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# The Combustion-Gas Chromatographic Determination of Minute Quantities of Sulfur in Metals

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The determination of minute quantities of sulfur in metals is an important problem in refinery processing. This paper will describe a combustion-gas chromatographic method which gives precise results. This method is applicable to various metals, including iron and steels. Standard samples containing 0.011% of sulfur show a standard deviation of 0.0001%. Titanium and copper containing from 0.004 to 0.008% of sulfur show a mean deviation of 0.0003%. The limit of detection is 10 $\mu$g. (0.001%) of sulfur in a 1.0 g. sample. It takes about 10 min. to determine the sulfur content by this method.

Because of the adverse effect of sulfur on the physical properties of pure metals, steel and cast iron, a method for controlling the sulfur content during refining is desirable. The determination of sulfur in metals is generally performed by a chemical method which measures the concentration of $SO_4^{2-}$ or $SO_3^{2-}$ ions formed by bubbling the combustion products (carbon dioxide, sulfar dioxide, water, etc.) through an aqueous solution of hydrogen peroxide. Several other methods[1-7] have been proposed for the determination of minute quantities, i. e., several micrograms, of sulfur. Colorimetric,[1-3] conductometric[4,5] and chromatographic - gravimetric[7] methods are available for the determination of extremely small amounts of sulfur in metals. For rapid analysis, a neutron-activation analysis[6] is used. Recently, a combustion-gas chromatographic method[8] has been proposed to determine carbon and sulfur simultaneously in ferrous metals.

This paper will describe a combustion-gas chromatographic method which is capable of determining sulfur accurately in various metals. The method is a simplification in the following three ways: a gas chromatograph was used for the analysis of the combustion gases; a simple chromatographic concentration technique[9] was used for isolating sulfur dioxide and pure copper powder or foil was used as the bedding material to burn titanium, silicon, etc., in a commercially-available H-F combustion furnace. Minute amounts of sulfur can be accurately determined by this method within ten minutes.

## Experimental

**Apparatus.**—A simple schematic diagram is shown in Fig. 1. The apparatus is simlar in principle to that described[8] elsewhere by the present authors and used for the determination of small amounts of carbon in pure iron and steel; it consists of a commercially-available combustion funace to ignite the sample and a gas chromatograph connected to the concentration column to isolate sulfur dioxide in the combustion products. Some changes have, however, been made in the apparatus and in the procedure used previously for the determination of carbon. A silica gel column

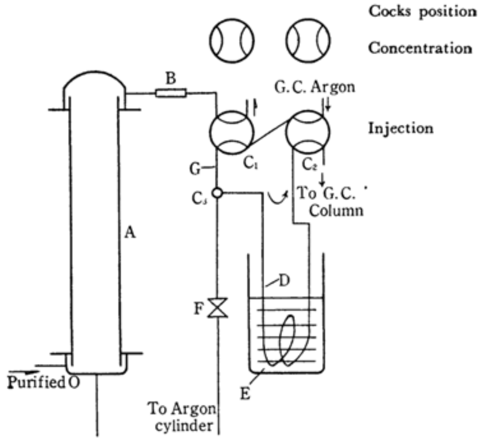

Fig. 1. Schematic diagram of apparatus and the basic flow system.
A. Combustion system, B. Drierite, $C_1$. Hard glass four-way cock, $C_2$. Four-way gas sampling cock. $C_3$. Three-way cock, D. Concentration column packed with silica gel, E. Warming bath of potassium carbonate, F. Needle valve, G. Glass capillary tube

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was used instead of an activated charcoal column, and accelerator was added.

Oxygen gas of a commercially-pure grade was introduced from a gas cylinder through the reducing valve. The gas was further purified by passing it through tubes of granular potassium hydroxide and of phosphorus pentoxide, thus removing the sulfur dioxide and water.

The combustion was carried out by the use a of Kokusai Denki H-F combustion furnace; the oxygen stream was regulated by means of a reducing valve attached to the gas cylinder.

The combustion products were led into concentration column, D, by stainless steel tubing (2 mm. in diameter.) through a Drierite, B, and a silica wool plug.

$C_1$ is a four-way cock which connects the concentration column, D, and the gas-sampling cock, $C_2$, of the gas chromatograph, as is shown in Fig. 1.

The Flikentite cuplets (crucibles) and the caps (made by the Nihon Kagaku Kogyo Co.) were prebaked for 3 hr. at a temperature of about 1500°C in a hydrogen stream; the cuplets were then baked for 4—5 more min. in the same manner as in the ordinary combustion procedure.

