Measurement Device for Ambient Carbonyl Sulfide by Means of Catalytic Reduction Followed by Wet Scrubbing/Fluorescence Detection

Kodai Abe, Koki Shimohira, Yusuke Miki, Yasuo Hirose, Shin-Ichi Ohira, and Kei Toda*

Cite This: ACS Omega 2020, 5, 25704–25711

ABSTRACT: A portable chemical analysis system for monitoring ambient carbonyl sulfide (COS) was investigated for the first time. COS is paid attention to from the perspectives of photosynthesis tracer, breath diagnosis marker, and new process-use in the manufacture of semiconductors. Recently, the threshold level value of COS was settled at 5 ppm in volume ratio (ppmv) for workplace safety management. In this work, COS was converted to H₂S by a small column packed with alumina catalyzer at 65 °C. Then, the H₂S produced was collected in a small channel scrubber to react with fluorescein mercuric acetate (FMA), and the resulting fluorescence quenching was monitored using an LED/photodiode-based miniature detector. The miniature channel scrubber was re-examined to determine its robustness and easy fabrication, and conditions of the catalyzer were optimized. When the FMA concentration used was 1 μM, the limit of detection and dynamic range, which were both proportional to the FMA concentration, were 0.07 and 25 ppbv, respectively. Ambient COS in the background level and even contaminated COS in the nitrogen gas cylinder could be detected. If necessary, H₂S was removed selectively by reproducible adsorbent columns. COS concentrations of engine exhaust were measured by the proposed method and by cryo-trap-gas chromatography-FPD methods. The CryT-GC-FPD method is troublesome and requires skilled analysts and long analysis time, thus it is not suited for onsite continuous monitoring. Recently, a quantum cascade laser was employed for long-path absorption spectroscopy (QCLS), cavity ring-down spectroscopy (CRDS), and off-axis integrated cavity output spectroscopy (OA-ICOS) to accomplish the long-distance COS measurement. However, the toxicity of COS has become an issue in this decade. For example, inhalation exposure of COS produces altered brainstem auditory evoked responses. EPA has determined a threshold limit value of 5 ppmv for workplace COS. According to the recent industrial use and revealed toxicity of COS, a monitoring method for COS is urgently needed. Nevertheless, a convenient and inexpensive monitoring method has not been developed for COS (see Table S2 for reported methods). Conventionally, gas samples collected in Tedlar bags are brought back to the laboratory to be analyzed offline by cryo-trapping/thermal desorption followed by gas chromatography-flame photometric detection (CryT-GC-FPD). The CryT-GC-FPD method is troublesome and requires skilled analysts and long analysis time, thus it is not suited for onsite continuous monitoring. Recently, a quantum cascade laser was employed for long-path absorption spectroscopy (QCLS), cavity ring-down spectroscopy (CRDS), and off-axis integrated cavity output spectroscopy (OA-ICOS) to accomplish the long-distance COS measurement. However, the toxicity of COS has become an issue in this decade. For example, inhalation exposure of COS produces altered brainstem auditory evoked responses. EPA has determined a threshold limit value of 5 ppmv for workplace COS. According to the recent industrial use and revealed toxicity of COS, a monitoring method for COS is urgently needed. Nevertheless, a convenient and inexpensive monitoring method has not been developed for COS (see Table S2 for reported methods). Conventionally, gas samples collected in Tedlar bags are brought back to the laboratory to be analyzed offline by cryo-trapping/thermal desorption followed by gas chromatography-flame photometric detection (CryT-GC-FPD). The CryT-GC-FPD method is troublesome and requires skilled analysts and long analysis time, thus it is not suited for onsite continuous monitoring. Recently, a quantum cascade laser was employed for long-path absorption spectroscopy (QCLS), cavity ring-down spectroscopy (CRDS), and off-axis integrated cavity output spectroscopy (OA-ICOS) to accomplish the long-distance COS measurement.

INTRODUCTION

Carbonyl sulfide (COS) is the most abundant volatile sulfur compound in the atmosphere, and its background level is in the range 0.51–0.53 part per billion in volume ratio (ppbv). Its lifetime in the atmosphere, 7 years, is much longer than those of other volatile sulfur compounds (dimethyl sulfide (DMS): 0.5 days, H₂S and SO₂: 2 days), and it is retained in high concentrations in the atmosphere. Concentrations of COS in various environments are summarized in Table S1. COS is naturally produced from sediments and plants, especially in coastal areas and lakes. Volcanos are geological sources of COS. Indirect production also includes oxidative conversion from DMS and CS₂. Anthropogenic emissions from the pulp, chemical fiber, pigment, aluminum and gas industries, agriculture, biomass burning, biofuel combustion, and food processing/waste can also produce COS. The elevated tropospheric COS levels impact the stratospheric aerosol layer. COS is recognized as a powerful tracer of ecosystem CO₂ exchange because COS is taken up by vegetation and hydrolyzed by carbonic anhydrase. Also, COS in exhaled breath is a potential biomarker for different disease pathologies, such as liver disease, organ rejection, and cystic fibrosis. Recently, COS has been recognized as an important process gas for the manufacturing of advanced semiconductors to prepare conducting carbon films for the deep trench walls in oxygen plasma-assisted chemical vapor deposition. However, the toxicity of COS has become an issue in this decade. For example, inhalation exposure of COS produces altered brainstem auditory evoked responses. EPA has determined a threshold limit value of 5 ppmv for workplace COS. According to the recent industrial use and revealed toxicity of COS, a monitoring method for COS is urgently needed.

