ice bath and pipet 1 ml. of the iodine solution into the cup of the iodine flask. Cautiously loosen the stopper so that the iodine is drawn into the flask without allowing any of the H_2S to escape. Wash the iodine into the flask with small portions of distilled water, being careful at all times not to remove the stopper completely. The partial vacuum will draw in the wash water without difficulty.

Shake the flask well so that all the H_2S will react with the iodine. Allow the flask to come to room temperature with occasional shaking. Titrate with the thiosulfate to the disappearance of the blue starch color, adding the starch indicator just before the endpoint.

If more than 1.5 mg. of $S^=$ are present add 2 ml. of the iodine solution. 1 ml. of 0.1 N I_2-KI is equivalent to 1.6 mg. sulfide sulfur.

2. In the presence of nitrate:

Nitrate interferes seriously with the procedure. Traces of nitrate will produce low results. To eliminate nitrate, evaporate the solution with 5 ml. of 70 per cent perchloric acid. Boil the solution vigorously to drive off all traces of nitrate. A criterion of sufficiently vigorous boiling is that no $HClO_4$ condenses in the distillation flask. A convenient apparatus for the evaporation is shown in Figure 2. Do not close the semi-ball joint completely but clamp it so that a small gap is left between the male and female parts of the joint.

Evaporate the solution until the volume is decreased to 1 - 2 ml. This will remove the nitrate in one evaporation. The residual perchloric acid will not react explosively with the reducing mixture. Cool the flask and proceed with the distillation as described above.

Precautions

1. Do not pass the nitrogen through the solution too rapidly.
2. Nitrate must be quantitatively removed.

Calculations

If x ml. of 0.01 N thiosulfate are used to titrate the excess iodine when 1 ml. of 0.1 N iodine is added, then:

$$[0.1 \text{ meq.} - (x \cdot 0.01)]\ 16 = \text{mg. } S^=$$

$$\text{mg. } SO_4^= = \text{mg. } S^= \times 2.99$$

Literature References

1. Luke, C. L., Ind. Eng. Chem., Anal. Ed. 6, 602 (1934)

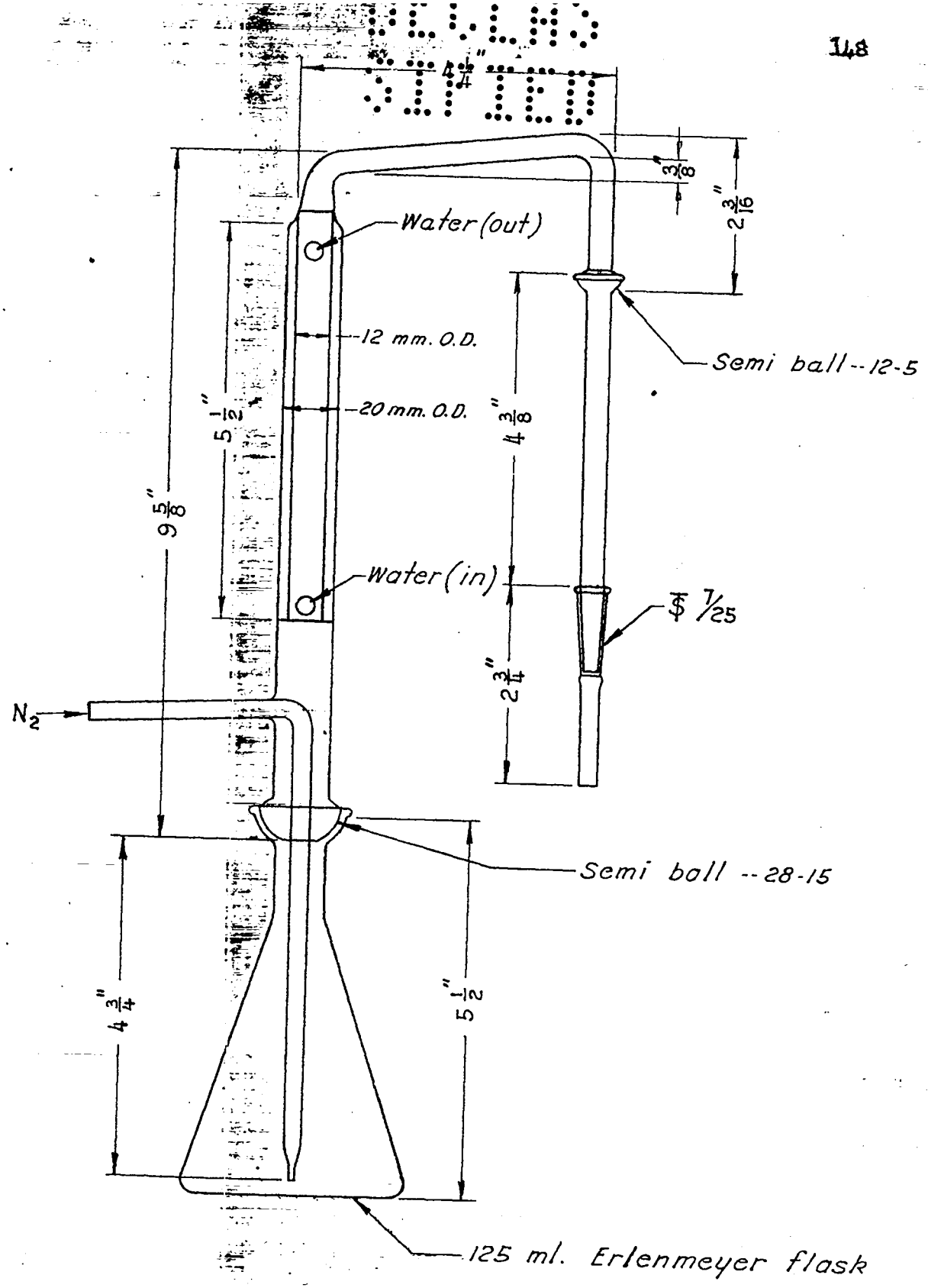
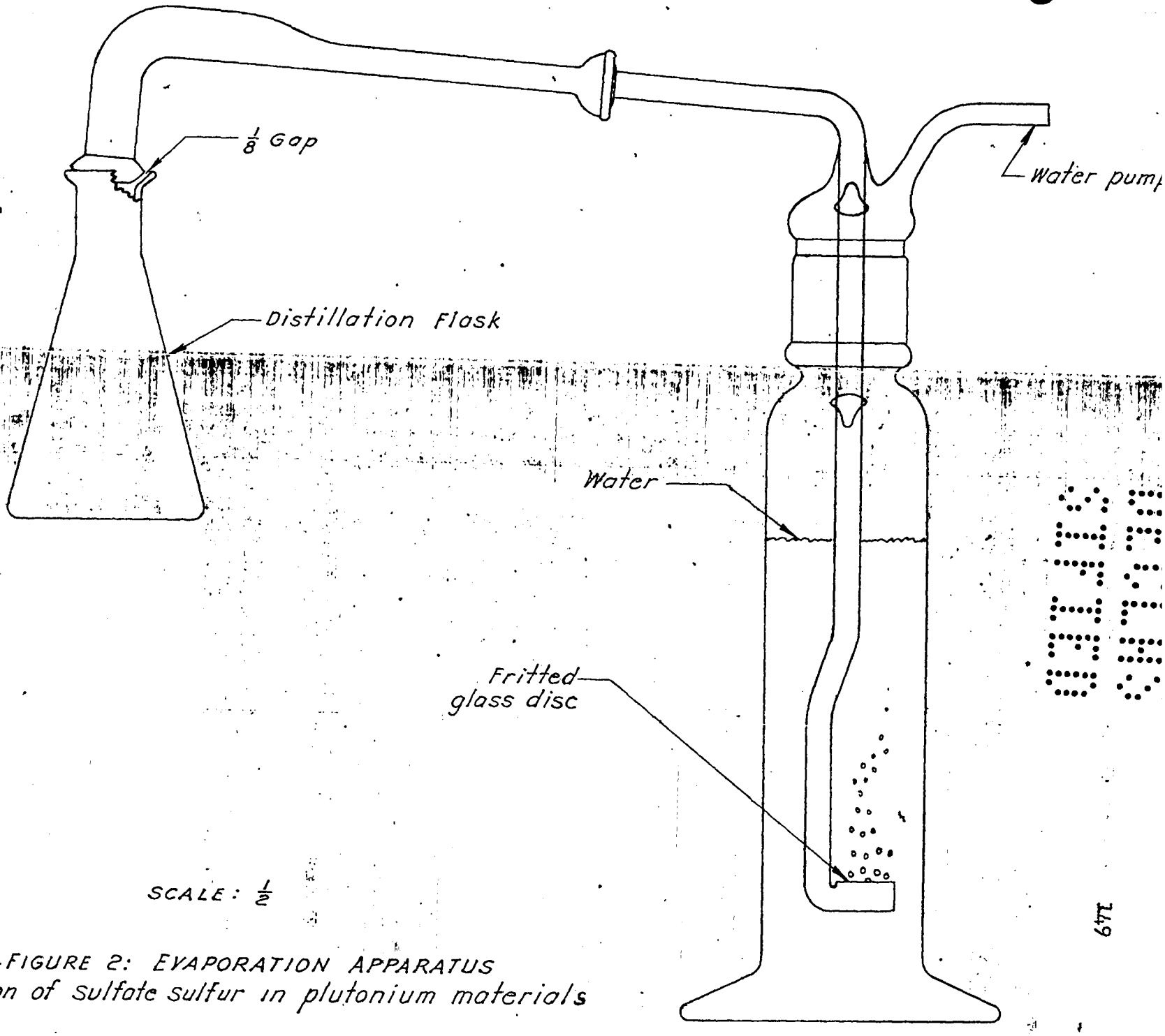


