Response Characteristics of Flame Thermionic Detector to Sulfur Compounds

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The response characteristics of flame thermionic detectors (FTDs) to sulfur compounds were studied. The optimum flow rates of air and hydrogen were obtained by investigating changes in the detector response and selectivity for hydrocarbons with respect to changes in the air and hydrogen flow rates. From these investigations, the response for sulfur compounds shows a high sensitivity at an air flow rate of about 6 ml min^{-1} , as well as 100 ml min^{-1} or 16 ml min^{-1} . Investigations were carried out concerning the detection limit, response linearity and selectivity for representative sulfur compounds (under these set of operational conditions). Disulfides were detected at especially high sensitivity, under 16 ml min^{-1} air flow rate conditions. The detection limit of dimethyl disulfides was $1.78 \times 10^{-10} \text{ g s}^{-1}$ ($S/N=2$), and the selectivity for hydrocarbons was $1.7 \times 10^3 \text{ gC/gS}$. Exact details concerning the negative surface ionization process on alkali metal surface are not completely known. The presumed ionization process for organic sulfur compounds is discussed in this paper.

Keywords Flame thermionic detector, sulfur compounds, negative surface ionization, gas chromatography

Flame thermionic detectors (FTDs) characteristically display highly selective and sensitive response to nitrogen, phosphorus and halogen compounds.¹⁻⁵ However, reported applications have been limited to nitrogen and phosphorus compounds. We were interested in whether the FTD's high selectivity could be extended to sulfur compounds. FPD (flame photometric detector) has been widely adopted for highly sensitive detection of sulfur compounds up to the present.⁶⁻⁸ However, the response of FPD for sulfur compounds was not linear and gave low selectivity.

Our investigations showed that FTDs have a fairly high selectivity for sulfur compounds, though not as high as that for nitrogen or phosphorus compounds; under certain conditions, however, high sensitivity to particular types of sulfur compounds can be achieved.

Experimental

Apparatus

The gas chromatograph (GC) system was assembled from a GC-14A equipped with an FTD-14 flame thermionic detector (both Shimadzu Corp., Kyoto, Japan). Figure 1 is a cross-section of the FTD-14. A rubidium sulfate (Rb_2SO_4) bead is sintered to a platinum wire and used as an alkali metal source. The bead is positioned above the effluent jet and is centered in the cylindrical outer collector just below an inner collector, which also serves as the exhaust pipe. The Pt wire on which the

bead is bonded bridges the coaxial collectors which are physically and electrically isolated by a ceramic filler. A power controller regulates the current in the collector-bead-collector loop to provide bead temperature control ($600\sim 800^\circ\text{C}$) and overcurrent protection, while an electrometer tap on the inner collector serves to monitor

Fig. 1 Cross-section of the FTD cell used in the experiments (FTD-14): 1, inner collector; 2, ceramic insulator; 3, outer collector; 4, rubidium bead; 5, quartz jet; 6, column; 7, electrometer; 8, power controller; 9, high voltage supply.

the ion current. A high-voltage DC source impresses a potential of *ca.* 200 V across the metallic tip of the quartz jet and the collector assembly. The column effluent is mixed with hydrogen before exiting the jet, while air is supplied around the base of the jet. The mixture is burnt in a high-entropy plasma which envelops the bead. The FTD-14 fits easily into the existing FID (flame ionization detector) position of the GC-14A; the only modification required is an addition of flow restriction to the FID flow controller, since the FTD-14 uses relatively low flow rates for air and H₂.

The column was a polyphenylether (5 ring), 10% on Shimalite TPA (60–80 mesh), 3 m/3 mm i.d., glass column.

The carrier gas was helium delivered at 44 ml min⁻¹, with a column temperature of 100°C, and an injection port/detector temperatures of 250°C.

All of the reagents were of analytical grade. Methyl mercaptan, methyl sulfide, thiophene, dimethyl disulfide, dibutyl disulfide, diphenyl disulfide, 2-methyl thiophene, and 3-methyl thiophene as representative sulfur compounds, and decane, as a typical hydrocarbon, were obtained from Wako Pure Chemical Industries Ltd.