Received: June 21, 2020
Accepted: September 17, 2020
Published: September 30, 2020
monitor COS, and the estimated limits of detection (LODs) were reported as 250 or 0.185 ppbv. Kooijmans et al. evaluated a QCLS for COS measurement at an ambient level of around 0.5 ppbv. OA-ICOS has been recently developed to continuously measure dissolved COS in seawater with the use of an equilibrator. These ‘physical (or optical)’ methods provide continuous measurement with a special laser light source and a precious optical system for aligning kilometers of the optical axis. In this work, a chemical approach was employed to achieve a low-cost and sensitive system for COS monitoring.

COS itself is inactive and difficult to measure chemically. However, COS can be converted to H2S by catalytic hydrolysis. Zhao et al. investigated Zn–Ni–Fe hydrotalcite and Zn–Al hydrotalcite as catalysts. Hydrolysis with the former catalyst was performed at a high temperature of 250 °C. With the latter, the reaction proceeded at 50 °C, but oxygen in the air damaged the catalyst in a few hours. Apart from these, effective organic polymer catalysts, alumina/titania-based catalysts, and liquid-phase hydrolysis were also recently reported. We have found that the conventional alumina catalyst works well for this purpose at a low temperature (<100 °C) with a long lifetime. The produced H2S can be analyzed by wet scrubbing, followed by fluorescence detection, as previously demonstrated.

The microsystem for H2S, called micro-gas analysis system (μGAS), is a highly sensitive portable device and could be applied for the measurement of CH3SH, HCHO, and breath NO for environmental and medical applications. However, fabrication of the microchannel scrubber, which is the key device of the μGAS, can be carried out only by skilled personnel. In this work, the channel scrubber was re-examined to make fabrication easier and the device more robust and maintaining the performance to establish a catalytic hydrolysis-miniature gas analysis system (CH-mGAS).

The flow diagram of CH-mGAS is shown in Figure 1a. The device is portable as shown in Figure S1. COS in an air sample was hydrolyzed in a catalysis reactor (CR). The H2S produced was collected at a honeycomb-patterned channel scrubber (HCS) in an alkaline absorbing solution and reacted with fluorescein mercuric acetate (FMA). Quenching of FMA fluorescence was monitored by a miniature fluorescence detector (μFD). If interference from ambient H2S must be considered, a H2S remover (Figure 1b) was placed at the sample inlet. See the Experimental Section for details of CH-mGAS.

RESULTS AND DISCUSSION

Miniature Channel Scrubber. We have previously developed a microchannel scrubber to collect water-soluble analyte gases. Fabrication of microchannels is advantageous for gas scrubbing. Similar approaches have been carried out by Guglielmino et al. for absorbance detection and Ueda et al. and Becker et al. for fluorescence detection of gaseous HCHO. An effective enrichment of the analyte gas was achieved by the microchannel scrubber, which could have a high ratio of the gas absorbing area to absorbing solution volume, and a small liquid volume of the scrubber makes the system response faster. However, the previous microchannel scrubber made of poly(dimethylsiloxane) (PDMS) was not robust for long operations. This was a serious disadvantage for field use. A gas-permeable membrane must be pasted strongly on the PDMS microchannel plate without adhesive; otherwise, the membrane could sometimes peel off from the PDMS plate due to the liquid flow pressure. If adhesive is used, it could spread out and clog the microchannel. Therefore, the device should be fabricated only by skilled personnel. To overcome this problem, new scrubbers were designed (Figures S2 and S3), so that the channels for absorbing solution could be fabricated by machining with a miniature end mill bit on a transparent poly(vinyl chloride) (PVC) plate. The gas absorbing channels were arranged in a honeycomb pattern, but the width and depth of the hexagon channels were 1.0 and 0.25 mm, while they were 0.22 and 0.06 mm in the previous device, respectively (Table 1, Figure S2). Though such an enlargement of the liquid channels might be disadvantageous due to the lowering of the absorbing-area-to-absorbing-solution volume ratio, higher collection efficiencies were obtained and comparable characteristics were achieved with the end-mill-machined device. This is because the pattern of gas channels was made the same as that of the liquid channels, while the gas channel of the previous PDMS device was a single large channel (Figure S3). Between the two newly developed devices, the bigger one had a better collection efficiency but the response speed was worse (Table 1); hence, the smaller PVC device was chosen as the best scrubber device.

Clear PVC is a good material for the plates of the device because of its transparency and durability to reagents. However, the system that comprised the PVC scrubber did not provide response signals to H2S at low concentrations (<1 ppbv) probably because Pb additives in the material interacted with H2S. This problem was solved by the silanization of the gas channels. Not only did the dead zone in the calibration curve disappear but also the slope of the calibration curve became 1.8 times greater after the inactivation of the channel device.

Optimizations of Hydrolysis. The conditions for COS hydrolysis were examined. We succeeded in converting COS to...
H₂S with the Al₂O₃ catalyst at a low temperature, as shown in the reaction in eq 1.

\[
\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2
\]  

(1)

High amounts of catalyst and a high catalysis temperature resulted in poor recovery, as shown in Figure 2a, b. This was probably due to the fact that the produced H₂S was decomposed on the catalyst.

