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**The Gravimetric Determination of Carbon in
Uranium-Plutonium Carbide Materials**

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THE GRAVIMETRIC DETERMINATION OF CARBON IN URANIUM-PLUTONIUM CARBIDE MATERIALS

by

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ABSTRACT

A gravimetric method for determining carbon in uranium-plutonium carbide materials was developed to analyze six samples simultaneously. The samples are burned slowly in an oxygen atmosphere at approximately 900°C, and the gases generated are passed through Schütze's oxidizing reagent (iodine pentoxide on silica gel) to assure quantitative oxidation of the CO to CO₂. The CO₂ is collected on Ascarite and weighed. This method was tested using a tungsten carbide reference material (NBS-SRM-276) and a (U,Pu)C sample. For 42 analyses of the tungsten carbide, which has a certified carbon content of 6.09%, an average value of 6.09% was obtained with a standard deviation of 0.01,₇% (the subscript indicates an approximate value) or a relative standard deviation of 0.28%. For 17 analyses of the (U,Pu)C sample, an average carbon content of 4.97% was found with a standard deviation of 0.01,₇% or a relative standard deviation of 0.24%.

I. INTRODUCTION

We developed a simplified method for determining carbon in uranium-plutonium carbide reactor fuels containing approximately 5% carbon. This method permits the simultaneous analysis of six samples or reference materials, allowing eight samples and four reference materials to be analyzed on a single system in a regular 8-h working period. Only a small glove box area is required because most of the system is located outside the alpha-containment

box. To oxidize CO to CO₂, Schütze's oxidizing reagent (iodine pentoxide on silica gel) is used at room temperature instead of CuO heated to 700°C.

Reliable combustion analysis requires a quantitative ignition of the sample, a process that is material dependent. In this method, complete combustion is assured by a slow heating-oxidizing process in which the sample is heated to 450°C during the first hour and to 900°C during the second hour. This controlled oxidation process prevents the sample from forming "cinders," which under rapid

oxidation conditions can trap carbon and cause low analysis results. This slow heating-oxidation process produces a fine oxide powder.

II. APPARATUS AND REAGENTS

Apparatus

Absorption Tubes. (See Fig. 1.) Nesbitt-type tubes to quantitatively collect the CO_2 . These tubes are packed with a uniform layer of glass wool on the bottom to evenly distribute the gas and eliminate clogging. Six absorption tubes are required.

Balance. Analytic with ± 0.1 -mg sensitivity.

Capsules. Tin, 4-mm i.d. and 20 mm deep for containing powdered standards or samples. LECO No. 501-059 or equivalent. The sample loading tool shown in Fig. 2 can be used.

Chamois skin. Dampened with distilled water and used to wipe absorption tubes immediately before weighing to prevent static electric charge on the tubes.

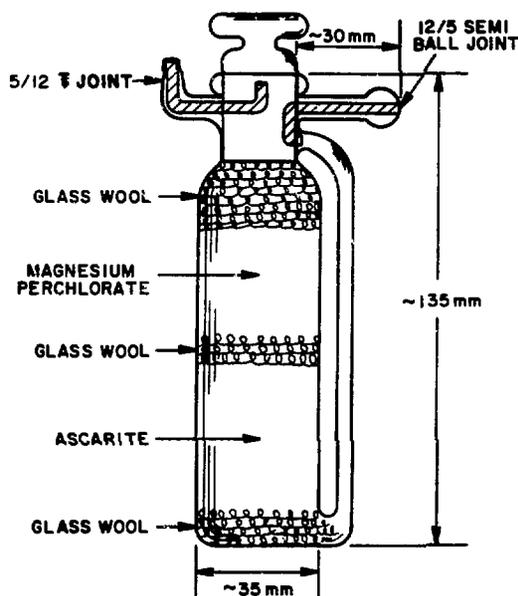


Fig. 1.
Absorption tube.

