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## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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**To cite this Article** Li, Kwong-Chi and Shooter, David(2004) 'Analysis of sulfur-containing compounds in ambient air using solid-phase microextraction and gas chromatography with pulsed flame photometric detection', *International Journal of Environmental Analytical Chemistry*, 84: 10, 749 – 760

**To link to this Article:** DOI: 10.1080/03067310410001729619

**URL:** <http://dx.doi.org/10.1080/03067310410001729619>

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# ANALYSIS OF SULFUR-CONTAINING COMPOUNDS IN AMBIENT AIR USING SOLID-PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY WITH PULSED FLAME PHOTOMETRIC DETECTION

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*(Received 26 May 2003; In final form 30 April 2004)*

A new analysis method for sulfur-containing compounds in air using solid-phase microextraction (SPME), gas chromatography and pulsed flame photometric detection (PFPD), SPME-GC-PFPD method, has been developed. The analysis method is simple, fast and easily performed. To demonstrate the usefulness and versatility of the method air samples collected in geothermal areas in Rotorua, at a muddy beach in Auckland (cities in New Zealand), and in a wastewater treatment plant were analysed. COS, H<sub>2</sub>S, CS<sub>2</sub>, SO<sub>2</sub>, CH<sub>3</sub>SH, (CH<sub>3</sub>)<sub>2</sub>S and CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SH were identified in the samples from Rotorua. It was noted that air quality in residential areas with respect to sulfur compounds was better than that around geothermal sources. Samples from the wastewater treatment plant contained COS, H<sub>2</sub>S, CS<sub>2</sub>, SO<sub>2</sub>, CH<sub>3</sub>SH, (CH<sub>3</sub>)<sub>2</sub>S and (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>. It was found that the emission of sulfur compounds was reduced in the course of the wastewater treatment process. The potential impact of the detected sulfur compounds on human health is briefly discussed.

*Keywords:* Sulfur compounds; SPME; PFPD; Air sampling bag

## INTRODUCTION

Natural sulfur-containing compounds (sulfur compounds) in the atmosphere such as hydrogen sulfide, dimethyl sulfide and dimethyl disulfide, are released from oceans, marshes, soils and vegetation [1,2]. Geothermal and volcanic activity are also sources of these compounds [3,4]. Natural emissions constitute about 24% of the total sulfur emission budget, and anthropogenic sulfur emissions, mainly SO<sub>2</sub>, contribute the remainder [4]. The public generally has a notion that a malodorous smell in the air is an indication of the presence of pollutants. Most sulfur compounds have a characteristic odor with low odor threshold limit which can cause annoyance to people,

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for instance the workers in wastewater treatment plants and Kraft pulp and paper mills. Muezzinoglu [5] in 2001 studied sulfur compounds in the air at the deltas of polluted creeks where an odor nuisance was recognized in the city of Izmir, Turkey. Furthermore, the International Labor Organization of the UN reports that some sulfur compounds even in low concentrations may cause harmful effects to the human respiratory system, and may be fatal in high concentrations.

Previously analyses of sulfur compounds in the atmosphere have been carried out using solid adsorbents or cryogenic trapping for concentrating the sulfur compounds, and gas chromatography for separating the analytes [6–8]. Wardencki [9] has reviewed the problems of sampling, extraction and analysis of environmental sulfur compounds in gas samples using gas chromatography. Devai and DeLaune [10] has identified hydrogen sulfide, carbonyl sulfide, methanethiol, dimethyl sulfide and carbon disulfide in the emissions from wastewater treatment plants using solid adsorbent preconcentration and gas chromatography. By trapping hydrogen sulfide, sulfur dioxide and other gaseous sulfur compounds separately with different extraction methods Muezzinoglu [5] found that hydrogen sulfide, dimethyl sulfide, 2-propanethiol, 2-butanethiol, thiophene, diphenyl sulfide and sulfur dioxide were present in the emissions from the polluted creeks in Izmir, Turkey.

