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**DETERMINATION OF GRAPHITIC CARBON
IN SULPHIDE-CONTAINING ROCKS AND ORES**

by

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SUMMARY OF RESULTS

A suitable method for the determination of graphitic carbon in sulphide-bearing ores and rocks is described.

A special acid decomposition effectively removes all sulphur, previous to the burning of the carbon in a conventional combustion train. Fouling of the apparatus with sulphur oxides is thus prevented.

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INTRODUCTION

The Mines Branch is constantly concerned with improving the efficiency, and thereby the economics, of methods and processes used for the recovery of gold from its ores. It has long been known that the presence of graphitic and other carbonaceous material in an ore interferes with the extraction of the gold by the cyanidation process.

In Canada, there are substantial quantities of ore containing varying amounts of carbon and carbonaceous substances and these have not been worked to any great extent, because of the lack of a suitable milling process. The Mines Branch is initiating a research program to develop an improved method for treating these ores, many of which contain significant amounts of sulphides and, for the intelligent guidance of this program, analyses giving the carbon content of a wide range of ores and concentrates are required.

Consequently, the Analytical Chemistry Sub-division of the Mineral Sciences Division, was requested to develop a reliable method for the determination of graphitic carbon in sulphide-containing gold ores and concentrates.

REQUIREMENTS OF THE METHOD

Since the gold ores under consideration may carry large quantities of sulphide minerals, it is essential that the method should provide for the elimination of the sulphur, previous to the combustion of the carbon. Otherwise, rapid fouling of the absorption bottles with sulphur gases could be expected.

Consideration had to be given too, to the removal of lead sulphate, which may be formed during the chemical treatment of the sample, because of the presence of galena in an ore. The chemical treatment used to eliminate the sulphides must have no effect on the graphite in the sample.

METHOD

The sample is treated with elemental bromine and acetic acid to oxidize the sulphur. Dilute nitric acid is added and the solution boiled. The addition of ammonium chloride and further boiling dissolves lead sulphate and the sulphur compounds are removed by filtration and washing.

The dried residue is burned in a stream of pure oxygen, in a combustion furnace, at a temperature of 1000°C, and the carbon dioxide formed is caught in an absorbent, such as ascarite (asbestos impregnated with sodium hydroxide). From the gain in weight of the absorbent, the amount of carbon present in the sample is calculated.

Equipment Required

1. A cylinder of commercial oxygen, 99% pure, or better, and free from organic matter.
2. A simple combustion furnace; similar to the multiple unit, hinged type, furnace made by The Heavy Duty Electrical Co., Milwaukee, Wisc.
3. Rheostat for controlling temperature of the furnace.
4. Thermocouple with pyrometer.
5. Porcelain (mullite) combustion tube, 27 in. long x 1 in. ID; one end reduced to take rubber tubing.
6. Vitrified ceramic boats, or nickel boats.
7. Fleming absorption bottles (2 required) filled with ascarite and anhydrone for CO₂ absorption.
8. Fleming purifying jars (2 required) charged with H₂SO₄, for removing water from the gas stream.
9. One "Sulsorber" (tube filled with specially prepared MnO₂) to remove sulphur oxides from the gas stream, in which traces may occur.
10. An absorption bottle filled with anhydrone to remove moisture from the gas stream.

Cost of the Equipment

It is estimated that the total cost of the equipment listed above would not exceed five hundred dollars.

Assembling and Operation of the Combustion Train

The units of the train are joined together with heavy-walled rubber tubing, using short lengths where possible. The entrance orifice of the combustion tube is stoppered with a rubber stopper, carrying a short length of glass tubing, to which is attached the rubber tubing conveying the oxygen.

The oxygen from a high pressure cylinder, equipped with a gas pressure regulating valve, is made to flow at the rate of about 50 ml per minute and is passed through the combustion train, the various units of which are assembled in the following order:-

1. A Fleming purifying jar containing concentrated H_2SO_4 to remove moisture.
2. A Fleming absorption bottle filled with ascarite in the lower compartment and anhydron in the upper compartment. This serves to remove any CO_2 that may be present as an impurity in the oxygen.
3. The combustion tube in the furnace, which is heated to $1000^\circ C$ and in the centre of which is located the boat containing the sample to be burned.

4. A tube filled with specially prepared MnO_2 ("Sulisorber") to remove any sulphur oxides.
5. A Fleming purifying jar containing concentrated H_2SO_4 , to remove moisture.
6. An absorption bottle filled with anhydron (magnesium perchlorate), as a further check against moisture and as a suitable desiccant to be placed immediately ahead of the absorption bottle (7).
7. A Fleming bottle similar to (2), which absorbs the CO_2 produced by the combustion of the sample.

A drawing of the assembled apparatus is given on page 6, Fig. 1.