Results and Discussion

Relationship between the detector response to sulfur compounds, and different hydrogen flow rates and air flow rates

In order to find the optimum hydrogen and air flow rates for the determination of sulfur compounds, detector responses and selectivities were obtained under different hydrogen and air flow rate conditions.

The sample was an acetone solution containing 10³ µg ml⁻¹ each of thiophene and dimethyl disulfides as sulfur compounds and 10⁴ µg ml⁻¹ of decane as the hydrocarbon.

Figure 2 shows how the detector response to these

Fig. 2 Relationship between the response to sulfur compounds and decane, and the hydrogen flow rate: 1, decane (10⁴ µg ml⁻¹); 2, thiophene (10³ µg ml⁻¹); 3, dimethyl disulfide (10³ µg ml⁻¹).

three compounds varies with a change in the hydrogen flow rate, the air flow rate being kept constant at 102 ml min⁻¹. The detector response to sulfur compounds increased with an increase in the hydrogen flow rate and was almost constant above 11 ml min⁻¹. The detector response to decane also increased with an increase in the hydrogen flow rate, making a sharp increase around 11 ml min⁻¹; it is relatively constant above this point.

Figure 3 shows how the selectivities for thiophene and methyl disulfide against decane vary with a change in the hydrogen flow rate. The data shown in Fig. 3 were calculated from the data used in Fig. 2. The selectivity is defined as the ratio between the mass sensitivity to sulfur compounds and decane. The selectivity for thiophene is maximized at about 6.5 ml min⁻¹ of the hydrogen flow rate; that for dimethyl disulfide is maximized at about 5.5 ml min⁻¹. When the hydrogen flow rate is increased above these points, the selectivities for thiophene and dimethyl disulfide decrease. When the hydrogen flow rate is increased to 11 ml min⁻¹, which gives the highest sensitivity for decane, no significant increase in the selectivity is obtained for thiophene and methyl disulfide. Figures 2 and 3 show that the optimum hydrogen flow rate is about 5.5 ml min⁻¹.

Next, the optimum air flow rate was obtained. Figure 4 shows how the detector responses to thiophene, methyl disulfide, and decane vary with changes in the air flow rate, the hydrogen flow rate being kept at 5.5 ml min⁻¹, as determined above.

The detector response to the sulfur compounds increased with the air flow rate and became maximized at about 120 ml min⁻¹; it gradually decreased if the air flow rate was increased to above 120 ml min⁻¹. Decane gives a similar response curve, though with a somewhat different slope. It is noteworthy that when the air flow rate is decreased to below 30 ml min⁻¹, thiophene and decane are hardly detectable; also, the detector sensitivity

Fig. 3 Selectivity for sulfur compounds vs. the hydrogen flow rate. The selectivity is mass sensitivity relative to decane: 1, thiophene; 2, dimethyl disulfide.

Table 1 FTD response to sulfur compounds

Sulfur compound	Structural formula	Selectivity ^a	Slope ^b	Minimum detectable quantity/g s ⁻¹
Methyl mercaptan	R-S-H	9.14	0.76	5.25×10^{-11}
Dimethyl sulfide	R-S-R	20.13	0.61	2.13×10^{-11}
Carbon disulfide	S=C=S	20.62	0.59	9.47×10^{-12}
Thiophene		24.68	0.83	1.84×10^{-10}
Dimethyl disulfide	R-S-S-R	12.30	0.71	1.05×10^{-10}

a. Selectivity is defined as the ratio between mass sensitivity to sulfur compounds and decane. b. Slope is slope of the curves in the linear response range $R-\text{CH}_3-$.

Fig. 4 Relationship between the response to sulfur compounds and decane, and the air flow rate: 1, dimethyl disulfide ($10^3 \mu\text{g ml}^{-1}$); 2, decane ($10^4 \mu\text{g ml}^{-1}$); 3, thiophene ($10^3 \mu\text{g ml}^{-1}$).