Solid-phase microextraction (SPME) is an alternative extraction technique. Much research has already demonstrated that SPME is simple, fast and effective for extracting analytes from various matrices [11–14]. SPME has been used to extract sulfur compounds for analysis from beer and wine samples [12,15]. A variety of detectors have been used to detect the sulfur compounds in chromatographic analyses [9]. A sulfur-selective detector, the pulsed flame photometric detector, has been used for example in the analysis of sulfur compounds in beer [15]. In this article, the application of a new analysis method for sulfur compounds in ambient air using solid-phase microextraction, gas chromatography and a pulsed flame photometric detector (SPME-GC-PFPD) is described. The analysis results obtained using this method for air samples collected in Rotorua (a city situated in a geothermal area in New Zealand), in a wastewater treatment plant and at a muddy beach in Auckland (New Zealand) are presented.

## EXPERIMENTAL

### Chemicals and Instrumentation

Throughout this study analytical-grade chemicals were used. Carbonyl sulfide, hydrogen sulfide and methanethiol were purchased from Matheson; carbon disulfide, sulfur dioxide, diethyl sulfide from BDH; ethanethiol, 1-propanethiol, 2-propanethiol, 1-butanethiol, 1-pentanethiol, 2-methyl-2-propanethiol, furfuryl mercaptan, dimethyl sulfide, *n*-butyl sulfide, *n*-butyl disulfide, thiophene, 2-methylthiophene, 2,5-dimethylthiophene and 2-ethylthiophene from Acros; 1,2-ethanedithiol, benzyl mercaptan, *p*-thiocresol, ethyl methyl sulfide, diethyl disulfide and 3-methylthiophene from Lancaster; *sec*-butyl sulfide from Aldrich; dimethyl disulfide from Merck.

An SPME fiber holder and SPME fibers coated with 75  $\mu\text{m}$  Carboxen-Polydimethylsiloxane (Carboxen-PDMS) were purchased from Supelco, USA. 600-mL Tedlar air sampling bags with septum ports and Teflon reducing ferrules (1/4" to

1/8") were purchased from Alltech Associates, Inc., USA, and Teflon/silicone septa [thickness 100 mil (2.54 mm)] from Supelco, USA.

A Shimadzu GC-17AAFV(ver. 3) coupled with an OI-Analytical 5380 pulsed flame photometric detector and a J & W Scientific GS-GasPro column (30 m × 0.32 mm i.d.) were used for the GC analysis.

### Pre-concentration and Injection of Analytes Using the SPME Fiber

The SPME fiber coated with 75  $\mu\text{m}$  Carboxen-PDMS was conditioned at 280°C in the injector of the gas chromatograph for 30 min before use. Before using the fiber for an analysis a blank run with the fiber was necessary to remove any compounds adsorbed on the fiber during storage. For extracting analytes from samples the fiber was retracted inside the protecting needle, and the needle inserted through the septum and exposed to the sample by pushing the fiber out of the needle for a pre-determined time. Once the sampling was finished the SPME fiber was withdrawn into the protecting needle which was then withdrawn from the septum. The protecting needle was immediately inserted into the injector of the gas chromatograph. The same procedure was followed for desorption from the fiber in the injector.

### Collection of Air Samples

The Tedlar air sampling bags were flushed with nitrogen gas three times prior to the collection of samples. With the samples being collected using the device shown in Fig. 1 anhydrous calcium chloride was used to remove moisture from the sampled air. Before collecting a sample the Tedlar air sampling bag was filled and emptied twice with the air at the sampling site using a hand pump. Air was then sucked into the Tedlar air sampling bag until it was almost fully filled. The sample was kept in a chilled box at 10°C during transportation, and in a refrigerator in the laboratory until it was analyzed. All samples were analyzed within two days of collection.

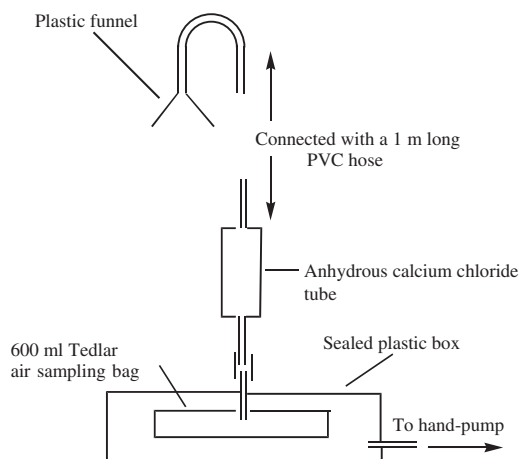


FIGURE 1 Schematic of the collection device for air samples (not to scale).

Ambient air samples were collected in Rotorua, in a wastewater treatment plant and at a muddy beach in Auckland for subsequent analysis of the ambient sulfur compounds.