**Table 1. Comparison of the Channel Scrubbers**

| channel scrubber device | PDMS          | PVC small | PVC big |
|-------------------------|---------------|-----------|---------|
| number of hexagonal unit| 499           | 44        | 68      |
| liquid channel          |               |           |         |
| width (mm)              | 2.2           | 1.0       | 1.0     |
| depth (mm)              | 0.06          | 0.25      | 0.25    |
| length (mm)             | 0.60          | 2.0       | 2.0     |
| volume (μL)             | 13            | 86        | 116     |
| gas absorbing area (mm²)| 210           | 340       | 460     |
| gas channel             | single        | honeycomb |         |
| width (mm)              | 14            | 1.0       | 1.0     |
| depth (mm)              | 3.0           | 1.5       | 1.5     |
| liquid flow rate (mL/min)| 0.12         | 0.20      | 0.20    |
| response (μM/H₂S ppbv)  | 0.060         | 0.037     | 0.046   |
| collection efficiency (%)| 35           | 68        | 85      |
| response T90% up (min)² | 1.8           | 1.4       | 2.4     |
| down (min)              | 1.4           | 1.3       | 1.3     |

“*The same device as in ref 53 was fabricated and examined in this study. 6 Gas channels of the PVC devices were honeycomb-patterned, same as the liquid channel. See Figure S2 for the design of the three scrubbers. T90% up and down is 90% response time when the H₂S concentration was changed from 0 to 50 ppbv and from 50 to 0 ppbv, respectively.*

Figure 2c shows response intensities for 50 ppbv H₂S without the catalyzer and 100 ppbv COS with the catalyzer in blue and green plots, respectively, obtained by changing flow rates of the test gases. The H₂S signal increased with an increase in the gas flow because the supply rate of the H₂S analyte was proportional to the flow rate. But the curve bends downward because diffusion through the PTFE membrane limited the supply of H₂S into the scrubbing solution. On the other hand, the signal for COS was constant above 0.4 L/min. This was because the conversion rate of the catalyst gradually became slow with the increase in the flow rate at this flow range (red curve). The hydrolysis conversion efficiency was maximum at the sampling rate of 0.4 L/min. From these results, we decided to use 4 g of the catalyst at 65 °C with 0.4 L/min sample flow rate as optimum parameters. In these conditions, the water vapor effect was examined by changing the temperature of the water vapor equilibrator. While excess water vapor (45 °C) decreased the response intensity again, the efficiency of conversion to H₂S was almost the same between 15 and 35 °C. The conversion rate of COS to H₂S increases with the increase in water vapor concentration, but too much water vapor clogs the micropore reaction sites by water deposition and decreases the hydrolysis rate. Therefore, the water bubbler was maintained at 25 °C or was used without temperature control for further experiments.

**Analytical Performance of the Device.** The fluorescence signal of FMA was quenched by the reaction of FMA with dissolved H₂S, which was converted from COS. Thus, the fluorescence signal decreased with the introduction of COS. Figure 3a shows the response chart obtained in optimized conditions for 0–125 ppbv COS, triplicated for each concentration. The FMA concentration used was 5 μM. By switching a three-way solenoid valve (35V in Figure 1a), baseline and response were alternatively obtained for 6 and 4 min, respectively, so that response peaks were obtained every 10 min. Good baseline stability and repeatable signals were obtained. A linear calibration curve was obtained from the results ($R^2 = 0.9984$). The limit of detection (LOD), obtained from three times the noise and the calibration curve, was 0.32 ppbv for COS. The dynamic range could be enlarged by increasing the FMA concentration of the absorbing solution. On the contrary, a higher sensitivity could be achieved with a lower FMA concentration. With 1 μM FMA, for example, the LOD obtained was 0.07 ppbv, and the calibration curve was linear up to the dynamic range of 25 ppbv ($R^2 = 0.9998$). The numbers in Figure 3 indicate concentrations of COS added in the test air. Even without COS mixing, obvious responses were observed as shown in the inset of Figure 3b. These responses were from COS existing in the experimental room. The air was used after passing through a Peltier dryer, silica gel/sodalime/active carbon columns, but COS was not removed by such conventional purifiers. Surprisingly, responses were obtained even for nitrogen supplied from a gas cylinder. COS removal is extremely difficult, and the proposed system can be used for quality control of gas manufacturing.

Wide range monitoring was performed by replacing the channel scrubber and 5 μM FMA solution with a short annular wet denuder 58 and 20 μM FMA solution. COS in ppbv levels was successfully monitored, as shown in Figure 3c, with a dynamic range of 7.5 ppbv ($R^2 = 0.9965$). The dynamic range for COS can be enlarged by an increase in the FMA concentration and a decrease in the collection efficiency of the scrubber.
obtained with keeping the solenoid valve (3SV in Figure 1a) on to remove the produced H2S. The COS hydrolysis column was maintained at 65 °C for conversion to H2S. Thus, the proposed system works well under normal measurement conditions.

Elimination of Interference. We tested other volatile sulfur compounds that may interfere with the analysis. The tested volatile sulfur gases were 200 ppbv of H2S and 1000 ppbv of CH3SH, SO2, DMS, dimethyl disulfide (DMDS), and CS2. H2S and CH3SH had a 91 and 20% response to the same concentration of COS, respectively. H2S introduced in the analytical device was partially decomposed in the catalyzer, and the response intensity for H2S was slightly smaller than that for COS. The collection efficiency and FMA reaction rate of CH3SH were lower, and the response to CH3SH was smaller than that of H2S.46 The other sulfur gases did not show interference at all (Table S1).

