Determination of the Total Sulfur Content Using a Sulfur Chemiluminescence Detector

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A sulfur chemiluminescence detector (SCD) was applied to measuring the total sulfur content. A non-stationary phase column was used in a GC-FID connected to the SCD in order to measure the total sulfur content without separating it. It was revealed that interference from hydrocarbons could be eliminated by optimizing the combustion condition of the FID burner. A calibration curve was obtained independent of the types of sulfur compounds. The experimental results are in good agreement with those obtained with conventional methods.

Keywords Total sulfur content, sulfur chemiluminescence detector, non-stationary phase column, gas chromatograph, fuel gas

The total sulfur content in distribution gas must be measured once a week in accordance with Gas Utility Laws. Recently, liquefied natural gas (LNG) has been used for gas distribution in Japan, Korea and other countries. Since LNG is purified from raw natural gas through a production process, it contains a significantly smaller sulfur content. It thus requires a substantially greater amount of gas and a longer period of time to determine the total sulfur content. Although a combustion method (JIS K 2301) is widely used to determine the total sulfur content of fuel gas in Japan, it has the following drawbacks: 1) the procedure is complicated, 2) it cannot be applied to concentrations below 1 ppm, and 3) it requires a large volume of sample gas (over 20 l).

We, therefore, attempted to establish a new, simple and rapid analytical method to determine the total sulfur content by employing a sulfur chemiluminescence detector (SCD), which is beginning to be used commercially as a sulfur-selective detector for gas chromatography. Although the flame photometric detector (FPD) is the most commonly used detector for sulfur analysis, it exhibits a nonlinear response to sulfur compounds and is likely to be adversely affected by coexisting compounds, such as hydrocarbons. The SCD a selective detector for sulfur, can overcome these problems. Its measurement principle is the detection of the characteristic chemiluminescence of SO with 0_3 appearing in the region of 260 - 480 nm. SO is produced by the combustion of sulfur compounds in a reductive hydrogen flame of an FID burner connected to an SCD. The features of the SCD can be summarized as follows: 1) it selectively detects sulfur compounds without any interference from other compounds, 2) it produces a nearly equimolar response to sulfur compounds and a linear response to sulfur weight, and 3) it is sensitive enough to detect even a few picograms of sulfur.

Experimental

Figure 1 is a schematic diagram of the entire experimental system. The SCD used in this experiment was a Sievers Research Inc. Model 350N, and a gas chromatograph equipped with an FID (GC-FID) was a Hewlett Packard HP5890.

A common gas chromatographic analysis uses a column with a stationary phase to separate the components in the sample. In this experiment, however, we used a non-stationary phase column because our intention was to analyze the total sulfur content in the sample gas without separating it. The column oven...
temperature was therefore kept constant at 200°C, so that all of the components in the sample gas would elude within a short period of time and would not separate along with a rise in the oven temperature.

In this experiment, the FID was used as a reductive hydrogen combustion burner to convert all of the sulfur compounds into SO.

**Results and Discussion**

**Confirmation of the basic performance**

To analyze the total sulfur content, a fundamental requirement is that the measurement sensitivity must depend solely on the sulfur weight, regardless of the types of sulfur compounds. To confirm the basic performance of the SCD, we measured each sulfur compound separated from the matrix, or hydrocarbon, using a separation column. The separation column used in the experiment was the non-polar OV-type GL Science Inc. Neutra Bond-1 (length, 25 m; inner diameter, 0.53 mm; liquid layer thickness, 2.0 µm). Helium was used as the carrier gas. The flow rate of the carrier gas was fixed at 5 ml/min, taking into consideration the HETP. The column oven temperature program consisted of a start at 35°C followed by a ramp of 10°C/min to 200°C.

Calibration curves were made for each of the various types of sulfur compounds, such as aliphatic sulfides, mercaptanes, cyclic sulfides, and inorganic sulfides. These are shown in Fig. 2. It is obvious that all of the sulfur compounds, irrespective of the type, can be expressed on the same calibration curve. The measurement error in using this single calibration curve is expected to be 10% or less.

**Effect of coexisting air**

An analysis revealed that the injection of air containing no sulfur compounds produced only a slight response. In addition, an injection of pure nitrogen produced no response, while one of oxygen produced a greater response than air. These results indicate that the blank response correlates positively to the concentration of oxygen in the sample. This response is so small that it can be ignored for a determination of the total sulfur content. For a microanalysis of sulfur compounds, however, the blank response should affect any determination.

To investigate the effect of coexisting air on the microanalysis of sulfur compounds, some test gases, which were prepared by adding various concentrations of COS to air, were injected at a constant volume. The results are shown in Fig. 3. As the figure clearly shows, there is no effect on the linearity of the SCD's response; however, the curve does not go through the original point because of the blank response. Since air does not affect the linearity of the calibration curve, we can correct the measurement value by subtracting the blank value. By correcting the blank value, an accurate determination of a sample which includes a small amount of sulfur compounds could be accomplished.

