Single Column Trapping/Separation and Chemiluminescence Detection for On-Site Measurement of Methyl Mercaptan and Dimethyl Sulfide

ARTICLE *in* ANALYTICAL CHEMISTRY · OCTOBER 2006

Impact Factor: 5.64 · DOI: 10.1021/ac060928v · Source: PubMed

3 AUTHORS, INCLUDING:

Shin-Ichi Ohira
Kumamoto University
61 PUBLICATIONS **741** CITATIONS
SEE PROFILE

Kei Toda
Kumamoto University
108 PUBLICATIONS **1,181** CITATIONS
SEE PROFILE

Anal. Chem. **2006,** *78,* 6252−6259

Single Column Trapping/Separation and Chemiluminescence Detection for On-Site Measurement of Methyl Mercaptan and Dimethyl Sulfide

Md. Abul Kalam Azad, Shin-Ichi Ohira, and Kei Toda*

Department of Environmental Science, Faculty of Science, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

A simple, automated method for the measurement of methyl mercaptan (CH_3SH) and dimethyl sulfide (DMS) has been investigated. These two sulfur gases have strong and unpleasant odors. The collection and separation are performed in sequence with a single short column packed with silica gel powder. CH_3SH and DMS are separated according to their desorption temperatures and introduced into a chemiluminescence cell in this order. These two gases emit strong chemiluminescence by reaction with ozone. The calibration curves obtained are linear, which is superior to flame photometric detection of these substances. The whole system, including a small cylinder for the carrier nitrogen, can be set in a portable box. The instrument is applicable to breath odor analysis, and automated measurement of room air can also be performed. In toilet air analysis, it was observed that levels of the sulfur gases increased after dark. With this instrument, sulfur gases at a ppbv level are successfully measured by a simple procedure without much interference.

The presence of volatile sulfur compounds (VSCs) in waste gases deserves special attention due to their very low odor threshold value, high toxicity, and potential corrosive effect.[1,2] The monitoring of VSCs is also important for research on natural environments and clinical diagnoses. VSCs are emitted from sediments, especially in coastal areas,[3] and are converted into SO_2 and sulfate, which affect the climate as cloud condensation nuclei. Dimethyl sulfide (DMS) is one of the characteristic gases emitted from the seawater surface and alga. In addition, VSCs are known to be key contributors to halitosis.[4−10] The intensity of clinical bad breath is significantly correlated with the level of intraoral VSCs.[11,12] Methyl mercaptan (CH_3SH) shows an independent association with noticeable oral malodor and is a more useful marker than H_2S.[13] CH_3SH and DMS odors linger longer after intake than that of H_2S. Breath analysis has attracted a considerable amount of scientific and clinical interest during the past decade. Exhaled levels of sulfur-containing compounds are elevated when liver failure and allograft rejection occurs.[14] Looking at a set of volatile markers may enable recognition and diagnosis of complex diseases such as lung cancer. Due to technical problems in sampling and analysis and a lack of normalization and standardization, huge variations exist between results of different studies. This is one of the main reasons why VSC breath analysis has not yet been introduced into clinical practice.[14]

It is generally difficult to collect, store, and analyze VSCs at trace levels because of their highly adsorptive, reactive, and volatile properties. VSC analyses require preconcentration because concentrations of these substances in environmental and breath samples usually fall in the ppbv−pptv ranges. Adsorption on solid adsorbents, such as Tenax and β,β'-ODPN, and subsequent measurement by gas chromatography with a sulfur-selective detector, e.g., a flame photometric detector (GC-FPD)[4,15,16] or pulsed flame photometric detector (GC-PFPD)[17] is commonly used for VSC determinations. GC-MS has also recently become popular for VSC analysis,[18] sometimes in combination with a three-stage cryogenic trapping system to reduce detrimental effects from the

* Corresponding author: (e-mail) todakei@sci.kumamoto-u.ac.jp.

(1) Smet, E.; Lens, P.; van Langenhove, H. *Crit. Rev. Environ. Sci. Technol.* **1998**, *28*, 89−117.
(2) Smet, E.; van Langenhove, H. *Biodegradation* **1998**, *9*, 273−284.
(3) Bodenbender, J.; Wassmann, R.; Papen, H.; Rennenberg, H. *Atmos. Environ.* **1999**, *33*, 3487−3502.
(4) Tangerman, A.; Meuwese Arends, M. T.; van Tongeren, J. H. M. *Clin. Chim. Acta* **1983**, *130*, 103−110.
(5) Yaegaki, K.; Sanada, K. *J. Periodontol.* **1992**, *63*, 783−789.
(6) Feller, L.; Blignaut, E. *J. S. Afr. Dent. Assoc.* **2005**, *60*, 17−19.
(7) Cchmidt, N. F.; Missan, S. R.; Tarbet, W. J.; Cooper, A. D. *Oral Surg. Oral Med. Oral Pathol.* **1978**, *45*, 560−567.
(8) Hunter, C. M.; Niles, H. P.; Lenton, P. A.; Majerus, G. J.; Vazquez, J.; Kloos, C.; Subramanyam, R.; Cummins, D. *Compendium Continuing Educ. Dent.* **1995**, *24* (9 suppl.), 25−28.
(9) Tonzetich, J. *J. Periodontol.* **1977**, *48*, 13−20.
(10) Amir, E.; Shimonov, R.; Rosenberg, M. *J. Pediatr.* **1999**, *134*, 338−343.
(11) Koshimune, S.; Awano, S.; Ghora, K.; Kurihara, E.; Ansai, T.; Takehara, T. *Oral Surg. Oral Med. Oral Pathol.* **2003**, *96*, 38−41.
(12) Oho, T.; Yoshida, Y.; Shimakazi, Y.; Yamashita, Y.; Koga, T. *J. Dent.* **2001**, *29*, 31−33.
(13) Awano, S.; Koshimune, S.; Kurihara, E.; Gohara, K.; Sakai, A.; Soh, I.; Hamasaki, T.; Ansai, T.; Takehara, T. *J. Dent.* **2004**, *32*, 555−559.
(14) Miekisch, W.; Schubert, J. K.; Nooeldge-Schomburg, G. F. E. *Clin. Chim. Acta* **2004**, *347*, 25−29.
(15) Tangerman, A.; Meuwese Arends, M. T.; van Tongeren, J. H. M. *J. Lab. Clin. Med.* **1983**, *106*, 175−182.
(16) Wardencki, W. *J. Chromatogr., A* **1998**, *793*, 1−19.
(17) Cheskis, S.; Atar, E.; Amirav, A. *Anal. Chem.* **1993**, *65*, 539−555.
(18) Kelly, T. J.; Kenny, D. V. *Atmos. Environ.* **1991**, *25A*, 2155−2160.