Fig. 5 Selectivity for sulfur compounds vs. the air flow rate. The selectivity is mass sensitivity relative to decane. 1, thiophene; 2, dimethyl disulfide.

to dimethyl disulfide is enhanced dramatically, as shown by the dotted line curve in Fig. 4. Only dimethyl disulfide is detected when the air flow rate is set to be below 30 ml min^{-1} . Figure 5 shows a plot of the selectivities for thiophene and dimethyl disulfide against decane, plotted against the air flow rates. The selectivities for the two sulfur compounds are maximized at around a 100 ml min^{-1} air flow rate, though the optimum point is a little different between them. When the air flow rate is decreased to below 30 ml min^{-1} , the selectivity for dimethyl disulfide greatly increases, as shown by the dotted line in Fig. 4; this is in sharp contrast to that for thiophene, which is considerably lower in this region. A discussion is given later on concerning this point.

Figures 4 and 5 show that the optimum air flow rate is 100 ml min^{-1} . According to the results described above, the following experiments were carried out with the hydrogen flow rate set at 5.5 ml min^{-1} and the air flow rate at 100 ml min^{-1} .

Detector response characteristics to sulfur compounds

Sulfur compounds were classified from their chemical

structures into five groups, and the representative compound of each group was determined. Table 1 gives the names, chemical structures, selectivities, and slopes of the curves in the linear response range, as well as the detection limits for these compounds.

Selectivity

All of the sulfur compounds are detected with sensitivities of only 10- to 20-times higher than that for decane. The sensitivities are not sufficiently selective.

Detection limit

The detection limits for these sulfur compounds are 10^{-10} – $10^{-12} \text{ g s}^{-1}$, which correspond to 0.50 ng of methyl mercaptan, 0.18 ng of dimethyl sulfide, 0.07 ng of carbon disulfide, 2.2 ng of thiophene, and 2.1 ng of dimethyl disulfide. Figure 6 shows, as an example, a chromatogram of 1.0 ng carbon disulfide. This chromatogram shows that the detection limit of carbon disulfide is below the 10^{-10} g quantity level.

Linearity

The measurement of the linear range has been made

Fig. 6 Gas chromatogram showing the minimum detectable quantity for CS_2 (1×10^{-9} g injected). Sensitivity, 2×10^{-11} A full scale; (1) CS_2 1×10^{-9} g.

with sulfur compounds in Table 1 as a test sample, showing that the straight portion of the working curves covers nearly 4 orders of magnitude for the sulfur compounds. The slopes of the working curves for sulfur compounds are shown in Table 1.

Characteristics of the response to sulfur compounds with a 16 ml min^{-1} air flow rate

In a study of the air flow rate dependency of the detector response to sulfur compounds, it was found that dimethyl disulfide is detected with high selectivity when the air flow rate is reduced to below 30 ml min^{-1} . A detailed investigation was carried out concerning this finding.

Figure 7 shows chromatograms of sulfur compounds obtained with the air flow rate set at 100 ml min^{-1} (optimum flow rate) and 16 ml min^{-1} . The sample was 1% decane solution of thiophene, dimethyl disulfide, 2-methyl thiophene, and 3-methyl thiophene. When the air flow rate was set to 16 ml min^{-1} , only dimethyl disulfide was detected; the other sulfur compounds and decane were not detected at all. An air flow rate of 16 ml min^{-1} gives a more stable base line than at 100 ml min^{-1} . A further investigation was carried out in order to see if other disulfides have the same tendency. The sample was 1% decane solution of dimethyl sulfide, thiophene, dimethyl disulfide, and dibutyl disulfide. Figure 8 shows chromatograms of this sample obtained with the air flow rate set at 16 ml min^{-1} and 100 ml min^{-1} (optimum flow rate). The glass column was OV-17, 2% on Chromosorb W (AW, DMCS treated), with a length of 1 m and an inner diameter of 3 mm. The column temperature was 100°C .