FIGURE 1. DISTILLATION APPARATUS.
Determination of sulfate sulfur in plutonium materials



SCALE: 1/2

FIGURE 2: EVAPORATION APPARATUS
Determination of sulfate sulfur in plutonium materials

IV C-1

MICROVOLUMETRIC ASSAY OF PLUTONIUM

Abstract

Pu as 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 1 N HNO_3, particularly in Hanford material 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 - 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.

It should be noted that, 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 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.

Reagents

1. H_2SO_4, concentrated.
2. H_2SO_4, 1 N.
3. Ceric sulfate, about 0.02 N in 1 N H_2SO_4.*
4. Saturated zinc amalgam.**
5. Solid CO_2 for generator.

Apparatus

1. Detachable syringe pipet controls for transferring all Pu solutions and for filling and emptying the burets.
2. Transfer weight-pipets with waxed tips (Figure 1).
3. Volumetric pipets, waxed tip, calibrated to contain 20 to 100 λ (Figure 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 (Figure 2).
6. Infra-red lamp and Variac.
7. CO_2 generator.
8. Reduction flask (Figure 3).
9. Electric stirrer.
10. Suction cup with syringe control (Figure 3).
11. Weight-burets 0.5 to 3.0 ml. capacity (Figure 1). The control constriction is waxed inside to allow free gravity drainage and the tip is waxed outside

* Standardized with Bureau of Standards $Na_2C_2O_4$.

** The amalgam may be prepared directly in the reduction flask by adding a few tenths of a gram of zinc to a milliliter of mercury. An excess of zinc sufficient to form a solid phase is permissible as long as the mixture is mobile.

[redacted]

to prevent drainage except when immersed in a solution or forced with a syringe. 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.

12. Titration cups made by cutting 15 ml. beakers to half height.

13. Beckman pH meter with calomel and platinum electrodes.

Procedure

HEED HEALTH SAFETY RULES OUTLINED IN SECTION I.

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 sample into the crucible rinse the pipet once with 1 N 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 and with a slow stream of air drawing over them heat them with the 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 re-dissolve the 4 sulfate precipitate; 0.4 to 0.5 ml. should be enough. Repeat the fuming and dilution three times.

2. Charge the reduction flask with saturated zinc amalgam; rinse with dilute H_2SO_4. Remove the rinse with the siphon and raise the CO_2 lead well above the surface. With a transfer pipet transfer the dissolved sample from Procedure 1 into the reduction flask using 2 ml. of 1 N H_2SO_4 for rinsing the

to prevent drainage except when immersed in a solution or forced with a syringe. 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.

12. Titration cups made by cutting 15 ml. beakers to half height.

13. Beckman pH meter with calomel and platinum electrodes.

Procedure

HEED HEALTH SAFETY RULES OUTLINED IN SECTION I.

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 sample into the crucible rinse the pipet once with 1 N 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 and with a slow stream of air drawing over them heat them with the 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 re-dissolve the +4 sulfate precipitate; 0.4 to 0.5 ml. should be enough. Repeat the fuming and dilution three times.

2. Charge the reduction flask with saturated zinc amalgam; rinse with dilute H_2SO_4. Remove the rinse with the siphon and raise the CO_2 lead well above the surface. With a transfer pipet, transfer the dissolved sample from Procedure 1 into the reduction flask using 2 ml. of 1 N H_2SO_4 for rinsing the

pipet, crucible, and flask neck. Lower the CO_2 lead into the solution and regulate the gas flow to a fraction of a cc. per second. Raise the lead just above the surface of the solution for the rest of the reduction except for occasional checks on the rate. Adjust the stirrer with the flattened end half immersed in the amalgam. Stir at a moderate rate. The minimum time of reduction for +4 valence is 1/2 hour. For a mixture of +4 and +6 it may require over an hour. A reasonably safe rule is 10 times the time required for the solution to turn from tan to blue-gray.

3. Turn on the pH meter. Select + MV scale.

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. Place the titration cup in the siphon. Stop the stirrer and lower the flask. Transfer the reduced solution as completely as possible, being careful not to draw up any amalgam. (Amalgam globules can be removed with platinum wire loops. Very little practice, however, is required to avoid this error.) Titrate with stirring immediately to within a few per cent of the end point — between 600 and 700 millivolts cell potential. Allow to stand.

5. Rinse the stirrer and flask sides with 1 ml. of 1 N H_2SO_4. Reduce this in the same manner as the sample for 12 to 15 minutes. (This procedure gives a minimum and reproducible blank.) Return the cup to the siphon and transfer the rinse. Titrate to the endpoint with small additions of ceric sulfate. The end point is at about 800 millivolts cell potential but should be determined by the operator from a titration curve. Interpolation of the end point is possible to 0.1 per cent from any potential between 700 and 900 millivolts provided a satisfactory curve has been obtained. Weigh the buret at several points within 1 per cent of the end point on either side. With some practice only an initial and a final weight are required.

Blank Procedure

Determine the reagent blank in the presence of plutonium in the following way. Take aliquots ranging from 0.01 to 0.100 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 amount in the small samples is the reagent blank correction. It should not exceed 10 γ of plutonium and should be reproducible to 2 or 3 γ.

Precautions

1. See Method of Sampling concerning errors resulting from storage of sample.

2. Although iron can stand for an hour after reduction and transfer before titration without error in excess of 0.1 or 0.2 per cent — and pure +3 valence Pu for 10 to 15 minutes with about the same error, it seems that the combination, iron and Pu, is air oxidized several times faster than Pu alone. Procedure as outlined above has been shown to give quantitative results with combinations of iron and Pu.

3. Significant errors in weight and erratic balance behavior has 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 a modification of Procedure

III D of this manual. 10 ml. flasks are substituted for 2 ml. ones. 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 plutonium concentration seems to be satisfied by this method.

Precision and accuracy

Mean deviations 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 on plutonium metal and tetrafluoride. The former assayed 99.9 per cent plutonium with a standard deviation of 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

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

T = mg. Pu per gram of ceric solution.