**Gas Chromatography.**—A Yanagimoto gas chromatograph, Model GCG 100, and a Minneapolis-Honeywell recorder, Model SY 153, with a full-scale sensitivity of 50 mV. were used. In order to measure a minute quantity of sulfur dioxide, the recorder was connected with an Ohkura DC. amplifier, Model AM 101, and employed at a full-scale sensitivity of 500 $\mu$V. The detector was a thermal conductivity cell with a pair of tungsten filaments; the current supply to the bridge circuit was adjusted to 150 mamp.

The argon gas, which was less than 0.01% impure, was used as the carrier gas at a flow rate of 50±2 ml./min.

The chromatographic column was a copper tube 50 cm. long and 6 mm. in diameter. It was packed with 30—64 mesh Celite 545 containing 30% tricresyl phosphate and was kept at the temperature of 40°C in a thermostat chamber.

The concentration column was a copper tube 10 cm. long and 6 mm. in diameter.; it was packed with 30—64 mesh silica gel. This column was used for concentrating only sulfur dioxide at room temperature. The concentrated gas was injected into the chromatograph at the temperature of 120°C.

**Procedure.**—The concentration column, D, was heated in a salt bath, with the argon gas allowed to flow through for several minutes, until the water absorbed in the silica gel had been removed. In order to remove the water from the combustion system, it was heated in oxygen gas.

The sample (approximately 1.0 g.) was weighed into a cuplet, together with the analytical-grade accelerators, i. e., 100 mg. of tin shot and 50 min. of chromium(III) oxide powder. The sample was placed in position, and then agron gas was passed through the apparatus for 2 min. The column, D, was connected with the combustion tube by turning cocks $C_1$, $C_2$ and $C_3$ to the positions shown in Fig. 1; the rate of oxygen flow was adjusted to 150 ml./min., and then the combustion was started.

The products of the combustion were collected in the column at room temperature for 3—5 min. while the sample was being burned. The three-way cock, $C_3$, was then turned 90° to cut off the oxygen flow. The sample cuplet was removed from the combustion tube to avoid overheating the silicone gaskets. By opening the needle valve, the oxygen in the column was expelled in 20—30 sec. by the argon stream at a flow rate of 50 ml./min. $C_3$ was then returned to the previous position, and the column was immersed in a potassium carbonate bath at 120—130°C. By turning $C_2$, the gases in the column were then injected into the gas chromatograph. A typical chromatogram is shown in Fig. 3.

The blank value for this method was obtained from the data derived from the ordinary results. The blank value was about 12 $\mu$g. of sulfur; this was very low in comparison with the amounts of sulfur in 1—2 g. samples of steel. A fluctuation of the blank values was, however, found between various kinds of crucibles used. The measurement of a peak area of sulfur dioxide was carried

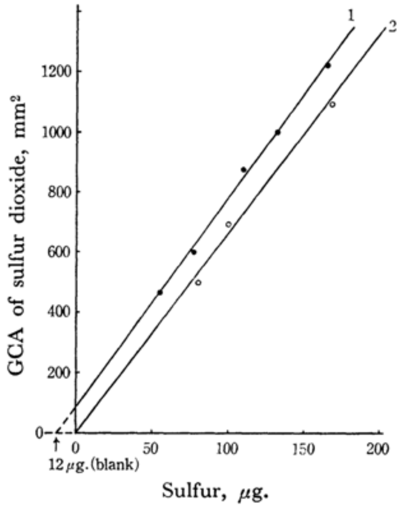

Fig. 2. Calibration curve for determining sulfur contents.

1. Values obtained using the samples of 0.5—1.5 g. 2. Values obtained by the use of a standard sulfur dioxde gas, under conditions such as 20°C, 758 mmHg.

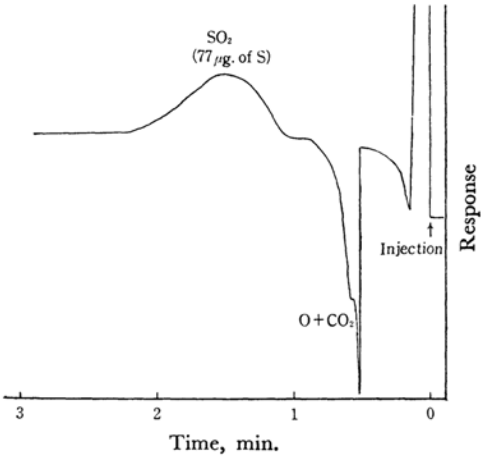

Fig. 3. A typical chromatogram.

out by the use of a planimeter or by the conventional appoximate method, while the sulfur content in the sample was obtained by the following equation:

$$\text{Sulfur, } \% = (a_t - a_b)/w \cdot K$$

where $a_t$: the area of the chromatogram of sulfur dioxide in sq. mm. for the sample; $a_b$: the area of the chromatogram of sulfur dioxide in sq. mm. for the blank test; $w$: the sample weight in mg. and $K$: the constant= 0.15 (μg. sulfur per sq. mm.), which was determined by using standard samples of known compositions or standard gas.