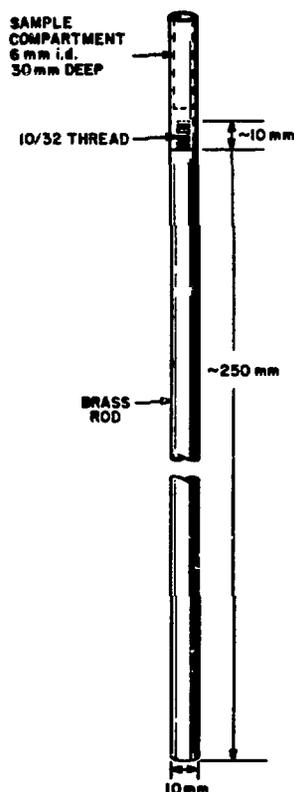


Fig. 2.
Sample loading tool.

Combustion tube. (See Fig. 3.) Fused silica tube with a 2-hole, No. 00 rubber stopper fitted with two stainless steel tubes. Six combustion tubes are required.

Combustion Furnace. (See Fig. 4.) Two heating elements with fused silica and lavite insulators enclosed in a box made from 5-mm-thick Transite. Capable of heating to 900°C .

Gas Purification Tube. (See Fig. 5.) A 300-mm column packed with magnesium perchlorate, Ascarite, and Schütze's reagent.

Oven. Capable of heating to 220°C with openings for inlet and outlet argon gas.

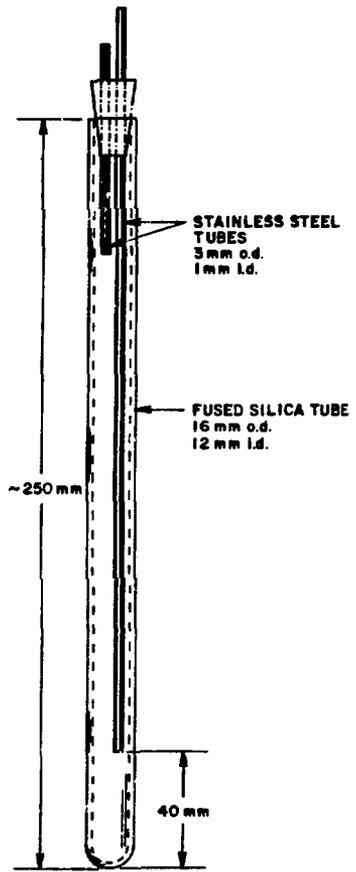


Fig. 3.
Combustion tube.

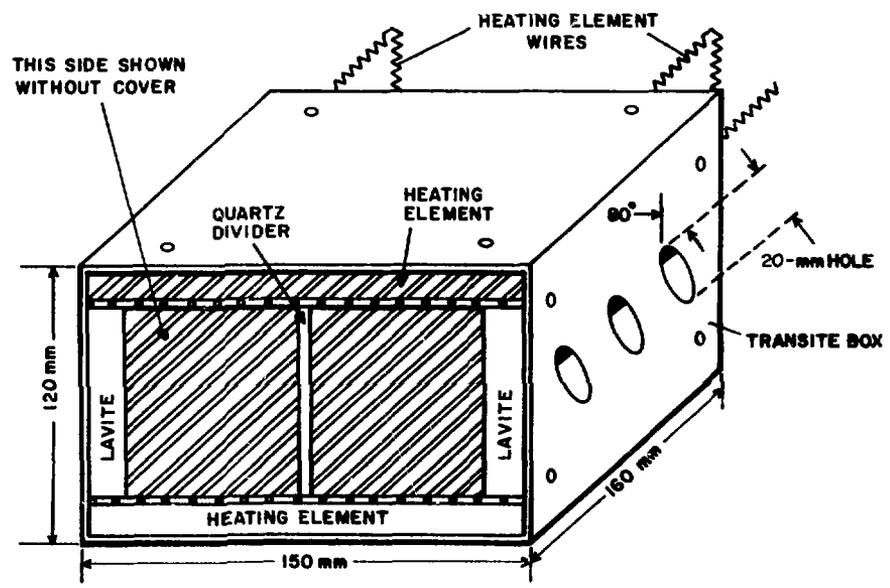


Fig. 4.
Combustion furnace.