10.1021/ac060928v CCC: $33.50
Published on Web 08/05/2006

huge amount of CO_2 present in breath air.[19] Solid-phase microextraction is another technique used to sample VSC gases.[20−22]

Light-emitting species are generated from VSCs not only by the reducing flame in a FPD but also by their reaction with ozone. Consequently, VSCs can be detected by chemiluminescence measurement. The chemiluminescence spectrum for VSCs extends from 280 to 400 nm and is centered around 360 nm.[23−25] In the 1980s, Kelly et al. combined a commercial NO chemiluminescence instrument with a GC to obtain a chemiluminescence chromatogram for VSCs.[26] Since the 1990s, the sulfur chemiluminescence detector, based on conversion of sulfur-containing substances into SO in a hydrogen/oxygen furnace and subsequent ozone-induced chemiluminescence, has become one of the most powerful tools for analytical chemists.[27−31] The first step needs high-power, high-temperature conversion with H_2, to obtain almost equivalent sensitivity on a per mole of sulfur basis. In 1998, fluorine-induced chemiluminescence was reported as a high-sensitivity DMS sensor.[32] However, even without the furnace pretreatment or the special gas, CH_3SH and DMS directly give significant chemiluminescence signals.[23,24,26]

On-site measurement is ideal for VSC analysis due to their instability. No instrument is currently available for automatic measurement of VSCs to the best of our knowledge.[33] We have already developed a diffusion scrubber-based instrument for continuous H_2S measurement[34,35] and used it for volcanic gas measurements[36] and gas emission analysis at tidal flat sediments.[37] CH_3SH and DMS are more important odorous species than H_2S, as mentioned above. Our system had been modified to measure CH_3SH by using two kinds of membrane scrubbers.[38] However, that was indirect CH_3SH measurement, and the sensitivity and reliability were not satisfactory for ppbv levels of CH_3SH. Here, a new method is presented for determination of the major odorous sulfur compounds, CH_3SH and DMS. This is based on a simple trap/separation system and gas-phase chemiluminescence measurement. Preconcentration and separation of gases is performed with the same column. The instrument is compact and suitable for use in the field. The present method allows on-site analysis of CH_3SH and DMS at ppbv levels and is applicable to odor measurement and breath analysis.

EXPERIMENTAL SECTION

Trapping/Separation Column. A single column was used for both trapping and separation of the sample gases. MTO-Davidson silica gel (grade 12, 60/80 mesh, Supelco, Bellefonte, PA) was packed in a mullite ceramic tube (2 mm i.d. × 3 mm o.d. × 20 cm, NewMullite, Nikkato Co., Osaka, Japan) with silanized quartz wool plugs in the ends. The effective adsorbent bed was 14 cm long. A nickel−chrome wire (d 0.2 mm × 35 cm, 15 Ω) was coiled around the ceramic tube as a heater. The heater was covered with glass wool and aluminum tape together with a thermocouple. The column temperature was regulated by a programmable temperature controller (E5AK-TAA2FB, Omron Co., Kyoto, Japan) with 30-V ac being applied to the heater via a solid-state relay. Before the first use, the column was cleaned for 2 h at 330 °C with a constant flow of nitrogen at 20 mL/min.

Chemiluminescence Detector. Figure 1 presents a schematic illustration of the chemiluminescence cell and photomultiplier tube (PMT) arrangement. The reaction cell was constructed without any special machined parts. The cell consisted of a quick-coupling flange tube (25 mm i.d. × 40 or 20 mm L, KF-25, ULVAC, Chigasaki, Japan) made of stainless steel. The inside of the tube was polished before use. Sample and ozone gases were introduced through concentric stainless steel tubes with outer diameters of 1/8 and 1/4 in., respectively. An optical convex lens (S51-20-30, Suruga Seiki, Shizuoka, Japan) and a spherical glass plate (d 21 mm × t 2.5 mm) were placed at the window of the reaction cell and fixed with O-rings. Light from the reaction cell was detected by a PMT (R3550A, Hamamatsu Photonics, Hamamatsu, Japan) placed at the window of the reaction cell. High voltage (HV) was applied to the PMT from a miniature HV supplier (Opton-1NC-12, Matsusada Precision, Kusatsu, Japan) which was powered by 12-V dc. The PMT voltage was adjusted to be 830 V to optimize the signal-to-noise ratio. The PMT current was converted into voltage with amplification factors of 0.1 V/nA (with 100 MΩ). The signal was amplified in the main circuit board 10 and 100 times for wide-range and high-sensitivity determinations, respectively.