We examined molecular sieve columns and alkaline absorbing solutions to remove H2S from the sample air. A bubbler was incorporated to supply water vapor for COS hydrolysis. An alkaline-added bubbler would work as a H2S absorber as well as a water vapor generator and effectively remove H2S. However, the removal efficiency dropped after 2 h of introducing 100 ppbv H2S (Figure 4). Although the lifetime doubled when the volume of the absorbing solution (0.1 M NaOH) was increased to 40 mL, the alkaline solution must be renewed every 4 h. The molecular sieve too removed H2S well. Finer powders (80/100 mesh) of the molecular sieve had longer lifetimes than the coarse adsorbent (1/8″), as shown in Figure 4. The molecular sieve column quantitatively removed 100 ppbv H2S for 3 h and 100 ppbv CH3SH for 2 h.

The molecular sieve column was reproducible. Two molecular sieve columns were connected in parallel at the sample inlet and used to remove H2S alternatively (Figure 1b). One of the columns not in use was heated at 200 °C with waste air flowing out from the sampling air pump. The H2S removal system could be used semipermanently by switching every 2.5 h with 2 h of heating and 0.5 h of cooling. The solid-state H2S remover did not interfere with COS analysis, and a good response was obtained for COS, as shown in Figure 5. Responses for the mixture of 50 ppbv COS, 500 ppbv H2S, and 500 ppbv SO2 were the same as those for 50 ppbv COS without H2S and SO2. Continuous and selective COS detection was succeeded by the reproducible H2S removal system.

Analysis of COS Emitted from Motorcycles. The developed system was evaluated for exhaust gases emitted from bicycle engines. Direct and continuous analysis of the exhaust by CH-mGAS together with IMR-MS was first evaluated. The exhaust gas from the bicycle placed outside the laboratory was introduced via a window into the CH-mGAS and ion molecule reaction-mass spectrometer (IMR-MS) placed in the laboratory. COS concentrations obtained by the two methods increased and decreased in a similar manner

![Figure 3. Responses of CH-mGAS.](image)

![Figure 4. Lifetime of the H2S removers.](image)
However, the values obtained by IMR-MS were much higher than those obtained by CH-mGAS. We assumed that COS concentrations obtained by IMR-MS were overestimated due to the coexistence of compounds, whose m/z was the same as that of COS, such as CH₃COOH produced by combustion. We tried to remove CH₃COOH vapor by an alkaline bubbler, and then the values obtained by the two methods were in the same order in the engine acceleration periods. However, the overestimation by IMR-MS was not removed well, and the difference between signals of CH-mGAS and IMR-MS became larger with the time of operation due to the sticky property of the interference species (Figure 6a).

After the engine was stopped, the output of CH-mGAS decreased quickly but the IMR-MS output did not reach zero within 40 min of the engine being stopped. This was probably due to the sticky organic acid being adsorbed in the sampling line and retained for a long time. Thus, COS in the exhaust gas cannot be measured by the mass spectrometer.

Next, batchwise comparison with gas chromatography was performed (Figure 7). The exhaust gas was collected in Tedlar bags and then measured by CH-mGAS (with the H₂S removal system) and CryT-GC-FPD. The exhaust gas samples contained COS but not in high concentrations (0.5–6 ppbv). According to CryT-GC-FPD analysis, H₂S existed in the exhaust, especially in the exhaust from old catalyst bikes, in several to several tens of ppbv, and SO₂ was between 10 and 30 ppbv (Table S2). Even in such conditions, the values obtained by the two methods agreed well, with good correlation ($R^2 = 0.945$) and a slope of 0.947, as shown in eq 2.

$$\text{COS mGAS (ppbv)} = 0.947 \times \text{COS GC-FPD (ppbv)} + 0.215 \quad (R^2 = 0.945)$$

Furthermore, the CH-mGAS measured the bag sample in minutes while CryT-GC-FPD required a long analysis time of more than 30 min. Also, the analysis operator needs to prepare a cryo-bath of acetone/dry ice or liquid argon beforehand to perform CryT-GC-FPD.

**CONCLUSIONS**

A new principle for measuring COS is proposed, which is based on online catalytic hydrolysis, followed by scrubbing/fluorescence detection, and an automated system, CH-mGAS, has been developed and characterized. The performance and features of the developed method is compared with those of conventional and reported methods in Table S2. CH-mGAS is the first analytical device to monitor COS chemically. The device shows good performance for COS sensing, and it is also portable and inexpensive. The LOD is dependent on the FMA concentration used, and the LODs are 0.07 and 0.32 ppbv when FMA concentrations are 1 and 5 μM, respectively. The sensitivity of the method with 1 μM FMA is comparable to those of optical methods, such as OA-ICOS, and the sensitivity and selectivity of the device are much higher than those of chemical ionization mass spectrometer simultaneously tested. Though it is difficult to monitor COS at an ambient level with the mass spectrometer due to low concentrations of COS and other compounds, the CH-mGAS was able to measure COS with good correlation and a simple procedure.
interference from coexisting compounds, the developed device can detect COS at the ambient level. Interference from H$_2$S can be removed by a molecular sieve column system. Data analyzed by CH-mGAS agree well with data analyzed by Cry-T-GC-FPD. Also, the device has good repeatability and good selectivity. COS in ambient air and a nitrogen cylinder could be detected. The sensing system has the potential to be used for ambient COS monitoring, breath COS analysis, and quality control of gas manufacturing. Further investigation must be carried out to establish the crucial determination of COS at ambient levels to evaluate applicability in monitoring photo-synthetic activity and atmospheric/oceanic COS content with incorporating calibration with 0.5 ppbv standard gas and further improvements of the system. In addition, it may also be applied in an alarm system for safety control in workplaces, such as semiconductor industries where COS is used for plasma-assisted vapor deposition. Wide range monitoring can be performed with FMA solution at high concentrations and with a short annular wet denuder.