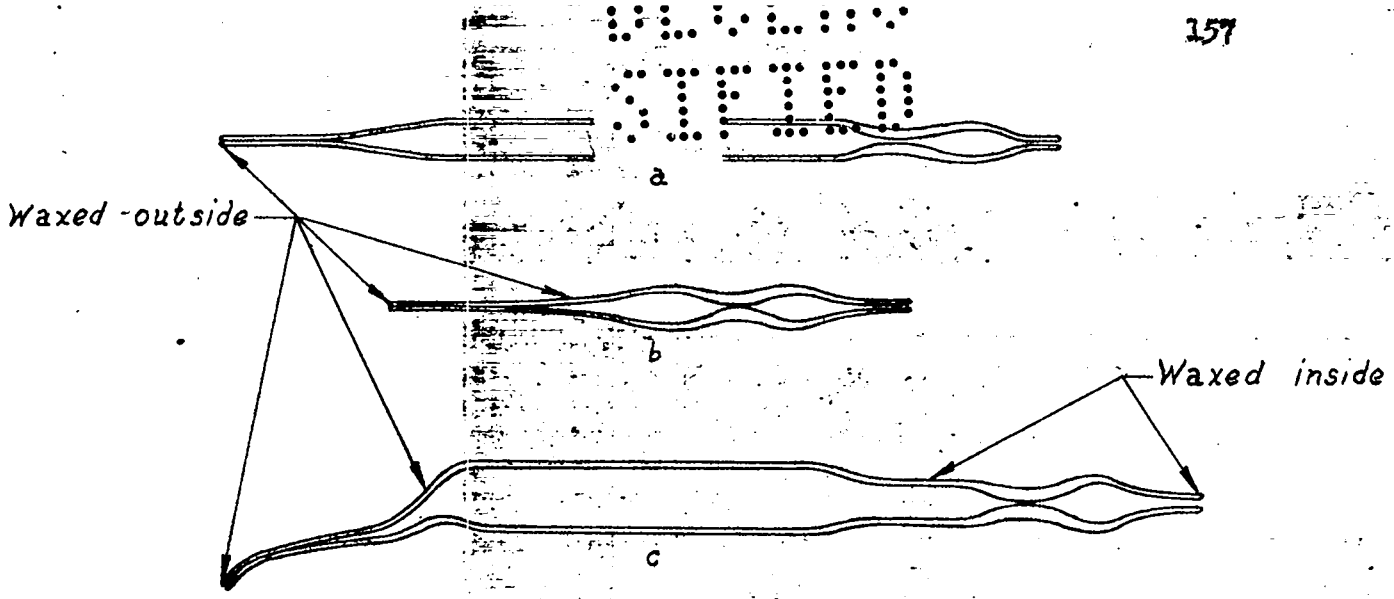


Figure 1 - a. Transfer pipet b. Volumetric pipet c. Weight buret

Scale $\frac{1}{1}$

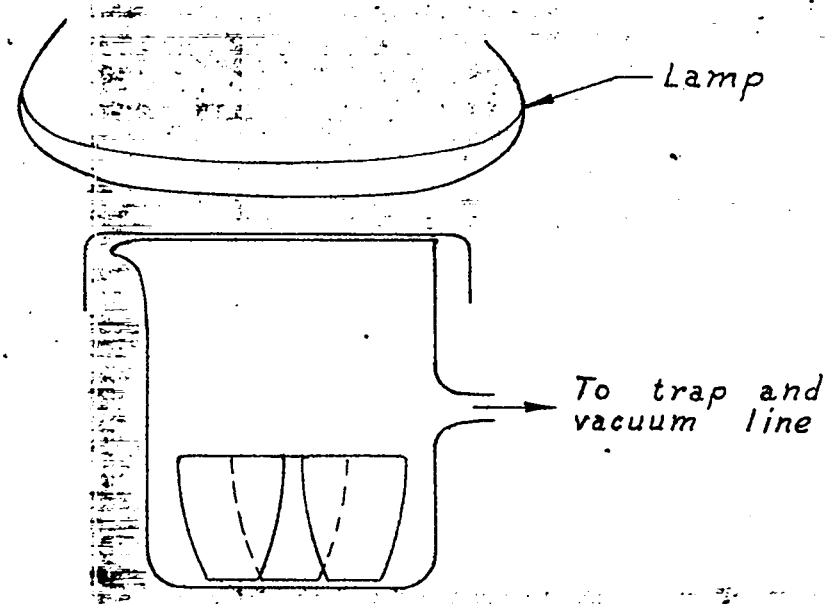


Figure 2 - Evaporation Chamber

Scale $\frac{1}{2}$

VOLUMETRIC ASSAY of PLUTONIUM

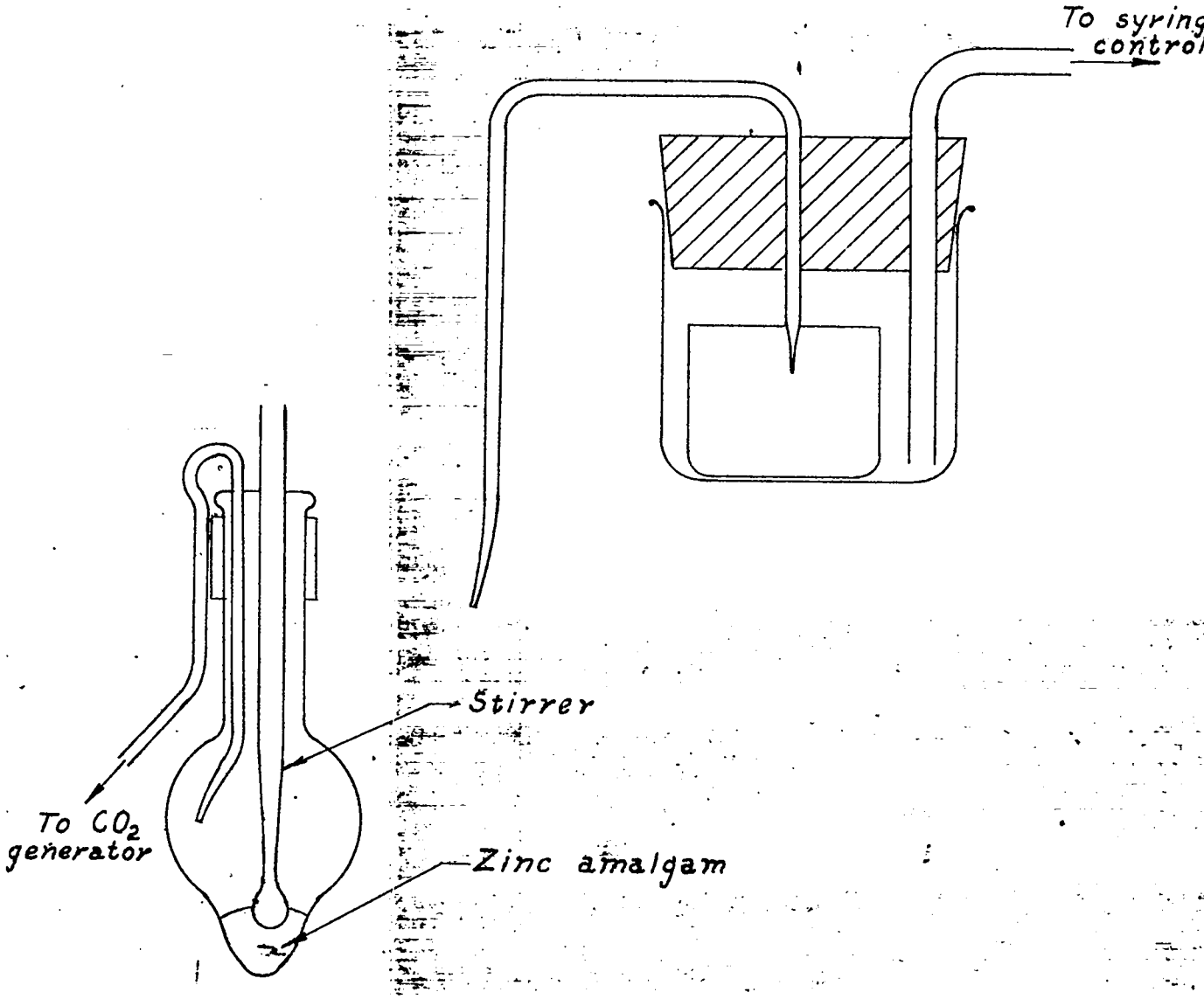


Figure 3 - Reduction flask and syphon cup

scale - $\frac{1}{1}$

VOLUMETRIC ASSAY of PLUTONIUM

MICROVOLUMETRIC ASSAY OF URANIUM

Abstract

Uranium as the +6 sulfate is reduced to the +4 state by means of zinc-amalgam. The +4 uranium is then titrated with standard ceric sulfate using a micro-weight buret.n The end point is determined by using orthophenanthroline-ferrous complex as an indicator.

Applicability

The method has been applied to uranium samples which do not contain plutonium. If iron is present, it must be determined separately and the titration result corrected accordingly.

Range and Accuracy

From 0.1 mg. to 5 mg. of uranium can be determined by the method here described. Best results are obtained with 1 mg. samples. In the analysis of uranyl sulfate controls the maximum observed deviation from the true value was 8%. The average deviation in 17 analyses was less than 1%.

Reagents

1. 2 N sulfuric acid.
2. 0.1 N potassium permanganate.
3. 4 per cent zinc amalgam.
4. Standard ceric sulfate, 0.02 N.*
5. Carbon tetrachloride.
6. Orthophenanthroline-ferrous indicator, approximately 0.01 M.
7. Dry ice.
8. Conc. H_2SO_4.
9. Conc. HNO_3.

