Large volume sample system for measuring sulfur isotopic compositions of carbonyl sulfide

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Abstract

Knowledge related to sulfur isotopic composition of carbonyl sulfide (OCS or COS), the most abundant atmospheric sulfur species, remains scarce. Earlier method developed for sulfur isotopic analysis for OCS using S^+ fragmentation is inapplicable for ambient air samples because of the large samples required (approx. 500 L of 500 pmol mol^{-1} OCS). To overcome this difficulty, herein we present a new sampling system for collecting approx. 10 nmol of OCS from ambient air coupled with a purification system. Salient system features are (i) accommodation of samples up to 500 L (= approx. 10 nmol) of air at 5 L min^{-1}, (ii) portability of 7 inch tubes (approx. 1 cm^3) for preserving samples, and (iii) purification OCS from other compounds such as CO_2. We tested the OCS collection efficiency of the systems and sulfur isotopic fractionation during sampling. Results show precision (1σ) of $\delta^{33}S(OCS)$, $\delta^{34}S(OCS)$, and $\Delta^{33}S(OCS)$ values, respectively, as 0.4 ‰, 0.2 ‰, and 0.4 ‰. Additionally, this report presents diurnal variation of $\delta^{34}S(OCS)$ values collected from ambient air at Suzukakedai campus of Tokyo Institute of Technology located in Yokohama, Japan. The observed OCS concentrations and $\delta^{34}S(OCS)$ values were, respectively, 447–520 pmol mol^{-1} and from 10.4 ‰ to 10.7 ‰. No significant difference was found between values obtained during the day and night. The observed $\delta^{34}S(OCS)$ values in ambient air differed greatly from previously reported values ((4.9 ± 0.3) ‰) for compressed air collected at Kawasaki, Japan, presumably because of sampling conditions and collection processes for that sample. Consequently, previous values of $\delta^{34}S(OCS) = (4.9 ± 0.3)$ ‰ were not representative samples for a global signal. When considering (10.5 ± 0.4) ‰ is postulated as the global signal of $\delta^{34}S(OCS)$, this revised $\delta^{34}S(OCS)$ value is consistent with previous estimation based on terrestrial and oceanic sulfur sources. The $\delta^{34}S(OCS)$ value explains the reported $\delta^{34}S(OCS)$ values for background stratospheric sulfate. The system presented herein is useful for application of $\delta^{34}S(OCS)$ for investigation of OCS sources and sinks in the troposphere to elucidate its cycle and its contribution to background stratospheric sulfate.

1   Introduction

Carbonyl sulfide (OCS) is the most abundant sulfur-containing gas in ambient air with atmospheric concentrations of approx. 500 pmol mol^{-1} in the troposphere (Chin and Davis, 1995; Montzka et al., 2007). In fact, OCS can be transported to the stratosphere because the average residence time of OCS is longer than two years (Brühlet et al., 2012). In the stratosphere, it
5   is converted to stratospheric sulfate aerosols (SSA) through atmospheric sink reactions (Crutzen, 1976). Therefore, OCS must be regarded as an important sulfur source for SSA, playing an important role in the Earth's radiation budget and in ozone depletion. Moreover, because leaves consume OCS whenever assimilating CO_2, but do not emit OCS to the atmosphere by respiration (Sandvalo-Soto et al., 2005), OCS can be a tracer of net ecosystem exchange into gross primary production (GPP) on land (Campbell et al., 2008). For those reasons, elucidating the OCS dynamics in the atmosphere is important to elucidate
10   the carbon cycle. Nevertheless, tropospheric OCS sources and sinks entail great uncertainty (Watts, 2000; Kremser et al., 2016) because of missing sources in the atmospheric budget of 230–800 Gg a^{-1} S equivalence as revealed by top-down modelling (Berry et al., 2013; Glatthor et al., 2015; Kuai et al., 2015).

