

**STUDY ON THE CHARACTERISTICS  
OF FLAME PHOTOMETRIC DETECTOR  
FOR GAS CHROMATOGRAPHY**

**TOSHIAKI SUGIYAMA**

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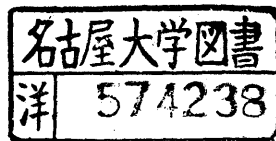
Study on the Characteristics  
of Flame Photometric Detector  
for Gas Chromatography

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A Dissertation  
for  
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## PREFACE

Determination of elements by flame photometry is among the relatively older arts in quantitative analysis. A detector by flame photometry for the detection of gas chromatographic effluents is, however, a new device in the field of modern gas chromatographic detectors. The basic principle is simple. A gas chromatographic effluent is burned in an air-hydrogen flame to emit a light peculiar to the effluent. The peculiar emission is isolated by a monochromator or filter and then detected by a photomultiplier tube. Hence, the effluent is selectively detected. This detector is generally called a flame photometric detector.

The availability of the intense emission of  $S_2$  bands for sulfur compounds in a fuel-rich air-hydrogen flame gives the flame photometric detector the possibility of its wider applications as a detector of a gas chromatograph, as well as the band of HPO for phosphorus-containing compounds. The bands of  $S_2$  are emitted mainly in the reaction zone and become very weak as the fuel ratio approaches the stoichiometric. The quadratic relationship between the intensity of the chemiluminescence of the  $S_2$  species and the sulfur concentration is observed by analytical spectrochemists. Exactly speaking, the analytical curve becomes more or less quadratic only at the lowest concentrations and somewhat linear above that.

This interesting feature of the responses of the flame photometric detector was observed for

various flame conditions (Chapter I) and many different sulfur-containing compounds (Chapter II). To clarify the characteristics and mechanism of the  $S_2$  emission in terms of the effect of some operating variables on the response of the detector, we assume the frequency of the collisions between sulfur atoms being formed from sulfur-containing compounds is too slow for the equilibrium of sulfur atoms and the  $S_2$  species to be reached within the available time in a flame (Chapter I). If virtually all of the sulfur-containing compounds has become the  $S_2$  species in the downstream portion of a flame, the analytical curve should be linear. If the equilibrium between the sulfur-containing compounds and the  $S_2$  species is established, the analytical curve should be quadratic in all concentration ranges, accurately. This assumption shows the prediction of the relationships between the intensity of the  $S_2$  bands emission and the sulfur concentration (Chapters I and IV). Similarly, an interference with some organic vapor was observed. By considering reaction kinetics, the major mechanism of the interference is found (Chapter III).

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## Chapter I

### Characteristics of $S_2$ Emission Intensity with a Flame Photometric Detector



## CHARACTERISTICS OF S<sub>2</sub> EMISSION INTENSITY WITH A FLAME PHOTOMETRIC DETECTOR\*

The molecular emission from sulfur compounds was studied by using a flame photometric detector and determining its intensity as a function of the composition of air-hydrogen flame and of the concentration of the sulfur compounds.

The relationship between the intensity of emission and the amount of sulfur in the compound is given by

$$i_E = i_0 (M)^n$$

where  $i_E$  is the intensity of the emission,  $M$  the amount of sulfur and  $i_0$  and  $n$  are constants for a given experimental flame condition. The value of  $n$  varies between 1.69 and 2.00, depending on the flame conditions.

The variations in the values of  $i_0$  and  $n$  are discussed by considering reaction kinetics. The recombination reaction of sulfur atoms in a flame, which is the rate-determining step, is affected by the experimental conditions. Therefore, the relationship between the intensity of the emission and the amount of sulfur-containing compounds varies considerably with the flow-rate of air and hydrogen in the burner.

\* J. Chromatogr., 77(1973) 309.

## INTRODUCTION

Flame photometry has been applied in gas chromatography in order to attain selective detection of the eluted gas components, by using the flame photometric detector (FPD)<sup>1-6</sup>. The use of the FPD for the selective detection of phosphorus and sulfur compounds was first introduced in 1966 by Brody and Chaney<sup>3</sup>. Since that time, this detector has been used extensively for the determination of residues of phosphorus- and sulfur-containing pesticides<sup>4,5</sup>.

The molecular emission due to the S<sub>2</sub> species from sulfur compounds is measured at 394 nm by a photomultiplier tube through an interference filter that transmits only in the region of 394 nm. The relationship between the response of the FPD and the amount of sulfur has been reported<sup>3,6</sup>. However, no systematic study has been published, on the characteristics of this detector.

The present work is an attempt to clarify the characteristics and mechanism of the molecular emission from sulfur compounds in terms of the effect of some operating variables on the response of the FPD. By considering reaction kinetics, we can explain the relationship between the response of the FPD and the flame conditions.

## EXPERIMENTAL

*Apparatus*

An FPD was equipped with an R268 photomultiplier tube operating at 720 V applied potential and a filter with maximum transmittance (32 %) at 394 nm with a

half-band width of 3.5 nm. This detector was supplied with air and hydrogen through flow meters, which were calibrated by using a soap-bubble flow meter. The detector was connected to a Yanagimoto G8 gas chromatograph (Fig. 1).

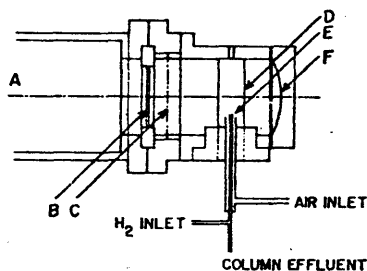


Fig. 1. Flame Photometric Detector.

- A: Photomultiplier tube,
- B: Optical filter,
- C: Lens,
- D: Quartz tube,
- E: Burner,
- F: Mirror.

The intensity of the molecular emission due to the  $S_2$  species from the sulfur compounds was measured by the FPD at varying flow-rates of air and hydrogen and over a wide range of concentrations of the sulfur compounds. The gas chromatograph was operated under the following conditions: column, glass tube (3 mm I.D. X 1.5 m) packed with 10 % of PEG 20M on Celite 545 (80-100 mesh); column temperature, 143 °C; and carrier gas, nitrogen at 22 ml/min and 0.56 atm.

A shielded burner, shown in Fig. 2, was used to obtain the spectra. Hydrogen containing the vapor of the sulfur compound and air were supplied separately to the burner. The spectra of the flames in the burner were determined with a Shimadzu SV50AL spectrophotometer.

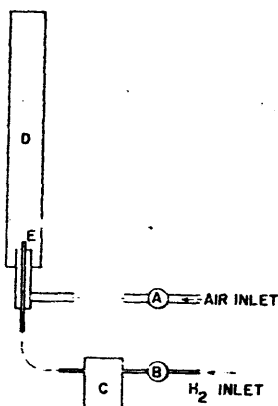


Fig. 2. Shielded burner. ,  
A and B: Flow meters,  
C: Saturation cell,  
D: Quartz tube (14 mm I.D.),  
E: Stainless-steel burner tip.

### Reagents

Di-*n*-butyl sulfide and benzo-*[b]*-thiophene of guaranteed grade were used without further purification. Benzo-*[b]*-thiophene was dissolved in acetone to a concentration of  $4.397 \times 10^{-4}$  g/ml for the gas chromatographic experiments. This solution was further diluted to the concentrations required for the individual experiments.

## RESULTS AND DISCUSSION

Fig. 3 shows a typical gas chromatogram obtained at flow-rates of 174 ml/min of air and 225 ml/min of hydrogen.

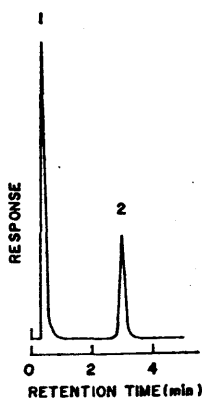


Fig. 3. Gas chromatogram:  
 $2.3 \times 10^{-8}$  g of sulfur in  
2  $\mu$ l of acetone solution.  
1: Acetone,  
2: Benzo-[*b*]-thiophene.