Instrumentation and Measurement Procedure. Measurements were performed using the system shown schematically in Figure 2. Sample was aspirated by a diaphragm pump (DA-55, ULVAC) and was normally bypassed via a dummy column, DC1, which was filled with the same silica gel as the trapping column to maintain a constant pressure in the flow system. When three-way solenoid valves (TV307Y-6G-01, SMC, Tokyo, Japan) were activated, the sample passed through the trapping column at 200 mL/min, while the carrier gas (nitrogen) went through a dummy Teflon column, DC2. After the sampling (typically 5 min), the three-way solenoid valves were switched to go to the measurement mode where the carrier flowed at 25 mL/min through the trapping column in the same direction as the sampling. During the first 1 min of the measurement mode, the column temperature was kept

(19) Ochiai, N.; Takino, M.; Daishima, S.; Cardin, D. B. *J. Chromatogr., B* **2001**, *762*, 67−75.
(20) Hyspler, R.; Crhova, S.; Gasparic, J.; Zadak, Z.; Cizkova, M.; Balasova, V. *J. Chromatogr., B* **2000**, *739*, 183−190.
(21) Grote, C.; Pawliuszyn, J. *Anal. Chem.* **1997**, *69*, 587−596.
(22) Giardina, M.; Olesik, S. V. *Anal. Chem.* **2003**, *75*, 1604−1614.
(23) Kummer, W. A.; Pitts, J. N.; Steer, R. P. *Environ. Sci. Technol.* **1971**, *5*, 1045−1047.
(24) Akimoto, H.; Finlayson, B. J.; Pitts, J. N. *Chem. Phys. Lett.* **1971**, *12*, 199−201.
(25) Glinski, R. J.; Sedarski, J. A.; Dixon, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 1126−1128.
(26) Kelly, T. J.; Gaffney, J. S.; Phillips, M. F.; Tanner, R. L. *Anal. Chem.* **1983**, *55*, 135−138.
(27) Yan, X. *J. Chromatogr., A* **2002**, *976*, 3−10.
(28) Gaines, K. K.; Chatham, W.H.; Farwell, S. O. *J. High Resolut. Chromatogr.* **1990**, *13*, 489−493.
(29) Benner, R. L.; Stedman, D. H. *Anal. Chem.* **1989**, *61*, 1268−1271.
(30) Gaffney, J.S.; Spandau, D.J.; Kelly, T. J.; Tanner, R. L. *J. Chromatogr.* **1985**, *347*, 121−127
(31) Burrow, P. L.; Birks, J. W. *Anal. Chem.* **1997**, *69*, 1299−1306.
(32) Hills, A. J.; Lenschow, D. H.; Birks, J. W. *Anal. Chem.* **1998**, *70*, 1735−1742.
(33) Environmental pollutants and their determination methods (in Japanese), http://www.jpo.go.jp/shiryou/s_sonota/map/ippan12/4/4−2.htm.
(34) Toda, K.; Dasgupta, P. K.; Li, J.; Tarver, G. A.; Zarus, G. M. *Anal. Chem.* **2001**, *73*, 5716−5724.
(35) Ohira, S.; Toda, K. *Lab Chip* **2005**, *5*, 1374−1379.
(36) Ohira, S.; Azad, M. A. K.; Kuraoka, R.; Tanaka, T.; Mori, K.; Toda, K. *Bunseki Kagaku* **2006**, *55*, 109−115.
(37) Azad, M. A. K.; Ohira, S.; Oda, M.; Toda, K. *Atmos. Environ.* **2005**, *39*, 6077−6087.
(38) Toda, K.; Ohira, S.; Tanaka, T.; Nishimura, T.; Dasgupta, P. K. *Environ. Sci. Technol.* **2004**, *38*, 1529−1536.

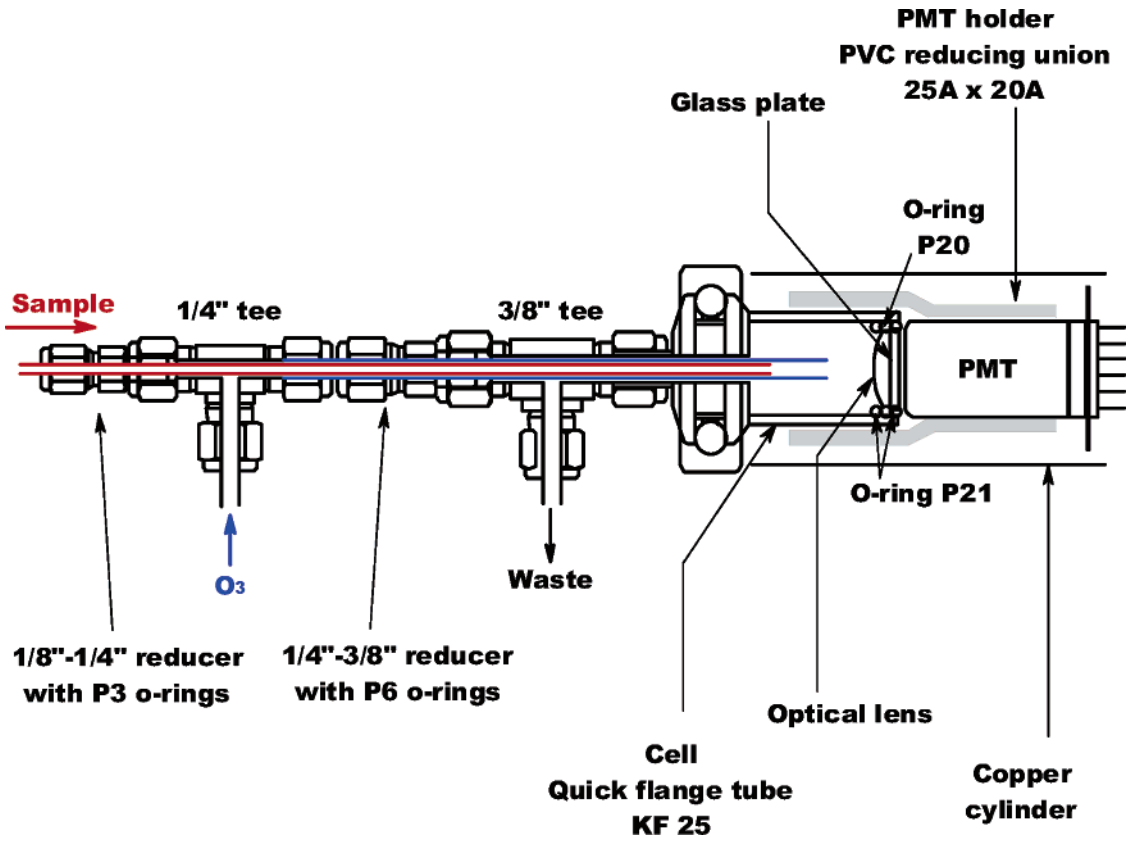

Figure 1. Schematics of the chemiluminescence cell. The 1/8- and 1/4-in. stainless steel tubes were fixed at the reducers with O-rings, so that the positions of the tubes were adjustable. A small Teflon tube (AWG 24) was inserted in the entire 1/8-in. tube to minimize the volume between the trapping/separation column and the cell.