Isotope analysis is a useful tool to trace sources and transformations of trace gases (Johnson et al., 2002; Brenninkmeijer, 2003). To quantify OCS sources and sinks in natural environments using isotope analysis, determination of
15   isotopic fractionation for reactions and ambient measurements is required. To date, isotopic fractionations occurring in the reactions of OCS have been determined for almost all OCS sink reactions in the stratosphere: OCS photolysis (Hattori et al., 2011; Lin et al., 2011; Schmidt et al., 2013) as well as reactions with OH (Schmidt et al., 2012) and O(^3P) (Hattori et al., 2012). Furthermore, an online method measuring sulfur isotopic compositions ($\delta^{33}S$, $\delta^{34}S$ and $\Delta^{33}S$ values) for OCS on a gas chromatograph (GC) - isotope ratio mass spectrometer (IRMS) using S$^+$ fragmentation ions (Hattori et al., 2015) supports
20   simple analysis of sulfur isotopic compositions for OCS over 8 nmol. Using this method, the sulfur isotopic fractionation during soil bacterial degradation and enzymatic degradation were ascertained based on laboratory experiments (Kamezaki et al., 2016; Ogawa et al., 2017). However, application of sulfur isotopic analysis to OCS for atmospheric samples has yet to be reported, probably because of the large sample amounts that are necessary (i.e. 500 L of 500 pmol mol^{-1} OCS). Consequently, an OCS collection method that can collect several nanomoles of OCS from ambient air at a pmol mol^{-1} level is required.

25   To date, several methods have been developed for concentration measurements using grab samples of air coupled with sampling/purification systems in the laboratory (e.g. Inomata et al., 1999; Xu et al., 2001; Montzka et al., 2004; Kato et al., 2012). Most systems collect 2–5 L of atmospheric samples for measuring OCS concentrations. The collected OCS is extracted in the laboratory with a combination of adsorbents at subambient temperatures: Tenax TA with dry ice/methanol (Inomata et al., 1999) or dry ice/ethanol (Hattori et al., 2015), glass beads with liquid oxygen (Montzka et al., 2004) or liquid
30   argon (Xu et al., 2001), 2,3-Tris (2-cyanoethoxy) propane with liquid oxygen (Kato et al., 2012). Grab sampling, however, is unrealistic when collecting 500 L of air. Therefore, we developed a large-volume sampling system for measuring sulfur isotopic compositions of OCS. We modified a large-volume sampling system developed for carbon isotope measurement for halocarbons such as chloromethane and bromomethane, which have concentrations of pmol mol^{-1} level in ambient air

(Bahlmann et al., 2011). Subsequently, we combined this sampling system and newly developed an online OCS purification system for separation from impurities such as CO_2, which is 10^6 times more abundant in air than OCS. For the current study, we describe the systems and its applications to atmospheric observation. We provide first results for diurnal variations of $\delta^{34}S(OCS)$ in ambient air from samples collected at Suzukakedai campus of Tokyo Institute of Technology located in

5 Yokohama, Japan.

2 Materials and methods

2.1 Samples

Commercial samples containing 10.5 % OCS balanced with high purity He (99.99995 % purity; Japan Fine Products Co. Ltd.,
10 Kawasaki, Japan) (sample A, Japan Fine Products Co. Ltd., Kawasaki, Japan) and 5.9 $\mu mol\ mol^{-1}$ OCS balanced with high purity He (sample B, Japan Fine Products Co. Ltd.) were used (Table 1). Furthermore, we synthesized OCS from three kinds of sulfur, designated as sample C (Fujifilm Wako Pure Chemical Corp., Japan), sample D (Sigma-Aldrich Corp. LLC, Missouri, U.S.A.), and sample E (a mixture of sulfur powders used for samples C and D) with a reaction with CO (99.99 % purity; Japan Fine Products Co. Ltd., Kawasaki, Japan) (Ferm et al., 1954; Hattori et al., 2015) (Table 2). The OCS concentrations for sample
15 A and sample B were calibrated from in-house synthesized OCS (i.e. 100 %), diluted by high-purity He. For the testing of repeatability and collection efficiency of the systems, we used three commercially available cylinders of compressed air samples in a collected in Kawasaki, Japan (Toho Sanso Kogyo Co., Ltd., Yokohama, Japan) (sample F (collected on 25 July 2017), sample G (collected on 2 July 2012) and sample H (collected on 2 December 2017). Sample G was used as sample E for Hattori et al. (2015). Its $\delta^{34}S(OCS)$ value was (4.9 ± 0.3) ‰, and it was postulated as the global representative value at that
20 moment. Storage experiments assessing the stability of the sampled OCS were carried out with air from another cylinder of compressed air (sample H).