#### *Intensity of Emission*

The intensity of the molecular emission, represented by peak heights, is given in Table I for various flame conditions and concentrations of the sulfur compound. The concentration of the sulfur compound in a carrier gas at the maximum of a peak is approximately proportional to the amount of sulfur compound injected, for a small sample size. The response to the sulfur compound of the FPD is, however, not linearly proportional to the concentration of the sulfur compound, but the relationship between the intensity of the emission and the concentration



Table I: Characteristics of S<sub>2</sub> Emission Intensity

Air flow-rate (ml/min)	M (ng as sulphur)	Hydrogen flow-rate (ml/min)			
		116	168	225	289
128	207	1598	462	224	153.4
		1598	456	223	153.8
	69.0	276	71.2	33.9	19.8
		278	70.0	32.7	20.8
	23.0	42.7	10.1	4.3	1.9
		41.6	10.2	3.9	1.9
	7.67	6.5	—	—	—
6.0		—	—	—	
152	207	3814	1594	899	573
		3830	1594	885	589
	69.0	730	315	148.8	90.8
		727	316	152.8	91.2
	23.0	87.8	36.8	21.1	10.8
		88.0	39.8	20.3	11.9
	7.67	12.5	5.5	2.6	—
13.2		4.7	—	—	
174	207	5306	3450	1984	1334
		5370	3450	2010	1350
	69.0	896	558	352	234
		875	559	352	238
	23.0	102.4	79.6	46.8	33.6
		100.8	76.0	47.4	30.4
	7.67	14.2	10.5	5.4	4.0
14.5		10.6	5.2	4.0	
195	207	5917	8333	5318	3485
		5792	8378	5312	3427
	69.0	945	1184	746	501
		927	1184	743	513
	23.0	114.4	131.6	78.6	47.8
		115.0	129.2	74.8	48.4
	7.67	15.8	21.8	12.8	9.1
17.0		19.5	12.5	8.0	

can be found from the following equation:

$$i_E = i_0 (M/M_0)^n \quad (1)$$

where  $i_E$  is the observed intensity of the molecular emission due to the S<sub>2</sub> species,  $M$  the weight of sulfur injected and  $M_0 = 2.30 \times 10^{-8}$  g of sulfur. The values of  $i_0$  and  $n$  are both constant under given experimental conditions.

Fig. 4 illustrates the relationship between the flow-rates of air and hydrogen and the value of the constant  $i_0$  (a) and that of the constant  $n$  (b).

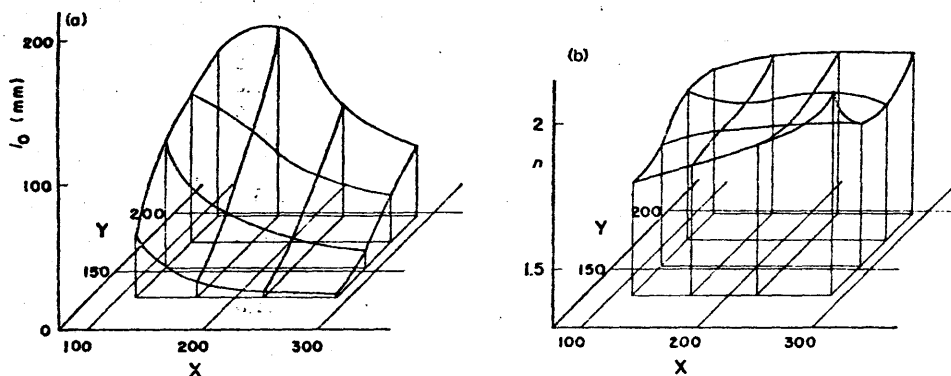


Fig. 4. Relationships between constant  $i_0$  (a) and exponent  $n$  (b) and flow-rates of air and hydrogen. X-axis: Hydrogen flow-rate (ml/min), Y-axis: Air flow-rate (ml/min).

#### *Effect of Air in the Flame*

Complete molecular emission spectra of the  $S_2$  species are shown in Fig. 5.

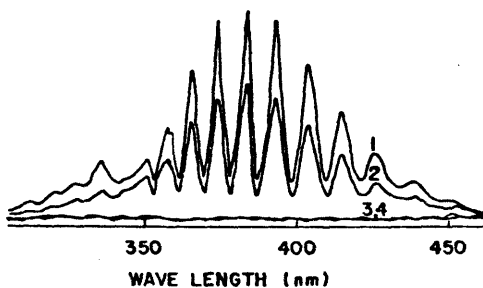


Fig. 5. Flame emission spectra of di-*n*-butyl sulfide.

Hydrogen flow-rate: 60 ml/min,  
 Air flow-rate: (1): 100 ml/min,  
 (2): 135 ml/min,  
 (3): 170 ml/min,  
 (4): 200 ml/min.

The flow-rate of hydrogen was maintained constant at 60 ml/min, while the flow-rate of air was varied between 100 and 200 ml/min. The intensity of the molecular emission decreased with increase in the ratio of the flow-rate of air to hydrogen in flames containing an excess of oxygen, and the following factors seem to affect the emission intensity:

- (1) the temperature of the flame is too high to allow the formation of the  $S_2$  species<sup>6,7</sup>,
- (2) oxygen in the flame prevents the formation of the  $S_2$  species from the sulfur atom by the competitive reactions:



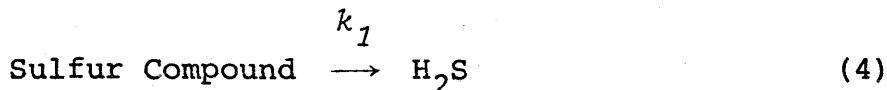
It can be seen from Fig. 5 that the decrease in the emission intensity is more affected by the latter factor than the former. Therefore, no characteristic response can be observed in the range of high air-hydrogen flow ratios (Table I).

#### *Effect of Hydrogen in the Flame*

In the range of low air-hydrogen flow ratios, a characteristic response of the FPD can be observed, as shown in Table I. The intensity of the emission decreased with increase in the hydrogen flow-rate at a constant flow-rate of air. The temperature of the air-hydrogen flame will be decrease as the flow-rate of hydrogen increases. The intensity of the molecular emission is approximately proportional to the temperature of the flame<sup>1</sup>.

### Mechanism of Emission

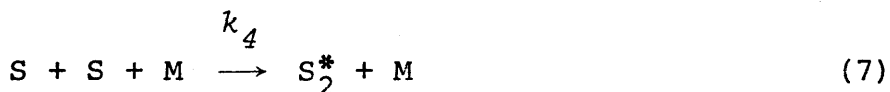
In a very hydrogen-rich flame,  $\text{H}_2\text{S}$  will be a dominant constituent of the products from organic sulfur-containing compounds<sup>8</sup>.



The formation of sulfur atoms is rapid<sup>9</sup>:



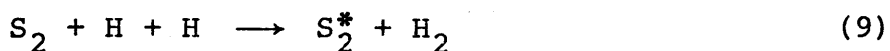
The simplest mechanism involves a rate-determining step that is a three-body recombination:



(where M is the third body) and which is followed by



The  $\text{S}_2$  species reacts as follows:



The concentration of  $\text{H}_2\text{S}$  corresponds with that of the sulfur compound, provided that  $\text{H}_2\text{S}$  is produced predominantly and stoichiometrically in reaction 4.

It can be assumed that

- (1) the reactants distribute uniformly in a cross section of a flame,
- (2) sulfur atoms are rapidly formed in a reaction zone,
- (3) reaction 7 is a rate-determining step.

The concentration of sulfur atoms is given by:

$$[S] = K_2 K_3 \frac{[H_2S][H]^2}{[H_2]^2} \quad (11)$$

$$= K[H_2S] \quad (12)$$

The rate of the formation of the  $S_2$  species is given by reaction 7, and then the concentration of  $S_2$  is

$$[S_2] = \frac{aK}{2} \left( 1 - \frac{1}{2aKk_4[M]t + 1} \right) \quad (13)$$

for a reaction time of  $t$  sec, where  $a$  is the initial concentration of the sulfur compound and  $[M]$  the concentration of the third body. The total number of the  $S_2$  species is given by

$$N_{S_2} = \frac{Av}{4k_4[M]} [x - \ln(x + 1)] \quad (14)$$

where  $A$  is the cross sectional area of a flame,  $v$  the velocity of  $S_2$  rising in a flame and  $x = 2aKk_4[M]t$ .