Table I. Accuracy and agreement with JISS value of the proposed method

| Sample designation | Sulfur, μg. Taken | Sulfur, μg. Found | Sulfur content wt. % | Standard deviation % |
|---|---|---|---|---|
| JISS No. 11 (tungsten steel, 0.011%S) | 110 | 118 | 0.0118 | |
| | | 118 | 0.0118 | |
| | | 114 | 0.0114 | |
| | | 118 | 0.0118 | |
| | | 122 | 0.0122 | |
| | | 112 | 0.0112 | |
| | | 116 | 0.0116 | |
| | | 116 | 0.0116 | |
| | mean | 116 | $0.011_6$ | $0.0001_3$ |
| | 165 | 161 | 0.0108 | |
| | | 163 | 0.0109 | |
| | | 170 | 0.0113 | |
| | | 164 | 0.0109 | |
| | mean | 164 | $0.010_9$ | $0.0001_2$ |
| JISS No. 5 (d) (basic open hearth steel, 0.023%S) | 230 | 230 | 0.0230 | |
| | | 230 | 0.0230 | |
| | | 235 | 0.0235 | |
| | | 230 | 0.0230 | |
| | | 222 | 0.0222 | |
| | | 233 | 0.0233 | |
| | | 230 | 0.0230 | |
| | | 228 | 0.0228 | |
| | | 228 | 0.0228 | |
| | mean | 230 | $0.023_0$ | $0.0003_6$ |
| | 115 | 115 | 0.0230 | |
| | | 118 | 0.0236 | |
| | | 115 | 0.0230 | |
| | | 116 | 0.0232 | |
| | | 118 | 0.0236 | |
| | | 121 | 0.0242 | |
| | | 121 | 0.0242 | |
| | mean | 118 | $0.023_5$ | $0.0005_1$ |

Table II. Sulfur contents in electrolytic irons

| Sample designation | No. of determinations | Sulfur % | Standard deviation % |
|---|---|---|---|
| SP-1 (plate, 0.006%S*) | 7 | $0.0059_4$ | 0.00034 |
| HP-1 (powder, 0.010%S*) | 9 | $0.0096_1$ | 0.00048 |
| HP-2 (powder, 0.010%S*) | 5 | $0.0087_6$ | 0.00055 |

* Sulfur content obtained by a combustion-conductometry.

The calibration was carried out with three samples measured manometrically using a standard gas of sulfur dioxide in the 1.0-ml. sampling cell used for quantitative gas analysis, where the system for sampling was evacuated to $10^{-3}$ mm. Hg by means of a rotary oil pump. The calibrated value was obtained from the relationship between the concentration and the chromatogram area. However, when the calibration was carried out by using the standard steel sample, this value was different from that obtained by using the gas.

## Results

The accuracy of this method and agreement of the results with those shown in JISS were tested by determining the sulfur content of JISS No. 11 and No. 5(d) and of the electrolytic iron samples; the results are shown in Tables I and II. The data were obtained from 1—2 g. samples to which suitable accelerators had been added.

The usefulness of this method was proved by determining the sulfur contents of cast iron, titanium, silicon, copper, chromium and manganese; the results are given in Tables III and IV. In these metals only copper was effectively burnt by the H-F combustion technique; commercial copper powder or foil could be used as the bedding material in place of iron powder. The data were obtained with 0.3—1.0 g. samples, with 1—1.5 g. of copper and with 0.1 g. of chromium(III) oxide used as the accelerators.

## *Discussion*

The use of a highly-sensitive gas chromatograph for the analyses of combustion gases enables us to determine sulfur contents as low as 10 μg. in pure metals; in this case, the blank value of this method can be kept below 3 μg. of sulfur by using the Leco. 528-31 cuplet. The determination of sulfur contents below 100 μg. is difficult in the conventional method. By using the Leco. cuplet, this method can also be applied to non-ferrous pure metals by the addition of special purified copper foil and some accelerators. It is of a great advantage to be able to use the Flikentite or the Leco. cuplet, since they require no complicated pretreatment, unlike as in the other combustion method. If the Flikentite cuplet prepared for carbon analysis was used for the determination of the sulfur content in cast iron, however, a lower value was obtained. For this reason, the study of the modification of refractory materials for the crucible is now being continued with the cooperation of other laboratories.

