APPLICATION NOTE

Gas Chromatography

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Determination of Sulfur Compounds in Air by Online TD-GC/FPD

Introduction

With the continual development of urbanization and industrialization, the effect of malodor pollution is more and more serious, and is regarded as one of the seven social effects of pollution. The major odor pollutants in air come from municipal solid waste treatment, waste water treatment, livestock and poultry and industrial manufacturing processes. The major odor pollutants are sulfur compounds, phenols, aldehyde compounds, organic amines, organic acids and organic solvents. Among these compounds, sulfur compounds possess the lowest odor threshold concentrations and are extremely toxic to people which can lead to serious safety and environment problems.

The European and American Standards (EN13725:2003 and BSEN 13725, 2002) are applicable to the measurement of odor concentration, using dynamic olfactometry with a panel of human assessors, while the triangle odor bags method is widely used in Japan (Yoshio, 2004)[1,2]. In 1993, the Chinese government issued "emission standards for odor pollutants" (GB14554-93) which summarized air quality requirements and standardized methods and calculation of results[3]. In these methods, the instrument measurement method can determine the odorific components and their exact concentration which plays a very important role in monitoring and governance of odor pollution sources.

A new method targeting eight sulfur compounds in air using a TurboMatrix on-line 300 thermal desorber (TD) and analyzed by a PerkinElmer Clarus® 580 gas chromatography (GC) flame photometric detector (FPD) is introduced in this study. Results indicate that this method has good linearity, precision and detection limits.

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Experimental

PerkinElmer Clarus 580 GC/FPD with TurboMatrix™ on-line 300 TD was used to perform these experiments with the conditions presented in Table 1. The Thermal Desorption transfer line was directly connected to a PerkinElmer Elite 5 column (60 m x 0.32 mm x 3 µm). An instrument timed event was added in the method to change the attenuation of FPD from -6 to -3 between the peak of ethanethiol and dimethyl sulfide in order to avoid signal saturation at higher concentrations for some compounds.

An air monitoring trap was used in this study to concentrate the target compounds. Of the air monitoring trap contains two layers of sorbents as shown in Figure 1. The weak adsorbent (graphitized carbon black) is toward the sample entrance/exit and the strong adsorbent (carbon molecular sieve) is behind the weaker one. The heavier components are adsorbed onto the weak sorbent while the lighter components are adsorbed onto the strong sorbent. This design prevents the irreversible adsorption of heavier compounds and leaves the trap clean after one desorption cycle.

Table 1. Analytical parameters.

Thermal Desorber Parameters		GC Parameters	
Sampling Time	20 min	Initial Oven Temp	50 °C
Pump Flow	50 mL/min	Oven Hold	2.0 min
Mode	Online	Ramp	15 °C/min
Concentrator Trap Low	-30 °C	2nd Oven Temp	200 °C
Concentrator Trap High	300 °C	Oven Hold	5.0 min
Concentrator Trap Hold	5.5 min	FPD Temp	280 °C
Concentrator Trap heating rate	40 °C/min	PMT Voltage	80%
Valve Temp	220 °C	Air Flow	95 mL/min
Transfer line Temp	220 °C	H^2 Flow	70 mL/min
Column Pressure	18 psi		
Inlet split	OFF		
Outlet split	4 mL/min		

Eight sulfur compounds were investigated as shown in Table 2. Calibration gas mixtures were purchased from Dalian special gases Co., Ltd and diluted by dynamic diluter (CMK).

Results and Discussion

The chromatogram of a calibration standard (Figure 2) shows baseline resolution of the selected compounds. Of the eight sulfur compounds, methanethiol and ethanethiol are easily

Table 2. Calibration points employed in this study.

Compound Name	Level1 (µg/m^3)	Level 2 (µg/m^3)	Level 3 (µg/m^3)	Level 4 (µg/m^3)
Methanethiol	1.00	2.50	5.00	12.50
Ethanethiol	1.00	2.51	5.02	12.55
Dimethyl sulfide	1.00	2.49	4.98	12.45
Carbon disulfide	0.99	2.48	4.97	12.42
Methylthioethane	0.99	2.48	4.95	12.38
Thiophene	0.99	2.49	4.97	12.43
Diethyl sulfide	0.98	2.45	4.89	12.23
Dimethyl Disulfide	1.03	2.58	5.16	12.91