### Analysis of Air Samples

Samples in the Tedlar air sampling bags were equilibrated at room temperature for an hour, followed by exposing an SPME fiber coated with 75  $\mu\text{m}$  Carboxen-PDMS to the sample for 15 min. The analytes adsorbed on the fiber was then desorbed in the injector of the gas chromatograph, and separated using a GS-GasPro column with the temperature programme: 50°C for 1 min, ramp at 20°C/min to 230°C, hold for 5 min, ramp at 20°C/min to 250°C hold for 14 min.

The sulfur compounds were detected with a PFPD and identified using the retention times of the sulfur compound standards listed in Table I.

This SPME-GC-PFPD analysis method has the following advantages: (1) no power requirement for collection of samples, making it suitable for remote sites and sites with restricted access; (2) no need for cryogenic devices for pre-concentration of the volatile analytes; (3) the SPME fiber provides both concentration and introduction of analytes; (4) it provides selective detection of sulfur compounds; (5) it is solvent-free.

### Evaluation of the Loss of Sulfur Compounds During Sampling

Sampled air was passed through anhydrous calcium chloride to remove moisture. It has been reported previously that this material does not absorb  $\text{H}_2\text{S}$ ,  $\text{COS}$ ,  $\text{CS}_2$ , thiols, sulfides and disulfides [16]. Other possible losses of sulfur compounds during sampling, which may have been caused by the use of PVC tubing (Fig. 1), was investigated as follows. A gaseous sulfur compound standard containing  $\text{CS}_2$  (2 ppbv/v),  $\text{CH}_3\text{CH}_2\text{SH}$  (20 ppbv/v),  $(\text{CH}_3)_2\text{S}$  (2 ppbv/v) and  $\text{CH}_3\text{SSCH}_3$  (2 ppbv/v) was drawn through a 1.5-m long PVC tube into a Tedlar air sampling bag. As a reference the standard was also drawn through a 3-cm long Nylon tube into a Tedlar air sampling bag. The samples and reference were then analyzed using the SPME-GC-PFPD method. It was found that there was no significant difference between the mean peak area

TABLE I GC retention times of selected sulfur reference compounds

<i>Sulfur compound</i>	<i>Retention time (min)</i>	<i>Sulfur compound</i>	<i>Retention time (min)</i>
COS	3.11	1-Butanethiol	12.35
$\text{H}_2\text{S}$	3.28	$(\text{CH}_3)_2\text{S}_2$	12.64
$\text{CS}_2$	5.87	$(\text{C}_2\text{H}_5)_2\text{S}$	14.55
$\text{SO}_2$	6.5–8.0 (broad peak)	2-Ethylthiophene	14.55
$\text{CH}_3\text{SH}$	7.29	1-Pentanethiol	14.80
$\text{C}_2\text{H}_5\text{SH}$	9.06	2,5-Dimethylthiophene	15.07
$(\text{CH}_3)_2\text{S}$	10.26	1,2-Ethanedithiol	15.58
2-Propanethiol	10.30	Benzyl mercaptan	15.77
Thiophene	10.33	Furfuryl mercaptan	17.63
1-Propanethiol	10.62	Diethyl disulfide	17.87
2-Methyl-2-propanethiol	11.57	<i>s</i> -Butyl sulfide	17.94
Ethyl methyl sulfide	12.10	<i>p</i> -Thiocresol	20.74
2-Methylthiophene	12.27	<i>n</i> -Butyl disulfide	29.02
3-Methylthiophene	12.30	<i>n</i> -Butyl sulfide	30.85

of the samples and reference for each sulfur compound (C.I. = 95%,  $n = 5$ ). Hence, it was concluded that there was no significant loss of sulfur compounds in the use of PVC tubing for collecting air samples.

### Reproducibility of the Analysis Method

The gaseous sulfur compound standard containing  $\text{CS}_2$ ,  $\text{CH}_3\text{CH}_2\text{SH}$ ,  $(\text{CH}_3)_2\text{S}$  and  $\text{CH}_3\text{SSCH}_3$  was used to evaluate the reproducibility of the analysis method. It was found that the RSDs for the analysis of these compounds were less than 9%, 17%, 12% and 20% respectively ( $n = 7$ ).