The intensity of the emission in reaction 8 is

$$I_{S_2} = [S_2] \quad (15)$$

On the other hand, the intensity in reaction 10 is

$$I_{S_2} \propto N_{S_2} \quad (16)$$

The calculated intensity can be compared with the molecular emission intensity observed.

Provided that the emission in reaction 10 contributes little to the over-all molecular emission of  $S_2$ , the theoretical relationship between  $a$  and  $I_{S_2}$  is shown in Fig. 6. The exponent  $n$  can be calculated by the following equation:

$$n = \frac{d(\log I_{S_2})}{d(\log a)}$$

$$= 1 + \frac{1}{2aKk_4[M]t + 1} \quad (17)$$

Fig. 7 shows the variation of  $n$ . The value of  $n$  can decrease with increase in the concentration,  $a$ , from 2 to 1.

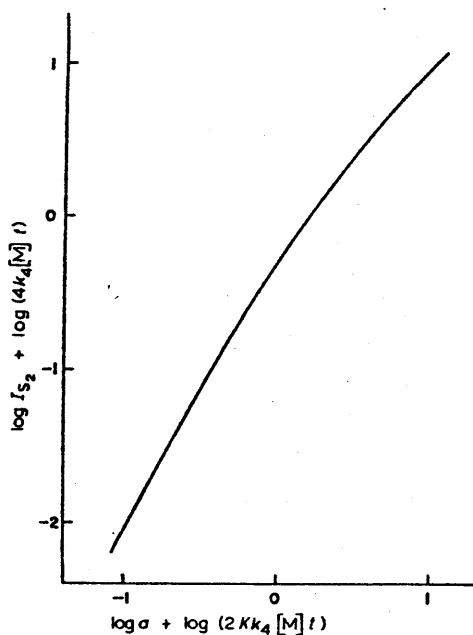


Fig. 6. Theoretical relationship between  $\log I_{S_2}$  and  $\log a$ .

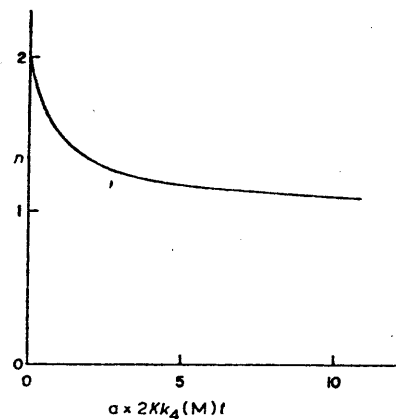


Fig. 7. Theoretical relationship between exponent  $n$  and initial concentration of sulfur atoms  $a$ .

Figs. 6 and 7 indicate the following criteria:

(1) When the air-hydrogen flow ratio is constant, an increase in the total flow-rate leads to a lower intensity of the molecular emission because the concentration of the sulfur compound decreases.

(2) The value of  $n$  varies with the flame conditions and is inversely proportional to the intensity of the molecular emission.

(3) Because of the decrease in the concentration of the sulfur compound, the intensity of  $S_2$  emission decreases and the value of  $n$  becomes larger with increasing hydrogen flow-rate.

These criteria can satisfy the effect of some operating variables on the intensity measured by the FPD. Consequently, the mechanism of the molecular emission due to the  $S_2$  species from the sulfur compound can be interpreted as follows. Reactions 4-7 occur in an air-hydrogen flame and reaction 7 is the rate-determining step. However, reaction 9 occurs to only a small extent. Eqn. 15, the relationship between the intensity of the  $S_2$  molecular emission and the amount of sulfur compound, therefore provides fairly complex functions of flow-rates of air and hydrogen, and of concentration of sulfur-containing compounds. Finally, the response of the FPD is shown by this mechanism to be proportional to about the second power of the amount of sulfur compounds, for small sample size<sup>10</sup>.

## Chapter II

### Intensity Characteristics of $S_2$ Emission for Sulfur Compounds with Flame Photometric Detector





## INTENSITY CHARACTERISTICS OF S<sub>2</sub> EMISSION FOR SULFUR COMPOUNDS WITH FLAME PHOTOMETRIC DETECTOR\*

*The effect of the bond-structure of sulfur atoms on the emissive response of sulfur containing compounds is examined with a flame photometric detector. The response of a flame photometric detector varies enormously with the type of the sulfur compounds. Butanethiol, the most sensitive compound, is more responsive than pentyl disulfide, the least sensitive, by a factor of about 100. Although the response for butanethiol and phenyl sulfide varies almost linearly with the concentration of the compounds, the response of the others relates in a non-linear manner to both the concentration or its square.*

\* J. Chromatogr. Sci., 11(1973)639.

## INTRODUCTION

The flame photometric detector (FPD), based on a principle patented by Draegerwerke<sup>11</sup> and developed further for use in gas chromatographic detector by Brody and Chaney<sup>3</sup>, selectively detects sulfur compounds in subnanogram quantities. Several applications of the FPD for gas chromatographic analysis have been reported recently<sup>5,6,12-19</sup>. Sulfur compounds with the sulfur in various oxidation states were found to produce slightly different responses per unit sulfur weight<sup>6,7,14,19</sup>.

The work reported in this paper is an attempt to define the response of the FPD for various types of sulfur-containing compounds. Not only the responses, but also the nature of the relationship of the concentration of sulfur compounds to the responses are made clear and seem to vary considerably with the types of bond-structure of sulfur atoms.

## EXPERIMENTAL

*Apparatus*

The device with which the emission of  $S_2$  species at 394 nm was measured was identical to that in the previous paper<sup>20</sup>. The FPD was connected to the outlet of a Hitachi K53 Gas Chromatograph equipped with a thermal conductivity detector. The detector was carried out with the flow rates of air of 174 ml/min and hydrogen of 225 ml/min.

The gas chromatographic column used was a 1 m X 3 mm I.D. stainless steel tube packed with 10 % of PEG 20M on Celite 545. With the carrier gas ( $H_2$ ) flow rate at 15 to 20 ml/min, the column temperature was varied to obtain 4 to 8 minute retention time with each compound. The injection temperature was kept 50 °C above the column temperature.

#### *Reagent*

The chemicals used were reagent grade, each of which was found to have a minimum purity of 99.5 % as determined by a gas chromatograph equipped with FID. The test solutions of the various compounds were as follows (in  $10^{-3}$  g/ml-acetone): thiophene: 2.131, benzo-[b]-thiophene: 2.174, butyl sulfide: 2.038, phenyl sulfide: 2.301, and pentyl disulfide: 1.904.

## RESULTS AND DISCUSSION

#### *Concentration of an Effluent Gas*

Provided that the response of a detector is proportional to the concentration of gas chromatographic effluents, the response on the recorder chart paper (in cm) can be given as follows:

$$h(t) = c W(t) \quad (1)$$

where  $W(t)$  is the concentration of a certain gas chromatographic effluent (in  $\text{mol}/\text{cm}^3$ ), and  $c$  the sensitivity factor for a substance and instrument within the range being used in the measurement (in  $\text{cm cm}^3/\text{mol}$ ). The amount of a sample injected in a gas chromatograph is  $M$  mol:

$$M = \int_0^{\infty} W(t) V dt \quad (2)$$

where  $V$  is the flow rate of a carrier gas through the detector (in  $\text{cm}^3/\text{min}$ ). The peak area concerned is

$$S = \int_0^{\infty} h(t) v_C dt \quad (3)$$

where  $S$  and  $v_C$  are the peak area of the sample (in  $\text{cm}^2$ ) and chart speed (in  $\text{cm}/\text{min}$ ), respectively.

$$\begin{aligned} S &= c v_C \int_0^{\infty} W(t) dt \\ &= \frac{c v_C}{V} M \end{aligned} \quad (4)$$

The sensitivity factor can be measured by Eqn. 4. Therefore, the concentration of the sample can be calculated by the next equation:

$$\begin{aligned} W(t) &= \frac{1}{c} h(t) \\ &= \frac{M v_C}{V S} h(t) \end{aligned} \quad (5)$$

In this paper, the thermal conductivity detector satisfying the above prerequisite was used, and the flow rate of the sample through the detector,  $W(t)V$  ( $= f$ , in  $\text{mol}/\text{min}$ ), was used as a graduation instead of the concentration of the sample ( $W(t)$ ).