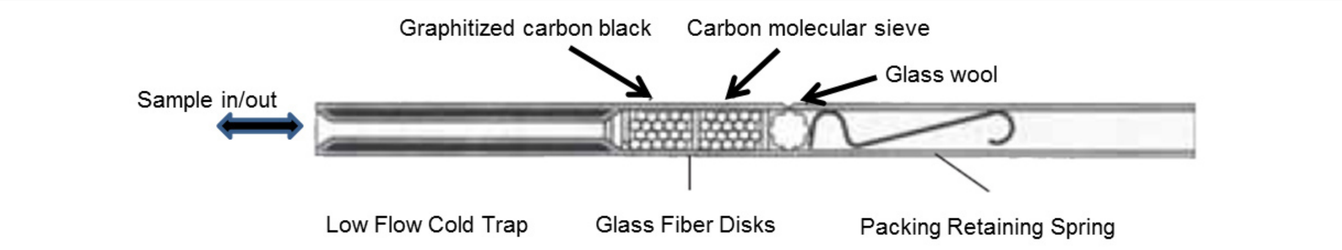

Figure 1. TurboMatrix Air Monitoring Trap.

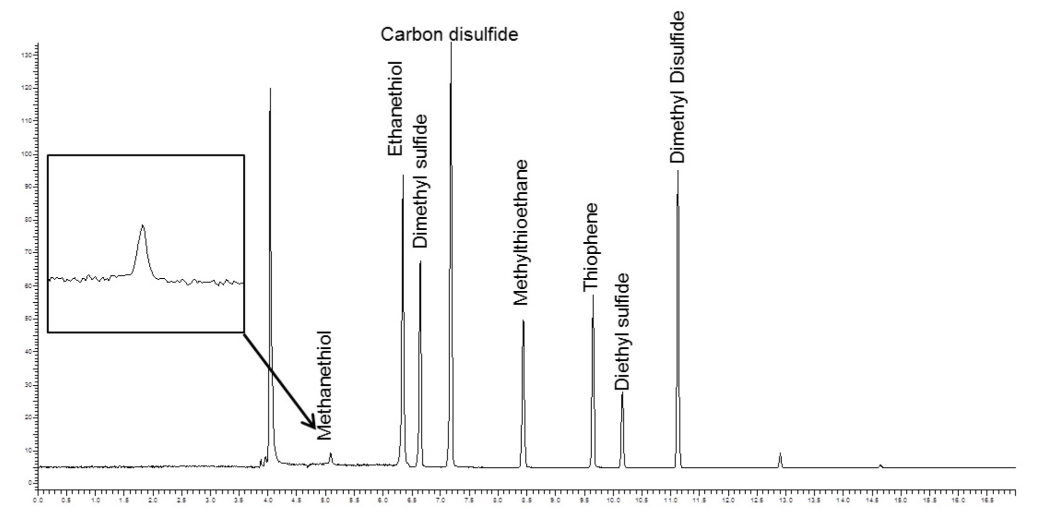

Figure 2. Chromatogram of eight sulfur compounds with 5.00 µg/m^3 of Methanethiol, 5.02 µg/m^3 of Ethanethiol, 4.98 µg/m^3 of Dimethyl sulfide, 4.97 µg/m^3 of Carbon disulfide, 4.95 µg/m^3 of Methylthioethane, 4.97 µg/m^3 of Thiophene, 4.89 µg/m^3 of diethyl sulfide and 5.16 µg/m^3 of Dimethyl Disulfide.

adsorbed on the internal plumbing because of the thiol (–SH) group. The response of methanethiol is lower than other sulphur compounds on the FPD and two adjustments were therefore made to minimize the adsorption of these analytes. Shortened plumbing and materials with low adsorption were used in this study to create a beautiful peak profile. The methanethiol peak is also shown in Figure 2 with symmetric profile and high sensitivity.

Tables 3 and 4 summarizes the results for precision, linearity, method detection limits (MDLs) and quantitation limits (MQLs). The determination coefficients (r^2) of all compounds were over 0.9981, showing the reliability of the analysis.

Table 3. Results for linearity.