When the air flow rate was set at 16 ml min^{-1} , only dimethyl disulfide and dibutyl disulfide were detected; the other sulfur compounds and decane were not detected

Fig. 7 Gas chromatograms of sulfur compounds obtained with the air flow rate set at 100 ml min^{-1} and 16 ml min^{-1} . Column; 10% PPE (5 ring) on Shimalite TPA, 60–80 mesh, $3 \text{ m} \times 3.0 \text{ mm i.d.}$. Temperature, column 100°C , injection port/detector 250°C ; hydrogen flow rate 6.0 ml min^{-1} ; sensitivity, 3.2×10^{-10} A full scale. (1) thiophene; (2) dimethyl disulfide; (3) 2-methyl thiophene; (4) 3-methyl thiophene; (5) decane.

Fig. 8 Gas chromatograms of sulfur compounds obtained with the air flow rate set at 16 ml min^{-1} and 100 ml min^{-1} . Column: 2% OV-17 on Chromosorb W (AW, DMCS treated), 80–100 mesh, $1 \text{ m} \times 3 \text{ mm i.d.}$, glass column; temperature, column 100°C , injection port/detector 250°C ; hydrogen flow rate 6 ml min^{-1} ; carrier gas He 40 ml min^{-1} ; sensitivity 3.2×10^{-10} A full scale. (1) dimethyl sulfide; (2) thiophene; (3) dimethyl disulfide; (4) decane; (5) dibutyl disulfide.

at all. Another experiment showed that diphenyl disulfide has the same tendency. The above-mentioned experiments show that when the air flow rate is set at 16 ml min^{-1} , disulfides are detected with far higher sensitivity than other sulfur compounds. Under this set of operational conditions, disulfides are detected with about 10^3 times higher sensitivity compared with hydrocarbons. It is also noteworthy that the 16 ml

min⁻¹ air flow rate provides a far more stable base line, compared with that at a 100 ml min⁻¹ air flow rate.

Our conclusion is that this set of operational conditions (when air flow rate is set at 16 ml min⁻¹) provides excellent efficiency in the analysis of disulfides. The disulfides analyzed were dimethyl disulfide, dibutyl disulfide and diphenyl disulfide. The response curve for dimethyl disulfide has a slope of 0.71 when the air flow rate is set at 100 ml min⁻¹, and 1.45 when it is set at 16 ml min⁻¹. The linear dynamic range for dimethyl disulfide is as wide as 10³. The selectivity for dimethyl disulfide is 1745 against decane, and the minimum detectable amount is 1.78×10⁻¹⁰ g s⁻¹ (at S/N=2). The optimum set of operational conditions was confirmed by measuring the detector response for different hydrogen flow rates; the detector response was highest when the hydrogen flow rate was set at 5.5 ml min⁻¹.

Negative surface ionization on alkali metal salt surface

Exact details concerning the negative surface ionization process⁹ on an alkali metal surface are not completely known. The following outlines the presumed ionization process for organic sulfur compounds. Effluents from the column are forced up against the alkali metal salt bead under the influence of the carrier gas pressure. The salt bead, which is a rubidium sulfate coating on a platinum wire, is heated 600–800°C by a current supplied from the power controller and detector cell transformer mechanism. The high temperature of the alkali bead and surrounding hydrogen plasma causes a thermal fragmentation of organic sulfur compounds liberating radicals containing sulfur. The high-entropy plasma state around the alkali bead is also supported by the high bead temperature; thus, numerous collisions occur. Through these collisions, the sulfur radicals gain electrons and become

negative ions; rubidium atoms become positive ions.

From these data it is assumed that an air flow rate of 100 ml min⁻¹ results in an extensive oxidation of the sulfur of SO_x species, which collide with the excited rubidium atoms, giving rise to SO_x⁻, as shown in Eq. (1); in this case, the detection of ionic oxides predominates,

With an air flow rate of 16 ml min⁻¹ the predominating mechanism is the formation of simple sulfide from the disulfide, and subsequent ionization (Eq. (2)) and detection

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