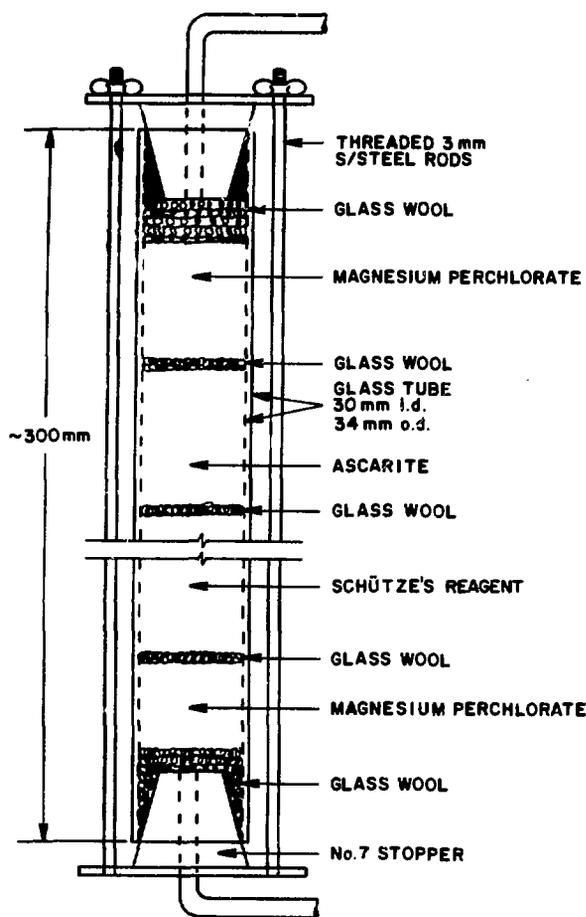


Fig. 5.
Gas purification tube.

Schütze's Reagent Preparation System. (See Figs. 6 and 7.) All glassware is made from borosilicate glass, all semiball (SB) joints are size 12/5, and all clamps (No. 12) are the screw type.

Schütze's Reagent tube. (See Fig. 8.) A 200-mm Schwartz absorption tube. Six tubes are required.

Tubing. Copper, 0.125 in. and 0.25 in., with appropriate connections, valves, and flow meters.

Tubing. Flexible, 0.125-in. i.d., lined with inert material to prevent the gas from picking up moisture. Bev-A-Line B-4 or equivalent.

Variac. 10-A variable transformer.

Reagents

Ascarite. Analytic Reagent (AR).

Carbon Reference Material. NBS-SRM-276, tungsten carbide containing 6.09% carbon.

Helium Gas. High purity.

Iodic Acid or Iodine pentoxide. AR.

Magnesium Perchlorate. AR.

Oxygen Gas. High purity.

Schütze's Oxidizing Reagent. See description of preparation in the appendix.

Silica gel. AR.

III. PROCEDURE

A. Determination of Blanks

(1) Connect the CO_2 absorption tubes (Fig. 1) to the system (Figs. 9, 10, and 11) and flush with O_2 at 80 to 100 cm^3/min for 30 min.

(2) Remove the CO_2 absorption tubes from the system one at a time, closing the inlet and outlet valves, wipe with a damp chamois skin, weigh, and record the weight (WB1). (The balance should be zeroed before weighing each set of tubes.)

(3) Connect the CO_2 absorption tubes to the system and flush with O_2 at 80 to 100 cm^3/min for 2.5 h.

(4) Remove the CO_2 absorption tubes from the system one at a time, closing the inlet and outlet valves, wipe with a damp chamois skin, weigh, and record the weight (WB2). (The balance should be zeroed before weighing each set of tubes.)

(5) Calculate the blank using the following equation.

$$\text{Blank} = \text{WB2} - \text{WB1}.$$

(6) Accept blanks in the range of ± 0.0003 g and do not apply any corrections. If a larger blank is obtained, repeat the blank determination.