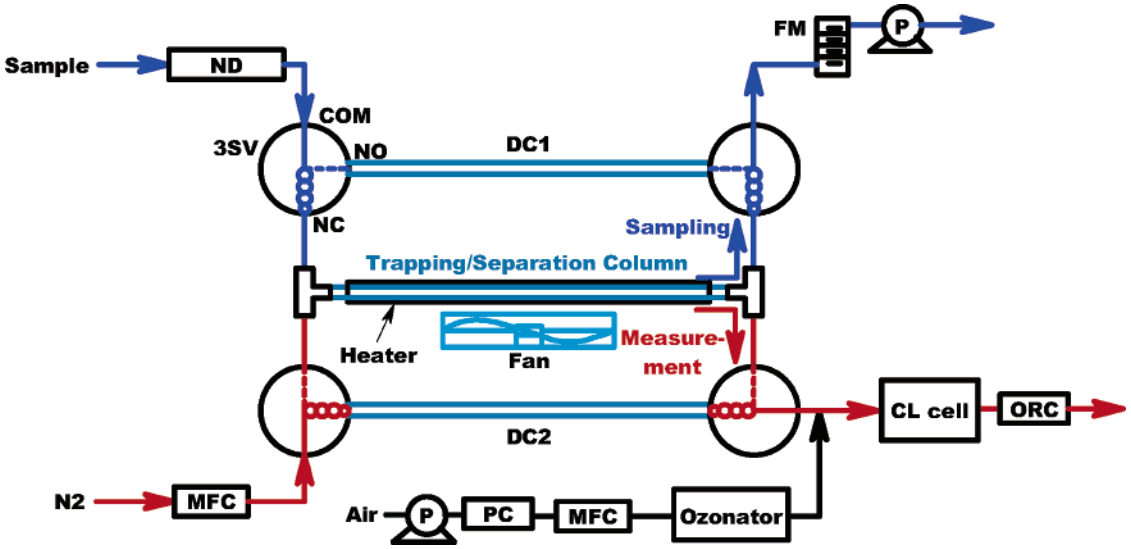

Figure 2. Flow diagram of the measurement system: ND, Nafion dryer; 3SV, three-way solenoid valve; FM, flow meter; DC1,2, dummy columns; MFC, mass flow controller; PC, air purification column packed with soda lime and activated carbon; P, air pump; CL cell, chemiluminescence cell; ORC, ozone removing column.

at room temperature to completely remove any remaining air. The column was then heated to the desired temperature stepwise with a constant carrier flow to purge the target gas to the chemiluminescence cell. The analyte gases were mixed with ozone flow (300 mL/min) in a tube-in-tube in the cell, and the chemiluminescence emitted was measured. After all gases were purged out, the column was cooled to room temperature by two 8-cm fans, to prepare it for the next measurement.

The ozone was prepared by passing air at 300 mL/min through an aluminum chamber that contained two ceramic electrode plates (W 25 mm × L 51 mm, 1100N (2501), Logy Electric, Tokyo, Japan). Pulse power was applied to the electrode from a control kit (LHV-9K-DC 12 V, Logy Electric) to generate ozone from the induced plasma. By using the two electrode plates, 0.6% ozone was generated in an air flow of 300 mL/min. The ozone-containing waste gas was discharged through an ozone-deactivating column.

The measurement was repeated automatically using two twin timers (H5CX from Omron, Kyoto, Japan). One was for solenoid valves (9 min off and 5 min on) and the other was for the fans (14 min on and 9 min off). When the cleaning of the column at 320 °C was finished, an alarm signal from the temperature controller reset the timers, and then column cooling was started with the fans. After 9 min of cooling, the four solenoid valves were turned on and 5 min of sampling started. After 5 min, the sample flowing through the column was changed back to the nitrogen carrier, and the fans were turned off. After 1 min of purging with nitrogen, the column temperature was changed according to the programmed profile. When the final he ating was completed, the temperature controller triggered the timers to reset for the next measurement cycle.

Test Gas Preparation. The working gases (2−100 ppbv) were prepared from 100 ppm standard gases by dynamic dilution with purified air. Cylinders of CH_3SH and DMS gas were purchased from Taiyo Nippon Sanso (Tokyo, Japan) and Sumitomo Seika Chemicals (Osaka, Japan), respectively. The dilution air was supplied by an oil-free compressor with a dehumidifier (dry air supplier P4-EAD, Yaezaki Koatsu, Tokyo, Japan) and was further purified by removing water and organic compounds by the use of a silica gel, soda lime, and activated charcoal column.

Sample Measurements. Human breath and septic tank headspace were analyzed by the present system. A Nafion dryer was placed at the sample inlet to remove water vapor from the real samples.

Breath samples and headspace gases from a septic tank were collected into 5-L cleaned Tedlar bags. In the case of breath sampling, a column (10.8 mm i.d. × 75 mm L) packed with calcium chloride was placed in front of the Tedlar bag inlet to reduce water vapor. The sampled breath and septic tank air were then measured in triplicate by the present system.

Diurnal variation of the gases in a toilet room was also examined. All parts of the apparatus were placed in an aluminum box. Alternating current power was obtained from a wall socket in the toilet. Nitrogen packed in a 1-L can was used for short measurements. When the measurements were over a longer period of time than 3 h, a 10-L gas cylinder was used. The measurement was repeated automatically by using the programmable temperature controller and the timers. All data were acquired with a data logger.