**Effect of coexisting hydrocarbons**

The performance of the SCD depends on the combustion conditions of the FID burner connected to the SCD, because the combustion conditions of the FID burner affect the formation of SO, resulting in a change in the sensitivity as well as the selectivity. Shearer et al. reported that SCD exhibits sulfur to hydrocarbon selectivities of 10^6 or greater on a weight-to-weight basis. It is necessary, however, to increase the selectivity by optimizing the combustion conditions in the FID burner to determine the total sulfur content in fuel gas.

To investigate the effect of coexisting hydrocarbons, the response of the SCD to two sample gases, methane and propane (each containing 20 ppm of COS), was
studied. When there is no interference by hydrocarbons to the response of the SCD, a linear response to sulfur weight should be exhibited, regardless of any coexisting gases. The results are shown in Fig. 4. When the injection volume exceeds a certain amount, the response tends to be saturated. The injection volume at which a "saturation trend" is observed is defined to be a critical volume. Since the critical volume is smaller for propane injection than for methane injection, it may correlate negatively with the number of carbon atoms in the hydrocarbons. The reason for this is believed to be that the response of the SCD becomes smaller than expected because intermediates produced by the combustion of hydrocarbons react with SO, which is the main chemiluminescent species. It is assumed that a hydrocarbon such as propane, containing a relatively larger number of carbon atoms, produces more intermediates at any given volume.

Moreover, as can be seen in Fig. 5, the response of the SCD to the sulfur weight is linear over a wide range when the base gas is air; however, the response exhibits a "saturation trend" when the base gas is either methane or propane. Therefore, although the SCD, itself, is not saturated, the response is saturated as a result of interference of the base gases.

Elimination of interference of coexisting hydrocarbons by combustion

To optimize the ratio of hydrogen to the air flow rate (H₂/air), methane test gas containing 20 ppm COS was used. As Fig. 6 shows, when the H₂/air ratio increases (in other words, the combustion atmosphere becomes reductive), the graph slope becomes sharper and the sensitivity improves. On the other hand, the critical volume decreases in a reductive atmosphere. The reasons for these phenomena are considered to be as follows: the amount of SO increases in a reductive atmosphere, thereby enhancing sensitivity, while hydrocarbons such as methane tend to undergo imperfect combustion, thus leading to the production of more undesirable materials, which react with SO.

Figure 7a shows that the critical volume decreases when H₂/air increases, leading to a greater SCD sensitivity. The detectable concentration in methane as H₂/air changes is shown in Fig. 7b. The detectable concentration is defined here to be the lowest concentration that can be measured without interference by the base gas, methane. Hence, if the base gas is propane, it would have a smaller value, since the magnitude of the
interference is believed to be proportional to the number of carbon atoms. Taking the interference of hydrocarbons into consideration, the $\text{H}_2/\text{air}$ is optimized at around a value of 0.55.

The response of the SCD is greatly dependent on the hydrogen flow rate; it exhibits a maximum value at a flow rate of 220 ml/min when $\text{H}_2/\text{air}$ is constant. These results indicate that the optimum combustion condition in the FID burner is a hydrogen flow rate of 220 ml/min and a total air flow rate of 400 ml/min.

**Measurable range**

After setting the flow rates of gases in the FID burner to their optimum condition, the measurable range was investigated. Since an injection of the test gas containing 9.33 mg/m$^3$ sulfur for 25 ml produced a peak whose $S/N$ was 22.2, the lower detection limit observed was 31 pg sulfur at $S/N=3$. The maximum injection volume used to measure the total sulfur content without any interference of methane is 500 µl. Therefore, the detectable concentration in methane is 0.062 mg/m$^3$.

Since the linearity of the calibration curve remains at around 10 ng sulfur, a concentration greater than 1000 mg/m$^3$ is to be measured. The dynamic range of this method is more than $10^5$, which is remarkable when compared with that of the combustion method, 2.5 to 20 mg/m$^3$.

**Comparison with conventional methods**

Table 1 compares the total sulfur measurement results obtained for TEST GAS 1 (COS methane base gas), TEST GAS 2 (mixed gas of TBM, DMS, and methane base gas), and TEST GAS 3 (coke oven gas) using the JIS K 2301 method and the GC-FPD method. The results of the GC-FPD method were obtained by a calculation using the data for each sulfur compound.

The measurement results of the three types of test gas agree with each other well. This means that the total sulfur content in gas, which contains very little (or no) oxygen, such as methane base gas or coke oven gas, can be accurately measured without interference from any coexisting hydrocarbons. By comparing the SCD method to the conventional method, it can be seen that the former is superior regarding the following points: 1) the sample gas volume can be as small as 0.1 ml; 2) the measurement range is as wide as $10^5$; 3) the lower detection limit is so low that a high sensitivity microanalysis can be performed; 4) after determining the calibration curve, the measurement can be completed within a few minutes; and 5) no special skills are required to conduct an analytical operation.

**References**


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