Compound Name	Linearity	
	Calibration Curve	r^2
Methanethiol	$Y=931.04X^2+1976.58X+4189.14$	0.99985
Ethanethiol	$Y=-5766.25X^2+87824.19X-20849.65$	0.99959
Dimethyl sulfide	$Y=12633.98X^2+24153.29X+40684.54$	0.99905
Carbon disulfide	$Y=44588.84X^2+87297.71X+82464.34$	0.99935
Methylthioethane	$Y=24975.68X^2+10736.23X+27697.44$	0.99989
Thiophene	$Y=42709.08X^2-18984.82X+61694.52$	0.99998
Diethyl sulfide	$Y=16384.08X^2+2279.01X+9960.55$	0.99993
Dimethyl Disulfide	$Y=109146.55X^2-121767.31X+174855.08$	0.99853

Method detection limits were determined by analyzing seven replicate samples at 1 μg/m^3. Reporting limits are calculated using a 1 liter sample volume. Precision was measured by analyzing six replicates at 5 μg/m^3.

Table 4. Results for precision, MDL and MQL.

Compound Name	RSD%	MDL (μg/m^3)	MQL (μg/m^3)
Methanethiol	2.82	0.419	1.675
Ethanethiol	3.07	0.131	0.524
Dimethyl sulfide	2.21	0.058	0.232
Carbon disulfide	2.16	0.058	0.232
Methylthioethane	2.66	0.064	0.258
Thiophene	2.30	0.069	0.275
Diethyl sulfide	2.15	0.075	0.301
Dimethyl Disulfide	2.32	0.084	0.335

The determination of sulfur emissions from stationary sources was established in EPA method 15 and 16 (Method 15, Method 16 USEPA)[4,5]. A gas sample is collected from the emission source and diluted with clean dry air (if necessary) with an aliquot analyzed by GC/FPD. The MDLs of selected sulfur compounds using EPA method 15, EPA method 16 and the method in this study were shown in Table 5. The MDLs obtained using the method in this study were far lower than those using other methods.

Measurements of Sulfur Compounds in Petrochemical Industry Zone

On-line monitoring of sulfur compounds in air was performed using a PerkinElmer TurboMatrix on-line 300 TD - Clarus 580 GC/FPD at a chemical industry park in Shanghai, China. The chromatogram of an air sample collected at 12:46:16 on Sept. 30 in 2016 is shown in Figure 3. The peak of Carbon disulfide is shown while the other compounds were not detected in the air sample. The change in concentration of Carbon disulfide is shown in Figure 4 with continuous monitoring from Sept. 30 to Oct. 8, 2016.

Table 5. MDL of sulfur compounds using different methods.

Method name	Sample Volume	Unit	Methanethiol	Dimethyl Sulfide	Dimethyl Disulfide	Carbon Ddisulfide
EPA Method 15	0.1 ml	ppb	-	-	-	500
EPA Method 16	10 ml	ppb	50	50	50	-
In this study	1 L	ppb	0.195	0.027	0.039	0.027

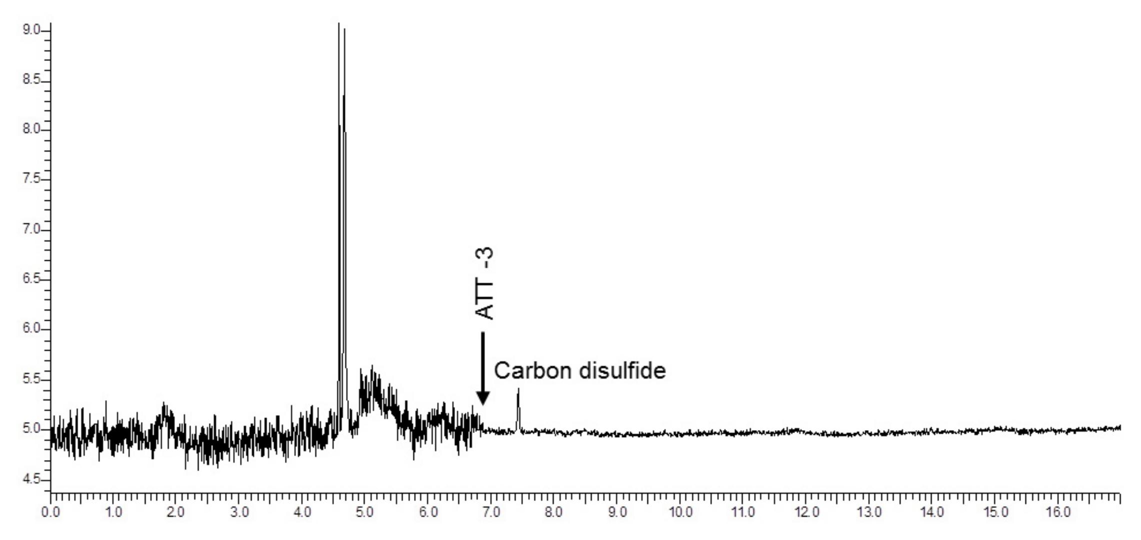

Figure 3. Chromatogram of sulfur compounds in air at 12:46:16 on Sept. 30 in 2016 at a chemical industry park in Shanghai, China.