## RESULTS AND DISCUSSION

### Atmospheric Sulfur Compounds in Rotorua, New Zealand

Seven locations in Rotorua were selected for the collection of air samples: Western Road in Ngongotaha and Rainbow Farm at Fairy Springs Road (situated in the outskirts of Rotorua); Linton Park and Harold Crescent (residential areas in the urban area of Rotorua); Kuirau Park; Sulfur Point and Sulfur Flat (geothermal areas in the urban area of Rotorua). Two samples were collected at one or two sites within each location. All samples, except one from the outlet of a fumarole at Sulfur Point, were collected at 1.5 m above ground level.

Selected examples of the chromatograms of sulfur compounds detected in two air samples are shown in Figs. 2 and 3. It was found that the sulfur compound composition of the duplicate samples collected from the same site in the residential areas differed slightly. The common sulfur compounds identified in both samples had large peak areas while one or two additional sulfur compounds with relatively small peak areas were often identified in at least one of the samples. The difference in the composition could have resulted from the variation with time in the composition of the air sampled in residential areas (one of the samples was collected 15 min later). Moreover, the duplicate samples collected from the geothermal areas contained the same sulfur compound composition. The relative peak areas of the identified sulfur compounds in the air samples from each location are given in Table II.

$\text{COS}$ ,  $\text{H}_2\text{S}$ ,  $\text{CS}_2$  and  $\text{SO}_2$  were the sulfur compounds found common to all the samples collected from the twelve locations with  $(\text{CH}_3)_2\text{S}$  being found in all samples except for the sample collected at site 1. Based on the peak areas of these five

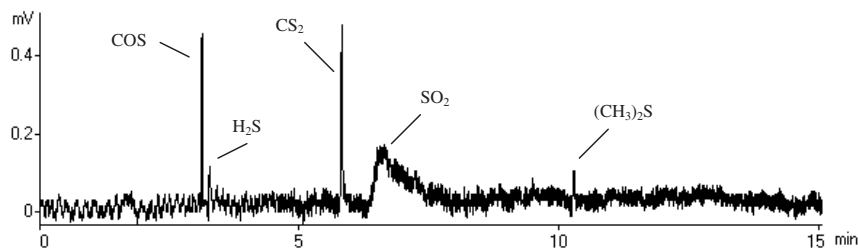


FIGURE 2 Chromatogram of a sample collected in a 600-mL Tedlar air bag at Linton Park (Deborah Place). The sample was analyzed using the SPME-GC-PFPD method with a 15-min SPME exposure.

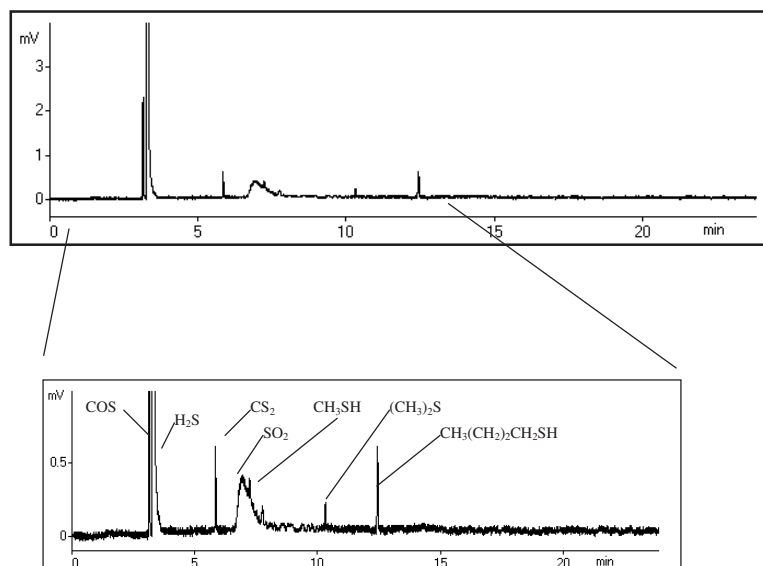


FIGURE 3 Chromatogram of a sample collected in a 600-mL Tedlar air bag at a thermal spring at Kuirau Park. The sample was analyzed using the SPME-GC-PFPD method with a 15-min SPME exposure.

compounds it was estimated that their concentrations were lower in residential areas (locations 1–5) than those (locations 6–12) close to the geothermal sources – a thermal spring, a mud pool and a fumarole.

