

A Study on the Distribution Characteristics of Sulfur Compounds in Ambient air using Continuous Monitoring Method in Incheon Area

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Abstract

This paper focuses on the applicability of a continuous monitoring method on trace sulfur compounds in the ambient air by TD and GC/PFPD. The target compounds for monitoring include H₂S (hydrogen sulfide), Methyl mercaptan, Dimethyl Sulfide, and Dimethyl disulfide. The result of QA/QC on monitoring instruments satisfies all the standards of Odor Measurement and Analysis Method, showing that the reproductivity of the compounds by concentration is within 10%, linearity is above 0.98 of a correlation coefficient, method detection limit is 0.16 ppb by MM standard, and recovery rate is over 70%. Monitoring was conducted for two years from March 2006 to February 2008. As a result of the monitoring, the average concentration of H₂S was 0.08 ppb, with the maximum concentration at 16.15 ppb. The result indicates that it is reasonable to do continuous monitoring as there appears a spontaneous event of high concentration by the condition of the site during monitoring odor-causing substances. Therefore, it is suggested that the continuous monitoring method used in this paper is appropriate to identify the characteristics of sudden occurrence and concentration variations of sulfur compounds.

Keywords: Odor, Sulfur compounds, Hydrogen sulfide, TD (Thermal Desorption), GC (Gas Chromatography), PFPD (Pulsed Flame Photometric Detector), QA (Quality Assurance), QC (Quality Control)

1. Introduction

Bad odor is defined as smell that gaseous stimulating substances including hydrogen sulfide, mercaptan, and amine stimulates human olfactory sense, presenting displeasure and aversion. Sulfur compound such as hydrogen sulfide is classified as defined malodorous substance under regulation and control^[1]. Sulfur compound is cause of bad odor of rotting eggs, and is known to come from industries such as petroleum refining facility, wood pulp facility, and sewage and human waste treatment facility^[2]. Discharged substance of sulfur series exists in ambient air as very small amount of tens or hundreds pptv^[3]. Such substance of sulfur series is known to have low intoxication concentration and great influence on bad odor^[4]. In addition, it is volatile and reactive; it disappears in short time after discharge

to atmosphere, unable to measure. Thus, it is difficult to be continuously observed and managed.

As large number of observative researches is under progress with recent development of technique to measure sulfur compound, high-sensitive detection devices such as Pulsed Flame Photometric Detector (PFPD) are introduced. It is, however, difficult to directly measure sulfur compound that exist with small amount in atmosphere. Therefore, low-temperature concentrating thermal desorption device that can enriched with micro amount of sulfur compound is utilized a lot recently^[5,6]. In case that there is moisture in sulfur compound when sampling for instrumental analysis, however, it reduces or interrupt adsorption capacity of sorbent tube, and causes unstable retention time or baseline of analysis chromatography^[7]. For measurement and analysis of various sulfur compounds, various systems shall be come together, and this causes more errors in sampling and analysis steps. Thus, influence and quality control for analysis instruments is important^[8].

This study is based sulfur compound auto sequential measurement method of Odor Analysis Method, uses Thermal Desorption (TD) system to concentrate sulfur

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compound in low temperature, and uses Gas Chromatography system with PFPD to detect sulfur compound with high sensitivity. In addition to minimize the influence of moisture, moisture dryer is used in front-end of thermodesorber^[9].

This study has evaluated field application possibilities four types of sulfur compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) through quality control and sequential measurement of auto sequential measurement method.