* Standardize by weight against Bureau of Standards sodium oxalate.

10. Conc. $HClO_4$.

Apparatus

1. Titration cup (Figure 1).

2. Microweight burets (Figure 1, IV C).

3. Syringe pipet control for filling burets.

4. CO_2 generator with outlets for titration cup and wash bottle.*

5. Electric stirrer with glass agitator.

6. Microliter pipets, 20 λ capacity.

7. Platinum crucibles, 10 ml.

8. Infra-red lamp.

Procedure

HEED HEALTH AND SAFETY RULES OUTLINED IN SECTION I.

1. In absence of nitrate

Fill the CO_2 generator with dry ice and bubble the gas stream through the wash bottle for 2 - 3 hours to sweep out the oxygen from the generator and from the water in the wash bottle. Clean the titration cup with cleaning solution and rinse thoroughly. Place the titration cup on the stand and adjust the CO_2 lead so that a fairly rapid stream of CO_2 will impinge on the surface of the solution to be placed in the cup.

Fill the rubber bulb completely with deaerated water and attach it to the cup with the stopcock open. Carefully compress the bulb so that the water is forced into the stem of the cup and displaces all of the air in the stem. Close the stopcock so that the deaerated water fills the stem.

* A Dewar flask fitted with a tight-fitting rubber stopper with an outlet to cup and wash bottle through a T; also a safety valve to relieve excess pressure. Fill the flask with dry ice and stopper. Allow a few hours to sweep out air before using.

Run into the cup 1 - 2 ml. of the zinc amalgam and then pipet into the cup the nitrate-free solution to be titrated. The volume of the solution should not be more than 5 - 6 ml. Adjust the stirrer so that both the amalgam and the solution are agitated. Keep the CO_2 stream running at all times during the determination. If the solution is neutral or basic add sufficient 2 N H_2SO_4 (usually 2 - 3 drops) to make the solution approximately 0.05 N. If the solution is more acid than this see (3) below.

Reduce for 5 minutes. After reduction add dropwise sufficient 0.1 N. $KMnO_4$ (1 drop is usually sufficient) to make the solution pink and reduce again for 10 minutes after the disappearance of the pink color. If during this second reduction, the solution bedomes turbid due to the formation of MnO_2, add another drop of the 2 N H_2SO_4 and allow sufficient time to reduce the MnO_2. If the turbidity does not disappear, add another drop of acid.

Following the 10 minute reduction period, stop the stirrer and add 2 - 3 ml. of CCl_4. Carefully open the stopcock and squeeze the bulb gently to force water around the amalgam and the CCl_4 layer, in this way washing the amalgam. Release the pressure on the bulb and allow the amalgam to run down into the bulb. Repeat this operation until all of the amalgam is in the bulb and the CCl_4 is drawn into the capillary. At this point there will be a layer of CCl_4 in the bottom of the cup and the reduced solution above. Raise the stirrer so that it will not agitate the CCl_4 layer too violently and wash the stirrer with 1 ml. of deaerated water. Add exactly 20 microliters of the orthophenanthroline indicator and be sure to wash out the microliter pipet because these pipets are usually calibrated "to contain".

During the second reduction period, fill the microweight buret with standard ceric sulfate and weigh. After adding the indicator, start the stirrer and titrate to a sharp change from red to colorless (or a very light blue). Add the ceric solution slowly near the end point using very small increments. The end point under proper conditions of acidity is a sharp color change which is stable for 5 minutes. Reweigh the buret; the difference is the weight of ceric sulfate solution used in the titration.

2. In presence of nitrate

Nitrate interferes seriously in the procedure. Even small amounts of nitrate will produce fading and irregular end points.

To remove nitrates before titrating, transfer the solution to a 10 ml. platinum crucible and carefully add (down the side) 2 drops of conc. H_2SO_4. Heat the solution under an infra-red lamp until the fumes of H_2SO_4 are evident. Transfer the crucible to a small hot plate and continue heating until all of the acid has been fumed off. Be careful to avoid spattering and do not ignite the residue. Take up the UO_2SO_4 in 1 - 2 milliliters of water and transfer quantitatively to the titration cup. Do not use more than 3 - 4 ml. for the transfer. This is necessary because the final volume should not be over 5 - 6 ml.

3. In presence of excess acid

If the acid concentration of the solution to be titrated is greater than 0.05 N, the end point will fade and be indeterminate. If this is the case, or if the acid is other than sulfuric, fume the solution as described under (2).

4. In presence of organic matter

Organic matter must also be removed. Place the sample in a 10 ml. platinum crucible and add 2 ml. of conc. HNO_3. Heat gently until the

oxides of nitrogen cease to evolve, and add 3 drops of conc. $HClO_4$. Heat the solution gently until the solution becomes colorless. Add more $HClO_4$ if necessary. After the solution becomes clear, proceed as under (2).

5. For U_3O_8

Dissolve the oxide in HNO_3 and proceed as under (2).

Indicator Blank

An appreciable amount of ceric ion is required to change the indicator and this blank must be known accurately; the quantity of indicator must be measured precisely. To do this care must be exercised in pipetting the small volume (20λ) of indicator. The indicator blank is determined by carrying out the complete procedure in the absence of uranium. Under the specified conditions, however, the blank which is equivalent to approximately 50 γ of U need be determined only once for the same batch of indicator.

Theoretical

Zinc amalgam will reduce the +6 uranium only to the +4 state. (Jones reductor, however, will produce a mixture of +3 and +4.)

$$UO_2^{++} + 2H^+ + 2e^- \longrightarrow UO^{++} + H_2O$$

Permanganate is used after the first reduction step because it effectively eliminates a positive error, the exact source of which is undetermined.

The oxidation by ceric ion involves a 2 electron change,

$$UO^{++} + 2Ce^{++++} + H_2O \longrightarrow UO_2^{++} + 2Ce^{+++} + 2H^+$$

therefore the equivalent weight of uranium in this reaction is 119.09. The effect of the high acid concentration is evident from the above equation. The hydrogen ion will tend to force the reaction to the left and cause the fading of the end point.

Precautions

1. A sufficiently rapid stream of pure CO_2 must be blown into the cup during all operations.
2. All air must be removed from the stem of the cup before introducing the amalgam.
3. The cup must be clean so that no mercury will stick to the sides.
4. Acidity of the solution must be approximately 0.05 N.
5. The indicator must be added quantitatively.
6. The end point is sharp and the increments near the end point must be small so as not to over-run the end point.
7. All nitrate and organic matter must be removed.

Calculations and Expression of Results

Results can be expressed in mg. of uranium or percentage composition. Let N be the milliequivalents of ceric ion per gram of solution; then

$$\text{mg. U} = 119.09 \cdot N \cdot (x-b)$$

where x is the grams of ceric sulfate solution used in the titration and b is the grams of ceric sulfate solution used for the indicator blank.