#### *Relationship Between Emission Intensity and Sulfur Concentration*

The intensity of the  $\text{S}_2$  molecular emission from various sulfur containing compounds, indicated as each peak height, is tabulated in Table I for

Table I: Response of Sulfur Compounds

Compound	Flow Rate of Sulfur Atoms $f_s \times 10^{-9}$ mol/min	Response (cm)
Thiophene	57.5	46.2
	79.0	79.0
	89.0	94.9
	102.8	124.8
	118.9	161.1
	170.3	326
Thiolane	39.5	32.0
	76.0	94.1
	109.5	173.1
	176	374
	182	400
	206	480
Butanethiol	65.1	124.8
	68.3	140.8
	149	317
	158	330
	223	470
	229	493
Thiophenol	48.8	9.20
	51.0	9.76
	61.5	12.50
	64.5	12.31
	95.0	29.3
	95.9	33.9
Benzo-(b)-thiophene	31.6	4.24
	57.1	12.02
	73.8	18.6
	87.4	24.2
	97.1	29.2
	100.2	31.2
Butyl sulfide	22.9	5.40
	29.9	8.76
	41.9	15.4
	55.2	27.8
	74.2	47.6
	102.1	85.2
Phenyl sulfide	29.8	4.72
	36.5	5.98
	41.1	6.42
	47.1	7.80
	53.0	8.16
	58.3	9.58
Pentyl disulfide	42.7	0.55
	47.1	0.60
	87.3	1.79
	114.0	2.91
	115.1	3.16
	152	4.59

various concentrations -  $f_S$  (in mol/min) - of the sulfur compounds. The responses of sulfur compounds to the FPD are not all linearly proportional to the concentration of them. The response to the FPD varies enormously with the type of sulfur compounds. The most sensitive compound, butanethiol, is more responsive than the least one, pentyl disulfide, by a factor of about 100. Alkylated sulfur compounds are, for the most part, more sensitive than others. On the other hand, dialkyl disulfide is much less sensitive.

The relationship between the intensity of the emission and the concentration of sulfur compounds can be expressed as follows:

$$i_E = i_0 (f_S / f_{S,0})^n \quad (6)$$

where  $i_E$  is the observed intensity of the molecular emission due to the  $S_2$  species (in cm-peak height), and  $f_S$  the amount of sulfur atoms entering the detector per unit time, determined by Eqn. 5.

$f_{S,0}$  is  $1.000 \times 10^{-7}$  mol/min of sulfur atoms.

The values  $i_0$  and  $n$  are both constant under a given experimental condition. These values are summarized in Table II. The value  $i_0$  shows the intensity of the emission per unit sulfur concentration. The order of the FPD response in this experimental condition is butanethiol > thiolane > thiophene > butyl sulfide > thiophenol > benzo-[b]-thiophene > phenyl sulfide > pentyl disulfide. Similarly, the exponent,  $n$ , reveals the concentration-response relationships which are found to differ significantly from one another in emitting features. The magni-

Table II: Constant Values  $i_0$  and  $n$   
 in  $i_E = i_0 (f_S/f_{S,0})^n$

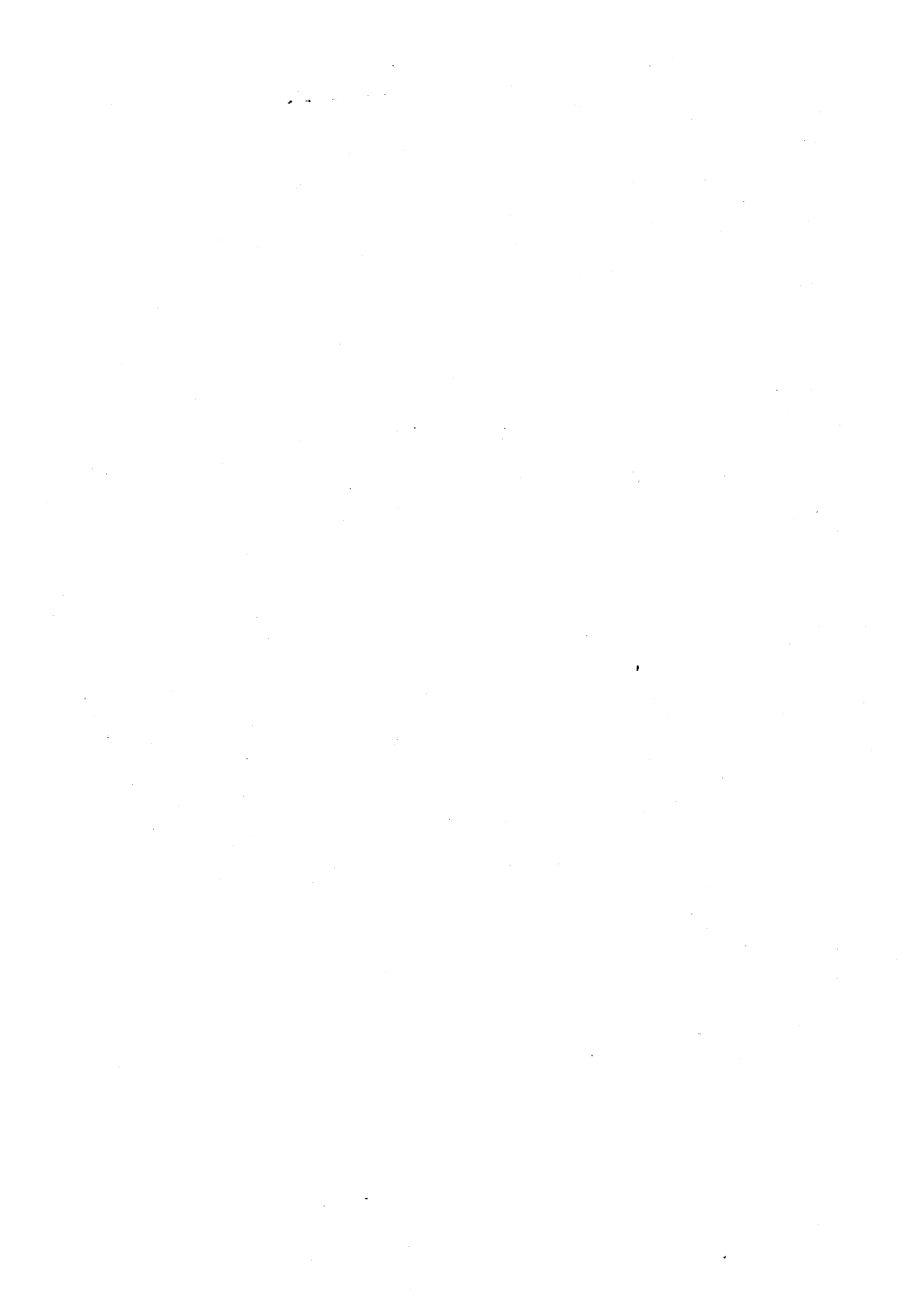
Compound	$i_0$ (cm)	$n$
Thiophene	120.8±4.2	1.799±0.041
Thiolane	147.9±1.3	1.645±0.006
Butanethiol	204.3±5.8	1.058±0.022
Thiophenol	33.1±3.8	1.892±0.167
Benzo-(b)-thiophene	30.95±0.44	1.718±0.014
Butyl sulfide	82.0±2.7	1.857±0.025
Phenyl sulfide	16.21±0.56	1.013±0.061
Pentyl disulfide	2.315±0.121	1.731±0.044

tude of  $i_0$  is found to be independent of the exponent,  $n$ . Although the intensity of the emission for butanethiol and phenyl sulfide seems to vary almost linearly with the concentration of sulfur atoms ( $n \approx 1$ ), the intensity for the others relates in a non-linear manner to both the concentration or its square. Examining the deviation from the quadratic relationship, the order is thiolane > benzo-[b]-thiophene > pentyl disulfide > thiophene > butyl sulfide > thiophenol.