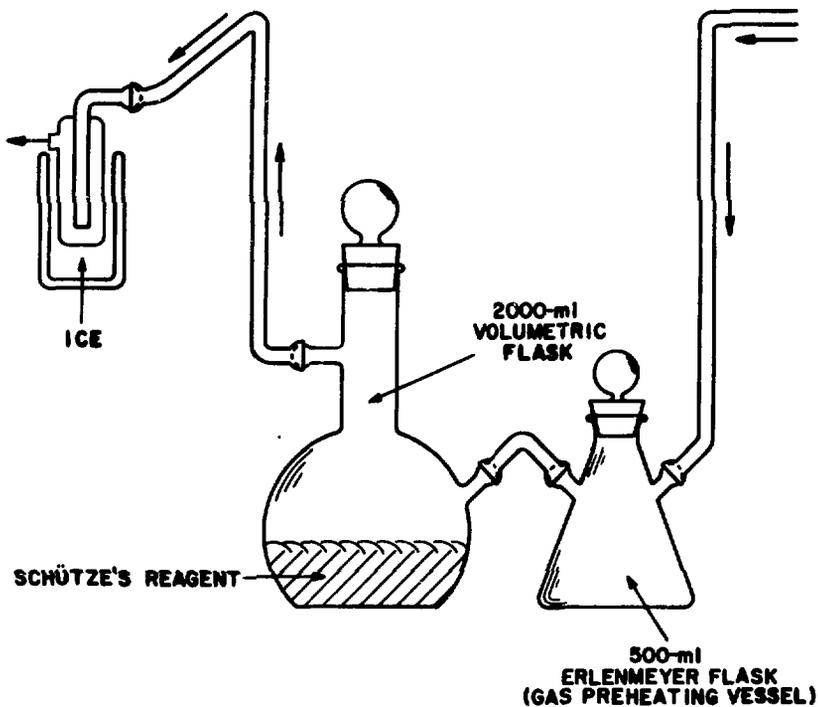


Fig. 6.
preparation system.

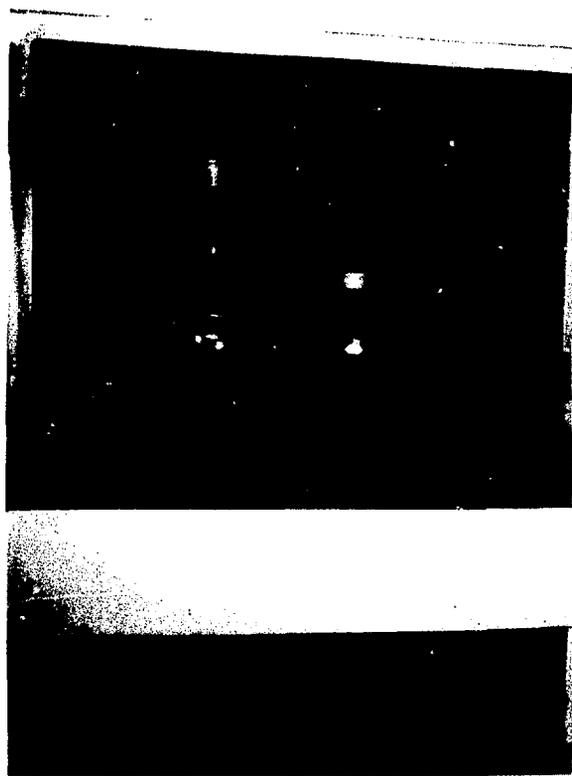


Fig. 7.
Schütze's reagent preparation system.