2.2 Sampling system

The sampling system was developed by modifying the system described by Bahlmann et al. (2011). A schematic diagram is depicted in Figure 1. Main comportments of the sampling system are 1/4 inch (0.64 cm) PTFE tubes, 1/8 inch (0.32 cm)
25 stainless steel tubes, 1/16 inch (0.16 cm) sulfinert® (Restek Corporation, PE, U.S.A.) treated stainless steel tubes, sulfinert® treated stainless steel ball valves V1, V2, V5, and V9, and stainless steel ball valves V3, V4, V6, V7 and V8 behind the sampling tube (Figure 1). Excluding union tees made of stainless steel immediately before the pump, union tees coming in contact with the sampled OCS are made of sulfinert® treated stainless steel (Figure 1). The sampling tube consists of an outer stainless steel tube (3/4 inch, 50 cm length) with an air inlet at the side 4 cm below the top and an inner 1/4 inch stainless steel
30 tube (Bahlmann et al., 2011). From top to bottom, the sampling tube package is the following: 0–30 cm, empty; 30–40 cm, silanized glass beads 2 mm; 40–43 cm, Tenax TA (60/80 mesh; GL Science Inc., Tokyo, Japan); 43–47 cm, Porapak N (80/100

mesh; Sigma-Aldrich Corp., Japan); 47–50 cm, empty, and adsorbents separated by plugs of precleaned glass wools (GL Science Inc., Tokyo, Japan). The adsorption tube consists of a stainless steel tube (with 1/4 inch (0.32 cm) outer diameter, 7 inch length) filled with Tenax TA. Before experiments, the sampling tube and the adsorption tube were conditioned, respectively, using 100 mL min^{-1} high-purity He flow at 160 °C for 6 h and 50 mL min^{-1} high-purity He flow at 330 °C for 6

5   h. We confirmed that possible contamination of OCS in the tubes was less than 10 pmol after conditioning.

During sampling, V1, V2, V3 and V4 were opened. Then atmospheric samples were drawn with a low volume diaphragm pump (LV-40BW; Sibata Scientific Technology Ltd., Saitama, Japan) through the sampling system with flow of (5.00 ± 0.25) L min^{-1}. The air was passed through a membrane filter (47 mm diameter, 1.2 μm pore, Pall Ultipor® N66 sterilizing-grade filter, Pall Corp., New York, U.S.A.) set in a NILU filter holder system (70 mm diameter, 90 mm length,

10   Tokyo Dylec Corp., Tokyo, Japan) to remove atmospheric aerosol. Then it was directed through a condenser (EFG5-10; IAC Co. Ltd., Japan) kept at approximately −15 °C to remove water vapour from the air. The air was then passed through the sampling tube cooled to less than −110 °C by vapour of the liquid N_2 in a dewar (MVE SC 20/20; Chart Industries Inc., Georgia, U.S.A.). The OCS was enriched in the sampling tube, whereas other main gases (N_2, O_2, Ar, etc.) were passed through the sampling tube.