2. Research Contents and Method

The objects of research are hydrogen sulfide, (H_2S), methyl mercaptan(CH_3SH), dimethyl sulfide(CH_3SCH_3), dimethyl disulfide(CH_3SSCH_3), etc., which are typical sulfur series classified as defined malodorous substance. The location is Seo-gu of Incheon where large waste landfill with possibly great amount of discharge of sulfur compound. In consideration that the measurement instrument used in this study is difficult be exposed to external environment, and installation of electricity and gas facility, the instrument is installed and operated in container located about 1km eastward from south of waste landfill (Fig. 1). The period of measurement is two years from March 2006 to February 2008. For measurement of sulfur compound in ambient air, mois-

ture dryer is used to remove moisture by primarily electric cooling system. Sample without moisture is concentrated with coldtrap of thermadesorber (thermal desorption, SPIS TD-3000, Donam instrument). The coldtrap is self produced using silica gel. Sample is concentrated in $-25^{\circ}C$, and it is sampled in 25 mL/min for 20 minutes. Concentrated sample heated up to $250^{\circ}C$ and desorbed by pressure reducing with syringe pump for better desorption efficiency. Desorbed sample is injected with GC through 100 μ L loop. Analysis instrument is GC/PFPD(DS 6200, Donam instrument, Korea) system attached with PFPD (Model 5380, O.I. detector was used for its appropriateness to analyze tiny amount of sulfur compound. Sulfur compound is separated by BP-1 column($50\text{ m}\times 0.32\text{ mm}\times 5\text{ mm}$). Detailed analytical conditions are presented in Table 1.

3. Results and Discussion

3.1. Quality Control

Assay reproducibility is measured for three times with standard sample of three substances with difference concentration (1, 2, and 5 ppb) (Table 2). Reproducibility with respective concentration has shown good result of under 10% of relative standard deviation (RSD) for overall object substances; the result of experiment is presented in Table 2. Only, in case of low mol-

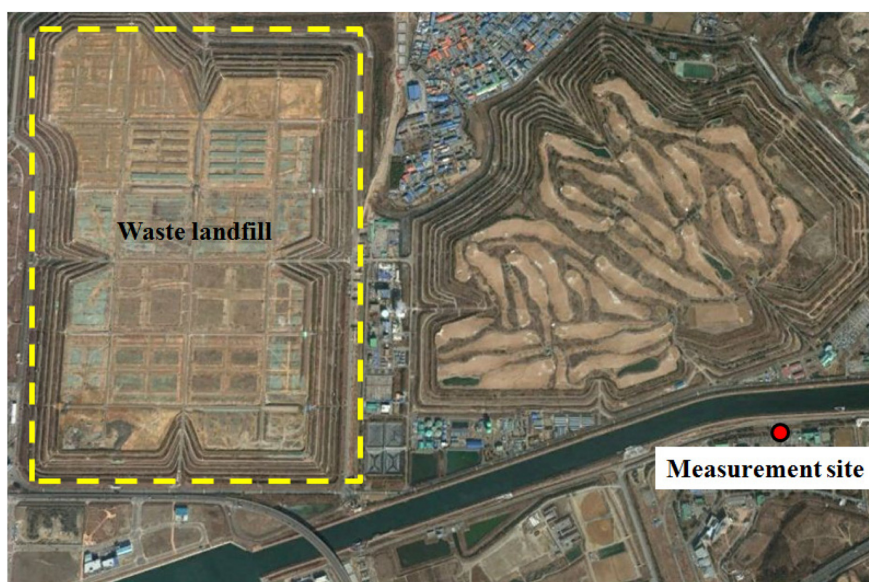


Fig. 1. Waste landfill and observation site in Incheon.

Table 1. Experimental condition of TD and GC/PFPD

TD condition		GC condition		
adsorbent	silica gel	column	BP-1 (50 m×0.32 mm×5 μm)	
sampling flow, time	25 mL/min, 20 min	oven	ramp	tamp. hold time
cold trap low temp.	-25°C	temp.	initial	70 4 min
desorption temp,	temp.	syringe pump	ramp 1	200 6.5 min
syringe pump flow	-25°C		(20°C/min)	
	-25~50°C	1 min(2 mL/min)	ramp 2	200 4.5 min
	50~250°C	1 min(1 mL/min)	Total	15 min
		1 min(2 mL/min)	PFPD condition	
column injection	100 μL		temp.	250°C
			H2	11.5 mL/min
			Air 1, 2	10 mL/min
			PMTvolt.	620