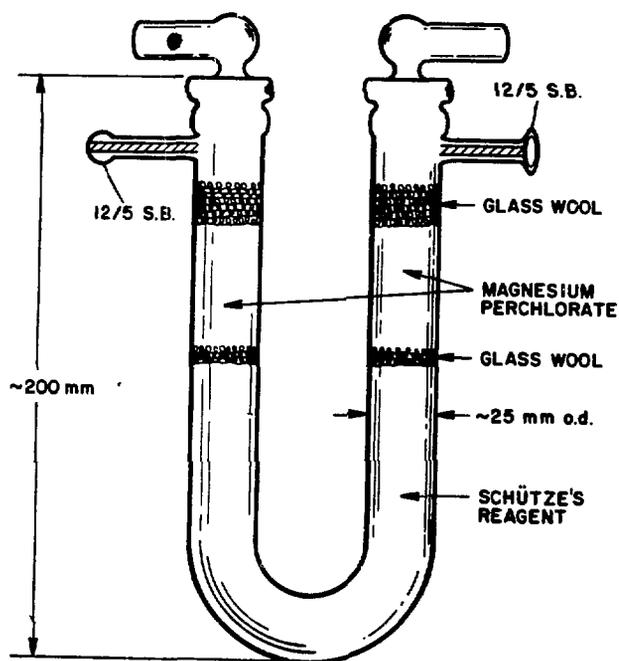


Fig. 8.
Schütze's reagent tube.

NOTE: FROM POINT (A) THE LINE IS SPLIT INTO 6 BRANCHES, WITH EACH BRANCH HAVING DUPLICATE EQUIPMENT TO THAT SHOWN UNTIL THE LINES REACH POINT (B), WHERE THEY ARE AGAIN COMBINED INTO ONE LINE.

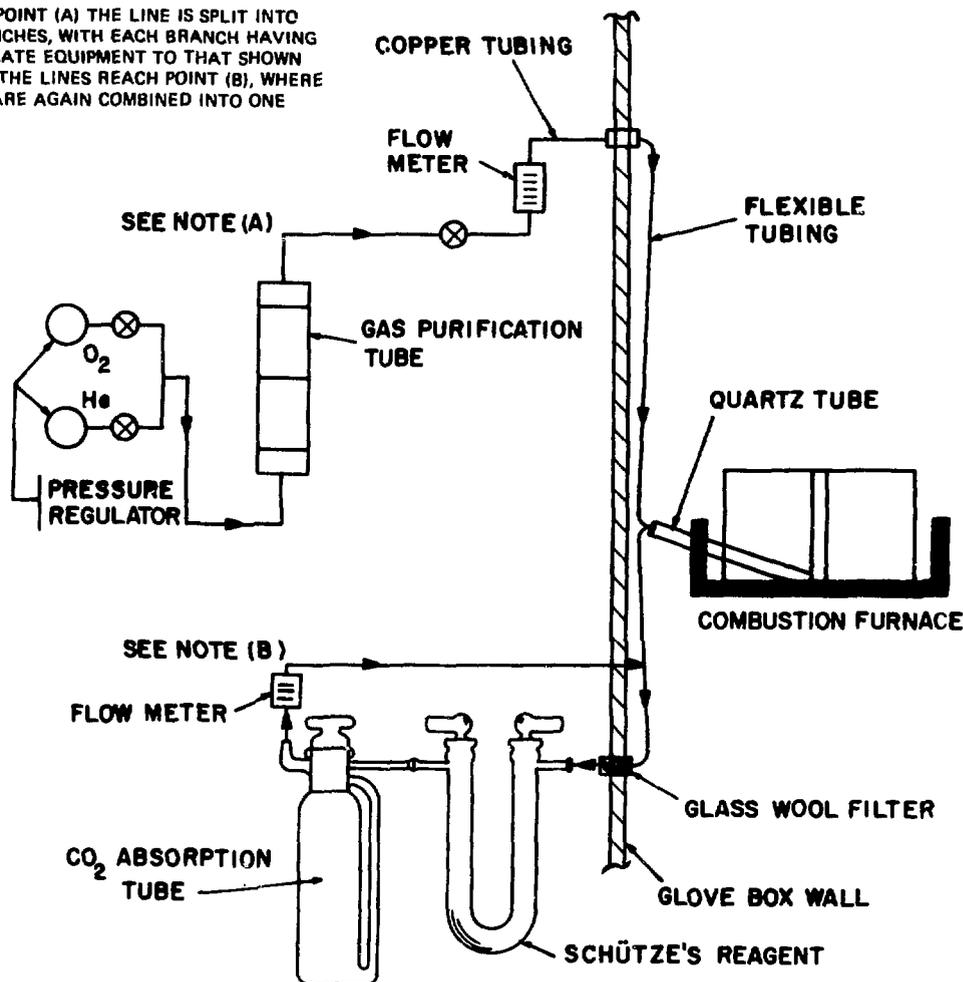


Fig. 9.
Carbon determination system.