15   After sampling, V1 and V4 were closed; V5, V6, V7, and V8 were opened. Then, the sampling tube was removed carefully from the dewar and was heated gradually to 130 °C. The vaporized gases in the sampling tube were passed to the adsorption tube cooled at −78 °C using dry ice/ethanol after removal of the remaining water vapour by a Nafion® dryer (MD-110-96S; Perma Pure LLC, New Jersey, U.S.A.). The flow rate was regulated (approx. 50 mL min^{-1}) by a needle valve equipped with a flow meter for 20 min. After the flow rate became lower than 10 mL min^{-1}, V4 was opened. The sampling

20   tube was flushed with pure N_2 (>99.99995 vol. %) with 50 mL min^{-1} for 40 min. After the transfer of samples, V6, V7 and V8 were closed. Then OCS was preserved in the adsorption tube. We initially confirmed that OCS did not pass through an adsorption tube at a flow rate lower than 50 mL min^{-1} using two adsorption tubes connected in series from the second adsorption tube: OCS was observed only from the first tube; not from the second tube.

2.3   Purification system

25   After sampling OCS from the air using the sampling system as described above, the collected OCS was purified and connected directly to the measurement system. The schematic system is shown in Figure 2. Excluding a fused silica capillary tube, all tubes and valves are made of stainless steel. Trap 1 is a 50 cm, 1/4 inch (0.64 cm) outer diameter (1/8 inch (0.32 cm) inner diameter) stainless steel tube. Trap 2 is a 30 cm, 1/8 inch (0.32 cm) outer diameter (1/16 inch (0.16 cm) inner diameter) stainless steel tube filled with Tenax TA (60/80 mesh; GL Science Inc.). Before the experiment, trap 2 is heated to 150 °C for

30   30 min at 30 mL min^{-1} with high-purity He for conditioning. Trap 3 is an empty stainless steel tube (1/16 inch (0.16 cm) outer diameter, 50 cm length). Trap 4 is a fused silica capillary tube (0.32 mm inner diameter, 50 cm length, GL Science Inc.). The GC1 (GC-8610T; JEOL Ltd., Tokyo, Japan) is equipped with a column packed with Porapak Q (80/100, GL Science Inc.) (1/8

inch (0.32 cm) outer diameter, 3 m length) to separate OCS from CO_2. The GC1 oven temperature for OCS purification was programmed to provide 30 °C for 5 min, ramping to 60 °C at 30 °C min^{-1}, followed by ramping to 230 °C at 30 °C min^{-1} from 40 min, and 230 °C for 1 min.

After the adsorption tube containing OCS was connected to the purification system, v3, v4, and v5 were opened and the air in the line was pumped out using a rotary pump (DA-60D; Ulvac Kiko, Miyazaki, Japan) for 5 min; v3, v4, and v5 were then closed. When the adsorption tube was heated at 130 °C and v2, v7, v8, and v6 were opened, gases in the adsorption tube passed through trap 1 cooled by dry ice (−78 °C) to remove trace remnant water vapour. Also, OCS was collected in trap 2, with Tenax TA cooled by dry ice/ethanol (−78 °C) with high-purity He flow rate of 30 mL min^{-1}. After 15 min, port valve (PV) 1 was changed. Trap 2 was then removed from dry ice/ethanol and was heated at 130 °C. The retention times of CO_2 and OCS were initially determined by injecting a mixture of 8 mmol of CO_2 and 10 nmol of OCS. They were, respectively, 3–10 min for CO_2 and 20–30 min for OCS at the flow rate of 25 mL min^{-1}. Trap 3 was cooled by liquid N_2 from 10 min; PV2 was changed from 15 min to 35 min after injection of samples to GC1 in order to introduce OCS to trap 3. OCS with high-purity He was passed through the column and collected in trap 3 for 20 min. After OCS collection in trap 3, the OCS was again transferred to trap 4 in liquid N_2 at 6 mL min^{-1} by high-purity He with removal of liquid N_2 from trap 3 to a cryofocus. Trap 4 was then removed from liquid N_2; the OCS passed through the GC2 and introduced directly to the detectors (quadrupole mass spectrometer (QMS) or IRMS depending on the experiments explained below).