Unexpectedly, the disulfide compound shows non-linear relationship between the response and the concentration; exponent,  $n$ , is 1.731. This value seems to point out that -S-S- in this disulfide doesn't lead directly to the emitting species,  $S_2$ , but decomposes to monatomic species after leading to  $S_2$ .

From these results, it is anticipated that analysts will have great difficulty determining sulfur-containing compounds with the FPD.





## Chapter III

### Interferences of S<sub>2</sub> Molecular Emission in a Flame Photometric Detector



## INTERFERENCES OF $S_2$ MOLECULAR EMISSION IN A FLAME PHOTOMETRIC DETECTOR\*

*The presence of gaseous non-sulfur-containing organic compounds in a carrier gas causes a decrease in the response of flame photometric detectors. The way in which such organic compounds interfered with the response of sulfur-containing compounds in the flame photometric detector was determined. The interference by organic compounds increases exponentially with increase in concentration of the substances. The interference by an organic compound is, however, independent of the concentration of sulfur-containing compounds in the presence of a certain concentration of the organic compound, and it was found that the decrease in the response of a flame photometric detector can be explained by inactivation of the excited  $S_2$  species by its combination or collision with an organic compound and/or its degradation products.*

\* J. Chromatogr., 80 (1973) 61.

## INTRODUCTION

Flame spectrophotometry has been used extensively for the analysis of sulfur-containing compounds<sup>3,5-7,12,13,15-18,21,22</sup>, which give rise to the S<sub>2</sub> band in a hydrogen-rich flame. The emission is highly dependent on the nature of the flame. The effect of other gaseous substances on the molecular emission of the S<sub>2</sub> species has been reported by Crider<sup>21</sup>, Rupprecht and Phillips<sup>12</sup> and Perry and Carter<sup>15</sup>, who found that the presence of other gaseous organic compounds in the carrier gas used to carry sulfur compounds into a flame photometric detector (FPD) led to a decrease in response, compared with that observed in their absence. Sulfur emission is obscured by the presence of hydrocarbons (methane, ethane, propane, butane and 2-methylpentane), alcohols (isobutanol and 3-pentanol) and carbon dioxide.

The object of this work was to explore the characteristics of the interference of organic compounds on the S<sub>2</sub> molecular emission. The interference was studied with an FPD and a spectrophotometer at various concentrations of organic compounds. The dependence of quenching on the concentration of organic compounds and the nature of the interference are discussed.

## EXPERIMENTAL

*Apparatus*

The device with which the emission of S<sub>2</sub> at

394 nm was measured was identical with that described in the previous paper<sup>20</sup>. Organic compounds were passed in a stream of hydrogen through a buffer tank of 500 cm<sup>3</sup> volume in order to study the interference that they caused.

The spectra of flames in a burner shielded with a 9.5 mm quartz tube were obtained with a Shimadzu SV50AL Spectrophotometer. Air and hydrogen were supplied to this burner, the hydrogen containing the vapor of the sulfur compound (di-*n*-butyl sulfide) and organic compounds being introduced into the air stream.

The concentrations of the compounds added to the hydrogen stream were determined with a Shimadzu GC-1C Gas Chromatograph equipped with a flame ionization detector. The chromatographic column consisted of a 3 mm I.D. X 1 m copper tube packed with 10 % of PEG 20M on 80-100 mesh Celite 545.

### *Reagents*

Di-*n*-butyl sulfide and benzo-[*b*]-thiophene of guaranteed grade were used. Benzo-[*b*]-thiophene was dissolved in acetone to a concentration of  $2.678 \times 10^{-3}$  g/ml for gas chromatographic experiments, and this solution was further diluted as required. The other chemicals used were of reagent grade.

## RESULTS AND DISCUSSION

### *Spectrum of the S<sub>2</sub> Band*

Fig. 1 shows the spectra of the molecular emis-

sion of  $S_2$  from di-*n*-butyl sulfide in the presence of the various concentrations of an organic compound (acetone) in the air stream. The presence of the acetone decreased the intensity of the emission, and this decrease is independent of wavelength and almost uniform over the whole wavelength range.

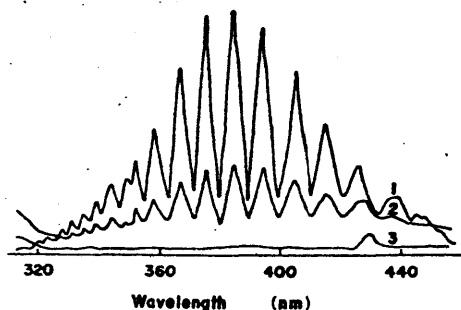


Fig. 1. Emission spectrum of  $S_2$  species obtained by introducing  $6 \times 10^{-7}$  mol/min of di-*n*-butyl sulfide into the hydrogen stream and acetone into the air stream and measuring under the following conditions:

slit width: 0.4 mm,  
 air flow-rate: 171 m-/min,  
 $H_2$  flow-rate: 343 ml/min,  
 acetone flow-rate:

- (1): 0 mol/min,
- (2):  $1.2 \times 10^{-4}$  mol/min,
- (3):  $2.3 \times 10^{-4}$  mol/min.

#### *Interference by Organic Compounds*

The interference with the molecular emission of  $S_2$  was measured with an FPD in the presence of vol-

atile organic compounds in the hydrogen stream. The intensity ratio,  $\Phi$ , of the  $S_2$  emission is defined as follows:

$$\Phi = \frac{\text{Response of FPD (compound present)}}{\text{Response of FPD (compound absent)}} \quad (1)$$

Benzo-[b]-thiophene was used as the sulfur-containing compound. The interference with the molecular emission caused by the organic compounds depends on the concentration of the compounds. The nature of the interference caused by ethanol and acetone for two different concentrations of benzo-[b]-thiophene is shown in Fig. 2.

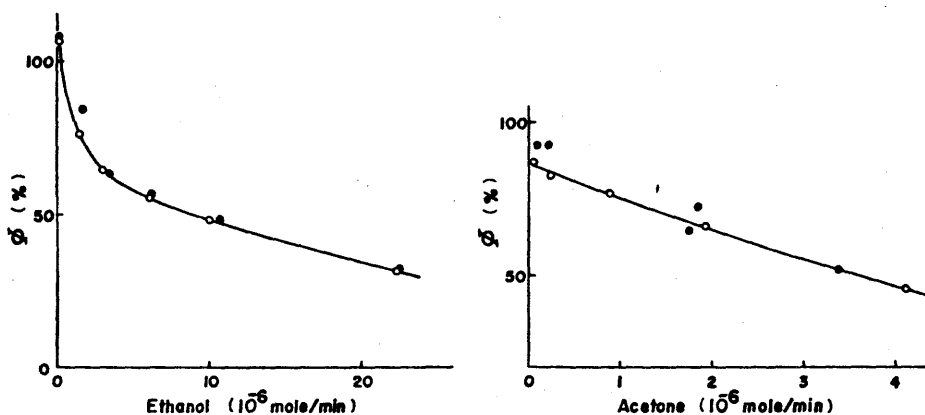


Fig. 2.  $S_2$  emission quenching: relationship between  $\Phi$  and flow-rate of interfering substances (ethanol and acetone) in the FPD.

Air-hydrogen flame: air flow-rate: 171 ml/min,  $H_2$  flow-rate: 343 ml/min.

Flow-rate of benzo-[b]-thiophene at the maximum point of peak:  $\circ$ :  $2.28 \times 10^{-9}$  mol/min,  
 $\bullet$ :  $7.02 \times 10^{-9}$  mol/min.



The decrease in the emission for the two concentrations of benzo-[*b*]-thiophene with increase in the concentration of the organic compounds is similar for both compounds, *i.e.*, the interference with the emission is almost independent of the concentration of the sulfur-containing compound.

Fig. 3 shows the interferences caused by four organic compounds, and can be seen to be similar in each instance. An exponential decrease in the emission intensity is caused by an arithmetic increase in the concentration of the organic compounds.