(7) Alternatively, determine the blank by obtaining WB1 as described in steps 1 and 2, flushing the system overnight with O_2 at 20 to 40 cm^3/min , and weighing the absorption tubes at the beginning of the next day after the O_2 flow has been increased to 80 to 100 cm^3/min for 30 min to obtain WB2. Calculate the blank using the following equation.

$$\text{Blank} = \frac{WB2 - WB1}{6}$$

Accept blanks in the range of ± 0.0003 g and do not apply any corrections.

B. Analysis of Samples or Standards

(1) Obtain the weight of each absorption tube by running either an overnight blank or a 2.5-h blank, or use the weight obtained from a previous standard or sample run (WS1).

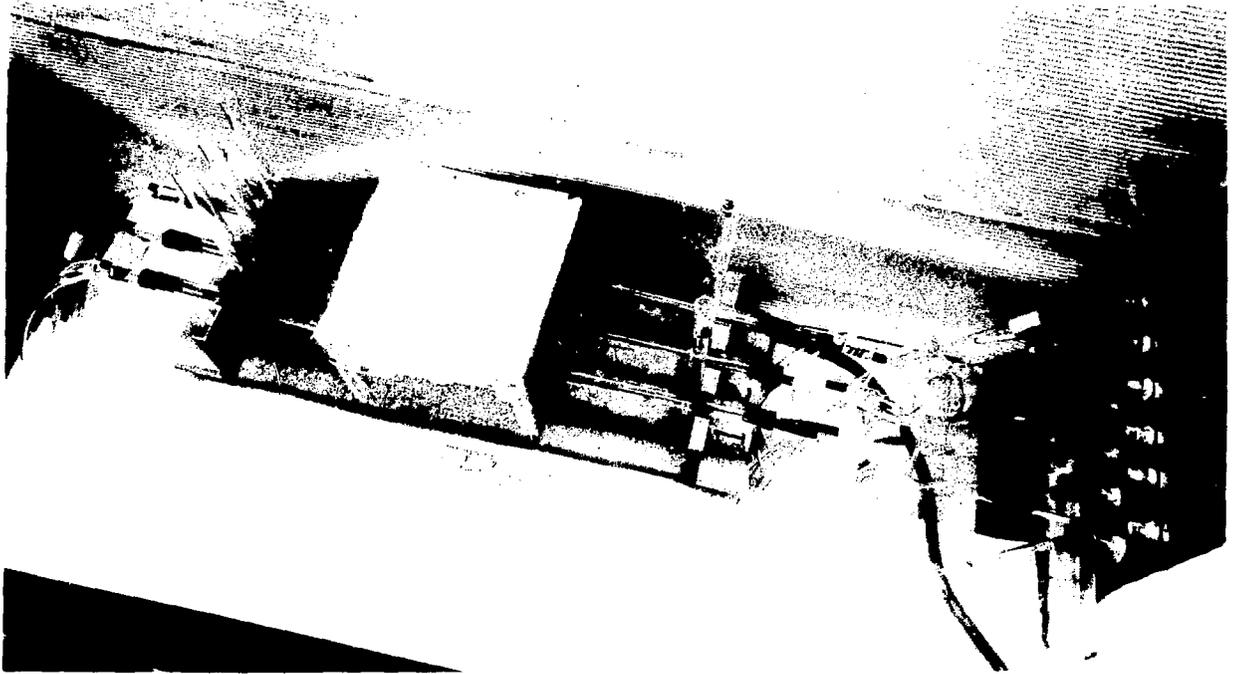


Fig. 10.
Combustion furnace.

(2) Quantitatively transfer the accurately weighed reference material or sample into a fused silica combustion tube, Fig. 3. (A tin capsule is used to contain the reference powder.)