Table 2. Precision and Method detection limit of sulfur compounds

	hydrogen sulfide	methyl mercaptan	dimethyl sulfide	dimethyl disulfide
STD 1 ppb RSD(%)	10.0	5.3	1.1	0.9
STD 2 ppb RSD(%)	1.5	0.9	2.2	1.0
STD 5 ppb RSD(%)	9.9	0.3	0.5	0.3
R ²	0.998	0.999	0.999	0.986
MDL (0.5 ppb)	0.22	0.16	0.15	0.04

ecule such as hydrogen sulfide and methyl mercaptan, reproducibility was relatively low in concentration. Result of reproducibility during retention time (RT) was under RSD 0.1% for all four substance; reproducibility for RT is quite stable.

Linearity test is done with standard substance of 1~10 ppb concentration. As the result of calibration, coefficients of determination (r^2) for four types of sulfur compounds were hydrogen sulfide 0.998, methyl mercaptan 0.999, dimethyl sulfide 0.999, and dimethyl disulfide 0.986, which satisfy condition over 0.98 offered by Odor Analysis Method.

Method detection limit (MDL) regulates methyl mer-

captan under 0.2 ppb in odor analysis method^[9]. This study has obtained method detection limit for concentration that has been from seven analysis based on standard sample of 0.5 ppb. The detection limit of methyl mercaptan in detection limit presented in Table 2 is 0.16 ppb, which satisfies standard of odor analysis method.

In order to measure recovery of sample for the cold-trap of thermal desorption device, standard sample was analyzed with different injection method. Standard sample diluted by 200 ppb is directly injected into loop, the last injection device of thermal desorption system, using syringe (Table 3(1)). The amount injected into loop is

Table 3. Recovery test of sulfur compounds

	Area average			Recovery (%) (2)/(1)	Recovery (%) (3)/(1)
	(1) 200 ppb 5 mL direct injection	(2) 200 ppb 5 mL TD injection	(3) RH 80%+200 ppb 5 mL TD injection		
hydrogen sulfide	761.79	632.29	558.84	83.0	73.4
methyl mercaptan	811.60	806.72	646.68	99.4	79.7
dimethyl sulfide	929.41	894.68	875.93	96.3	94.2
dimethyl disulfide	1959.26	1949.72	1687.46	99.5	86.1

100; it is level of 2 ppb if converted to actual concentration in atmosphere. Standard sample of same concentration is injected into cold-trap of thermal desorption device and analyzed for measurement of recovery factor (Table 3(2)). In addition, in order to find recovery rate due to influence of moisture, sample of same concentration including 80% moisture is injected into coldtrap and analyzed (Table 3(3)).

The result of recovery rate is presented in Table 3. As

the result, the recovery rate is 83~99% without moisture. With moisture of 73~94%, the recovery rate is somewhat lower. It satisfies suggestion by odor analysis method : over 80% recovery rate for H₂S and 60% recovery rate for relative humanity 80%.

3.2. Field Measurement Result

The analysis result for overall measurement period is presented in Table 4. For data treatment for overall data,

Table 4. Summary of concentration of sulfur compound in this study (Mar. 2006~Feb. 2008)

06.03~07.02	hydrogen sulfide	methyl mercaptan	dimethyl sulfide	dimethyl disulfide
mean (ppb)	0.06	0.02	0.05	0.03
S.D (ppb)	0.51	0.13	0.16	0.12
max (ppb)	16.15	2.2	2.09	2.25
detection frequency (%)	3.99	2.25	14.53	12.17
07.03~08.02	hydrogen sulfide	methyl mercaptan	dimethyl sulfide	dimethyl disulfide
mean (ppb)	0.11	< 0.01	< 0.01	< 0.01
S.D (ppb)	0.70	< 0.01	0.04	0.01
max (ppb)	14.54	< 0.01	1.16	0.23
detection frequency (%)	3.63	< 0.01	0.64	0.14