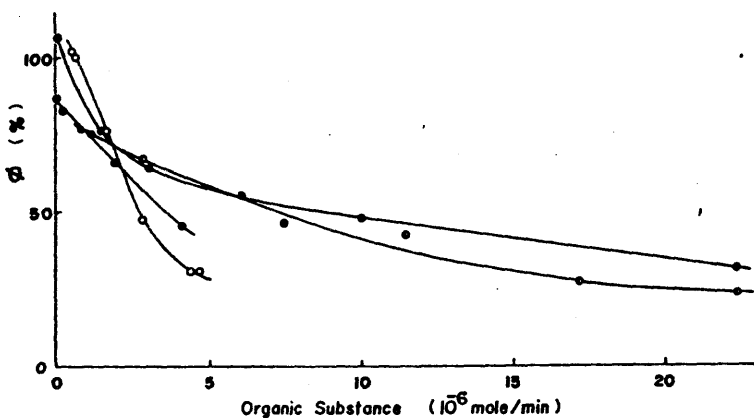
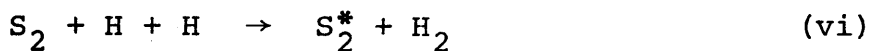
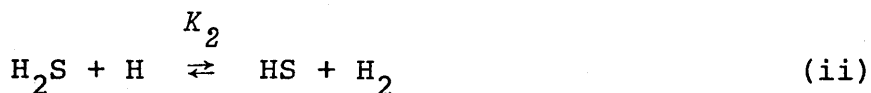
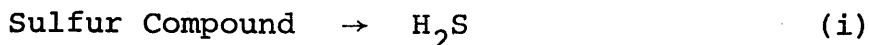


Fig. 3.  $S_2$  emission quenching. Flame conditions: air flow-rate: 171 ml/min,  $H_2$  flow-rate: 343 ml/min. Interfering substances: ○: cyclohexane (flow-rate of benzo-[*b*]-thiophene;  $f_S = 2.59 \times 10^{-9}$  mol/min), ○: acetone ( $f_S = 2.28 \times 10^{-9}$  mol/min), ●: methanol ( $f_S = 5.18 \times 10^{-9}$  mol/min), ●: ethanol ( $f_S = 2.28 \times 10^{-9}$  mol/min).

*Interference with the S<sub>2</sub> Molecular Emission*

The processes involved in the molecular emission of S<sub>2</sub> from sulfur-containing compounds are as follows<sup>20</sup>



The emission in reaction vii contributes little to overall S<sub>2</sub> molecular emission.

The following effects are probably responsible for the interference caused by organic compounds.

(1) An organic compound or its degradation products may absorb light due to the molecular emission of S<sub>2</sub>. From Fig. 1, the interference caused in the molecular emission is found not to be due to the absorption of light by an organic compound, since the decrease in emission was uniform over the whole wavelength range.

(2) The presence of an organic substance may cause an increase in the flame temperature, which may become too high to allow the formation of the

$S_2$  species. In this study, a hydrogen-rich flame was used so that only an increase in flame temperature could be caused by contamination with organic compounds. On the contrary, the addition of such compounds will cause a decrease in temperature owing to an increase in heat capacity.

(3) Hydrogen atoms in a flame may combine with scavengers (Sc), and the following reaction will reduce hydrogen atoms:



so that the concentration of sulfur atoms may become small.

In this case, the scavengers are organic compounds or their degradation products (radicals and ions).

The concentration of hydrogen atoms is given by

$$[H] = [H]_0 \exp(-k_g [Sc] t) \quad (2)$$

where  $t$  is the reaction time and  $[H]_0$  is the concentration of hydrogen atoms in the absence of scavengers. The concentration of sulfur atoms is given by

$$[S] = K_2 K_3 \frac{[H_2 S] [H]_0^2}{[H_2]^2} \exp(-2k_g [Sc] t) \quad (3)$$

The decrease in the concentration of sulfur atoms is dependent on  $[Sc]$ . Provided that nothing except the concentration of hydrogen atoms changes in the presence of scavengers, then the extent of the

decrease in the number of sulfur atoms is independent of the concentration of the sulfur compound. The ratio of the decrease in the number of the  $S_2$  species at the various concentrations of sulfur compounds was therefore shown to be constant in the presence of a certain concentration of an organic compound. The intensity of the  $S_2$  emission is given by

$$I_{S_2} = I_0 [S]^n \quad (4)$$

where  $I_0$  and  $n$  are both constant. The value of  $\phi$  is given by

$$\begin{aligned} \phi &= \frac{I_{S_2}}{I_{S_2,0}} \\ &= \exp(-2nk_g [Sc] t) \end{aligned} \quad (5)$$

When ethanol is used as the scavenger (Fig. 2), the value of  $k_g$  calculated from Eqn. 5 is  $10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ . This value is much lower than rate constants for the recombination reactions ( $10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ ), e.g.,  $H + C_2H_6$ ,  $H + C_3H_8$ ,  $H + C_4H_{10}$ , etc.<sup>23</sup>.

(4) Sulfur atoms formed in reaction iii may combine with scavengers. The competitive reactions will prevent the formation of the  $S_2$  species:



It is assumed that the concentrations of organic compounds and their degradation products are much less than that of the third body (M). A qualitative consideration of these reactions must account for the effect of scavengers. The reaction of S to  $S_2$  is second-order and the reaction of S and Sc to produce S-Sc is pseudo-first-order, so that making the concentration of sulfur atoms low will tend to decrease more rapidly the chance of the occurrence of the reaction to form  $S_2$  than that to form S-Sc. Therefore, the conversion of the sulfur atoms into the  $S_2$  species decreases with the decrease in the concentration of sulfur atoms in these competitive reactions. In this mechanism, the value of  $\phi$  is shown to decrease with the decrease in the concentration of sulfur-containing compounds. However, the value measured is independent of the concentration of the sulfur-containing compound.

(5) The  $S_2$  species in the excited states may be inactivated by collision with scavengers. The intensity of the molecular emission will decrease as the number of excited  $S_2$  species ( $S_2^*$ ) decreases by reaction x:



The concentration of excited  $S_2$  species that actually emit light is given by

$$[S_2^*] = [S_2^*]_0 \exp(-k_{10} [Sc] \bar{t}) \quad (6)$$

where  $[Sc] \gg [S_2^*]$ ,  $\bar{t}$  is the mean lifetime of the excited  $S_2$  species and  $[S_2^*]_0$  is the concentration

of the excited  $S_2$  species in the absence of scavengers. The decrease in the ratio of the concentration of the excited  $S_2$  followed by chemiluminescence is independent of the magnitude of  $[S_2^*]_0$  for a certain concentration of scavengers. The value of  $\phi$  is given by

$$\phi = \exp(-k_{10} [Sc] \bar{t}) \quad (7)$$

$[S_2^*]$  decreases exponentially with  $[Sc]$ .

When ethanol is used as the scavenger (Fig. 2), the value of  $k_{10}$  calculated from Eqn. 7 is  $10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$  where  $\bar{t}$  is  $10^{-7} \text{ sec}$  (Ref. 24). This value can be compared with the rate constants for re-combination in a flame<sup>23</sup>.

#### CONCLUSION

The magnitude of the interference caused by organic compounds on the molecular emission due to the  $S_2$  species increases exponentially with the concentration of volatile organic compounds. The value of  $\phi$  is independent of the concentration of sulfur-containing compounds in the presence of a certain concentration of the organic compound. The decrease in the intensity of the  $S_2$  molecular emission is based on the inactivation of the excited  $S_2$  species by combination or collision with an organic compound and/or its degradation products.



## Chapter IV

### Characterization for the Selective Detection of Sulfur Compounds by Flame Photometry





## CHARACTERIZATION FOR THE SELECTIVE DETECTION OF SULFUR COMPOUNDS BY FLAME PHOTOMETRY\*

*The molecular emission of the  $S_2$  species from sulfur compounds has been studied by using a flame photometric detector. From the measurements of the response of the flame photometric detector, we have proposed a mechanism for the emission of  $S_2$  in reactions of sulfur atoms.*

*The mechanism was confirmed by experimental results measured with the flame photometric detector and spectrophotometers. It was found that the  $S_2$  molecular emission arises mostly from a three-body recombination reaction and that the rate of this recombination is too slow for equilibrium to be attained sufficiently rapidly.*

*The response to sulfur-containing compounds of the flame photometric detector in gas chromatography represents an extremely complex function of the concentration of sulfur compounds.*

\* J. Chromatogr., 85(1973)45.