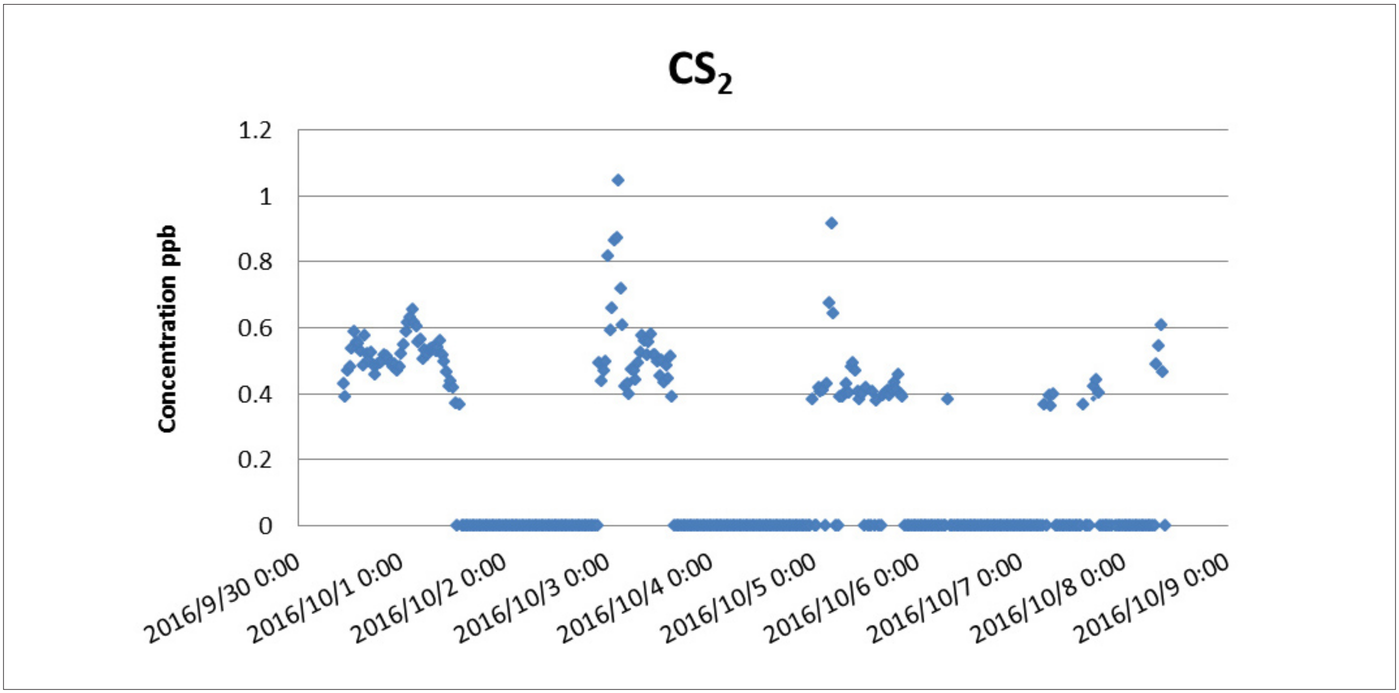

Figure 4. Change in concentration of carbon disulfide with continuous monitoring from Sep. 30 to Oct. 8 2016.

Summary

In this study, the determination of eight sulfur compounds in air was easily performed with a PerkinElmer TurboMatrix on-line 300 TD - Clarus 580 GC/FPD system. All of the target compounds presented superior detection limits, stability and linearity. The analytical results exceed method criteria for EPA method 15 and 16.

Reference

1. BSEN 13725, 2002, Air quality – Determination of odor concentration by dynamic olfactometry
2. Nagata Yoshio, 2004, Measurement of odor threshold by triangle odor bag method, Odor measurement review
3. GB14554-93, 1993, Emission standards for odor pollutants
4. Method 15, Determination of hydrogen sulfide, carbonyl sulfide, and carbon disulfide emissions from stationary sources, USEPA
5. Method 16, Semi continuous determination of sulfur emissions from stationary sources, USEPA

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