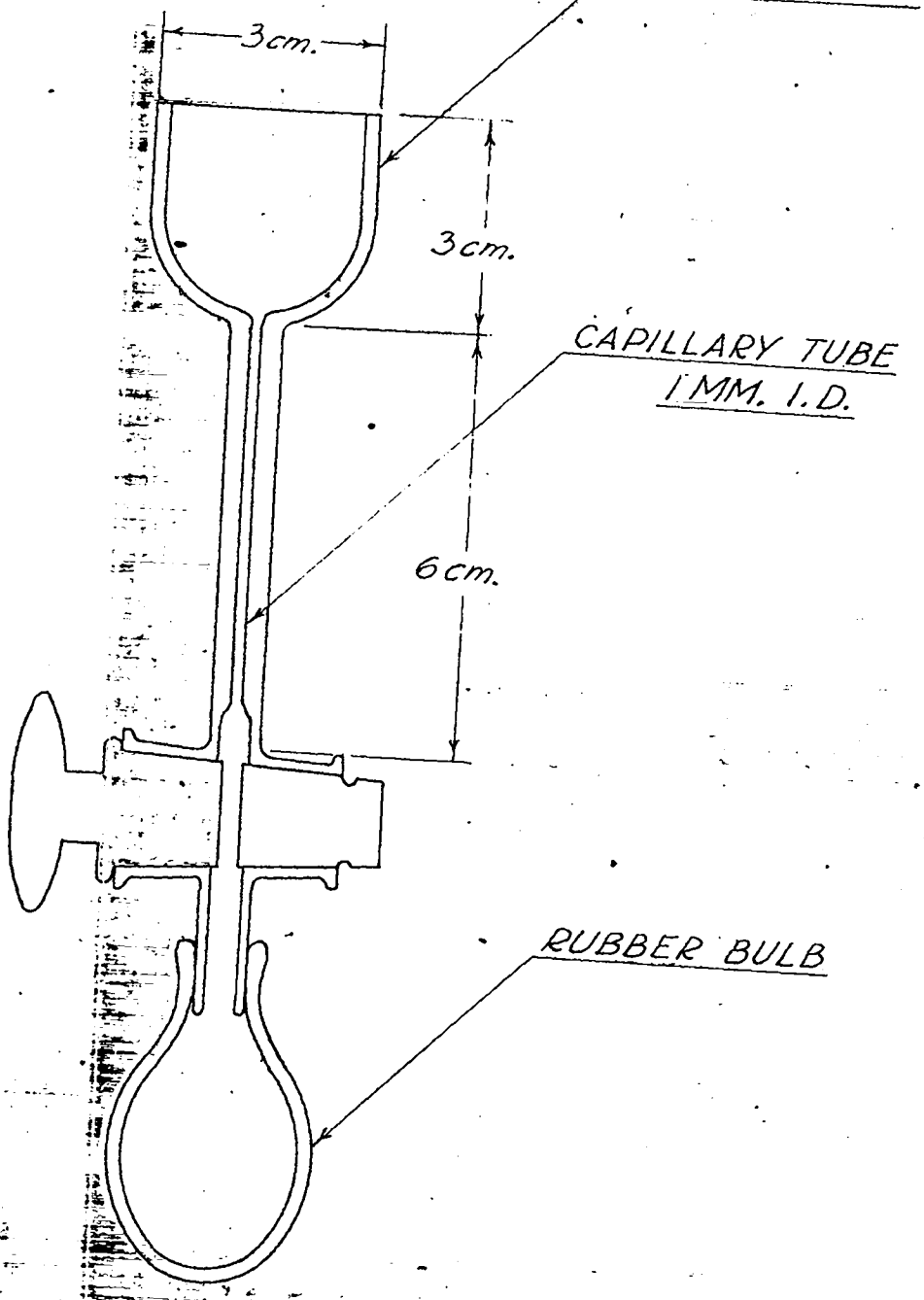


FIGURE 1. TITRATION CUP FULL SCALE

MICROVOLUMETRIC ASSAY OF URANIUM

V

GRAVIMETRIC PROCEDURES

GRAVIMETRIC DETERMINATION OF MOLYBDENUM IN MOLYBDENUM-URANIUM ALLOYS

Abstract

The molybdenum after oxidation with HNO_3, is precipitated, filtered, ignited, and weighed as $PbMoO_4$. Precipitation of uranium is prevented by buffering the solution with NH_4Ac.

Applicability

The method has been used successfully for molybdenum-uranium alloys with Mo content varying between 0.5 and 50 per cent.

Method of Sampling

The alloy is sampled by cutting or drilling. Iron introduced by these operations is removed by a magnet.

Size of Sample

The sample size shall be such that the weight of $PbMoO_4$ shall be about 0.1 gram.

Reagents

1. HNO_3, concentrated, c.p.
2. NH_4OH, concentrated, c.p.
3. NH_4Ac, 50 per cent solution.
4. $Pb(Ac)_2$, reagent solution; (40 g. $Pb(Ac)_2 \cdot 3H_2O$ per liter with enough HAc to produce a clear solution).
5. NH_4NO_3, 2 per cent solution.
6. HAc, glacial.
7. Methyl red indicator.

Apparatus

1. Four beakers, 400 ml.
2. Four watch glasses, plain, 4 inch.
3. Graduate, 50 ml.

4. Graduate, 10 ml.
5. Two stirring rods, 6 inch.
6. Hot plate, electric.
7. Wash bottle.
8. Two policemen.
9. Two Fisher burners.
10. Two clay triangles.
11. Two ring stands.
12. Two iron rings.
13. Dessicator containing $CaCl_2$.
14. Tongs.
15. Two No. 2 B Gooch crucibles; 2 Gooch adapters; 2 filter flasks, 500 ml.; medium Gooch grade asbestos; (or 2 3-inch funnels; No. 42 Whatman filter paper, and filter paper pulp).

Procedure

1. Weigh to the nearest 0.1 mg. duplicate samples of the alloy of such size that each will give about 0.1 g. of $PbMoO_4$.
2. Place sample in 400 ml. beaker covered with a watch glass. Cover sample with 3 - 5 ml. conc. HNO_3 and warm until dissolved with addition of more acid if necessary.
3. Dilute solution to about 150 ml. and add 4-5 drops of methyl red indicator.
4. Add 5 ml. glacial HAc.
5. Add concentrated NH_4OH with stirring until the precipitate which first forms redissolves with difficulty.
6. Add a 50 per cent solution of NH_4Ac until the color of indicator changes to yellow and than add a 20 ml. excess.
7. Heat solution to boiling and add slowly, with stirring, 1 ml. $Pb(Ac)_2$

reagent solution for each 0.01 gram of Mo present. (Avoid a large excess.)

8. Allow precipitate to settle on steam bath for a few minutes. Add a few more drops of precipitant to test for completeness of precipitation.

9. Decant solution onto tared Gooch crucible or No. 42 Whatman ashless filter paper (the use of some filter paper pulp will aid filtration and washing if filter paper is used) and wash three times by decantation with 2 per cent NH_4NO_3 solution. Transfer precipitate to paper or Gooch crucible using stream from wash bottle containing hot 2 per cent solution of NH_4NO_3, policing the precipitate to remove traces from the sides of the beaker.

10. If a Gooch crucible was used, heat at dull red heat to constant weight and weigh as $PbMoO_4$. If a paper was used, dry, burn off paper carefully and finally ignite to constant weight and weigh as $PbMoO_4$.

Equations

(1) $Mo^{\circ} + HNO_3 \longrightarrow MoO_4^{=}$

(2) $MoO_4^{=} + Pb^{++} \longrightarrow PbMoO_4$

Calculations

$Mo = PbMoO_4 \times 0.2614$

$$\text{Per cent Mo} = \frac{0.2614 \times \text{wt. } PbMoO_4 \times 100}{\text{wt. sample}}$$

References

1. Scott's Standard Methods of Chemical Analysis, I, pp. 589-590, New York, D. Van Nostrand Co., 1939.

2. W. F. Hillebrand and G. E. F. Lundell, Applied Inorganic Analysis, pp. 253-254, New York, John Wiley and Sons, 1929.

MICROGRAVIMETRIC DETERMINATION OF GALLIUM IN PLUTONIUM-GALLIUM ALLOYS

Abstract

Gallium as $GaCl_3$ is separated from plutonium by extraction with isopropyl ether. The $GaCl_3$ is re-extracted from the ether by shaking with water and is determined gravimetrically as the 8-hydroxyquinolate, $Ga(C_9H_6ON)_3$.

Applicability

The method has been used in analyzing Pu-Ga alloys with a gallium content ranging from 0.5 to 2.0 weight per cent.

Size of Sample and Limit of Sensitivity

Sufficient sample is taken to give approximately 1 mg. of gallium. Good results can be obtained, however, with as little as 0.5 mg. of gallium.

Reagents

1. Isopropyl ether. Shake with alkaline permanganate and redistill.
2. Mercury, c.p.
3. HCl, 12 N, standardized.
4. Sodium acetate solution, 20 per cent.
5. Alcoholic 8-hydroxyquinoline solution, 5 per cent.
6. Phenolphthalein indicator.
7. Ammonium hydroxide, conc.

Apparatus

1. Shaking tubes (see Figure 1).
2. Pipet, 1 ml., calibrated in hundredths.
3. Transfer pipets (see Figure 2).
4. Steam bath.
5. Buret, 1 ml.
6. Shaking machine.
7. Electric oven.
8. Beakers, 30 ml.

9. Rubber policemen.

10. Munroe crucibles, 10 ml., and filtering apparatus.

11. Semi-micro balance.

Procedure

HEED HEALTH AND SAFETY RULES OUTLINED IN SECTION I.

1. Preparation of sample and extraction.

a. Cut metal specimens each approximately 100 mg. in weight and weigh each sample accurately to 0.2 mg.

b. Calculate the volume of 12 N HCl needed to dissolve the Pu,* and the volume of additional HCl and H_2O needed to bring the resulting solution to 7.3 N in HCl in a volume of 1.00 ml.**

c. Pipet the calculated volume of H_2O into the shaking tube and drop in the metal sample. Add the total calculated volume of HCl slowly from the 1 ml. buret. The reaction will start immediately upon the addition of the first drop of acid. Keep the tube inclined while adding the acid to prevent the possibility of spray emerging from the tube.

