

The Analysis of Sulfur Compounds of Odorous Material in Kunsan Industrial Complex

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Abstract

In this study, we investigated the gas chromatography (GC) and pulsed flame photometric detection (PFPD) system for the analysis of four major reduced S compounds including hydrogen sulfide (H₂S); methyl mercaptan (CH₃SH); dimethyl sulfide (DMS); and dimethyl disulfide (DMDS) contained in environmental samples. To analyze these compounds in high concentration range (above ppb level), we developed a high mode analytical setting with the loop-injection system. By contrast, we also established a low mode setting for the analysis of low concentration samples (ppt-level samples from ambient air) by the combination with thermal desorption unit (TDU). Comparative analysis of both settings revealed that relative detection properties of four S compounds are systematic enough. The results of high mode analysis indicated that the patterns were systematic among compounds: H₂S exhibited the lowest sensitivity, while DMDS showed the strongest one. The results were also compared in terms of sensitivity reductions for all compounds by dividing slope ratios between low and high mode system. Although low mode system exhibited significant reductions on the order of a few tens times, their detection characteristics were highly consistent as it was shown in the high mode setting. To learn more about absolute and relative relations between two different modes of S analysis, future studies may have to be directed to cover more complicated nature of GC/PFPD performance. Hydrogen sulfide(H₂S) was over in summer about low level of olfactory sense 410 ppt, Methyl mercaptan(CH₃SH) was over in apring and summer about low level of olfactory sense 70, Dimethyl sulfide(DMS) was not over in four season about low level of olfactory sense 2,200 ppt. Carbon disulfide(CS₂) was not over in four deason about low level of olfactory sense 210,000, Dimethyl disulfide(DMDS) was not over in summer about low level of olfactory sense 2,000.

Keywords: Hydrogen sulfide, detection, malodor, PFPD detection, high mode, Low mode

Introduction

The operating technich of various air pollutants have been improving continuously. One of major odorous materials, improvement of measurement technich of reduced sulfur is encouragement. The classical measurement technich of these materials are flame photometric detector (FPD), pulsed UV fluorescence (PUVF), lead acetate tape (LAT), and The hyper sensitive measurement technich are sulfur chemiluminescence detector (SCD), pulsed flame photometric detector (PFPD).^{1,2}

Owing to these analytical method and technich using developed GC/PFPD, we can detect pg of H₂S, DMDS. But in environmental atmosphere, if these compounds is generally ppt in low level, we do not possible to detect components of these material. Therefore to solve analytical problem of low level sample, we use preconcentration method using thermal desorption unit(TDU).³

In this study, to estimate analytical performance according to processing method differentiation of GC system, we estimate to effect of detecting characterization about exchanged process method, TDU. And we examined source of sulfur compounds and examined precious investigation at surrounding area and source.

Materials and methods

1. Composition of analytical system : high level mode

We used GC system with PFPD (O.I. Co., Model 5380) to detect sulfur component⁴. In high level mode, we used loop injection method instead of direct sample injection to GC inlet. For this, we selected loop of proper dose (10, 50, 100, 250, 500 μ L), and composed indirect injection method with 6 rotary valve (Fig. 1).

2. Composition of analytical system : low level mode

To detect ppt level of sulfur, we composed online thermal desorption system (TDU-UNITY, Markes, LTD, UK) with GC/PFPD analytical system.

The UNITY on-line composed pump and Mass Flow Controller(MFC). In this system, for low temperature and concentration of sulfur component, we used trap with filling adsorber as Carbopack B and Silicagel. And we used Peltier cooling method at -15 $^{\circ}$ C instead of liquid nitrogen.

3. Process and standard of system

First, at high level mode, we handled with changing of 6 valve load and inject mode. And after adapting samples to loop in sampling mode, we set adapted sample transfer to inject mode. Second, at low level mode, we transmitted samples to cold trap in TDU directly, and then we induced cooling condensing of sulfur component.