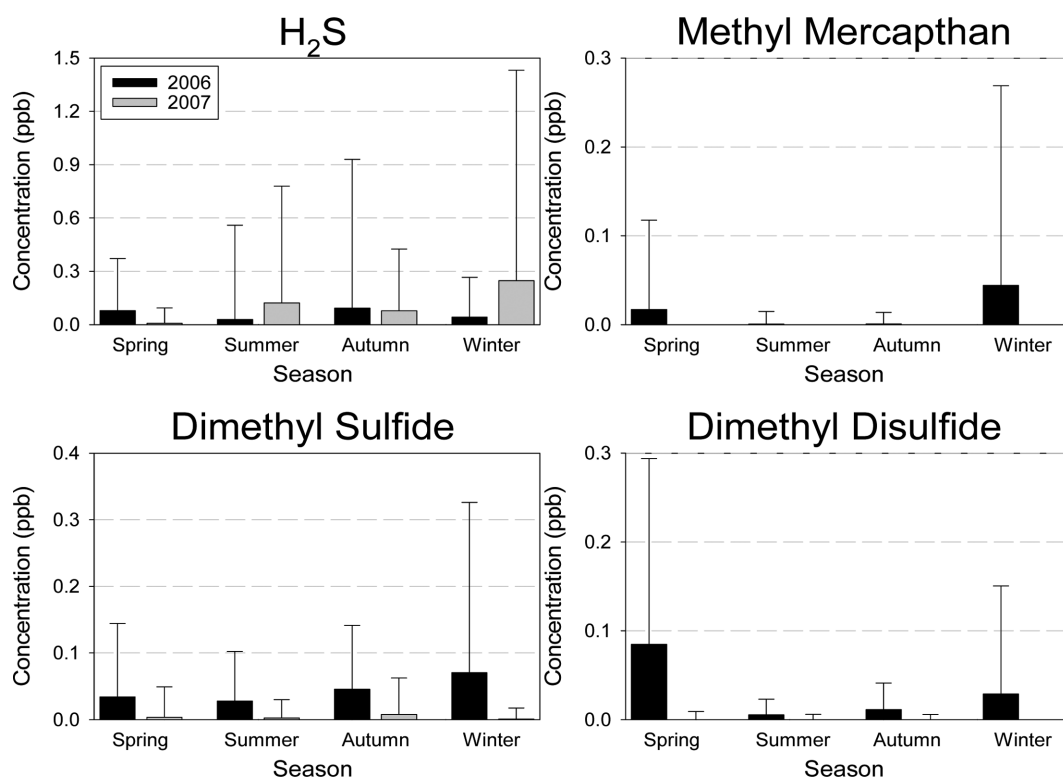


Fig. 2. Seasonal variation of sulfur compounds.

undetected data is considered and treated as 0. average concentration of hydrogen sulfide, typical one of sulfur compounds, was researched to be 0.006 ppb in 2006 and 0.11 ppb in 2007, and detection frequency was relatively similar frequency of respectively 3.99% and 3.63%. Substance other than hydrogen sulfide has shown high concentration and detection frequency of 2006. Unlike 2006 that showed detection frequency of 2.25~14.53%, it was under 1% lower in 2007. Concentration distribution by season for sulfur compounds is shown in Fig. 2.

Overall substances did not show clear changing aspect seasonally; rather, change by measuring year was large. Concentration of hydrogen sulfide in summer and fall was relatively high both in 2006 and 2007, and it was the highest in winter of 2007. Substances other than hydrogen sulfide was somewhat high concentration in spring and summer of 2006; however, the concentration

rapidly decreases in 2007. Thus, it was unable to find seasonal property change of reclaimed waste or generated irregularly.

The monthly variation of concentration for hydrogen sulfide, the major substance that cause bad odor among sulfur compounds, in Fig. 3. Generally detected concentration was high in summer of 2006, and summer and winter of 2007; deviation of concentration during this period was large as well. Overall discharging characteristic of H₂S was not influenced by seasonal effect, and detection characteristic was also irregular. Such result indicates that it is typical substance causing bad odor.