---

* In order that quantitative results may be obtained in the extraction procedure, the acidity must be carefully adjusted to 7.3 N. At this normality the distribution ratio of gallium between isopropyl ether and water is a maximum.

The equation for dissolving Pu in acid is as follows:

$$2\ Pu + 6\ H^+ \longrightarrow 2\ Pu^{+3} + 3\ H_2 \uparrow$$

The equivalent weight of Pu is therefore 239/3 = 79.7. If W is the weight of the sample in mg. and N is the actual normality of the HCl, the volume (in ml.) of acid necessary to dissolve the metal is W / (79.7)(N).

** The volume of N-normal HCl required to make 1 ml. of 7.3 N HCl is 7.3/N ml. The total acid requirement is

$$V_a = \left[\frac{W}{(79.7)(N)} + \frac{7.3}{N}\right] \text{ml.}$$

and the water required is $V_W = (1.00 - V_a)$ ml.

It is evident that a number of approximations have been made in these calculations. For example, the volume change that accompanies the dissolving of the metal is neglected, the volumes of water and 12 N acid are assumed to be additive, and the sample is assumed to be 100 per cent Pu (no correction being made for the gallium present).

d. When the sample is in solution, add 4 drops of mercury to reduce the iron present* and stopper the tube with a well-greased ground glass stopper. Place the tubes in the shaking machine and shake for 5 minutes.

e. Remove the tubes from the machine and add 1 ml. of isopropyl ether being careful to wash down the stopper with the first portion added. Re-grease the stopper if necessary and shake for 20 minutes.

f. After the shaking allow the Pu-Hg layer to separate from the ether and swirl gently so that a sharp separation takes place. Transfer the ether layer to a second shaking tube by means of the smaller of the transfer pipets. Wash the pipet by drawing up an equal volume of ether and add the ether washings to the second tube.

g. With the same pipet again add 1 ml. of isopropyl ether to the first tube, stopper (greasing stopper if necessary) and shake for another 20 minute interval.

h. Transfer the ether layer to the second tube. Add a small quantity of ether to the first tube with the same pipet, invert several times to wash the sides of the tube and transfer the ether layer to the second shaking tube.

i. Still using the same pipet add 5 ml. of water to the second tube.

j. Add a glass bead to the second tube, stopper with a well-greased stopper and shake for 10 minutes.

k. Transfer the lower aqueous layer by means of the larger transfer pipet to a 30 ml. beaker containing 5 ml. of 20 per cent sodium acetate, 1 drop of phenolphthalein, and 1 drop of ammonium hydroxide. While the pipet is passing through the upper ether layer, expel air through the pipet so that no ether is permitted to enter. Fill the pipet with water and add these

* $FeCl_2$ will not be extracted by isopropyl ether.

washings to the beaker.

l. Add 5 ml. of water to the shaking tube with the same pipet, and shake for 10 minutes.

m. Transfer the water layer to the beaker and add a small quantity of water to the shaking tube, stopper, invert a few times, and transfer this aqueous layer to the beaker. The total volume in the beaker should now be between 15 and 20 ml.

2. Precipitation.

Cover the beaker with a watch glass and heat below the boiling point until most of the color of the indicator has disappeared. Wash down the cover glass and add, dropwise, 15 drops of the alcoholic 8-hydroxyquinoline (5 per cent), waiting between drops for the yellow precipitate to form. Place on the steam bath and digest for an hour.

3. Transferring, Washing and Drying of the Precipitate

a. Transfer the precipitate to a weighed 10 ml. platinum Munroe crucible using hot water to wash out the precipitate. Transfer as much as possible by washing before using a policeman. Extreme care must be taken in the transfer since the precipitate is difficult to handle because of its tendency to crawl and become finely dispersed.

b. Wash the precipitate in the Munroe crucible 3 times with hot water. Inspect the beaker with a magnifying glass to see that all the precipitate has been transferred.

c. Dry in an electric oven at 120° C. for one hour. Cool for one hour in the balance room and weigh as $Ga(C_9H_6ON)_3$.

Precautions

1. The acidity of the HCl solution must be accurately adjusted before extraction.

2. The transfer of the precipitate is difficult and care must be used. Use

plenty of hot water for the operation.

Calculations

mg. Ga = mg. precipitate x 0.1389

$$\text{per cent Ga} = \frac{\text{mg. Ga}}{\text{sample wt. in mg.}} \times 100$$