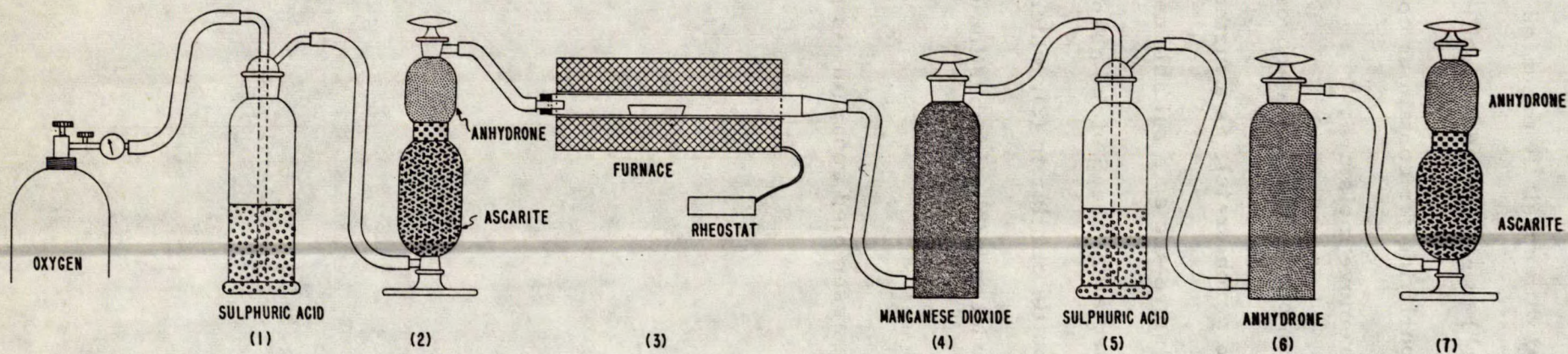


FIGURE 1-COMBUSTION TRAIN FOR THE DETERMINATION OF GRAPHITE IN ORES.

PROCEDURE

Weigh 0.5-5.0 g of the finely pulverized sample, depending on whether the graphite content is high, or low, and transfer it to a 400 ml beaker.

Add 10 ml of a mixture consisting of 3 parts of acetic acid and 2 parts of liquid bromine. Allow to stand at room temperature for 15 min and then heat at a low temperature for about 5 min. Do not boil; just allow to simmer. Remove from the heat and add, cautiously, 30-50 ml of 1:2 HNO₃. Boil 10 min, or until the bromine has been expelled and a solution, free from elemental sulphur, is obtained. Add about 10 g of NH₄Cl and boil a few minutes more. This will dissolve any PbSO₄ that may have been produced from galena, if present in the ore, and it will also assure that all arsenic and antimony are in solution.

Dilute the solution to about 150 ml with water and stir. Then, while still warm, filter through a Gooch crucible which has been prepared with ignited asbestos and which has a removable bottom. Wash well with hot water. Carefully remove the bottom of the crucible, with the pad of asbestos and sample adhering to it, and then transfer the asbestos and sample to a combustion boat. Any sample residue adhering to the side of the crucible may be recovered with the aid of a little damp asbestos.

Dry the boat and contents in an oven at 110°C.

Prepare a blank by using approximately the same quantity of ignited asbestos as was used for filtering the sample. Make up a Gooch crucible with it and, after washing, transfer the asbestos to a combustion boat and dry at 110°C.

When the sample and blank have been thoroughly dried and are ready for burning, the assembled combustion train, with the furnace heated to 1000°C, should be tested for leaks and, if found satisfactory, the blank should be determined as follows:-

Pass oxygen, at the rate of about 50 ml per min, through the train for 15 min. Close the absorption bottle (# 7) and disconnect it from the train. Place it near the balance to cool for 10 min. Momentarily open a stop-cock, to equalize the pressure in the vessel, and then weigh it.

Replace it in the train and push the boat, containing the blank, into the centre of the combustion tube. Again pass in oxygen at about 50 ml per min for 15 min. Then disconnect # 7 absorption vessel again, allow it to cool 10 min, open stop-cock momentarily and re-weigh. The increase in weight is the blank and usually amounts to less than 2 mg. A second blank should be run and if the agreement between the two is satisfactory, then the sample is burned in exactly the same manner and the increase in weight of the absorption bottle, less the blank, is the weight of the CO₂ produced by the combustion of the carbon in the sample.

Calculate the per cent carbon in the sample.

EXPERIMENTAL RESULTS

Several samples of graphite, obtained from different sources, were treated both by the simple dilute hydrochloric acid digestion and by the acetic acid-bromine-nitric acid digestion and then their carbon content determined by combustion. Results were in good agreement, showing that the severely oxidizing acid mixture did not affect graphitic carbon.

In Table 1 below are given the results obtained in a series of these tests. The graphite used was a powder supplied by the Foundry Section of the Physical Metallurgy Division.

Approximately 50 mg samples were used (which would represent about 5% graphite in a 1 g sample of ore).

TABLE 1

Recovery of Carbon from Graphite after Treatment
with Acid and Oxidizing Mixtures

| Sample | Weight graphite taken (mg) | Treatment previous to burning | Weight C obtained (mg) | % C Sample |
|--------|----------------------------|---|------------------------|------------|
| 1 | 50.6 | Nil. Burned as received. | 50.2 | 99.3 |
| 2 | 50.8 | Boiled with 1:2 HCl. | 50.2 | 98.8 |
| 3 | 51.0 | $C_2H_4O_2$ -Br digestion + 1:2 HNO_3 and boiling. | 50.6 | 99.3 |
| 4 | 50.2 | Added to 1.0 g of sulphide ore. $C_2H_4O_2$ -Br digestion + 1:2 HNO_3 + NH_4Cl and boiling. | 49.9 | 99.5 |

The sulphide ore with which sample No. 4 was mixed, consisted mainly of pyrite and galena. Oxidation of the sulphur by the acid mixture resulted in precipitation of some lead sulphate; but this was dissolved by the addition of ammonium chloride followed by boiling. Filtration and washing then gave a residue which was free from sulphur compounds and which was suitable for the determination of the carbon by combustion.