## INTRODUCTION

Flames that contain sulfur compounds as additives emit bands of  $S_2$ ,  $SO$ ,  $SH$  and  $CS$  and a continuum, and the various emissions are highly dependent on the nature of the flames. Of these emissions,  $S_2$  has proved to be the most useful for spectrochemical analysis.

The principle discovered by Dräger and Dräger<sup>11</sup> for the detection of sulfur and phosphorus compounds was first applied to produce a detector for gas chromatography in 1966 by Brody and Chaney<sup>3</sup>.

Since that time, this detector has been used extensively in the determination of residues of sulfur- and phosphorus-containing pesticides, natural gases, volatiles in smoke, etc.<sup>5-7,12,13,15-18,22</sup>.

In this flame photometric detector (FPD), a quadratic analytical curve was usually given for sulfur; the emission intensity varies as the square of the sulfur concentration<sup>5</sup>. Such curves were also observed by Dagnall *et al.*<sup>7</sup> and Mizany<sup>6</sup>.

Sugden *et al.*<sup>8</sup> studied the reactions of sulfur in hydrogen flames, and showed the manner in which the non-equilibrium concentration of  $H$  and  $OH$  affects the emission intensity of the sulfur species.

The theory was tested by measuring the dependence of the  $SO$ ,  $SH$  and  $S_2$  emission intensities on the distance from the reaction zone and on the concentration of total sulfur. On the other hand, Fair and Thrush<sup>9</sup> discussed the dependence of the  $S_2$  emission intensity on the concentration of hydrogen sulfide using an electrodeless radiofrequency discharge tube.

They tried to interpret the relationship between the S<sub>2</sub> emission intensity and the concentration of hydrogen sulfide at various reaction times. Nevertheless, the proposed mechanisms of emission of the S<sub>2</sub> species cannot adequately explain the experimental results.

We have observed the characteristics of the FPD in the sulfur mode<sup>20,25,26</sup>. In previous papers, a mechanism of the S<sub>2</sub> emission in reactions of sulfur atoms was developed by measuring the intensity of the emission with an FPD. In this paper, the mechanism was confirmed from the relationship between the intensity of the molecular emission of S<sub>2</sub> and the condition of the flames.

## EXPERIMENTAL

### *Apparatus*

The FPD used in this study to determine the intensity of the S<sub>2</sub> emission was identical with that described earlier<sup>20</sup>. The intensity of the molecular emission due to the S<sub>2</sub> species from a sulfur compound was measured at various flow-rates of air and hydrogen and over a wide range of concentrations of the sulfur compound.

### *Reagent*

Di-*n*-butyl sulfide of guaranteed grade was dissolved in acetone so as to give a concentration of  $4.403 \times 10^{-3}$  g/ml. This solution was further diluted to give appropriate concentrations required in the experiments.

## RESULTS AND DISCUSSION

*Intensity of S<sub>2</sub> Emission*

The intensity of the S<sub>2</sub> emission varies with the flow-rate of hydrogen, and the influence of this flow-rate on the intensity ( $i_E$ ) of the molecular emission of S<sub>2</sub> is shown in Fig. 1. The intensity decreases with increasing flow-rate of hydrogen.

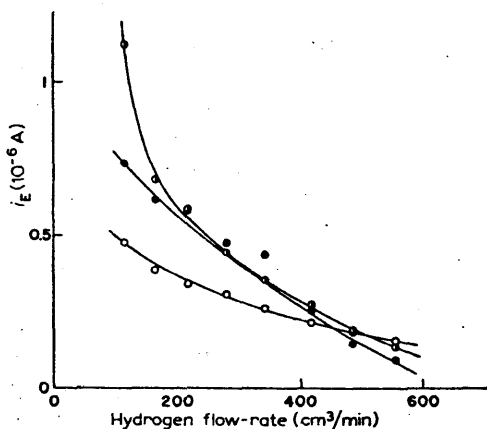


Fig. 1. Emission intensity of S<sub>2</sub> band for the following flame conditions: air flow-rate: ●: 107 ml/min, ◐: 140 ml/min, ○: 171 ml/min, flow-rate of di-*n*-butyl sulfide ( $f_S$ ):  $2.48 \times 10^{-8}$  mol/min.

The dependence of the emission intensity of S<sub>2</sub> on the concentration of the sulfur compound was measured for two flame conditions. The intensity is not linearly proportional to the concentration of di-*n*-butyl sulfide. The relationship between the intensity of the S<sub>2</sub> emission and the concentra-

tion of the sulfide,  $f_S$ , can be written as:

$$i_E = i_0 (f_S)^n \quad (1)$$

Both  $i_0$  and  $n$  are constant over a narrow concentration range under experimental conditions used.

Fig. 2 shows the plot of  $\log(i_E)$  against  $\log(f_S)$ .

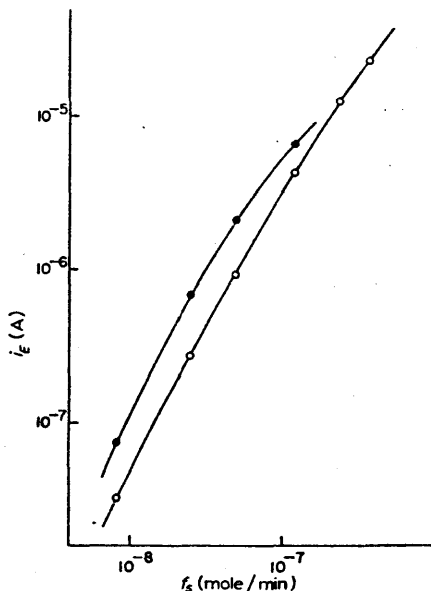


Fig. 2. Analytical curves for di-*n*-butyl sulfide,  $\log(i_E)$  vs.  $\log(f_S)$ , at flow-rates of air of 140 ml/min and hydrogen of 165 ml/min (●) and 417 ml/min (○).

$f_S$  is determined from the Eqns. in Ref. 25.

The relationship between the  $S_2$  emission intensity and the concentration of the sulfide is quadratic only at the lowest concentration; a plot of  $\log(i_E)$

against  $\log(f_s)$  is taken as linear over a narrow range and so the slope of the line can be represented by  $n$ . However, an almost first-order dependence of the emission intensity on the concentration of the sulfide is observed at concentrations higher than  $5 \times 10^{-8}$  mol/min at a flow-rate of hydrogen of 165 ml/min and higher than  $2 \times 10^{-7}$  mol/min at a flow-rate of hydrogen of 417 ml/min. The slope of the curve,  $n$ , at a flow-rate of hydrogen of 417 ml/min is steeper than that at 165 ml/min at the same concentration of di-*n*-butyl sulfide.

Fig. 3, which is taken from Fig. 10 in Ref. 8, calculated and redrawn, shows the time dependence of the emission intensity expressed as the  $S_2$  band emission intensity (3950 Å) versus distance from the reaction zone.

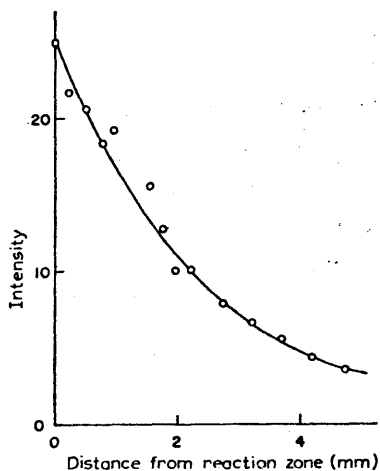


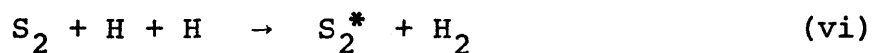
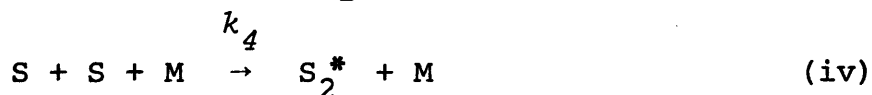
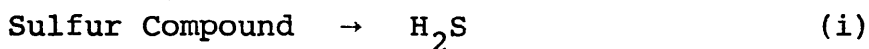
Fig. 3.  $S_2$  band emission intensity at 3950 Å.

