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No. 6/18

THE DETERMINATION OF CARBON IN URANIUM
TETRAFLUORIDE

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THE DETERMINATION OF CARBON IN URANIUM TETRAFLUORIDE

1. OUTLINE OF METHOD

After the uranium tetrafluoride is dried at 110°C , it is heated in a stream of oxygen in a combustion tube. The fluoride evolved is absorbed by magnesium oxide. The carbon dioxide formed is absorbed in a dilute sodium hydroxide solution and determined conductometrically with a modified General Electric conductance bridge (G.E.C. catalogue no. SP 1220).

2. APPLICATION

The method is applicable to the determination of more than 10 p.p.m. carbon in uranium tetrafluoride.

3. APPARATUS

- (1) A sketch of the apparatus used is appended. (See Figures 1 and 2.) The amount of granular manganese dioxide should not exceed a 3-inch length in a u-tube with an internal diameter of $\frac{3}{8}$ inch. Larger amounts retain carbon dioxide and lengthen the determination.
- (2) The silica combustion tube is closed at the entrance end by a special metal end-piece (G.E.C. catalogue no. SP 1200), which enables the combustion boat to be removed without interruption of the oxygen stream. The tube is cemented into this end-piece, and a rubber gasket is used to take up the difference in diameters. Clear 'Bostik' is a suitable adhesive for this purpose.
- (3) The magnesium oxide asbestos plug is positioned as shown in Figure 2.

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LABORATORY METHOD NO. 6/18

- (4) The platinum baffle is made from a piece of perforated platinum foil and protects the rubber bung at the exit end of the combustion tube from exposure to excessive heat.
- (5) Thermocouples are used to measure the furnace temperatures. The combustion furnace can be moved backwards and forwards.
- (6) Rubber connections in the combustion train must be kept as short as possible.
- (7) The rotameter used to measure the oxygen flowrate should read up to 100 ml/min. A Fisher and Foster type OF 1/16 - 10-4/36 flowrater is satisfactory.
- (8) Thermostat
The thermostat must be capable of controlling the temperature to within 0.05°C . A 0°C to 50°C thermometer, with $1/10^{\circ}\text{C}$ graduations, is used.
- (9) Conductivity cell
A perspex conductivity cell (G.E.C. catalogue no. SP 1210) is used. This cell has a helical-gas passage.
- (10) Combustion boats
Clay combustion boats are satisfactory for igniting samples. They must be ignited at 1000°C in a muffle furnace for 1 hour before being used to remove carbonaceous material. (Note 1.) These boats can be used several times. Silica boats are used for standardizing the apparatus. These are also ignited before use.
- (11) Resistance box
A 4-decade, 1111-ohm, resistance box is used.

4. REAGENTS

- (1) Sodium hydroxide: 0.8% (w/v) solution
Dissolve 4.0g A.R.-grade pellets in water and dilute to 500ml with water. Store in a well-stoppered plastic bottle.
- (2) Lissapol N: 2% (v/v) solution. (Note 2.)
- (3) Sucrose solution: 1ml = 1mg C
Dissolve 1.187g sucrose in water and dilute to 500ml with water.

- (4) Ascarite: 20-30 mesh
- (5) Anhydrone: 14-22 mesh
- (6) Manganese dioxide
Battery grade, granular manganese dioxide.
- (7) Magnesium oxide - Asbestos
20g of magnesium oxide is mixed with 4g of acid washed Gooch asbestos fibre and ignited at 950°C for half an hour.

5. SIZE OF SAMPLE

The amount of sample used should contain between 50 and 3000Y.C.
For uranium tetrafluoride a 1g sample is usually correct.

6. PROCEDURE

6.1. Calibration of Apparatus

- (1) Adjust the thermostatic bath temperature to 30°C, switch on the furnaces and pass oxygen at a rate of 80 ml/min (setting 9.5 on rotameter). (Note 3.) Adjust the temperature of the larger furnace to 850°C and that of the small furnace to 500°C.
- (2) Rinse the conductivity cell with water and allow it to drain. Close the drain plug and introduce 5ml 0.8% (w/v) sodium hydroxide solution and 2 drops of 2% Lissapol. Weigh the cell on a balance and introduce 43.0g (± 0.1 g) of water. Stopper the cell, put it into a bath that is thermostatically controlled, and connect to the combustion train.
- (3) Place aliquot portions of standard sucrose solution containing 1.000mg carbon in each of six silica combustion boats and evaporate to dryness in an oven set at approximately 100°C.
- (4) Remove from the oven and place one boat in the cool portion of the combustion tube. The furnace heating the combustion tube should, at this stage, be placed as near the exit end of the tube as possible.
- (5) Allow one hour for the cell to attain the temperature of the bath, and then measure the conductance at 20-minute intervals as follows:

LABORATORY METHOD NO. 6/18

- (i) Connect the leads from the cell to the terminals marked C1, and the resistance box to the terminals marked 'Res. Box' on the conductance bridge. Switch on the bridge.
 - (ii) Select the 'low' position on the range switch. Set the dials of the resistance box to 1000.0 ohms, and the rotary switch on the left to the position marked 'Int. Std.'
 - (iii) Close the tap on the exit side of the combustion tube and switch off the thermostat stirrer. Adjust the 'Standardize' rheostat to give minimum reading on the microammeter. Switch to the high-sensitivity position and adjust the rheostat more closely. (Zero current in the microammeter is indicated by a minimum reading.) The resistance-box dials now read directly in micromhos the conductance up to 11 110 micromhos.
 - (iv) Switch the rotary switch to position C1 and adjust the first three dials of the resistance box, and the capacity switches to give a minimum microammeter reading. Switch to the high-sensitivity position and adjust the resistance and capacity alternately until the smallest reading can be seen on the microammeter. The resistance-box dials then indicate directly the conductance of the cell. Open the tap at the exit side of the combustion tube and switch on the thermostat.
- (6) Continue measurements until the rate of increase in conductance readings becomes constant. Record all readings and the time at which they were taken.
- (7) With a piece of stainless-steel rod move the combustion boat to the edge of the furnace. Replace the plug in the tube closure and move the furnace until the boat is in the hottest position. Record the time at which the heating of the boat was commenced.
- (8) Continue measuring the conductance of the absorbing solution at 20-minute intervals until the readings stop decreasing. (This usually takes approximately 90 minutes from the time

that heating began.) Correct the final reading for the blank and plot the conductance decrease (in micromhos) per mg carbon versus the mean conductance during the determination. Assume that the conductance increased at a steady rate of 0.2 micromhos per minute in the absence of a sample. If the second (final) steady reading of conductance has taken 100 minutes after the heating of the sample began, the true reading is (100×0.2) , i.e. 20 micromhos less than the apparent reading.

- (9) Remove the boat from the furnace and allow it to cool approximately 12 inches from the combustion tube closure. Move the furnace back to its position nearest the exit end of the tube. After cooling for approximately 10 minutes remove the boat from the tube. Repeat the procedure described from paragraphs (5) to (9) with each of the other five standard carbon samples.
- (10) Draw a graph of conductance decrease per milligram of carbon against the mean conductance reading during determination. This graph will be curved.

6.2. Determination of Carbon in Uranium Tetrafluoride

- (1) If the conductance of the absorbing solution is less than 7000 micromhos, replace it with fresh solution, prepared as described in paragraph (2). Measure the conductance of the solution every 20 minutes for blank determination as described in paragraph (5). Normally a single blank determination suffices for a day.
- (2) Dry a convenient quantity of uranium tetrafluoride in an oven at approximately 100°C , cool, and store in a dust-free atmosphere.
- (3) Heat an ignited clay combustion boat in the tube furnace (at 850°C) for approximately 15 minutes, while the oxygen is passed. Move the boat to the cool portion of the combustion tube and allow to cool for approximately 15 minutes. Remove the boat from the tube by gripping it with tongs (to avoid contamination from handling), and quickly and evenly

spread a 1g sample of the uranium tetrafluoride in it. Replace the boat in the cool part of the combustion tube and close the tube. Subsequent samples may be placed in the same boat without re-heating. The U_3O_8 from the previous determination must be tipped out of the boat before the new sample is placed in it.

- (4) Move the boat to the edge of the furnace and replace the plug in the tube closure. Measure the conductance until the increase in conductance is constant as in paragraph (5). Move the furnace so that the boat is in the hottest position. Continue to measure the conductance at 20-minute intervals until it does not decrease. Correct the final reading for the blank as described in section 6.1, paragraph (8).
- (5) Use the calibration graph to convert the conductance drop to the amount of carbon in the sample, and calculate the carbon content of the uranium tetrafluoride.
- (6) When switching off the apparatus, close the tap at the exit end of the combustion tube to prevent the absorbing solution from sucking back.

7. NOTES

- (1) The clay boats adsorb carbon dioxide if they are left in air for any length of time. (A clay boat that had stood in air for 24 hours after igniting in a muffle furnace was found to contain 30YC; a boat that had stood 1 week gave 80YC.) It is for this reason that they are heated in the apparatus before the sample is transferred to them.
- (2) Available from Imperial Chemical Industries, Limited.
- (3) This flowrate is obtained by setting the regulator on the cylinder to approximately 1 litre/min, and reducing this flowrate to the desired level with the needle valve. If the regulator on the cylinder is set at too high a pressure there is a danger of the joints blowing apart when the tap is closed for conductance measurements.

LABORATORY METHOD NO. 6/18

- (4) The asbestos/magnesium oxide plug must always be covered by the tube furnace when the combustion train is being used. The asbestos/magnesium oxide plug must be renewed after 25 determinations.

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- A. Precision needle valve
- B. Rotameter
- C. Silica tube, 15 in long, approx. 1 in dia. with ca. 5 in palladized asbestos.
- D. 7 in Tube furnace
- E. Arnold bulbs, used as traps
- F. Arnold bulbs with H_2SO_4
- G. 1/2 in dia. U-tube with Ascarite
- H. 1/2 in dia. U-tube with Anhydrous
- I. Tube closure
- J. 14 in Tube furnace
- K. Clear silica tube, 36 in long, 1 1/16 in. o.d., 15/16 in. i.d.
- L. Platinum baffle
- M. Glass tap
- N. 3/8 in dia. U-tube, with 2-3 in manganese dioxide
- O. Conductance cell

FIGURE 1

PURIFICATION, COMBUSTION, AND ABSORPTION TRAIN

1. Clear silica tube (K in FIGURE 1)
2. Magnesium oxide and asbestos plug (20.0g magnesium oxide mixed with 4.0g asbestos)
3. Asbestos plug
4. Perforated refractory disc
5. Refractory rod
6. Rubber stopper at outlet
7. Platinum baffle

FIGURE 2
COMBUSTION TUBE (K IN FIGURE 1)