Comparable Measurements with GC-FPD. The above samples were also measured by GC-FPD coupled with a trap/desorption system, at the same time as the present method. The GC-FPD trap/desorption is conventionally used for odorous sulfur measurements.[39] A Tenax TA column was placed in a dry ice/methanol bath,[40] and the sample from the Tedlar bag was trapped at 50 mL/min for 10 min in the Tenax column, and then purged with helium for 1 min. The bath was then changed to a hot water bath (90 °C) to warm the column for 30 s, and the desorbed gases were introduced into the GC system. Separation was carried out with a Teflon column (i.d. 2.36 mm × 3 m) packed with β,β'-ODPN, Uniport HP 60/80 mesh. A Shimadzu 14A gas chromatograph was used with 20 mL/min helium as the carrier gas. Hydrogen (60 mL/min) and compressed air (40 mL/min) were used for the detector flame.

(39) Rank Odors Analysis (in Japanese), http://www.gls.co.jp/product/catalog-28/01/73.html.

(40) Inomata, Y.; Matsunaga, K.; Murai, Y.; Osada, K.; Iwasaka, Y. *J. Chromatogr., A* **1999**, 864, 111−119.

RESULTS AND DISCUSSION

Chemiluminescence Reaction Cell. A simple reaction cell was designed and constructed to detect CH_3SH and DMS with high sensitivity. There was no machined block, and the cell was light, simple, low cost, and easy to construct. The cell was made with a mirror-finished stainless steel tube, which had a volume 20 or 10 mL. The sample with carrier gas and ozone was introduced into the cell through concentric tubes where ozone entered via the outer tube. Substantial variation in the chemiluminescence intensity was observed with changes in sample/carrier−ozone flow rates and the gas inlet tube positions in the reaction cell. Optimum chemiluminescence intensity with minimum noise was observed at a 25 mL/min sample/carrier flow rate. The chemiluminescence intensity was not significantly influenced by the gas inlet tube's position in the reaction cell but the positioning did help to minimize the signal noise. The 1/4-in. tube was positioned 10 mm away from the optical lens, and the 1/8-in. tube was 10 mm upstream from the end point, inside the 1/4-in. tube. A 300 mL/min ozone flow rate was found to be optimal for maximum chemiluminescence intensity. Air was better than oxygen for the ozone source. When air is used in the ozonizer instead of oxygen, trace levels of NO_x are generated in the ozone stream, which enhances the chemiluminescence reaction.[26]

Minicolumn for Trap and Separation. VSC levels in air are usually too low for direct determination. Therefore, a preconcentration and isolation step must be included in the analytical method. These steps were performed with only one column in this system. Solid adsorbents were packed in a ceramic tube (Mullite) for both preconcentration and separation of the gases. Mullite tube has a higher thermal conductivity (5.0 W/(m K)) than glass tube (1.1 W/(m K)) and is resistant to chemical attack to above the maximum temperature range of the investigation (330 °C). As a thin-wall ceramic tube was available, a column with a small heat capacity was obtained. This is important for rapid temperature control and low power consumption. A good temperature profile over the whole effective area of the column was obtained. The surface temperature of the column was constant within ±5 °C at 300 °C.

In this study, cryogenic trapping was avoided in order to reduce the experimental complexity. Several kinds of solid adsorbents were examined at ambient conditions, with single or multiple beds of adsorbents to trap the sulfur gases: e.g., silica gel, molecular sieves, carbosieve S III, Tenax TA, and activated charcoal. The adsorbents were investigated with a view to their trapping efficiency and their ability to separate the gases. In our investigation, the silica gel was the most suitable adsorbent with respect to not only trapping efficiency[41] but also separating ability.

In the present study, the key factor in the gas separation was selective elution of the gases from the adsorbent according to their desorption temperature. The gases are adsorbed on the silica gel surface by molecular attraction such as van der Waals interactions. In general, the attraction becomes higher with increases in the molecular size, and every gas has a specific desorption temperature on a specific adsorbent. Accordingly, a

(41) Devai, I.; Delaune, R. D. *Org. Geochem.* **1996**, *24*, 941−944.

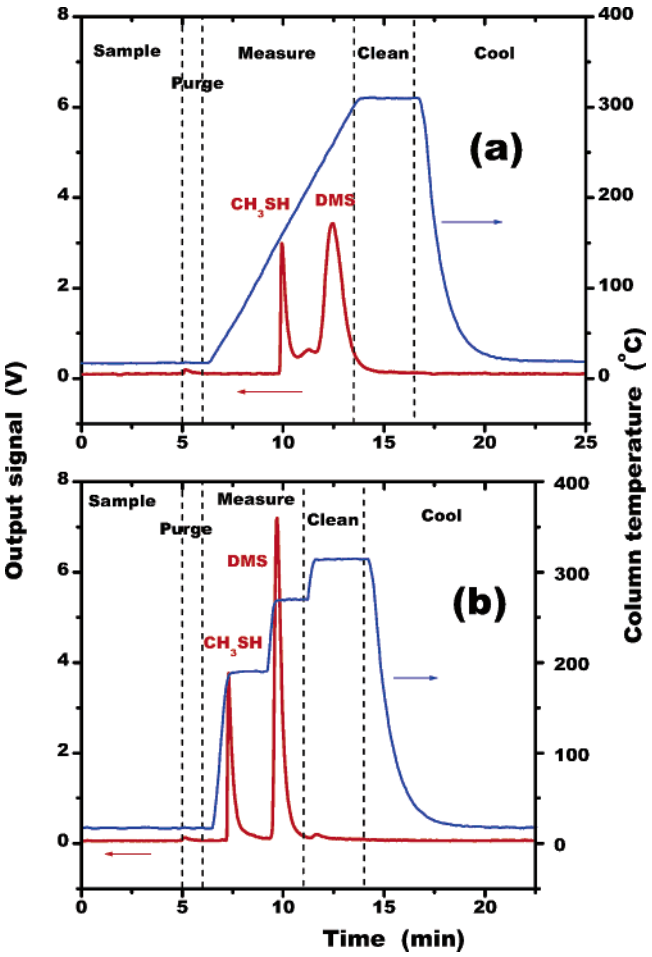

Figure 3. Chromatograms obtained by ramped (a) and stepwise (b) increases in the column temperature. The test gas was a mixture of 8 ppbv CH_3SH and DMS.