Flame conditions:  $N_2:H_2:O_2 = 4:4.7:1$ . (This figure has been adapted from Fig. 10 by Sugden *et al*<sup>8</sup>.)

Figs. 1 and 5 in Ref. 9 suggest the dependence of the  $S_2$  emission on the concentration of sulfur atoms in an electrodeless radiofrequency discharge tube at reaction times of 0 and 0.208 sec, respectively. At zero reaction time, the intensity of emission obeys the relationship  $I = I_0 [H_2S]^2$ , where  $[H_2S]$  is the concentration of hydrogen sulfide added. However, at a fixed reaction time (0.208 sec), the  $S_2$  emission intensity does not increase appreciably when the pressure of the hydrogen sulfide is raised.

#### *Mechanism of Emission*

The processes involved in the molecular emission of  $S_2$  from sulfur-containing compounds are advanced as follows<sup>20</sup>



The emission in reaction vii contributes little to the over-all  $S_2$  molecular emission.

The concentration of sulfur atoms is given by



$$\begin{aligned}
 [S] &= K_2 K_3 \frac{[H_2S][H]^2}{[H_2]^2} \\
 &= K[H_2S]
 \end{aligned} \tag{2}$$

The rate of formation of the  $S_2$  species is given by

$$\frac{d[S_2]}{dt} = k_4 [S]^2 [M] \tag{3}$$

Then, the concentration of  $S_2$  for a reaction time of  $t$  sec is

$$[S_2](t) = \frac{aK}{2} \left( 1 - \frac{1}{2aKk_4[M]t + 1} \right) \tag{4}$$

where  $a$  is the initial concentration of the sulfur compound and  $[M]$  the concentration of the third body.

The emission intensity in a whole flame is

$$I_{S_2} = [S_2](t_0) \tag{5}$$

where  $t_0$  is the reaction time at the top of the flame. On the other hand, the intensity of emission in part of the flame at a reaction time of  $t$  sec is given by

$$I_{S_2}(t) = \frac{d[S_2](t)}{dt} \tag{6}$$

Hence,

$$I_{S_2}(t) = \frac{a^2 K^2 k_4 [M]}{(2aKk_4[M]t + 1)^2} \tag{7}$$

The theoretical intensity of  $S_2$  emission in the whole of a flame has been shown in Fig. 6 in Ref. 20 to be a function of the initial concentration of a sulfur compound. It agrees very closely with Fig. 2 in this paper. At flow-rates of hydrogen of 165 ml/min and air of 140 ml/min, the value of  $k_4$  calculated from the dependence of the emission on the concentration of sulfur atoms is  $10^{17} \text{ cm}^6 \text{ mol}^{-2} \text{ sec}^{-1}$  on the assumption that K and M are 1 and  $N_2$ , respectively. This value can be compared with rate constants for the combination of other atoms in a flame, e.g.,  $H + H + M$ ,  $H + OH + M$ ,  $N + N + M$ , etc.<sup>23</sup>.

Sugden *et al.*<sup>8</sup> showed that the molecular emission intensity of the sulfur species varies with the concentration of hydrogen atoms only. Comparing the emission intensity of  $S_2$  with that of SO measured by them, the decrease in the intensity of  $S_2$  species with the distance from reaction zone should be identical with SO according to their theory, but they are, in fact, entirely different. In the flame with an  $N_2 : H_2 : O_2$  ratio of 4 : 4.7 : 1 (Figs. 7 and 10 in Ref. 8), a 0.98-th order dependence of the  $S_2$  emission intensity on the concentration of hydrogen atoms is found, provided that the intensity of SO emission is proportional to the fourth power of the concentration of hydrogen atoms. These emissions, therefore, do not seem to follow the mechanism of Sugden *et al.*

The measurements and mechanism described by Fair and Thrush<sup>9</sup> have provided good expressions for the dependence of the  $S_2$  emission intensity on the concentration of sulfur atoms. However, the exper-

imental results cannot be completely represented by their mechanism.

Our proposed mechanism will now be applied to above spectrophotometric experimental results. Firstly, the theoretical dependence of the  $S_2$  emission intensity on the reaction time is shown in Fig. 4, derived from Eqn. 7. The dependences in

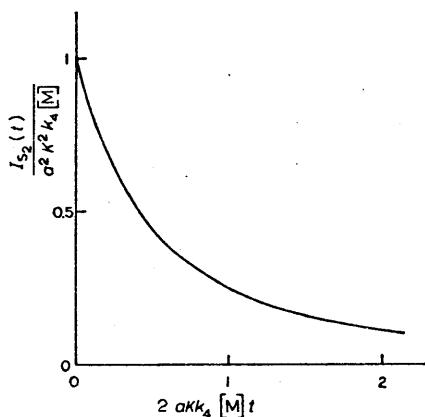


Fig. 4. Theoretical relationship between emission intensity and reaction time.

both Fig. 3 and Fig. 4 are similar. Furthermore, the emission intensity at zero reaction time ( $t = 0$  sec) is shown to be proportional to the square of the concentration of sulfur atoms by Eqn. 7.

Fig. 5 shows the concentration dependence of  $I_{S_2}(t)$  at a reaction time of  $t$  sec. These express satisfactorily the dependence of the molecular emission intensity of the  $S_2$  species from sulfur compounds on the concentration of sulfur atoms as measured by Fair and Thrush (Figs. 1 and 5 in Ref. 9).

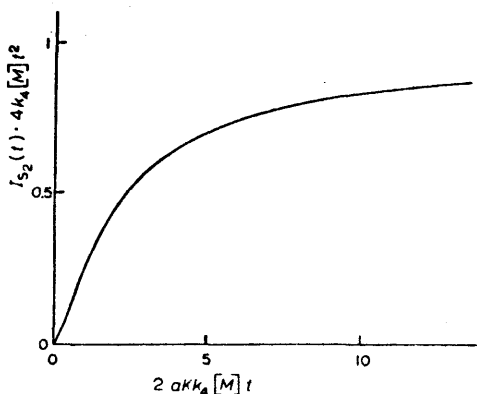
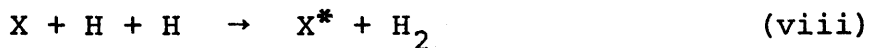


Fig. 5. Theoretical relationship between the  $S_2$  emission intensity at a reaction time  $t$  and the initial concentration of sulfur atoms  $a$ .

#### *Luminescent Radiation by Hydrogen Atoms*

The radicals present in a flame recombine if they can transfer their surplus energy to a third body in a triple collision. Such a recombination is possible in a collision with an atom in a hydrogen-rich flame:



where  $X^*$  represents an excited emitting species. The excited species lose its surplus energy in the form of a light quantum:



The emission of the  $S_2$  species can be compared with that of an atom of a metal such as sodium. The formation of a sodium atom is a much smoother reaction than that of  $S_2$ , because the latter involves

a three-body recombination (reaction iv). Therefore, the conversion of a sulfur compound into  $S_2$  will be vanishingly small compared with the conversion of a sodium salt into atoms. These emission species must be excited by the three-body collision with hydrogen atoms (reaction viii) in order to emit light. The emission of  $S_2$  after reaction viii, therefore, becomes much less in intensity than that of Na. However, the  $S_2$  emission process involves emission of light in reaction v, which is not attended by reaction viii (*i.e.*, reaction vi). Although the emission of sodium atoms follows according to reaction ix<sup>27</sup>, the emission of  $S_2$  in reaction vii is consequently presumed to contribute little toward the over-all  $S_2$  molecular emission.

#### CONCLUSION

The concentration and time dependences of  $S_2$  chemiluminescence provide good evidence that it is associated with the recombination of two sulfur atoms. It is considered that the bulk of the  $S_2$  molecular emission arises from the three-body recombination reaction. The rate of the recombination is too slow for equilibrium to be attained sufficiently rapidly and so it is the rate-determining step in the emitting process. It is therefore apparent how and why the response of the FPD to sulfur-containing compounds provides an extremely complex function of the concentration of sulfur compounds.

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