2.4 Determination of the concentration and sulfur isotopic composition of OCS

2.4.1 Concentration measurement

The OCS concentration was measured using a GC2 device (7890A; Agilent Technologies Inc., CA, U.S.A.) equipped with a capillary column (0.32 mm inner diameter, 25 m length, and 10 μm thickness; HP-PLOT Q, Agilent Technologies, CA, U.S.A.) and a connected quadruple mass spectrometer (Q-MS) (5975C; Agilent Technologies Inc., CA, U.S.A.). The GC2 oven program was set as 60 °C for 15 min, ramped to 230 °C at 60 °C min^{-1}, then 230 °C for 1 min. To make a calibration line for the quantification of OCS amount in the samples F and G and atmospheric samples, sample B was injected with volume of 0 μL, 200 μL, 400 μL, and 800 μL for low amount ranges for sample F and G, and 0.5 mL, 2.2 mL, 4.4 mL, 8.8 mL, 11 mL, 13.2 mL, 17.6 mL, and 22 mL for high amount ranges for ambient air. The precision (standard deviation (1σ) relative to mean) of the OCS amount by a syringe injection was ± 3 % for both calibration lines. For determination of OCS concentrations of samples F and G, samples F and G were stored in 50 mL two-neck glass bottles with atmospheric pressure and were introduced to the purification system from a glass bottle attached instead of an adsorption tube. The measured OCS concentrations for samples F and G were, respectively, (380 ± 15) pmol mol^{-1} and (160 ± 5) pmol mol^{-1}. The OCS concentrations for the samples F and G were lower than that of typical atmospheric OCS concentrations (400–550 pmol mol^{-1}) (Montzka et al., 2007), even though the samples were compressed air collected from the ambient atmosphere.

2.4.2 Isotope ratio determination

For the determination of sulfur isotopic compositions of OCS, OCS was passed through the GC2 after a purification system as described above. Then it was introduced directly to the IRMS (MAT253; Thermo Fisher Scientific Inc., Berlin, Germany) via an open split interface (ConFlo IV; Thermo Fisher Scientific Inc.). Reference OCS (sample A in this study) was purified with

5   liquid N_2 (−196 °C) and then introduced via a conventional dual inlet system because purified OCS, which is toxic, is not commercially available in Japan (Hattori et al. 2015). In addition to the method introducing OCS to IRMS as described above, conventional syringe injection line, which was previously used for Hattori et al. (2015) and Kamezaki et al. (2016), was also used for comparison or calibration. Briefly, the syringe-injected OCS was collected in stainless steel tubes (10.5 mm inner diameter, 150 mm length) cooled at −196 °C by liquid N_2 with vacuum by a diaphragm pump. After transfer of OCS to the

10   trap, the two-way six port valve was changed. Then liquid N_2 was removed from the trap. Subsequently, OCS was transferred and collected in a capillary tube covered by a stainless steel tube containing liquid N_2 for 13 min before being introduced into the GC-IRMS system.

      In the IRMS ion source, electron impact ionization of OCS produced S^+ fragment ions. The sulfur isotope ratios in OCS were therefore determined by measuring the fragment ions $^{32}S^+$, $^{33}S^+$, and $^{34}S^+$ using triple faraday collector cups, and

15   typical precision (1σ) of the replicate measurements ($n = 3$) are, respectively, 0.4 ‰, 0.2 ‰, and 0.3 ‰ for $\delta^{33}S$, $\delta^{34}S$, and $\Delta^{33}S$ values. The raw δ value for each sample were calibrated against the 5.9 μmol mol^{-1} of in-house OCS standard gas, previously calibrated against the international sulfur isotopic standard and measured in independent runs on the same day as sample measurements (Hattori et al., 2015). A reference OCS gas was introduced for 20 s at three times started at $t = 350$ s, 825 s, and 1025 s. The reference gas at $t = 350$ s was used as the reference for all calculations of OCS sulfur Isotopic compositions. To

20   remove hydrogen sulfide and ethane from ambient samples, from $t = 300$ s, the effluent from the GC column was kept off the MS line using back-flushed helium flow.