smaller molecule would desorb at a lower temperature. In this work, this simple principle was employed for the gas separation. The temperature of the gas-trapping column was ramped up while maintaining a continuous carrier flow. The gases were eluted according to their desorption temperatures and were detected by their subsequent chemiluminescence reactions. The gas separation was investigated with ramped and stepwise increases in the column temperature. Figure 3 shows chromatograms obtained by the two ways of increasing the temperature after trapping of 8 ppbv CH_3SH and DMS for 5 min. When the temperature of the column was increased at a constant rate of 42 °C/min, peaks appeared around 160 and 240 °C for CH_3SH and DMS, respectively. In the chromatogram (Figure 3a), we can see there was a small peak between the CH_3SH and DMS peaks, at ~180 °C. That small peak was recognized as CH_3SH, by performing several additional experiments. When clean air or only DMS was used as sample, no such peak was observed. That peak was observed only when CH_3SH was measured. The CH_3SH molecule has a smaller critical diameter (4.5 Å) than that of DMS and is supposed to enter easily into the cavities of porous silica gel. The reason for the two peaks for CH_3SH might be that a fraction of CH_3SH molecules is retained within the internal cavities of silica gel and then desorbs at a higher temperature (180 °C) than the normal desorption temperature. When the column temperature was increased stepwise, the CH_3SH signal appeared at 190 °C as a single peak. The DMS peak appeared at 270 °C. Better resolution between peaks and a higher peak intensity was observed in the stepwise increase (Figure 3b). In addition, the time needed for the stepwise temperature increases was shorter than that required for ramping the temperature up. Consequently, stepwise increases in the column temperature were employed for the further experiments. After DMS desorption, the column was cleaned at 320 °C.

Performance of the Measurement System. The performance of the present method was examined with the prepared test gases. Figure 4 shows the first five and last five chromatograms obtained when measurements of 10 ppbv CH_3SH and DMS were repeated 20 times. Good repeatability was obtained. Relative standard deviations for 10 ppbv CH_3SH and DMS were 3.2 and 1.9%, respectively. CH_3SH responses were smaller than those of DMS. This was because trapping efficiency was not perfect (70%) in case of CH_3SH.

Figure 5 shows calibration curves for CH_3SH and DMS. Linear calibration plots were obtained to over 100 ppbv for CH_3SH.

$$\text{peak height (V)} = 0.8634\text{CH}_3\text{SH (ppbv)} - 2.299 \qquad r^2 = 0.9987 \quad (1)$$

Response to low concentrations of CH_3SH was small compared to high concentrations. This is probably due to loss of CH_3SH during the trap and desorption steps. For a low concentration of CH_3SH (<10 ppbv), a quadratic equation was used for the calibrations. On the other hand, the linearity for DMS was very good from 0 to 60 ppbv.

$$\text{peak height (V)} = 1.1387\text{DMS (ppbv)} - 1.233 \qquad r^2 = 0.9994 \quad (2)$$

But, the calibration plot shifted downward from the linear in high concentrations over 60 ppbv. The reason for the shift was not clear, but a possible reason might be less reactivity of DMS to ozone than that of CH_3SH. It is reported that the cause of nonlinearity in the calibration plot may result from heterogeneous processes in the sulfide oxidation.[26] Limits of detection corresponding to three times the blank signal deviation were 0.3 ppbv for CH_3SH and 0.05 ppbv for DMS.

As shown in Figure 5, the calibration curves are linear over the measurement range. This is one of the merits of the chemiluminescence method. In the case of conventional FPD, the light-emitting species is S_2* and the light intensity is proportional to the square of the analyte concentration, as is well known. (Recently, HSO* has become known as another emitter in FPD, which provides linear intensity of chemiluminescence from 600 to 850 nm.[42]) On the other hand, the analyte generally becomes SO in the reaction with ozone, and then SO_2* is formed by a second reaction with ozone.[26]

Interference Examination. Interference from other gases was examined. NO is known as a chemiluminescence emitter, and the most popular NO analyzer is based on its chemiluminescence by reaction with ozone. As shown in Table 1, however, there is no effect from NO. The NO chemiluminescence is centered at 1200

(42) Aue, W. A.; Sun, X.-Y. *J. Chromatogr., A* **1993,** 633, 151−162.

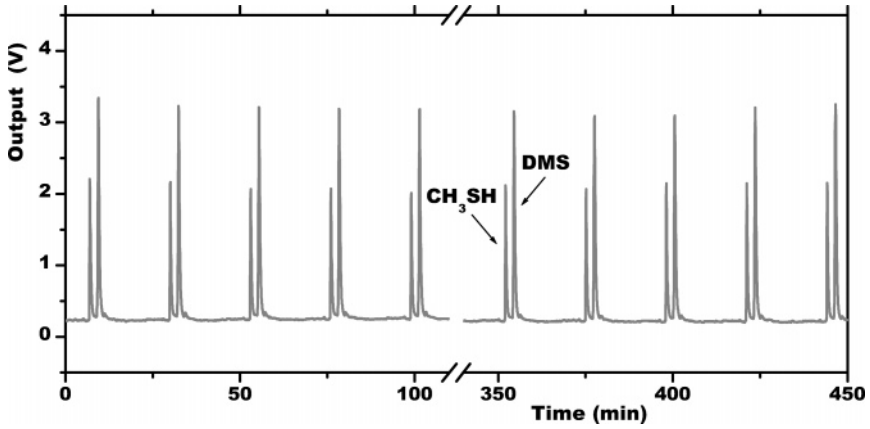

Figure 4. Chromatogram of standard gas mixture measured by the present system for 10 ppbv CH_3SH and DMS obtained with the shorter (20 mm) cell. The measurement was repeated 20 times, and the first 5 and the last 5 chromatograms are shown in the panel.