(3) Disconnect the CO₂ absorption tubes that will be used to analyze the reference materials and samples.

(4) Flush the system with He at 80 to 100 cm³/min for 15 min while loading the reference material.

(5) Connect the fused silica combustion tubes to the system and continue the He flush at 80 to 100 cm³/min for 30 min.

(6) Turn off the He flow and start the O₂ flow at 80 to 100 cm³/min.

(7) Connect the CO₂ absorption tubes to the system.

(8) Turn on the furnace with the Variac set to allow the temperature to reach approximately 450°C. After 1 h, increase the Variac setting to allow the temperature to reach approximately 900°C and maintain this setting for 1 h.

(9) After the furnace has been on for 2 h, turn it off and continue flushing the system with O₂ at the same flow rate for 30 min.

(10) Remove the CO₂ absorption tubes, one at a time, closing the inlet and outlet valves, wipe with a damp chamois skin, weigh, and record the weight (WS2).

(11) The percent carbon in the sample or standard is calculated using the following equation.

$$\% \text{ Carbon} = \frac{\text{WS2} - \text{WS1}}{\text{SWT}} \quad (27.2919) ,$$

where

WS1 = CO₂ absorption tube original weight in grams,

WS2 = CO₂ absorption tube final weight in grams, and

SWT = sample or reference material weight in grams.

(12) Cool the furnace for 2 h before another analysis is made.

(13) Transfer the plutonium material to a residue bottle. Wash the combustion tubes with distilled water and dry in an oven.

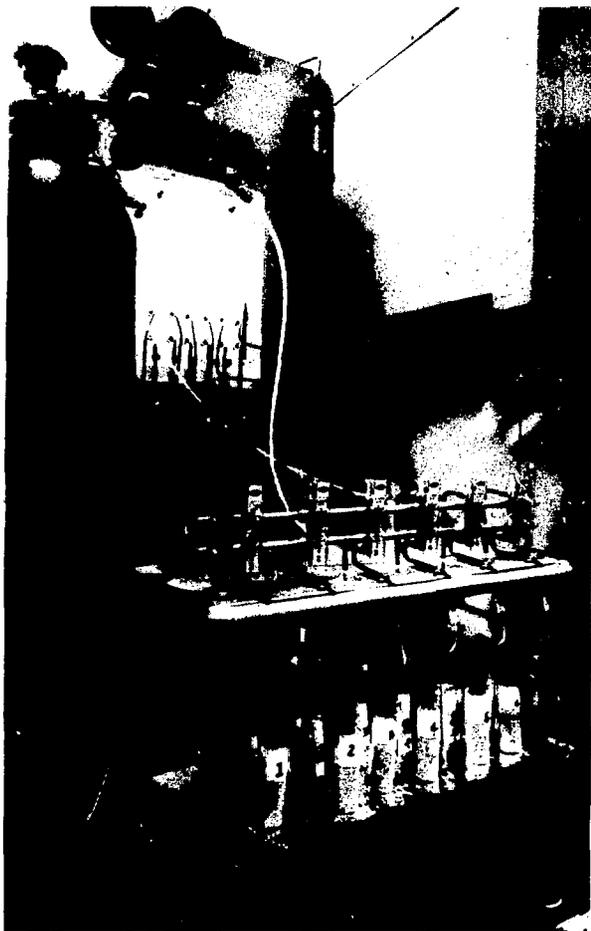


Fig. 11.
Gas purification/absorption system.

(14) When not in use, pass O_2 through the system continuously at 10 to 20 cm^3/min . The system will be ready for use at any time after a short purge with O_2 at 80 to 100 cm^3/min .