Hourly variation of overall data for hydrogen sulfide is presented in Fig. 4. While seasonal or monthly variation of concentration did not show development of change, hourly variation showed evident difference. The time zone with highest concentration of hydrogen sulfide was 5~6 right before sunrise and 20~21 right after sunset. Generally concentration was higher in night than in day.

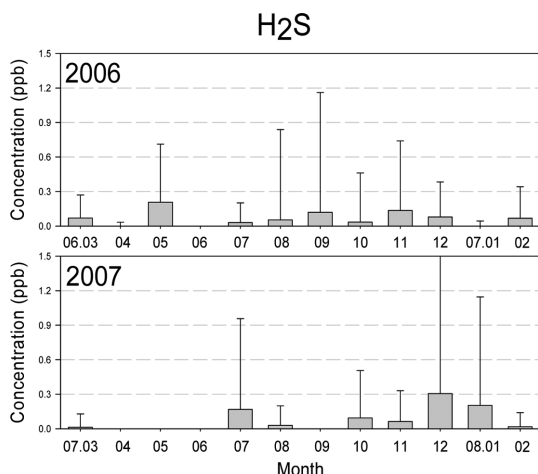


Fig. 3. Monthly variation of Hydrogen sulfide Concentration.

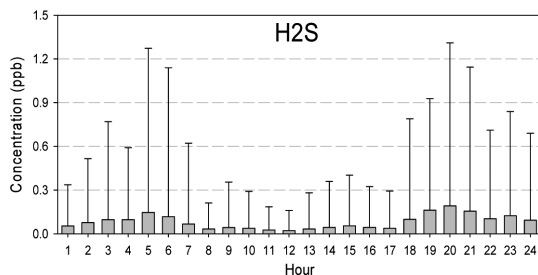


Fig. 4. Hourly variation of hydrogen sulfide concentration.

3.3. Analysis Result on Weather

In general, weather factors are important in dispersion of bad odor. Especially atmospheric stability, wind velocity, wind direction, temperature, relative humidity, sun's radiation, mixing height, etc. are known as most important factors. This study has studied the relationship of realtime measured weather data with hydrogen sulfide and dimethyl sulfide, which are malodorous substances with high frequency.

Concentration frequency and level by wind direction for hydrogen sulfide and dimethyl sulfide, the object malodorous substances, is presented in Fig. 5, using open air (D. Carslaw, 2011) of R statistics package. Hydrogen sulfide showed the highest frequency at 75°~105°, and the highest average concentration level at 225°~255°. Dimethyl sulfide is similar to hydrogen sulfide; however, it showed the highest frequency at 105°~135° and highest average concentration level at 225°~255°. For wind direction, hydrogen sulfide and dimethyl sulfide showed the highest frequency at 75°~135° and highest concentration level at 225°~285°.

Frequency and average concentration of hydrogen sulfide and dimethyl sulfide for wind velocity are shown in Fig. 6. Malodorous substances are similar to existing result of studies in inverse correlation. The

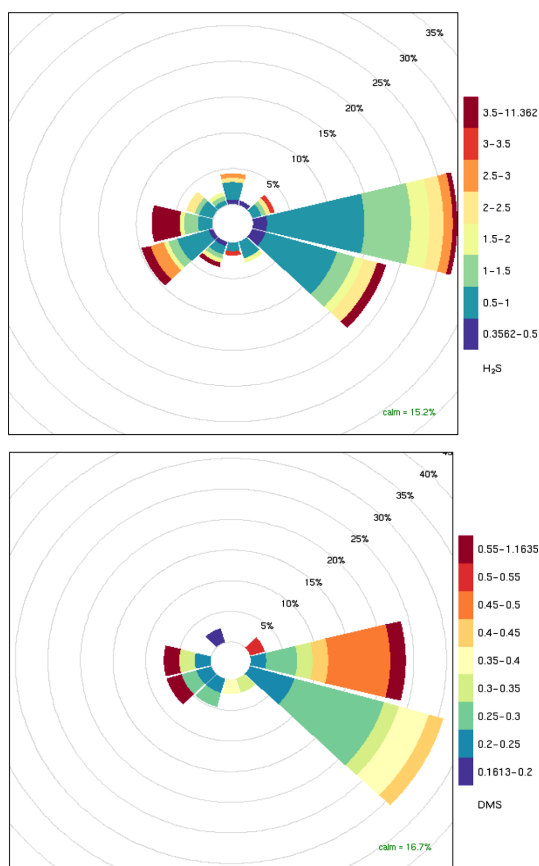


Fig. 5. Pollution rose of hydrogen sulfide (up) and dimethyl sulfide (down).