Rotorua is well known as a city with the characteristic smell of sulfur in the air. It is often thought that  $\text{H}_2\text{S}$  is responsible for the odor. However, as detailed above, a variety of sulfur compounds other than  $\text{H}_2\text{S}$  were identified in the air samples. Each sulfur compound would have contributed its characteristic odor with the odor of a mixture of sulfur compounds differing in quality from that of individual sulfur compounds. An example of this effect is the masking of one odor by another odorous compound. Table III lists the characteristic odors and threshold odor limits of the sulfur compounds identified in the samples. Based solely on the odor threshold limits of the listed sulfur compounds, each sulfur compound contributed its own characteristic odor. It was noted that the odor of the ambient air in the residential area differed from that in geothermal areas in the quality of smell. As seen in Table III, sulfur compounds have adverse health effects on humans. The Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH) and the American Conference of Governmental Industrial Hygienists (ACGIH) in the USA have established air quality guidelines and exposure limits for airborne sulfur compounds. Bates *et al.* [17] suggest that some of the elevated disease rates in Rotorua such as diseases of the nervous system and the eye were at least consistent with what one might expect to find if sufficient exposures to hydrogen sulfide and/or mercury were occurring. A short-term exposure to airborne sulfur compounds may thus cause irritation to the eyes and respiratory tract, headache, nausea and dizziness. Based on the peak areas of sulfur compounds obtained from the samples it is estimated that, as expected, sulfur compounds were present in higher concentrations around the geothermal areas than in residential areas. These compounds, especially those in the gaseous emissions direct from fumaroles, may therefore cause health

TABLE II Relative peak areas of sulfur compounds identified in air samples collected from areas in Rotorua

Site <sup>a</sup>	<i>COS</i>	<i>H<sub>2</sub>S</i>	<i>CS<sub>2</sub></i>	<i>SO<sub>2</sub></i>	<i>CH<sub>3</sub>SH</i>	<i>C<sub>2</sub>H<sub>5</sub>SH</i>	<i>(CH<sub>3</sub>)<sub>2</sub>S</i>	<i>CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>SH</i>	<i>CH<sub>3</sub>CH<sub>2</sub>SCH<sub>3</sub></i>	<i>CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SH</i>
Residential areas										
1a	*	—	**	—	*	*	—	—	—	—
1b	*	*	**	*	*	*	—	—	—	—
2a	**	*	***	*	—	—	*	—	—	—
2b	*	—	**	—	—	—	—	—	—	—
3a	**	*	**	*	—	—	*	—	—	—
3b	*	—	**	*	—	—	*	—	—	—
4a	*	—	*	*	—	—	*	—	—	—
4b	*	*	*	*	—	—	*	—	—	—
5a	*	*	*	*	—	—	*	—	—	—
5b	*	—	**	*	—	—	*	—	—	—
Geothermal areas										
6	***	*****	**	**	*	—	*	—	—	*
7	***	*****	***	*	—	—	***	—	—	****
8	***	*****	**	**	***	—	*	—	—	*
9	*****	*****	*****	*****	***	—	**	—	—	*****
10	*****	*****	*****	*****	*****	****	****	*	*	***
11	**	*****	***	***	**	—	*	—	—	****
12	**	*****	*****	*	*	—	*	—	—	**

1 = Western Road, Ngongotaha; 2 = Rainbow Farm, Fairy Springs Road; 3 = Linton Park, Deborah Place; 4 = Linton Park, Rimuvale Street; 5 = Recreational Reserve, Harold Crescent; 6 = Kuirau Park (close to a thermal spring); 7 = Kuirau Park (100 m from site 6 and close to a mud pool); 8 = Sulfur Point (edge of the lake); 9 = Sulfur Point (50 m from site 8 and next to a mud hole); 10 = A fumarole at Sulfur Point (50 m from sites 8 and 9); 11 = Sulfur Flat (away from the cluster of small fumaroles); 12 = Sulfur Flat (next to a small fumarole); \* peak areas  $\leq 500$  units; \*\* 500 units < peak areas  $\leq 1000$  units; \*\*\* 1000 units < peak areas  $\leq 4000$  units; \*\*\*\* 4000 units < peak areas  $\leq 8000$  units; \*\*\*\*\* 8000 units < peak areas; <sup>a</sup>a and b are the two samples collected at the same site.