The sulfur contents in the silica gel column as found by the actual combustion are given in Table V. The data were obtained with an oxygen stream with a flow rate of 150 ml./min. at room temperature. From this table, it is clear that an oxygen flow of 6 min. is sufficient.

TABLE III. DETERMINATION OF SULFUR CONTENTS IN CRAY CAST IRON

| Sample designation | No. of determinations | Sulfur % | Deviation from mean, % | Accelerator |
|---|---|---|---|---|
| P-732 (0.019%S*) | 3 | 0.0176 | ±0.0007 | $Cr_2O_3$ 0.1 g.<br>shot Sn 0.5 g. |
| P-733 (0.019%S*) | 4 | 0.0163 | 0.0003 | |
| P-506 (0.045%S*) | 5 | 0.0440 | 0.0020 | |
| P-507 (0.064%S*) | 6 | 0.0613 | 0.0047 | |

* Sulfur content obtained by a combustion-conductometry.

TABLE IV. SULFUR CONTENTS OF METALS

| Designation | No. of determinations | Sulfur % | Deviation from mean, % | Accelerator |
|---|---|---|---|---|
| Titanium rod | 4 | $0.0085_4$ | $\pm 0.0003_2$ | (bedding metal<br>SP copper<br>1—1.5 g.<br>$Cr_2O_3$ 0.1 g. |
| Lump silicon | 3 | $0.0057_7$ | $0.001_2$ | |
| Electrolytic copper | 6 | $0.0041_5$ | $0.0001_9$ | |
| Electrolytic chromium | 4 | 0.0508 | $0.006_4$ | |
| Electrolytic manganese | 5 | 0.0135 | $0.001_2$ | |

TABLE V. COLLECTION OF SULFUR DIOXIDE BY SILICA GEL COLUMN*

| Collection time min. | Chromatogram area, sq.mm. | Sulfur, μg. | |
|---|---|---|---|
| | | Taken | Found |
| 1.9 | 192 | 59 | — |
| 2.5 | 334 | 59 | — |
| 3.1 | 438 | 59 | 54 |
| 6.1 | 465 | 59 | 59 |
| 10 | 459 | 59 | 58 |
| 20 | 468 | 59 | 59 |
| 3.5 | 764 | 100 | 101 |
| 6.0 | 762 | 100 | 101 |
| 10 | 742 | 100 | 99 |
| 15 | 736 | 100 | 98 |

* The seize is of 4 mm. in diameter and 10 cm. long.

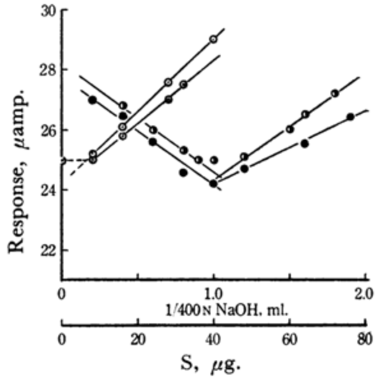

Fig. 4. A typical titration of $SO_4^{2-}$ by H-F conductometry.

-◑- -●- plots on 1.0 ml. of 1/400 N sulfuric acid

—⊙— plots on the solution washed sulfur trioxide absorbed in the concentration column with a little neutral water

Some investigators[2,9,10] have described how materials with sulfur contents of above 90% were converted into sulfur dioxide by the complete combustion of the metal. Similar results seem to be obtained by the present experiment. If sulfur trioxide is formed in the combustion products, the results obtained are erratic, because sulfur trioxide is absorbed in the concentration column. The experiment was carried out to measure the concentration of $SO_4^{2-}$ ions by means of highly-sensitive conductometry using a Shimadzu H-F titrator. The above-mentioned $SO_4^{2-}$ ions were present in the 20 ml. of water used to wash the column. The titration curves of an aqueous solution containing 1.0 ml. of 1/400 N standard sulfulic acid and those of this washed solution are shown in Fig. 4. The sulfur content as $SO_3$ was below 8 μg.; this quantity is below the limit of detection by conductometry.

Combustion times of 5—6 min. were found to be effective in the oxidation of metals. Copper, used as the bedding material in these experiments, burned smoothly at high temperatures (above 1600°C). In the reaction it was dissolved in crucible materials; copper is one of the metals with the lowest sulfur content. When it is then used together with the Leco. crucible, which shows a small blank value, the correction becomes small.

Because a small amount of lump silicon was available for performing the complete combustion, 200—300 mg. of the samples was used with 2 g. of the foil copper; satisfactory burnings were still obtained with titanium, however, when only 1 g. samples and 1—1.5 g. of copper powder were used.

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