The sensitivity of PFPD using pulse is more than 10~100 times to FPD. For component deliberation of analytical samples, we used DB-VRX (60m x 0.32mm, 1.8 μ m) column. And instrument condition related to analysis are as follows :

[1] Basic condition for both low and high mode analysis

Detector temp. of PFPD: 220 °C

Flow rate (ml/min): Air(1) = 10, Air(2) = 10, H₂ = 11.5, N₂ (Carrier) = 1.2

[2] Additional condition for low mode analysis only

Cold trap : low = -15 °C, high = 300 °C, hold time = 5.0 min

Outlet split : 5.0 ml/min (5:1 split ratio)

Flow path temp. : 80 °C

Results and Discussion

1. Detection characterization of high level mode

In Fig. 1, we showed detection result of standard samples concentration and loop area about 4 kinds of hydrogen sulfide series. And we excluded 10,000 ppb of standard sample because of off-scale at comparative thing.

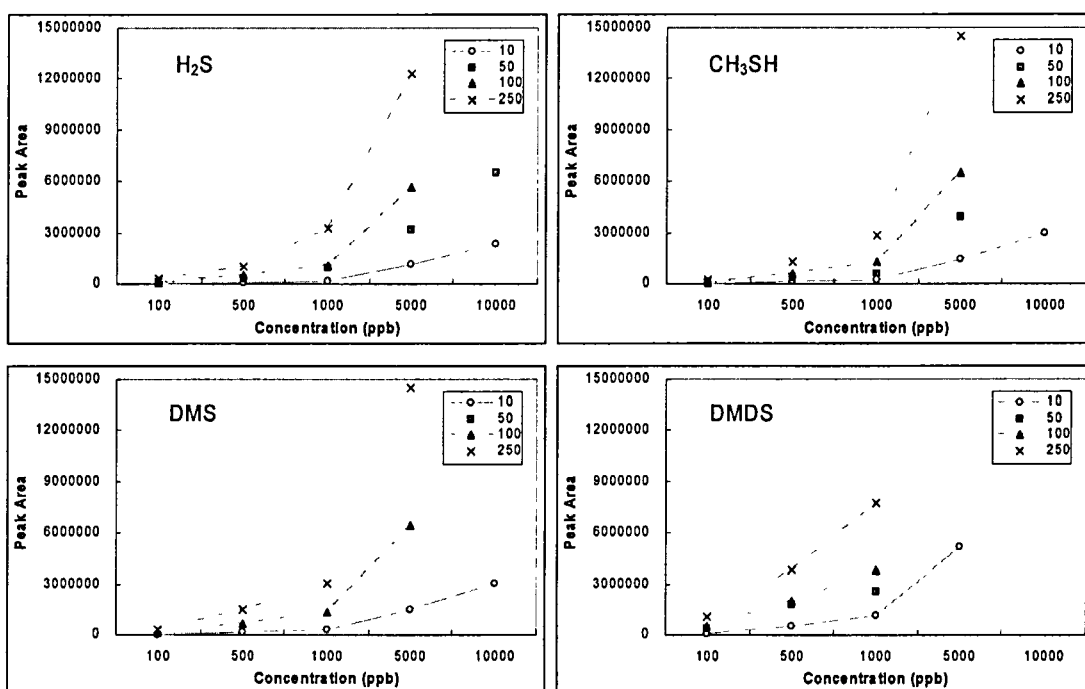


Fig. 1. Performance of high mode, loop-injection system: four different loops with the volume capacity of 10, 50, 100, and 250 µl, as shown as four different symbols, were used to analyze equimolar gaseous S standards prepared at five different concentrations of 100, 500, 1000, 5000, and 10000 ppb. Note that 50 µl results for DMS is not available.