TABLE III Characteristics of sulfur compounds identified in the air samples

<i>Sulfur compound</i>	<i>Odor characteristic, odor threshold limits</i>	<i>Short-term exposure effects</i>	<i>Occupational exposure limit (OEL)</i>
COS	Typical sulfide odor	No available information	No available data
H <sub>2</sub> S	Rotten egg 0.1–0.2 ppm	Hydrogen sulfide causes headache, dizziness, cough, sore throat and nausea through inhalation. It may cause lung edema and effects on the central nervous system. Exposure to high concentration may result in unconsciousness and death	TLV: 10 ppm (as TWA) (ACGIH 2000)
CS <sub>2</sub>	Pungent 1.2 ppm	Inhalation of carbon disulfide vapor may cause headache, nausea, dizziness, unconsciousness and death. Exposure between 200 and 500 ppm may cause death	PEL: 20 ppm in air (TWA)(OSHA)
SO <sub>2</sub>	Pungent 3–5 ppm	Sulfur dioxide causes irritation to the eyes and respiratory tract resulting in burning of the eyes, coughing and chest tightness. Short-term exposures to high levels of sulfur dioxide can be life-threatening. Exposure to 100 ppm in air is considered immediately dangerous to life and health	PEL: 2 ppm in air (TWA)(OSHA)
CH <sub>3</sub> SH	Pungent, sulfidy, decayed cabbage 0.001 ppm	Inhalation of methyl mercaptan may cause cough, headache, nausea, shortness of breath, sore throat and lung edema. It may cause effects on the central nervous system, resulting in respiratory failure. Exposure at high levels may result in death	TLV: 0.5 ppm (as TWA) (ACGIH 1992–1993)
C <sub>2</sub> H <sub>5</sub> SH	Sulfidy, earthy, decayed cabbage 0.0003–0.001 ppm	Inhalation of ethyl mercaptan may cause dizziness, headache, nausea, vomiting. It may cause effects on the central nervous system, resulting in convulsions and respiratory failure	TLV: 0.5 ppm (ACGIH 1995–1996)
(CH <sub>3</sub> ) <sub>2</sub> S	Decayed vegetables 0.1 ppm	Inhalation of dimethyl sulfide may cause slight irritation to respiratory tract	No available data
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> SH	Strong obnoxious odor like garlic or skunk 0.001–0.050 ppm	Inhalation of 1-butanethiol may cause cough, dizziness, drowsiness, headache, nausea, vomiting, shortness of breath, weakness and confusion. Exposure far above the OEL may cause effects on the nervous system and lowering of consciousness	TLV: 0.5 ppm (as TWA) (ACGIH 1999)

TLV: Threshold Limit Value-Time-Weighted Average (TLV-TWA) – the time-weighted average concentration for a conventional 8-h workday and a 40-h workweek, to which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. (From ACGIH, USA.); PEL: Permissible Exposure Limit – the maximum occupational exposure permitted under the OSHA regulations. (From ACGIH, USA.); Information from the International Labor Organization – UN specialized agency.

impacts to the population. Further study on the impacts on human health of sulfur-compound emissions in geothermal areas is recommended.

### Atmospheric Sulfur Compounds in a Wastewater Treatment Plant

Air samples were collected within a wastewater treatment plant, which was built to serve a population of 7500 in a residential suburb of Auckland, New Zealand. Seven locations: the screen, the fully aerated lagoon, the partially aerated lagoon, the wetland, the UV disinfection unit and the land disposal irrigation, were selected for the collection of duplicate samples using the Tedlar air bags. The samples were analyzed using the SPME-GC-PFPD method within two days of collection. Selected examples of the chromatograms of the sulfur compounds detected in two air samples are shown in Figs. 4 and 5. Table IV lists the sulfur compounds identified in the samples from all seven sites.

COS, CS<sub>2</sub>, CH<sub>3</sub>SH and (CH<sub>3</sub>)<sub>2</sub>S were found to be present in all samples. By considering the dependence of detector response to the number of S atoms in a sulfur

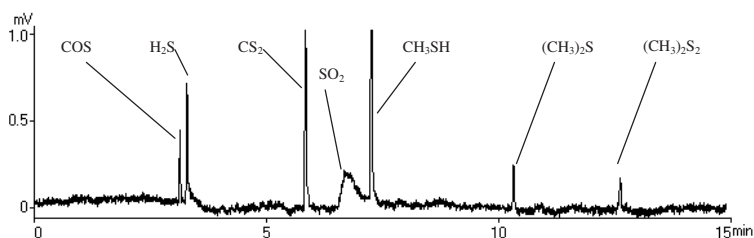


FIGURE 4 Chromatogram of a sample collected in a 600-mL Tedlar air bag at the fully aerated lagoon. The sample was analyzed using the SPME-GC-PFPD method with a 15-min SPME exposure.