**EXPERIMENTAL SECTION**

**Reagents.** COS test gases were prepared by dilution of standard cylinder gas (100 ppm COS balanced with nitrogen, Japan Fine Products, Kawasaki, Japan) with purified air using mass flow controllers. Gas dilutions (uncertainty of the first step dilution accuracy was within 2.7%) were conducted twice to obtain ppbv levels of COS. The gas absorbing solution was 0.1 M NaOH with the addition of 1 or 5 μM FMA. FMA was purchased from Sigma Aldrich (St. Louis, MO). A molecular sieve 3A (pore size 30 μm, 1/8″, Nacalai Tesque, Kyoto, Japan, or 80/100 mesh, Shimadzu, Kyoto, Japan) was used for selective H$_2$S removal. A minicolumn packed with soda lime No.2 (Wako Pure Chemical, Osaka, Japan) and active carbon (Nacalai) was used to remove H$_2$S produced by hydrolysis of COS to obtain a baseline signal. Alumina catalyst NT-9710 (50 m$^2$/g) was obtained from Nissan Girdler Catalyst (Tokyo, Japan). A silanizing agent (L-25, Fuji Systems, Tokyo) was used to make the gas channels inactive.

**Analytical System.** The flow diagram of the developed system is shown in Figure S1. All components were installed in a portable box (Figure S1). The air sample was aspirated using a miniature airpump (CM-15-12, Enomoto Micro Pump, Tokyo) and controlled by a flow sensor and a needle valve (PFMV510 and AS1002F, SMC, Tokyo) at a flow rate of 0.4 L/min. The COS air sample was passed through a humidifying bubbler and a catalytic reactor to convert COS to H$_2$S. The produced H$_2$S was collected in an alkaline FMA reagent solution in the honeycomb-patterned channel scrubber. In the case of wide range measurement, a short annular wet denuder, comprising a porous polypropylene tube (o.d. 2.7 mm × i.d. 1.8 mm × effective length 10 mm, Accurel PP S6/2, Membrana, Wuppertal, Germany) jacketed in a 1/4″ Teflon tube, was used instead of the channel scrubber. Fluorescence quenching by the absorbed sulfide was monitored by a microfluorescence detector that comprised a blue LED (NSPB800s, $\lambda_{max}$ 460 nm, Nichia, Anan, Japan) and a photodiode (OPT301M, Texas Instruments, Dallas, TX) covered with a plastic long-pass filter (SC-52, Fujifilm, Tokyo, Japan) to cut off light <520 nm. The FMA solution flowed through the other channel side by a micro-ring pump (RP-Q1.2N-P20A-DC3V, Aquatech, Osaka, Japan) with a flow dumper made of silicone tubing (o.d. 6 mm × i.d. 4 mm × 30 mm) and a Teflon tubing coil (i.d. 0.3 mm × 1 m) connected in series.

**Analysis of COS Emitted from Engines.** To validate the developed system, exhaust from bicycle engines were measured by an ion molecule reaction-mass spectrometer (IMR-MS) (Airsense Net, V&F Analyse-und Messechnik GmbH, Absam, Austria) and Cry-T-GC-FPD together with the CH-mGAS device. The continuous analysis was performed using a bicycle placed outside the laboratory and the exhaust was aspirated via a window to CH-mGAS and IMR-MS placed in the laboratory. An impinger containing 0.1 M NaOH solution was placed occasionally at the sample inlet to eliminate acidic gases. Also, batchwise analysis was conducted by collecting 3 L of exhaust gas in a Tedlar bag. The bag samples were analyzed by Cry-T-GC-FPD, IMR-MS, and CH-mGAS. See the Supporting Information for details of Cry-T-GC-FPD analyses.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02985.

Concentrations of COS in various environments; comparison of COS analytical methods; pictures of CH-mGAS; designs of previous and new channel scrubbers; repeatability test of CH-mGAS; effect of ambient temperature on the measurement results; interference from the other sulfur gases; and comparative analysis with IMR-MS and Cry-T-GC-FPD (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Kei Toda — Department of Chemistry, Kumamoto University, Kumamoto 860-8555, Japan; Email: todakei@kumamoto-u.ac.jp

**Authors**

Kodai Abe — Department of Chemistry, Kumamoto University, Kumamoto 860-8555, Japan

Koki Shimohira — Department of Chemistry, Kumamoto University, Kumamoto 860-8555, Japan

Yusuke Miki — Tsukuba Laboratory, Taiyo Nippon Sanso Co., Tsukuba, Ibaraki 300-2611, Japan

Yasuhiro Hirose — Tsukuba Laboratory, Taiyo Nippon Sanso Co., Tsukuba, Ibaraki 300-2611, Japan

Shin-Ichi Ohira — Department of Chemistry, Kumamoto University, Kumamoto 860-8555, Japan; Email: orcid.org/0000-0002-5958-339X

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c02985

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by KAKENHI, Grants-in-Aid for Basic Research (B) (16H04168) and (A) (19H00955), Bilateral Programs Joint Research Projects (open partnership) from the Japan Society for the Promotion of Science, and the A-STEP Regional Value Program (VIP29217943622) from Japan Science and Technology Agency.
REFERENCES

(1) Kettle, A. J.; Kuhn, U.; von Hobe, M.; Kesselmeier, J.; Andreae, M. O. Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks. *J. Geophys. Res.: Atmos.* 2002, 107, No. ACH-25.