Literature References

Project Report LA-417

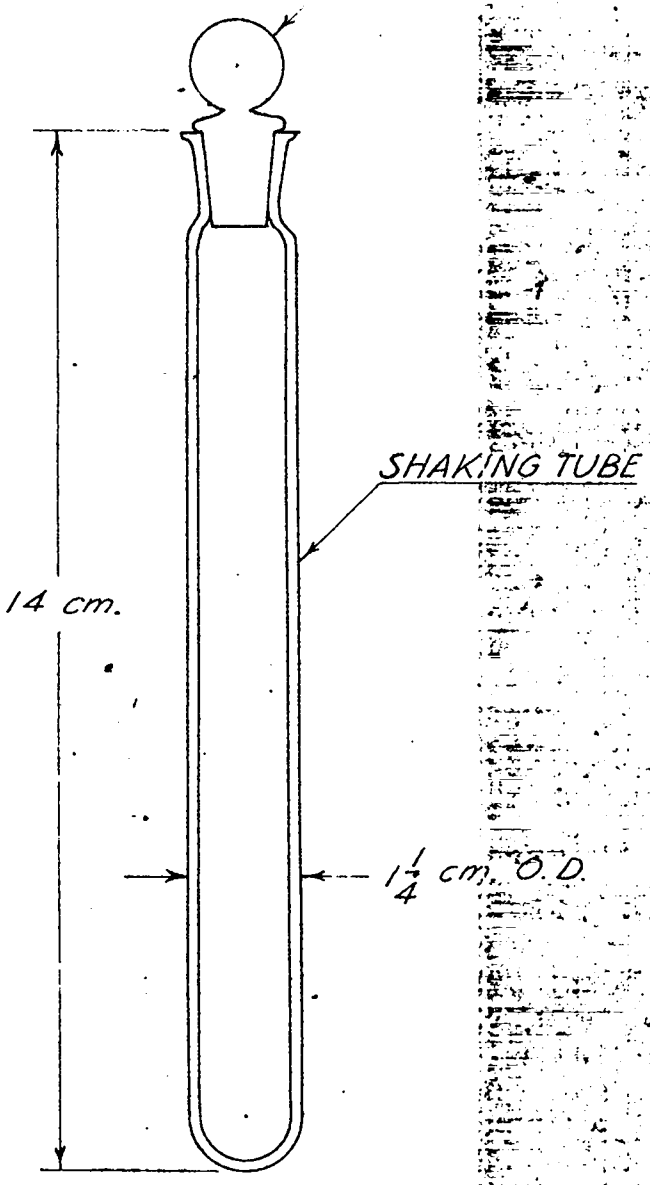


FIGURE 1 SHAKING TUBE FULL SCALE

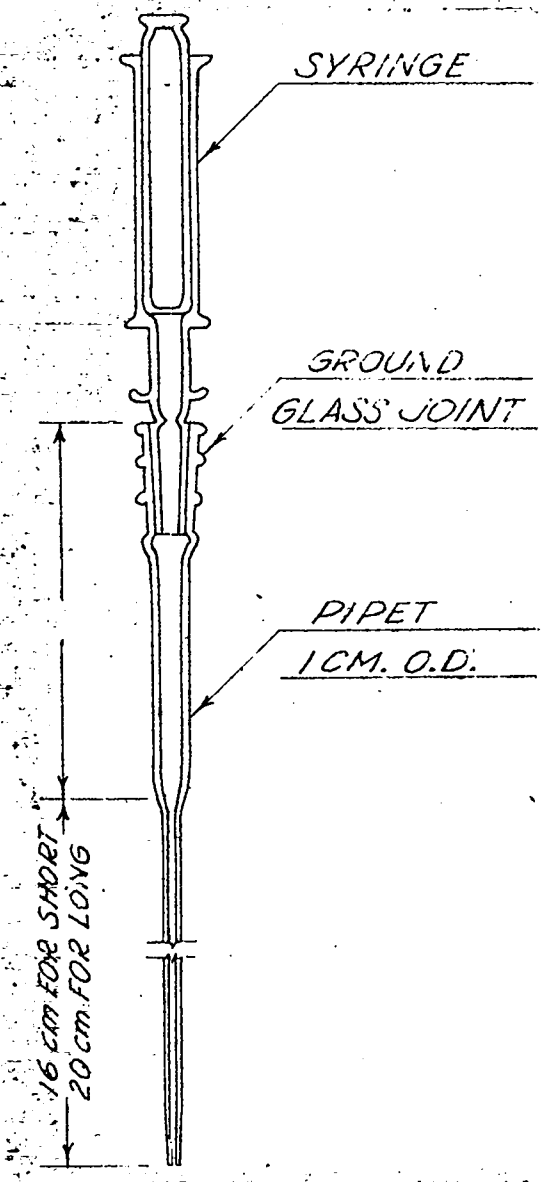


FIGURE 2 TRANSFER PIPETS HALF SCALE

MICROGRAVIMETRIC DETERMINATION OF GALLIUM IN PLUTONIUM-GALLIUM ALLOYS

GRAVIMETRIC DETERMINATION OF CARBON IN URANIUM TETRAFLUORIDE

Abstract

The sample, intimately mixed with MgO, is burned at 1000° C. in a stream of oxygen. Fluorine not retained by the MgO is trapped by PbO_2. The carbon dioxide formed by oxidation of carbon in the sample is quantitatively absorbed on Ascarite and weighed.

Applicability

The method has been used only for uranium tetrafluoride, but it is expected that it would give equally satisfactory results with certain other halogen-bearing inorganic materials.

Method of Sampling

The fluoride should be finely powdered by grinding in a clean porcelain mortar and uniformly mixed by any of the well-known methods.

Size of Sample and Limits of Sensitivity

Samples of the order of one to two grams are used. The limits of sensitivity are approximately 50 ppm of carbon on a 1 gram sample and 25 ppm on a 2 gram sample.

Reagents

1. Ascarite (soda-asbestos).
2. Dehydrite [Arthur H. Thomas, anhydrous $Mg(ClO_4)_2$].
3. Magnesium oxide, C-free; it is ignited in a muffle at 1000° C. for several hours.
4. PbO_2 made according to Pregl.*

* Digest a good grade of PbO_2 two to three hours on a steam bath with concentrated HNO_3 to dissolve basic oxides of lead. Decant the HNO_3 from the now black PbO_2 and wash by decantation with water until all of the HNO_3 is removed. Pour the PbO_2 slurry into a shallow dish and dry in an oven at 105° C. Cut up the dried cake into cubes about 3 - 5 mm. on edge and rotate in a bottle to round the edges. Discard the very small pieces and the dust.

5. H_2SO_4, concentrated, c.p.

6. Tank oxygen, 99.5 per cent minimum purity.

Apparatus

1. Multiple-unit organic combustion furnace (Figure 1).

2. Fused quartz combustion tube, 20 mm. o.d. x 100 cm.

3. Porcelain combustion boats, size 6 (Coors).

4. U-tube containing Dehydrite.

5. 4 U-tubes containing Ascarite and Dehydrite.

6. Bubbler containing concentrated H_2SO_4.

7. Variac resistor.

8. Thermocouple and pyrometer.

9. Boat hook and rake.

10. Mullite or porcelain mortar and pestle.

11. Radioactive source (1 mg. radium).

Procedure

1. Fill the combustion tube with PbO_2 pellets. These are held in place by rolled copper gauze plugs as shown in Figure 2, Detail A.

2. With the furnaces maintained at the correct temperatures, i.e., approximately 1000° C. for the small unit and approximately 190 - 200° C. for the large units, adjust the oxygen flow to about 1 - 2 bubbles per second and burn out the combustion tube approximately 6 - 8 hours.

3. Connect the Dehydrite tube and the weighed Ascarite tube and its tare as shown in Figure 1 and Figure 2, Detail B. (Handle tubes with dry clean cotton gloves.) Allow the tubes to remain on train for 30 minutes under conditions as given in (2) above. The Dehydrite tube is not removed from place until the combustion tube filling is renewed.

4. Remove the Ascarite tube and its tare from the train and close the stop-

cocks. Place the tubes on a suitable rack directly over a radioactive source (1 mg. of radium) and allow to remain 15 minutes for dissipation of accumulated static charges. Momentarily open stopcock to allow tubes to attain atmospheric pressure. Place the absorption tube on the left balance pan and its tare on the right pan and weigh. It is a good plan at this point to place the radioactive source in the balance and reweigh the tubes after 5 minutes to insure that all static charges are dispelled. The 30 minute absorption and weighing procedure is repeated until there is obtained a weight increase of less than 0.2 mg. per 30 minute absorption period. The combustion tube is then ready for use. It is kept closed from the air when not in use.

5. Weigh to the nearest mg. a 1 to 2 gram sample of the fluoride and transfer to a small porcelain or mullite mortar. Add an approximately equal amount of ignited MgO and intimately mix by grinding. With a spatula transfer the mixture to a pre-ignited No. 6 porcelain boat. It is not desirable to use a brush to transfer traces of the mixture adhering to the mortar because brush hairs may be introduced. Spread the mixture out evenly in the boat and overlay with one to two grams of ignited MgO.

6. With the furnaces maintained at the correct temperatures, i.e., approximately 1000° C. for the small unit and approximately 190 - 200° C. for the large units, connect the weighed Ascarite tube and its tare as shown in Figure 1 and Figure 2, Detail B. (Use cotton gloves.) Make sure that the stopcocks are properly aligned. After testing the assembly for leaks adjust the oxygen flow to about 1 - 2 bubbles per second.*

* To test for leaks count the rate of bubbling in the H_2SO_4 bubbler at the exit end of the train and also the rate in the bubbler (not shown in Figure 1) between the combustion tube and the oxygen tank. The rates will be the same if the system is air-tight.

7. Remove the stopper from the front end of the combustion tube and by means of a boat hook place the boat directly beneath the small combustion unit. Quickly replace the stopper. No further adjustment of the oxygen flow is necessary.

8. After 30 minutes remove the Ascarite absorption tube and its tare from the train and close the stopcocks. Replace these with another weighed set to determine the blank (see Blank Procedure). Place the used tubes on a rack directly over a radioactive source (1 mg. of radium) and allow about 15 minutes for dissipation of accumulated static charges. Momentarily open stopcocks to allow tubes to attain atmospheric pressure. Place the absorption tube on the left balance pan and its tare on the right pan and weigh. It is a good plan at this point to place the radioactive source in the balance and reweigh the tubes after 5 minutes to insure that all static charges are dispelled.

9. Remove the blank set of absorption tubes after thirty minutes and weigh as above.

Blank Procedure

Determine the blank by leaving the burned sample in the furnace and replacing the absorption tubes with another weighed set for 30 minutes. Since the PbO_2 loses much of its efficiency after about 20 determinations and since low blanks cannot be obtained if PbO_2 is absent, this method of obtaining the blank serves to indicate when the PbO_2 should be renewed.

Uranium tetrafluoride loses all of its fluorine at 1000° C.; most of it is retained by reaction with the MgO. That escaping retention by the MgO is converted to PbF_2 on the PbO_2 and retained.* In this manner blanks

* Neither MgO alone nor MgO used in conjunction with a silver wool tube filling (see Report CC-433) will retain all the fluorine. Both these procedures gave high and erratic blanks; e.g. about 5 mg. with MgO alone and about 2 mg. with added Ag wool.

are reduced to the order of 0.2 mg. or less, which is that found on the train without a sample.

Precautions

1. The MgO used must be ignited to remove all carbon. Most MgO contains more or less $MgCO_3$. It is well to determine the carbon left after ignition of each batch of MgO. It was found to be negligible when the ignition was done at 1000° C. for several hours.
2. Blanks should be determined frequently since the PbO_2 loses its efficiency after about 20 determinations.
3. In the dry air of Los Alamos static charges are very easily built up on glass. These are large enough to make prohibitive the wiping of the absorption tubes as is usually done. By handling the tubes with cloan dry cotton gloves, the necessity for wiping is eliminated and static charges are greatly reduced. Even so it has been found necessary to use a radioactive source to remove the small charges formed as they are otherwise but slowly dispelled.

Calculation and Expression of Results

The carbon content is usually reported as parts per million and is calculated as follows:

Wt. (g.) C = [Wt. (g.) increase of Ascarite tube, 1st 30 min. minus wt. (g.) increase of Ascarite tube, 2nd 30 min.] x 0.273

$$\text{ppm C} = \frac{\text{wt. (g.) C} \times 10^6}{\text{wt. of sample in grams}}$$

Literature Reference

Project Report CC-433.