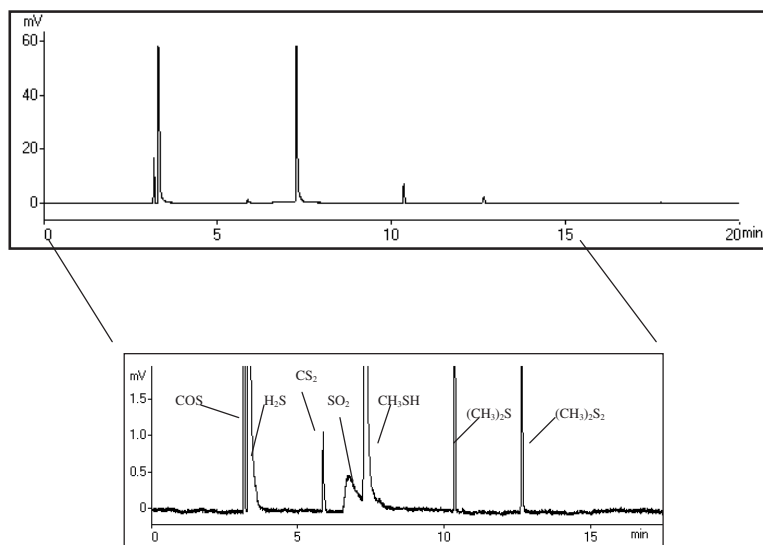


FIGURE 5 Chromatogram of a sample collected in a 600-mL Tedlar air bag at the inlet tank. The sample was analyzed using the SPME-GC-PFPD method with a 1-min SPME exposure.

TABLE IV Relative peak areas of sulfur compounds identified in the samples collected at the wastewater treatment plant

Site <sup>a</sup>	COS	H <sub>2</sub> S	CS <sub>2</sub>	SO <sub>2</sub>	CH <sub>3</sub> SH	(CH <sub>3</sub> ) <sub>2</sub> S	(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>
1a	**	*	***	—	*	**	**
1b	**	*	***	—	*	*	—
3a	**	***	***	*	***	*	*
3b	*	**	***	*	**	*	*
4a	*	*	***	—	**	*	—
4b	*	*	***	—	***	*	—
5a	*	*	***	—	**	*	—
5b	*	*	**	—	—	*	—
7a	*	—	***	—	*	**	—
7b	**	—	***	—	*	**	—
2	*****	*****	*****	*****	*****	*****	*****
6	***	*****	***	—	***	***	—

1 = 1.5 m above the ground at the inlet screen; 2 = Inside the inlet tank; 3 = 1.5 m above the ground at the monitor site of the fully aerated lagoon; 4 = 1.5 m above the ground at the side-track of the partially aerated lagoon; 5 = 1.5 m above the ground at the wetland; 6 = Inside the UV disinfection unit; 7 = 1.5 m above the ground at the land disposal irrigation area; \* peak areas ≤ 500 units; \*\* 500 units < peak areas ≤ 1000 units; \*\*\* 1000 units < peak areas ≤ 4000 units; \*\*\*\* 4000 units < peak areas ≤ 8000 units; \*\*\*\*\* 8000 units < peak areas; <sup>a</sup>a and b are the two samples collected at the same site.