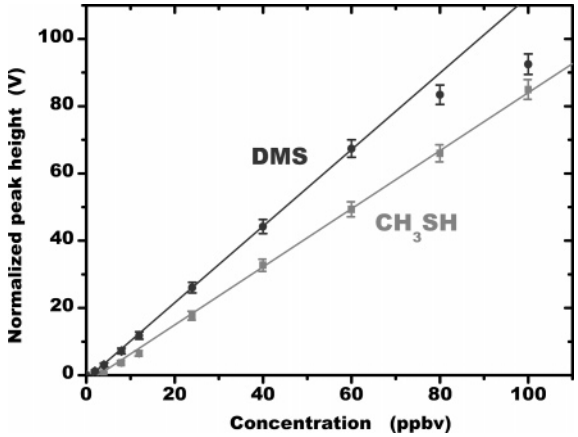

Figure 5. Calibration curves for CH_3SH and DMS measured by the present system.

Table 1. Chemiluminescence Characteristics of Sulfur Gases, NO, and Iroprene

gas	desorption temp (°C)[a]	concn (ppb)	response (V)[b]	relative response
DMS	240	10	3.11	1.00
CH_3SH	160	10	2.40	0.773
H_2S	150	10	0.0294	0.0094
COS	90	10	0.0380	0.0122
CS_2	100	20	0.522	0.0839
NO		100	nd	0
isoprene	190	185	0.748	0.0117

[a] Desorption temperatures were determined in ramped mode of the trap/separation system. [b] Response intensities were measured with the stepwise increases in the column temperature.

nm and starts from 600 nm. The PMT used did not respond to light over 650 nm, and a very poor signal was obtained even at 1000 ppbv NO in direct measurements. In the trap/separation chemiluminescence, no recognizable signal was observed for 100 ppbv NO, even in the high-sensitivity mode.

Olefins are other compounds that may interfere with reduced sulfur compounds.[23] The potential of interference by isoprene was investigated, because a considerable amount of isoprene is present in human breath.[43,44] The chemiluminescence of isoprene was 3 orders less than the DMS intensity in direct chemiluminescence measurements. When isoprene prepared from a permeation tube was measured by the present trap/separation system, the desorption temperature was near that for CH_3SH, but no significant peak was observed, as reported in Table 1.

Chemiluminescence intensities observed for COS and CS_2 were low compared to the intensity for DMS. In a real-world monitoring environment, these are not present in significant amounts and there is not much potential for them to interfere with CH_3SH detection. Desorption temperatures of COS and CS_2 were 90 and 100 °C in the system where the temperature was ramped, which was much lower than the desorption temperature for CH_3SH. When the column temperature was increased stepwise, the CS_2 peak appeared very quickly at 190 °C and could be distinguished from the CH_3SH peak.

One of the major sulfur gases, H_2S, desorbed from silica gel at ~150 °C, which was close to the CH_3SH desorption temperature. Therefore, it was difficult to separate H_2S and CH_3SH. Fortunately, the chemiluminescence signal of H_2S was much smaller than that of CH_3SH. Furthermore, the recovery of H_2S in the silica gel trap system was poor because of its high volatility and reactivity. Accordingly, in the trap/separation and chemiluminescence system, the H_2S signal was only 1/100 that of CH_3SH. There is no need for concern about H_2S interference in CH_3SH determination in normal odor analysis. If the H_2S level is much higher than that of CH_3SH (more than 20 times), H_2S interference may become a matter of concern. In that case, H_2S could be selectively eliminated by a small column (16 mm i.d. × 10 cm) packed with glass wool treated with 5% Na_2CO_3/5% glycerin placed downstream of the Nafion dryer. In the beginning, a filter paper impregnated with Na_2CO_3/glycerin was used the same as for elimination of HONO gas.[45] The present glass wool device was much more efficient than the filter paper and removed H_2S completely with negligible loss of CH_3SH.

Recoveries of both gases were affected by the humidity of the sample. The peak intensity of CH_3SH was significantly reduced 40−50% for a highly humid sample, whereas the DMS peak was

(43) Španěl, P.; Davies, S.; Smith, D. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 1733−1738.

(44) Lechner, M.; Moser, B.; Niederseer, D.; Karlseder, A.; Holzknecht, B.; Fuchs, M.; Colvin, S.; Tilg, H.; Rieder, J. *Respir. Physiol. Neurobiol.* **2006**, in press.

(45) Takeuchi, M.; Okochi, H.; Igawa, M. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 757−764.

Table 2. Measurement of Breath and Headspace of Septic Tank Samples by the Present Trap/Separation Chemiluminescence System and a GC-FPD System

sample		sampling date	CL system		GC-FPD[a]	
			CH_3SH	DMS	CH_3SH	DMS
breath	(sex, age)					
A	M, 31	Jan 27, 13:30	13.2 ± 0.0	18.8 ± 0.6	12.9 ± 0.3	23.2 ± 0.3
B	M, 45	Jan 27, 18:30	26.3 ± 2.1	9.23 ± 0.49	28.8 ± 0.0	7.75 ± 0.28
C	F, 23	Jan 30, 14:00	9.57 ± 0.10	9.14 ± 0.29	9.64 ± 0.69	9.30 ± 0.72
D	F, 24	Jan 31, 18:00	13.2 ± 0.3	5.07 ± 0.15	10.5 ± 0.39	4.83 ± 0.24
E	M, 28	Jan 31, 12:30	10.1 ± 0.6	7.13 ± 0.25	8.50 ± 0.10	6.85 ± 0.19
F	M, 28, smoker	Jan 30, 17:30	10.8 ± 0.29	9.59 ± 0.45	nd	nd
G	M, 26, smoker	Jan 31, 11:00	18.2 ± 0.4	11.4 ± 0.07	nd	nd
headspace						
septic tank 1		Jan 27, 15:30	2.30 ± 0.14	11.6 ± 0.7	nd	11.0 ± 0.6
septic tank 2		Jan 31, 17:30	1.12 ± 0.10	11.1 ± 0.8	nd	9.80 ± 0.48

[a] The LODs for GC-FPD were CH_3SH 2.4 ppbv and DMS 2.1 ppbv. nd, not detected. Each sample was measured three times.

reduced by 10−20%. Therefore, a Nafion dryer[3,46−48] was used during the trapping. In our examination, loss of CH_3SH and DMS in the Nafion dryer was negligible. In the case of breath sampling, the air was pre-dehumidified through a calcium chloride tube to prevent water condensation in the Tedlar bag.