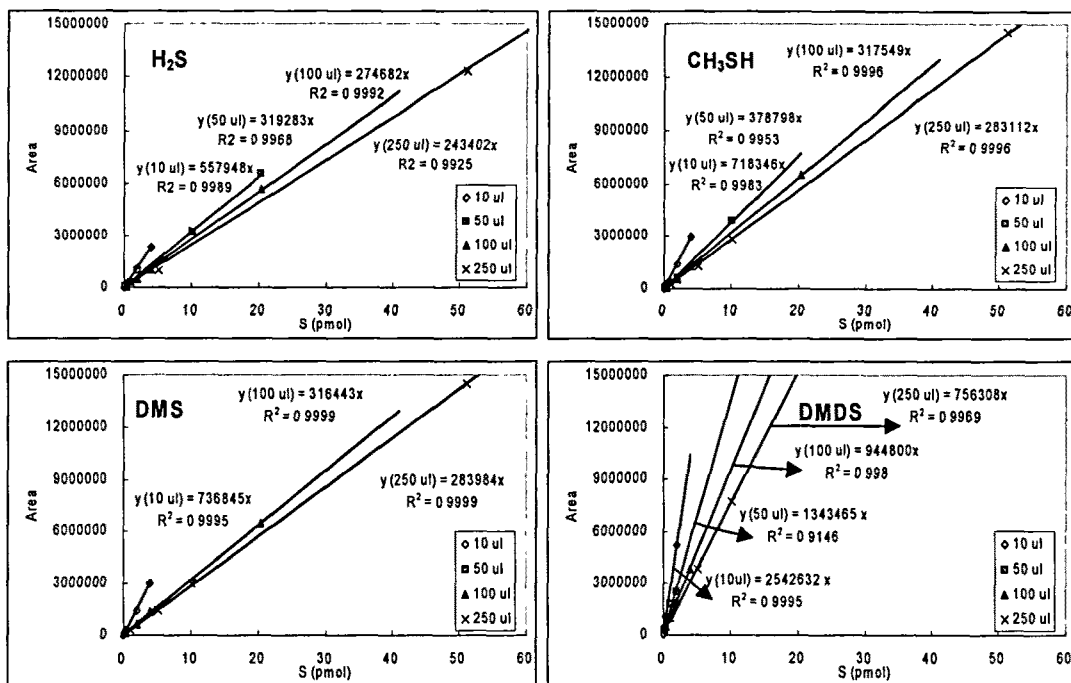


Fig. 2. Changes in GC/PFPD calibration slopes as a function of loop size capacity. All data shown in Fig 1 are modified to show relationships between absolute S injected (pmol) vs integrated area.

In Fig. 2, using same result showed Fig. 1, we showed results with changed method for compare differentiation of sensitivity. According to these comparison, we can find to corrective inclination at various view point. The summary of inclination are as follows: [1] There is differentiation of relative sensitivity continuously in 4 components. It is confirmed that slope of component are $H_2S < CH_3SH \sim DMS < DMDS$. [2] As the loop size is small, the slope of calibration curve is increased fastly, and the sensitivity of detection system was increased also. The slope of sensitivity increasing related to loop area confirmed 100 % continuously in all components. According to this study, as the volume of injection sample was increased, the shape and size of peak was thick and occurred to low sensitivity. In the case of H_2S , the slope of 250 μl loop was 243,400 and that of 10 μl was 557,950. And DMDS showed most high sensitivity. The slope of 250 μl loop was 756,310, and that of 10 μl loop was 2,542,630. The result of 10 μl loop, the slope of DMDS was 4.6 times to H_2S . Instead, the result of 250 μl loop showed most weak sensitivity, then the ratio of inclinations was 3.1. The slope of DMDS/DMS showed 2.7-3.5 times according to loop volume. Hydrogen sulfide was most reactive material, and that represents most low sensitivity. Instead DMDS, having two sulfur atoms, we think that the relative sensitivity of PFPD was higher than other mono sulfuric component.

2. Low level mode of detection characterization relative to high level mode

When we compare to the detection result of low concentration mode relative to high level mode, we can anticipate that the low sensitivity occurred distinguishly. But the size of calibration slope at low level mode, the differentiation of sensitivity of components showed $H_2S < CH_3SH < DMS < DMDS$.