(2) Lelieveld, J.; Roelofs, G. J.; Ganzeveld, L.; Feichter, J.; Rodhe, H. Terrestrial sources and distribution of atmospheric sulfur. *Philos. Trans. R. Soc. B* 1997, 352, 149–158.

(3) Seinfeld, J. H.; Pandis, S. N. Atmospheric Trace Constituents. In *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 3rd ed.; Seinfeld, J. H.; Pandis, S. N., Eds.; Wiley, 2016; pp 18–68.

(4) Yang, Z.; Kanda, K.; Tsuruta, H.; Minami, K. Measurement of biogenic sulfur gases emission from some Chinese and Japanese soils. *Atmos. Environ.* 1996, 30, 2399–2405.

(5) Stimler, K.; Montzka, S. A.; Berry, J. A.; Rudich, Y.; Yakir, D. Relationships between carbonyl sulfide (COS) and CO2 during leaf gas exchange. *New Phytol.* 2010, 186, 869–878.

(6) Yi, Z.; Wang, X. Carbonyl sulfide and dimethyl sulfide fluxes in an urban lawn and adjacent bare soil in Guangzhou, China. *J. Environ. Sci.* 2011, 23, 784–789.

(7) Watts, S. F. The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide. *Atmos. Environ.* 2000, 34, 761–779.

(8) Delaune, R. D.; Devai, I.; Lindau, C. W. Flux of reduced sulfur gases along a salinity gradient in Louisiana coastal marshes. *Estuarine, Coastal Shelf Sci.* 2002, 54, 1003–1011.

(9) Whelan, M. E.; Min, D.-H.; Rhee, R. C. Salt marsh vegetation as a carbonyl sulfide (COS) source to the atmosphere. *Atmos. Environ.* 2013, 73, 131–137.

(10) Bodemberger, J.; Wassmann, R.; Papen, H.; Rennenberg, H. Temporal and spatial variation of sulfur-gas transfer between coastal marine sediments and the atmosphere. *Atmos. Environ.* 1999, 33, 3487–3502.

(11) Devai, I.; DeLaune, R. D. Formation of volatile sulfur compounds in salt marsh sediment as influenced by soil redox condition. *Org. Geochem.* 1995, 23, 283–287.

(12) Angert, A.; Said-Ahmad, W.; Davidson, C.; Amrani, A. Sulfur isotopes ratio of atmospheric carbonyl sulfide constrains its sources. *Sci. Rep.* 2019, 9, No. 741.

(13) Du, Q.; Mu, Y.; Zhang, C.; Liu, J.; Zhang, Y. H.; Liu, C. Photochemical production of carbonyl sulfide, carbon disulfide and dimethyl sulfide in a lake water. *J. Environ. Sci.* 2017, 31, 146–156.

(14) Richards, S. R.; Rudd, J. W. M.; Kelly, C. A. Organic volatile sulfur in lakes ranging in sulfate and dissolved salt concentration over five orders of magnitude. *Limnol. Oceanogr.* 1994, 39, 562–572.

(15) Belviso, S.; Nguyen, B. C.; Allard, P. Estimate of carbonyl sulfide (COS) volcanic source strength deduced from COS/CO2 ratios in volcanic gases. *Geophys. Res. Lett.* 1986, 13, 133–136.

(16) Muller, E.; Philippot, P.; Rollion-Bard, C.; Cartigny, P. Multiple sulfur-isotope signatures in Archean sulfates and their implications for the chemistry and dynamics of the early atmosphere. *Proc. Natl. Acad. Sci. U.S.A.* 2016, 113, 7432–7437.

(17) Oppenheimer, C.; Kyle, P.; Eisele, F.; Crawford, J.; Huey, G.; Tanner, D.; Kim, S. C.; Mauldin, L.; Blake, D.; Beyersdorf, A.; Buhr, M.; Davis, D. D. Atmospheric chemistry of an Antarctic volcanic plume. *J. Geophys. Res.: Atmos.* 2010, 115, No. D04303.

(18) Vasiliakos, C.; Maggos, T.; Bartris, J. G.; Papagiannakopoulou, P. Determination of atmospheric sulfur compounds near a volcanic area in Greece. *J. Atmos. Chem.* 2005, 52, 101–116.

(19) Modiri Gharehveran, M.; Shah, A. D. Indirect photochemical formation of carbonyl sulfide and carbon disulfide in natural waters: role of organic sulfur precursors, water quality constituents, and temperature. *Environ. Sci. Technol.* 2018, 52, 9108–9117.

(20) Lee, C.-L.; Brühl, C.; Lelieveld, J.; Crutzen, P. J.; Tost, H. The role of carbonyl sulfide as a source of stratospheric sulfate aerosol and its impact on climate. *Atmos. Chem. Phys.* 2012, 12, 1239–1253.

(21) Yang, F.; Qubaja, R.; Tatarinov, F.; Stern, R.; Yakir, D. Soil–atmosphere exchange of carbonyl sulfide in a Mediterranean citrus orchard. *Atmos. Chem. Phys.* 2019, 19, 3873–3883.