compound molecule and comparing the peak areas of these four sulfur compounds, it was concluded that the concentrations of COS, CS<sub>2</sub>, CH<sub>3</sub>SH and (CH<sub>3</sub>)<sub>2</sub>S were highest in the samples collected at the inlet, and second highest in the samples collected at the UV disinfection unit. The concentrations of these compounds were much lower (Table IV) in the samples collected at sites 1, 3, 4, 5 and 7. Both the inlet tank and the UV disinfection unit had little ventilation, therefore higher sulfur compound concentrations were expected. A comparison of the peak areas obtained (Table IV) suggests that the emission of sulfur compounds was lower from the effluent in the UV disinfection unit than from the influent in the inlet tank. Such a reduction demonstrates that the emission of odorous sulfur compounds was reduced in the course of wastewater treatment. Sulfur or nitrogen compounds, organic acids or aldehydes have been identified in sewage treatment works odors [18]. Given that sulfur compounds have lower odor threshold limits than amines, organic acids and aldehydes [19], they are most likely the dominant species responsible for the odors observed in sewage treatment works. Each sulfur compound contributes its odor characteristics to the sulfury odors noted in the air around a wastewater treatment plant. On the basis of the peak area, indicating that sulfur compounds in the open air were present in low concentrations (Table IV), the emission to open areas from the wastewater treatment plant may not cause any offensive odor problems to plant workers or the public. However, the significant sulfur compound emissions in enclosed areas, such as the inlet tank and the UV disinfection unit might cause a health risk to workers. Therefore safety measures, such as good ventilation, should always be taken in such enclosed areas while conducting maintenance.

### Atmospheric Sulfur Compounds at a Muddy Beach

Air samples were collected with the Tedlar sampling bags at a muddy beach in Auckland. It was low tide at the time of collection, and samples were collected 1.5 m above the sediment. The samples were then taken back to the laboratory and analyzed on the same day. Figure 6 shows the chromatogram obtained for one sample collected

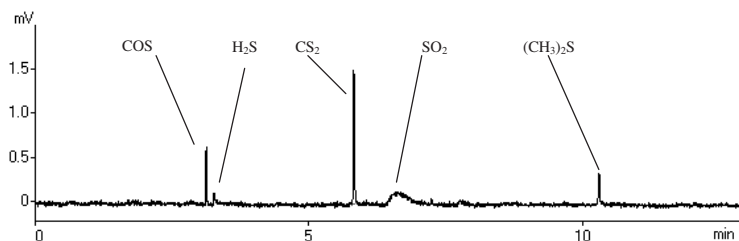


FIGURE 6 Chromatogram of a sample collected in a 600-mL Tedlar air bag at the beach. The sample was analyzed using the SPME-GC-PFPD method with a 15-min SPME exposure.

at the beach. Five sulfur compounds, COS, H<sub>2</sub>S, CS<sub>2</sub>, SO<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>S, were detected. With the exception of SO<sub>2</sub> these compounds have been described as the sulfur species emitted from coastal wetlands [2].

## CONCLUSIONS

The method used for the analysis of atmospheric sulfur compounds using SPME, GC and PFPD is simple, fast and easily operated. This has been demonstrated by the collection and analysis of samples of ambient air in Rotorua, in a wastewater treatment plant and at a muddy beach in Auckland, New Zealand. It was found that the samples from Rotorua contained COS, H<sub>2</sub>S, CS<sub>2</sub>, SO<sub>2</sub>, CH<sub>3</sub>SH, (CH<sub>3</sub>)<sub>2</sub>S and CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SH. In addition to these sulfur compounds, C<sub>2</sub>H<sub>5</sub>SH, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>SH and CH<sub>3</sub>CH<sub>2</sub>SCH<sub>3</sub> were identified in the samples collected directly from a fumarole. It is concluded that the smell of sulfur in Rotorua results from a mixing effect of these sulfur compounds rather than just from H<sub>2</sub>S. As expected it was also found that the air quality in Rotorua with respect to sulfur compounds was better in residential areas than close to geothermal sources.

The samples collected from a wastewater treatment plant contained COS, H<sub>2</sub>S, CS<sub>2</sub>, SO<sub>2</sub>, CH<sub>3</sub>SH, (CH<sub>3</sub>)<sub>2</sub>S and (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>. Relatively low concentrations of sulfur compounds were detected in the open air. However, the higher concentrations detected inside the inlet tank and the UV disinfection unit might be harmful to the maintenance workers without good ventilation. It was also noted that the emissions of sulfur compounds were reduced in the course of wastewater treatment. The method was also capable of easily detecting the sulfur compounds characteristic of wetlands. The results presented in the paper clearly show that the SPME-GC-PFPD method can be used to pre-concentrate and identify sulfur compounds in ambient air. Although quantification of a suite of compounds is time consuming, we plan to enhance our knowledge of reduced sulfur compounds in the environment by both identifying and quantifying sulfur compounds in air samples collected in the vicinity of a variety of geothermal areas in New Zealand.

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