Application to Breath Odor and Septic Tank Air Analyses. Human breath samples and headspace samples from a septic tank were measured by the single column trapping/separation method. The same samples were simultaneously measured by a cryogenic trapping GC-FPD system. Data shown in Table 2 give concentrations of CH_3SH and DMS contained in breath and septic tank samples obtained by both methods. The data obtained by the two methods were mostly in good agreement. However, some of the breath samples could not be measured by GC-FPD. For example, the gas levels of breath samples F and G were not low when analyzed by the present method, but they were not detected by the GC-FPD system. Interestingly, these samples were from a tobacco smoker, and it is probable that the sulfur gases reacted with tobacco ingredients, causing them to disappear in the trapping column. The cryogenic trapping used in the GC-FPD method is supposed to collect many kinds of gases. In the GC-FPD analyses, we originally used 2 min of heating for desorption as reported for atmospheric analysis;[37] however, breath samples gave no peaks with that desorption time. When the warming was shortened to 30 s, peaks were obtained for the samples. This suggested that the trapped sulfur gases reacted with co-trapped species, causing them to disappear during the heating for the desorption. Thus, the breath measurement using cryotrapping was difficult. On the other hand, room-temperature silica gel does not retain the reactive compounds, and the reliability is supposed to be better.

A difference between the data was observed in case of the CH_3SH concentration in the headspace sample, the GC-FPD system was unable to detect low levels of CH_3SH. The septic tank gas did not contain a very high level of sulfur gases. In contrast to the breath air, there was more DMS than CH_3SH in the septic tank. The CS_2 concentration was relatively high in the septic tank headspace, and a CS_2 peak was observed just before the CH_3SH peak in the present method. The peak height corresponded to 10 ppb CS_2. The trap/separation chemiluminescence instrument was easier to operate, more sensitive, and less affected by contaminants. The two major odorous compounds were successfully measured by the present instrument.

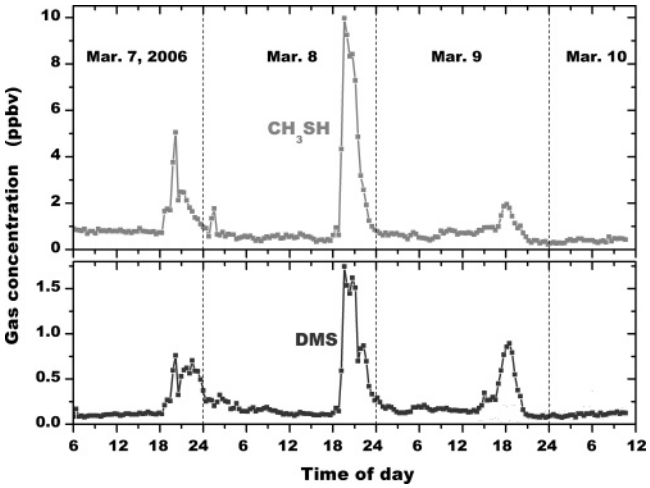

Figure 6. Trend in CH_3SH and DMS levels in toilet air. The gases were measured over 3 days in a rest room.

Automated Measurements of Toilet Air. The present instrument is suitable not only for batchwise measurement but also for semicontinuous automated measurement. Figure 6 is on-site measurement data obtained by placing the instrument in a toilet room. The measurements were automatically repeated 220 times for 3 days. The instrument was checked with standard gases before and after the experiment, and the responses were the same within 10%. The same trapping/separation column could be used for 3 days. H_2S was also analyzed on the last day by a micro gas analysis system.[33] CH_3SH was present at ppbv levels, and DMS and H_2S were present at sub-ppbv levels. The gas levels were lower than expected. The experiment was performed in winter during which microorganism activity was supposed to be low. Furthermore, only a few people used the toilet during the experiment, because it was during the spring break. Thus, the smell from the toilet was not strong. Even in this situation, the odorous sulfur

(46) Harrison, R. M.; Nedwell, D. B.; Shabbeer, M. T. *Atmos. Environ.* **1992**, *26A*, 2381−2387.
(47) Goldan, P. D.; Kuster, W.C.; Albritton, D. L.; Fehsenfeld, F. C. *J. Atmos. Chem.* **1987**, *5*, 439−467.
(48) Mactaggart, D. L.; Adams, D. F.; Farwell, S. O. *J. Atmos. Chem.* **1987**, *5*, 417−437.

gases could be measured and daily variations were obtained. Interestingly, both gas levels increased drastically after dark. The gas levels reached a maximum in the early evening every day. After that, they decreased: this seemed to be because the sulfur source was consumed in a few hours. DMS was retained a bit longer than CH_3SH. This suggests that the lifetime of DMS is longer than that of CH_3SH. Generation of sulfur gases during the night has been reported in the literature,[35,40] but details of the mechanism are not clear at this time. The instrument presented here may help the investigation of gas emissions.

CONCLUSIONS

A simple and reliable instrument for measurement of CH_3SH and DMS, the odorous sulfur compounds, has been developed. Both collection and separation are performed with the same column, and a simple measurement system was established. The calibration curve is linear, and it detects lower concentrations of the sulfur gases than those by FPD. An ac power source is required, but the instrument is portable and can be used for on-site analysis. The measurement is repeated automatically, and the instrument can be used for time variation analysis. The measurement cycle is repeated every 23 min in a typical protocol. If the H_2S concentration is expected to be more than 20 times the CH_3SH level, H_2S removal is recommended by using glass wool impregnated with Na_2CO_3. However, usually there is no concern of interference in natural sulfur gas measurements. The instrument proposed here is expected to be used not only for environmental research but also for odor analysis and breath analysis.

Received for review May 19, 2006. Accepted July 10, 2006.

AC060928V