IV. RESULTS

We tested this method by determining the carbon in a National Bureau of Standards, Standard Reference Material #276 (NBS-SRM-276) and in a (U,Pu)C sample. For 42 determinations of carbon in NBS-SRM-276 (NBS certified carbon content of 6.09%), an average content of 6.09% was obtained with a standard deviation of 0.01₇% (the subscript indicates an approximate value) and a relative standard deviation of 0.28%. See Table I. For 17 analyses

TABLE I
CARBON ANALYSES OF NBS-SRM-276

Run	Percent Carbon Measured in Duplicate Determinations	
1	6.08	6.11
2	6.10	6.10
3	6.08	6.09
4	6.09	6.08
5	6.08	6.09
6	6.09	6.09
7	6.09	6.07
8	6.10	6.09
9	6.06	6.08
10	6.07	6.10
11	6.08	6.09
12	6.09	6.10
13	6.08	6.07
14	6.07	6.10
15	6.08	6.09
16	6.09	6.12
17	6.11	6.07
18	6.11	6.06
19	6.13	6.07
20	6.09	6.09
21	6.09	6.07

Average 6.09

Standard Deviation = $\pm 0.01_7\%$

Relative Standard Deviation = 0.28%

of the (U,Pu)C sample, an average carbon content of 4.97% was found with a standard deviation of 0.01₂% and a relative standard deviation of 0.24%. See Table II.

We used various types of flexible tubing for connecting the combustion tube to the gas inlet and outlet lines of the drybox. Rubber tubing was satisfactory but tended to crack and develop leaks in less than 2 months. Tygon tubing was very long lasting, but it continuously gave up moisture to the gas passing through it. Tubing that has a Tygon exterior and a thin film or lining of an inert material like Teflon proved to be the most satisfactory because it is long lasting and does not contribute any significant materials to the purge gas.

TABLE II
CARBON ANALYSES OF A (U,Pu)C SAMPLE

Run	Percent Carbon Measured
1	4.98
2	4.99
3	4.96
4	4.95
5	4.95
6	4.98
7	4.97
8	4.97
9	4.96
10	4.96
11	4.97
12	4.97
13	4.95
14	4.97
15	4.97
16	4.98
17	4.98

Average 4.97

Standard Deviation = 0.01₂%

Relative Standard Deviation = 0.24%

Various types of absorption tubes for collecting the CO₂ were tested. The conventional Schwartz "U" absorption tubes, about 100 mm long, were used

first, but their small capacity necessitated frequent replacement. The absorption tubes shown in Fig. 1 are lightweight, have a large capacity, and can be weighed on a single-pan balance. We found that one loading of the reagents lasted for 15 to 20 analyses of 0.5- to 1-g samples containing 6% carbon.

Most combustion methods use hot CuO or other heated oxidants to oxidize CO to CO₂, but one key to this new method is the use of Schütze's oxidizing reagent at room temperature. We modified a method for preparing 50-g quantities of Schütze's reagent described by Smiley.¹ See the appendix. Using simplified heating and flushing systems, we prepared a 500-g batch in minimal operator time (less than 2 h). This was necessary because of the large quantities of Schütze's reagent used to load the system initially, but the reagent lasts for many months even during continuous operation. The brown band of iodine that forms on the light yellow reagent is a clear indication of how much of the reagent has been depleted.

ACKNOWLEDGMENT

We thank the Los Alamos Scientific Laboratory Group CMB-11 for supplying the (U, Pu)C samples used in our precision studies.

REFERENCES

1. G. W. Smiley, "Note on Reagent for Oxidation of Carbon Monoxide," Nuclear Science Abstracts 3, 391-392 (1949).

APPENDIX

PREPARATION OF SCHÜLTE'S OXIDIZING REAGENT

(1) Dissolve 50 g of iodine pentoxide or 53 g of iodic acid in 250 ml of water.

(2) Add the solution to 500 g of coarse (6- to 16-mesh) silica gel and mix well. Dry at approximately 150°C for 18 to 19 h.

(3) Cool to room temperature, add 100 ml of 18M H₂SO₄, mix well, vent the container frequently, and store overnight in a closed container.

(4) Pack the mixture into a glass, 2000-ml volumetric flask (Fig. 6), flush the tube with dry argon at 250-300 cm³/min while heating the mixture to approximately 220°C for 2 h.

(5) Turn off the heat but continue the argon flow until the reagent is cool.

(6) Store the reagent in a capped glass bottle under argon.