In table 1, when we used 500 μ l at high level mode, the ratio of slope showed 18.5 (DMS, DMDS) to 43.9 times (H_2S). Instead, When we used 10 μ l at high level mode, the ratio of slope showed DMS (19.9) < CH_3SH (30.6) < DMDS (40.7) < H_2S (59.5). As a result, the declinnation of sensitivity of hydrogen sulfide was most high at high level mode. And also the process of low level mode declined the sensitivity 10 times over. But in spite of declined sensitivity, low level mode system depending thermal desorptor showed that the relative detection characterization maintained moderately over.

Table 1. Comparison of slope ratios between high and low detection mode.

Exp date	H_2S	CH_3SH	DMS	DMDS
A. Ratios using a high mode with the loop capacity of 500 μL				
04-8-27	36.8	23.6	16.9	22.6
04-9-5	51.0	26.8	20.0	14.4
Average	43.9	25.2	18.5	18.5
SD	10.1	2.29	2.14	5.80
B. Ratios using a high mode with the loop capacity of 10 μL				
04-1-09	58.4	29.6	15.1	27.9
04-5-8	63.1	28.8	23.2	55.8
04-9-23	57.1	33.5	21.4	38.4
Average	59.5	30.6	19.9	40.7
SD	3.14	2.52	4.27	14.1

3. Analysis of sulfuric compounds

We analyzed samples within 24 hr after sampling at 4 sites from April, 2004 to February, 2005. When hydrocarbon compounds with sulfur and phosphorus ignited in FID typed flame, it made component induced chemical radiation. Only some interval light wave of these lights with lightening filter arrived at lightening amplifier and transferred to electric circuit. And we detected sulfur to S_2 molecule and phosphorus to HPO molecule. And then we analyzed using GC/PFPD that it detects concentration induced chemiluminescence.

Conclusion

To understand analytical characterization of deoxidized sulfur being high level(source) and low level(environmental atmosphere), we estimated detecting characterization of GC/PFPD system about hydrogen sulfide, mainly 4 deoxidized sulfur compounds. We knew that deoxidized sulfur compounds showed detecting characterization regularly or anticipately. When we operate to high level mode showed basic detecting characterization, we found sensitivity differentiation within

components remarkably. Our result of calibration slope was $H_2S < CH_3SH \sim DMS < DMDS$, it reflected dose of sulfur in components. Related to high level mode system, low level mode system for analyzing low level sample showed sensitivity down notably. Because of the lose in system according to low level mode, after all it showed that sensitivity down occurred about 10 times over. But in the low level mode, the relative calibration tendency maintained between sulfur components continuously.

Analytical result in investigated area was Table 2 and Fig. 3. And Table 3 is the Name, measurement method, and low level of olfactory sense of odorous material. Number of analytical components of odorous material was hydrogen sulfide and 5 materials of sulfur series. Hydrogen sulfide(H_2S) were 51.5 ppt< in spring, 40.9 - 1683 ppt in summer, 52.7 - 109 ppt in fall, 92.7 - 223 ppt in winter by investigation sites. It was not over olfactory sense minimum perception level 410 ppt except summer. Methyl mercaptan(CH_3SH) were 19.0-106 ppt in spring, 66.0 - 135 ppt in summer, 6.9 - 23.2 ppt in fall, 9.22 - 23.9 ppt in winter by investigation sites. It was over olfactory sense minimum perception level 70 ppt in spring and summer. Dimethyl sulfide(DMS) were 440-1090 ppt in spring, 215 - 387 ppt in summer, 14.4 - 86.7 ppt in fall, 19.8 - 418 ppt in winter by investigation sites. It was not over olfactory sense minimum perception level 2,200 ppt during 4 season and all sites. Carbon disulfide(CS_2) were 537 - 841 ppt in spring, 1469 - 1736 ppt in summer, 73.2 - 257 ppt in fall, 330 - 438 ppt in winter by