(22) Kits, F.; Gomez-Brandón, M.; Eder, B.; Ettemadi, M.; Spielmann, F. M.; Hammerle, A.; Insam, H.; Wohlfahrt, G. Soil carbonyl sulfide exchange in relation to microbial community composition: insights from a managed grassland soil amendment experiment. *Soil Biol. Biochem.* 2019, 135, 28–37.

(23) Sehnert, S. S.; Jang, L.; Burdick, J. F.; Risby, T. H. Breath biomarkers for detection of human liver diseases: preliminary study. *Biomarkers* 2002, 7, 174–187.

(24) Studer, S. M.; Orens, J. B.; Rosas, I.; Krishnan, J. A.; Cope, K. A.; Yang, S.; Conte, J. V.; Becker, P. B.; Risby, T. H. Patterns and significance of exhaled-breath biomarkers in lung transplant recipients with acute allograft rejection. *J. Heart Lung Transplantation* 2001, 20, 1158–1166.

(25) Kamboures, M. A.; Blake, D. R.; Cooper, D. M.; Newcomb, R. L.; Barker, M.; Larson, J. K.; Meinardi, S.; Nussbaum, E.; Rowland, F. S. Breath sulfides and pulmonary function in cystic fibrosis. *Proc. Natl. Acad. Sci. U.S.A.* 2005, 102, 15762–15767.

(26) Steiger, A. K.; Zhao, Y.; Pluth, M. D. Emerging roles of carbonyl sulfide in chemical biology: sulfide transporter or gasotransmitter? *Antioxid. Redox Signal.* 2018, 28, 1516–1532.

(27) Kim, J. K.; Cho, S. I.; Kim, N. G.; Jhon, M. S.; Min, K. S.; Kim, C. K.; Yeom, G. Y. Study on the etching characteristics of amorphous carbon layer in oxygen plasma with carbonyl sulfide. *J. Vac. Sci. Technol., A* 2013, 31, No. 021301.

(28) Bartholomaeus, A. R.; Haritos, V. S. Review of the toxicology of carbonyl sulfide, a new grain fumigant. *Food Chem. Toxicol.* 2005, 43, 1687–1701.

(29) Haritos, V. S.; Dojchinov, G. Carboxic anhydrate metabolism is a key factor in the toxicity of CO2 and COS but not CS2 toward the flour beetle Tribolium castaneum [Coleoptera: Tenebrionidae]. *Comp. Biochem. Physiol., Part C: Toxicol. Pharmacol.* 2005, 140, 139–147.

(30) Herr, D. W.; Graff, J. E.; Moser, V. C.; Crofton, K. M.; Little, P. B.; Morgan, D. L.; Sills, R. C. Inhalational exposure to carbonyl sulfide produces altered brainstem auditory and somatosensory-evoked potentials in Fischer 344 rats. *Toxicol. Sci.* 2007, 95, 118–135.

(31) EPA, U. S., Provisional peer-reviewed toxicity values for carbonyl sulfide (CASRN 463-58-1). *Superfund Health Risk Technical Support Center, N. C.* 2015, 118, 20–28.

(32) Bielecki, Z.; Stacewicz, T.; Wojtas, J.; Mikołajczyk, J. Application of quantum cascade lasers to trace gas detection. *Bull. Pol. Acad. Sci. Tech.* 2015, 63, S15–S25.

(33) Banik, G. D.; Maity, A.; Som, S.; Pal, M.; Pradhan, M. An external-cavity quantum cascade laser operating near 5.2 µm combined with cavity ring-down spectroscopy for multi-component chemical sensing. *Laser Phys.* 2018, 28, No. 045701.

(34) Kooijmans, L. M. J.; Uitstal, N. A. M.; Zahnisser, M. S.; Nelson, D. D.; Montzka, S. A.; Chen, H. Continuous and high-precision atmospheric concentration measurements of COS, CO2, CO and H2O using a quantum cascade laser spectrometer (QCLS). *Atmos. Meas. Tech.* 2016, 9, 5293–5314.
(39) Lennartz, S. T.; Marandino, C. A.; von Hobe, M.; Andreae, M. O.; Aranami, K.; Atlas, E.; Berkelhammer, M.; Bingemer, H.; Booge, D.; Cutter, G.; Cortes, P.; Kremsner, S.; Law, C. S.; Marriner, A.; Simó, R.; Quack, B.; Uher, G.; Xie, H.; Xu, X. Marine carbonyl sulfide (OCS) and carbon disulfide (CS2): a compilation of measurements in seawater and the marine boundary layer. Earth Syst. Sci. Data 2020, 12, 591–609.

(40) Lennartz, S. T.; Marandino, C. A.; von Hobe, M.; Cortes, P.; Quack, B.; Simo, R.; Booge, D.; Pozzer, A.; Steinhoff, T.; Arevalo-Martinez, D. L.; Kloss, C.; Bracher, A.; Röttgers, R.; Atlas, E.; Krüger, K. Direct oceanic emissions unlikely to account for the missing source of atmospheric carbonyl sulfide. Atmos. Chem. Phys. 2017, 17, 385–402.

(41) Zhao, S.; Yi, H.; Tang, X.; Jiang, S.; Gao, F.; Zhang, B.; Zuo, Y.; Wang, Z. Q. The hydrolysis of carbonyl sulfide at Low temperature: a review. Sci. World J. 2013, 2013, 1–8.