highest average concentration for hydrogen sulfide was 1.5~2.0 m/sec, and for dimethyl sulfide was 1.0~1.5 m/sec; frequency was highest at 0~0.5 m/sec.

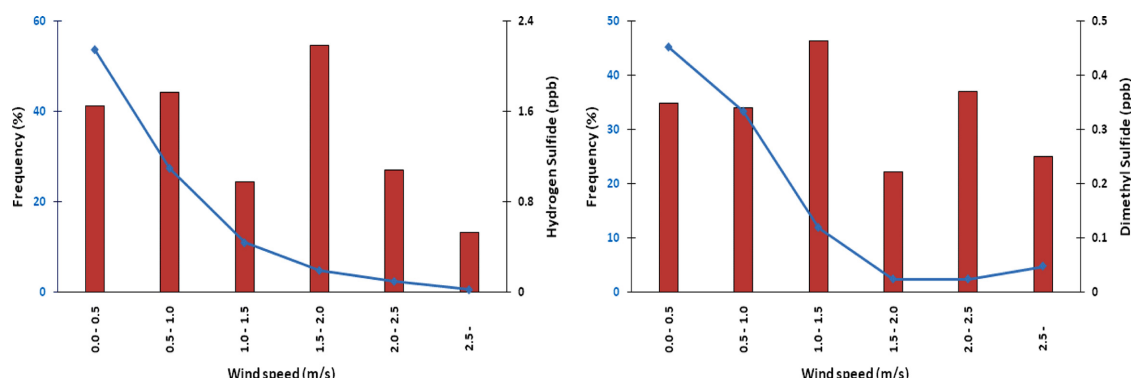


Fig. 6. Average concentration of hydrogen sulfide and frequency at various wind speed (left), average concentration of dimethyl sulfide and frequency at various wind speed (right).

4. Conclusion

This study uses TD and GC/pulsed flame photometric detector for four types of sulfur compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide) with micro amount in atmosphere; it is result of evaluation of field application possibility through quality control and continuous measurement of auto sequential measurement method at Seo-gu, Incheon, where large source of bad odor, for two years.

As the result of performance evaluation of analysis device, reproducibility of peak area was under 10%, and reproducibility of RT was under 0.1%. The result of linearity test based on reproducibility was over 0.98. method detection limit was 0.16 ppb based on methyl mercaptan. Recovery rate without moisture was 83~99%, and with 80% moisture was 73~94%. The overall result for quality control for device seems to satisfy suggestion by odor analysis method.

Monitoring hydrogen sulfide for 2 years resulted concentration detection frequency relatively similar for both 2006 and 2007; for others, detection concentration and frequency rapidly decreased in 2007, suggesting change in property of odor source. While seasonal or monthly variation of major malodorous substance, hydrogen sulfide, was quite irregular; however, dawn and night time showed the highest concentration.

As the result of analyzing concentration and frequency with weather factors, hydrogen sulfide and dimethyl sulfide showed highest frequency at 75°~135°, and highest concentration level at 225°~285°. The highest average concentration of hydrogen sulfide was at

wind velocity of 1.5~2.0 m/sec, and dimethyl sulfide was at 1.0~1.5 m/sec, indicating influence from source near measurement point.

Since malodorous substance shows irregular occurrence and generation of momentary high-concentration, field measurement requires long-term continuous measurement as the result of performance test of auto sequential monitoring system in this study, it is found to be appropriate for continuous measurement on sulfur compound; continuous measurement seems to provide consistent monitoring and systematic management for sulfur compound.

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