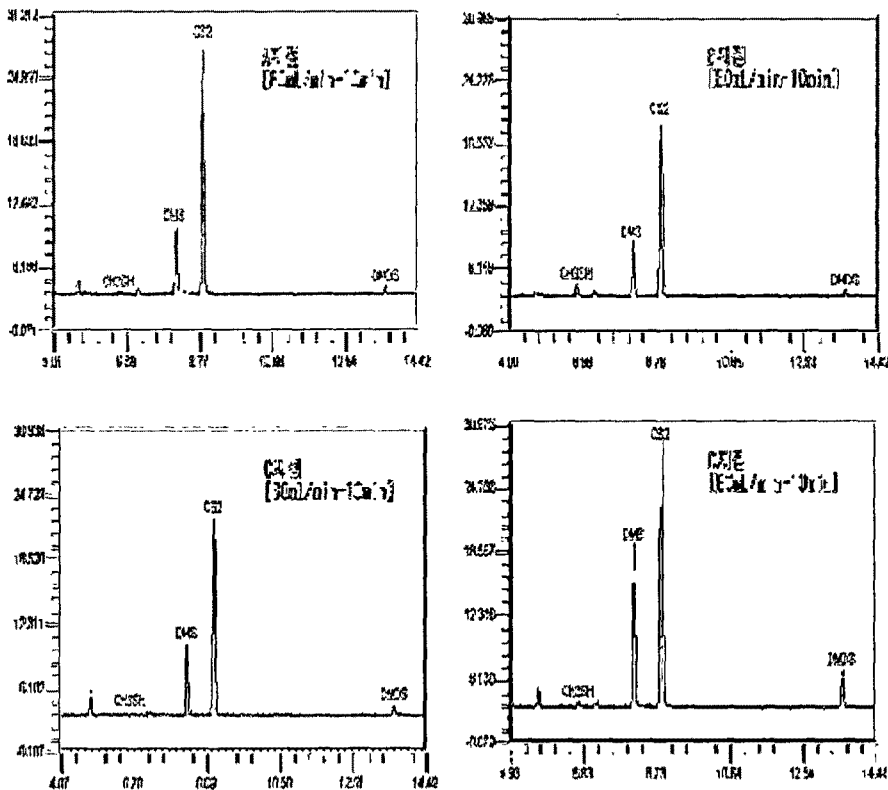


Fig. 3. Analytical results of sulfur compounds at 4 sites.

Table 2. The results of sulfur concentration at four sites by season.

Pollutants	M.N	A-1				A-2				A-3				A-4					
		Short Name	Unit	hongbosanup				nechodong				osikdodong				Incinerator company			
				1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th
H ₂ S	ppt	<51.5	168	66.2	122	<51.5	58.2	297	92.7	<51.5	40.9	109	120	<51.5	1683	52.7	223		
CH ₃ SH	ppt	19.0	135	14.2	23.9	106	66.0	23.2	14.6	35.6	74.3	6.9	9.22	43.5	66.9	7.3	22.5		
DMS	ppt	506	308	25.1	33 0	440	215	14.4	25.6	489	293	21.4	19.8	1090	387	86.7	418		
CS ₂	ppt	706	1605	73.2	438	537	1736	83.5	341	557	1469	257	386	841	1710	133	330		
DMDS	ppt	46.2	69.9	397	5.76	36.3	48.0	41.8	<1.79	58.5	229	69	6.33	225	41.1	<0.23	<1.79		

Table 3. Name, measurement method, and low level of olfactory sense of odorous material

	Pollutants	method	Pollutants	
	Short Name		Full name	Low level of olfactory sense
hydrogen sulfur and sulfur series	H ₂ S	GC/PFPD	Hydrogen sulfide	410 ppt
	CH ₃ SH	GC/PFPD	Methyl mercaptan	70 ppt
	DMS	GC/PFPD	Dimethyl sulfide	2200 ppt
	CS ₂	GC/PFPD	Carbon disulfide	210000 ppt
	DMDS	GC/PFPD	Dimethyl disulfide	2000 ppt

investigation sites. It was not over olfactory sense minimum perception level 210,000 ppt. And dimethyl disulfide(DMDS) were 36.6 - 225 ppt in spring, 41.1 - 229 ppt in summer, 0.23 - 397 ppt in fall, 1.79 - 6.33 ppt in winter by investigation sites. It was not over olfactory sense minimum perception level 2,000 ppt during 4 season and all sites.

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