(42) Zhao, S.; Yi, H.; Tang, X.; Kang, D.; Wang, H.; Li, K.; Duan, K. Characterization of Zn–Ni–Fe hydrotalcite-derived oxides and their application in the hydrolysis of carbonyl sulfide. Appl. Clay Sci. 2012, 56, 84–89.

(43) Zhao, S.; Yi, H.; Tang, X.; Song, C. Low temperature hydrolysis of carbonyl sulfide using Zn–Al hydrotalcite-derived catalysts. Chem. Eng. J. 2013, 226, 161–165.

(44) Mi, J.; Liu, F.; Chen, W.; Shen, L.; Cao, Y.; Au, C.; Huang, K.; Zheng, A.; Jiang, L. Design of efficient, hierarchical porous polymers endowed with tunable structural base sites for direct catalytic elimination of COS and H2S. ACS Appl. Mater. Interfaces 2019, 11, 29950–29959.

(45) He, E.; Huang, G.; Fan, H.; Yang, C.; Wang, H.; Tian, Z.; Wang, L.; Zhao, Y. Macroporous alumina- and titania-based catalyst for carbonyl sulfide hydrolysis at ambient temperature. Fuel 2019, 246, 277–284.

(46) Palma, V.; Vaiano, V.; Barbata, D.; Colozzi, M.; Polo, E.; Barbato, L.; Cortese, S.; Miccio, M. Study of the carbonyl sulphide hydrolysis reaction in liquid phase. Chem. Eng. Trans. 2019, 73, 247–252.

(47) Toda, K.; Dasgupta, P. K.; Li, J.; Tarver, G. A.; Zarus, G. M. Fluorometric field instrument for continuous measurement of atmospheric hydrogen sulfide. Anal. Chem. 2001, 73, 5716–5724.

(48) Toda, K.; Ohira, S.-I.; Tanaka, T.; Nishimura, T.; Dasgupta, P. K. Field instrument for simultaneous large dynamic range measurement of atmospheric hydrogen sulfide, methanethiol, and sulfur dioxide. Environ. Sci. Technol. 2004, 38, 1529–1536.

(49) Toda, K.; Ohira, S.-I.; Ikeda, M. Micro-gas analysis system μGAS comprising a microchannel scrubber and a micro-fluorescence detector for measurement of hydrogen sulfide. Anal. Chim. Acta 2004, 511, 3–10.

(50) Ohira, S.-I.; Toda, K. Micro gas analysis system for measurement of atmospheric hydrogen sulfide and sulfur dioxide. Lab Chip 2005, 5, 1374–1379.

(51) Toda, K.; Kuwashara, H.; Kajiwara, H.; Hirota, K.; Ohira, S.-I. Gas analyzer for continuous monitoring of trace level methanethiol by microchannel collection and fluorescence detection. Anal. Chim. Acta 2014, 841, 1–9.

(52) Toda, K.; Tokunaga, W.; Gushiken, Y.; Hirota, K.; Nose, T.; Suda, D.; Nagai, J.; Ohira, S.-I. Mobile monitoring along a street canyon and stationary forest air monitoring of formaldehyde by means of a micro-gas analysis system. J. Environ. Monit. 2012, 14, 1462–1472.

(53) Yanaga, A.; Hozumi, N.; Ohira, S.-I.; Hasegawa, A.; Toda, K. Formaldehyde vapor produced from hexamethylenetetramine and pesticide: Simultaneous monitoring of formaldehyde and ozone in chamber experiments by flow-based hybrid micro-gas analyzer. Talanta 2016, 146, 649–654.

(54) Toda, K.; Koga, T.; Kosuge, J.; Kashiwagi, M.; Oguchi, H.; Arimoto, T. Micro gas analyzer measurement of nitric oxide in breath by direct wet scrubbing and fluorescence detection. Anal. Chem. 2009, 81, 7031–7037.

(55) Ohira, S.-I.; Someya, K.; Toda, K. In situ gas generation for micro gas analysis system. Anal. Chim. Acta 2007, 588, 147–152.

(56) Ohira, S.-I.; Toda, K. Micro gas analyzers for environmental and medical applications. Anal. Chim. Acta 2008, 619, 143–156.

(57) Guglielmino, M.; Allouch, A.; Serra, C. A.; Calvé, S. L. Development of microfluidic analytical method for on-line gaseous formaldehyde detection. Sens. Actuators, B 2017, 243, 963–970.

(58) Ueda, M.; Teshima, N.; Sakai, T. Development of formaldehyde standard gas generator based on gravitational dispensing-vaporization and its application to breath formaldehyde determination. Bunseki Kagaku 2008, 57, 605–611.

(59) Becker, A.; Andrikopoulos, C.; Bernhardt, P.; Ocampo-Torres, R.; Trocquet, C.; Le Calve, S. Development and optimization of an airborne formaldehyde microfluidic analytical device based on passive uptake through a microporous tube. Micromachines 2019, 10, 807.

(60) West, J.; Williams, B. P.; Young, N.; Rhodes, C.; Hutchings, G. J. Low temperature hydrolysis of carbonyl sulfide using γ-alumina catalysts. Catal. Lett. 2001, 74, 111–114.

(61) Akimoto, M. Role of reduction sites in vapor-phase hydrolysis of carbonyl sulfide over alumina catalysts. J. Catal. 1980, 62, 84–93.