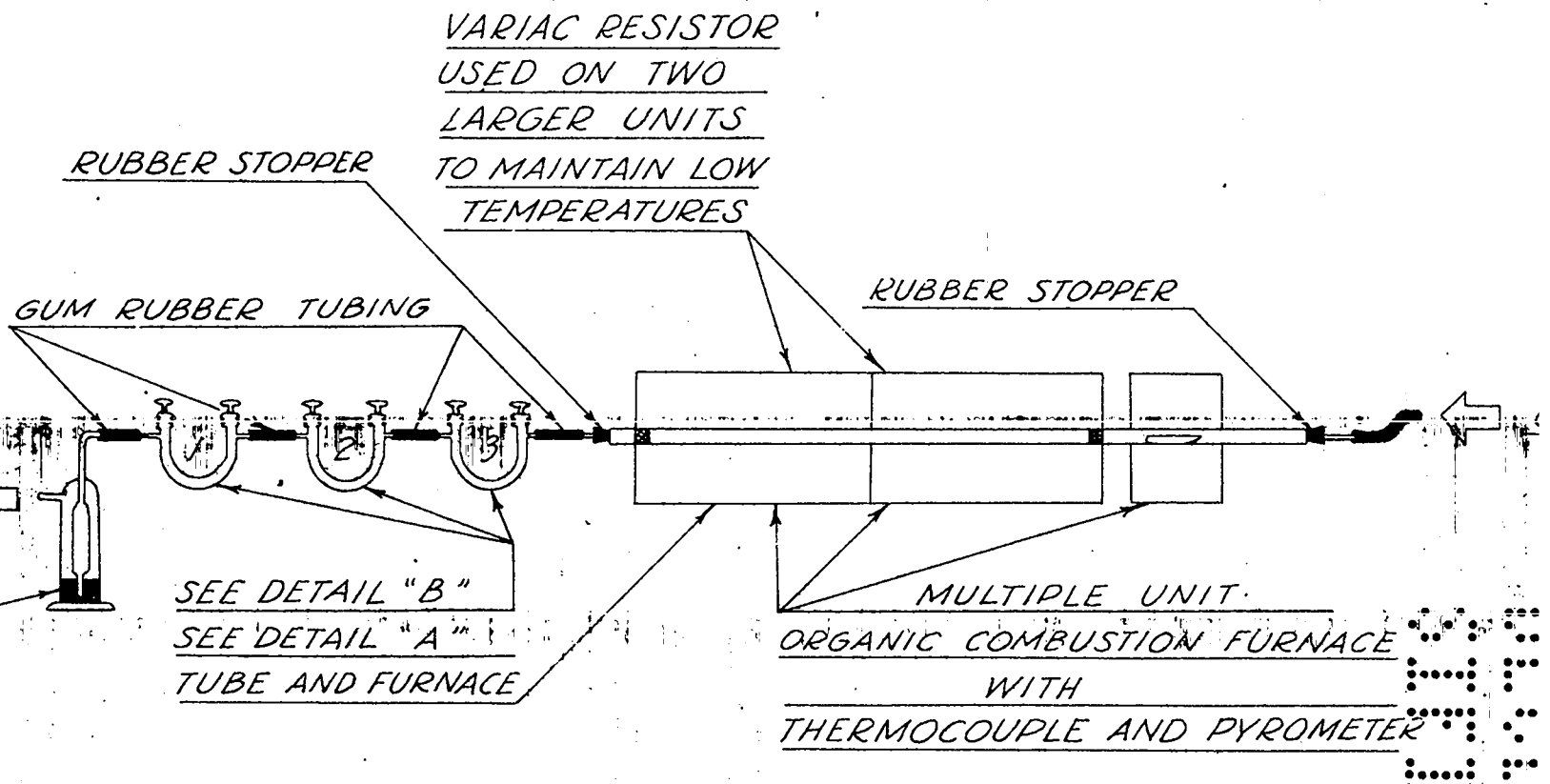
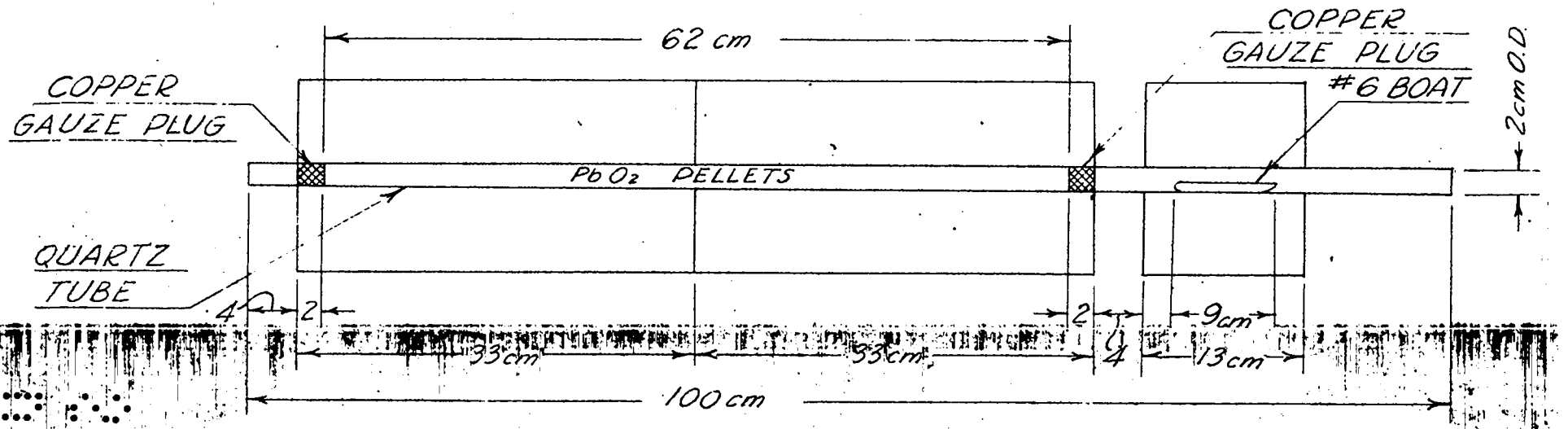
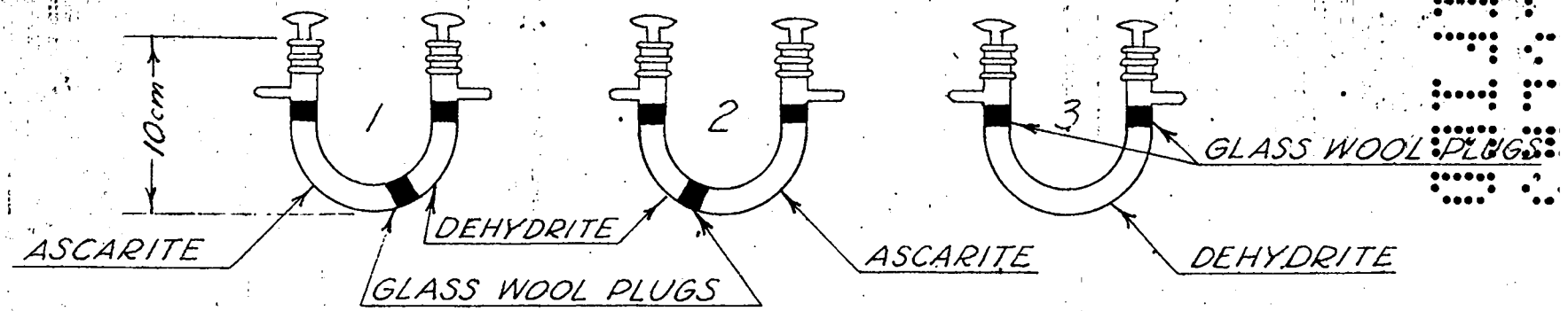


FIGURE 1 COMBUSTION TRAIN ASSEMBLY SCALE: 1/10

DETERMINATION OF CARBON
IN URANIUM TETRAFLUORIDE



DETAIL A COMBUSTION TUBE FILLING SCALE: 1/5



DETAIL B ABSORPTION TUBE FILLING SCALE: 1/4

FIGURE 2 DETAILS OF COMBUSTION TRAIN

DETERMINATION OF CARBON IN URANIUM TETRAFLUORIDE

APPROVED FOR PUBLIC RELEASE

UNCLASSIFIED

UNCLASSIFIED