      Sulfur isotopic compositions are typically reported using

$$\delta^x S = {}^x R_{\text{sample}} / {}^x R_{\text{reference}} - 1, \qquad (1)$$

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where ${}^x R_{\text{sample}}$ represents the isotopic ratios (${}^x S/^{32}S$, where $x = 33$ or 34) of the samples and standards. The sulfur isotopic compositions are reported relative to the Vienna Canyon Diablo Troilite (VCDT), and are quoted as per mil values (‰). In addition to the δ values, capital delta notation ($\Delta^{33}S$ value) is used to distinguish mass-independent fractionation (MIF; or non-mass-dependent fractionation) of sulfur, which causes deviation from the mass-dependent fractionation (MDF) line. The $\Delta^{33}S$

30   value describes the excess or deficiency of ^{33}S relative to a reference MDF line. It is expressed as

$$\Delta^{33}S = \delta^{33}S - [(\delta^{34}S + 1)^{0.515} - 1]. \qquad (2)$$

3 Results and Discussion

3.1 Sampling efficiency of OCS

To test the sampling and desorption efficiency, the cylinder containing sample F was connected to a flow meter and the flow was adjusted to 6 L min^{-1} with a needle valve. 5 L min^{-1} were drawn through the sampling system with a pump and the

5 remainder was vented into the air to maintain atmospheric pressure at the sampling inlet. The vent flow was measured with a flow meter (ACM-1A; Kofloc, Tokyo, Japan). To ascertain the trapping efficiency OCS was sampled for 10 min, 50 min, and 100 min with blank test intervals as presented in Figure 3a (see section 2.2 for sampling procedure). The sampling times corresponded to sampling volumes of (50 ± 2.5) L, (250 ± 13) L and (500 ± 25) L and the respectively and the corresponding OCS amounts were (0.77 ± 0.04) nmol, (3.9 ± 0.2) nmol, and (7.7 ± 0.4) nmol respectively.

10   Recovery and precision (1σ) for OCS amounts collected for sampling times of 10 min, 50 min, and 100 min were, (0.9 ± 0.1) nmol ($n = 3$), (3.6 ± 0.2) nmol ($n = 3$) and (7.4 ± 0.3) nmol ($n = 2$), respectively. The OCS blanks were smaller than 15 pmol. These results indicate that yield of OCS during sampling and transferring from the sampling tube to the adsorption tube is almost over 95 %. The memory effect of the system between the sampling run is expected to be less than 1% when sampling OCS amount over 3 nmol (approx. 50 min). Figure 3b presents a comparison of OCS amount between observed OCS

15 amounts and OCS amounts calculated based on OCS concentration in sample F and sampling time, showing that all results fall on the 1:1 line. This suggests that almost 100 % of OCS for sampling runs were collected in the sampling tube and were transferred successfully to the adsorption tube. Although the collected OCS amount in 10 min was slightly larger than the expected OCS amount, the OCS amounts in 100 min were slightly lower than the expected OCS amount. This result indicates that a small OCS blank during the sampling and a purification system might exist but that it might not be significant, as

20 discussed above.

3.2 Accuracy of the sulfur isotopic analysis of OCS via sampling/purification systems

To assess the OCS recovery during purification in particular with respect to the different trapping steps, known OCS amounts were injected into the purification system we sequentially bypassed all traps and the GC1. These tests revealed an OCS loss of less than 2 % and suggest a complete recovery of OCS within the given limits of uncertainty (±3 %). To assess the

25 dependency of the sulfur isotopic measurements on the OCS amount, different amounts of OCS using sample B were tested. We slowly introduced aliquots of 3 nmol, 6 nmol, 10 nmol, and 15 nmol of sample B into a stream (5 L min^{-1}) of high purity N$_2$ ($>$99.99995 vol. %, Nissan Tanaka Corp., Saitama, Japan). For each experiment a total volume of 500 L N$_2$ was processed. The OCS blank for this experiment was (0.30 ± 0.16) nmol ($n = 3$) when we flushed with 500 L of pure N$_2$ stream. For comparison, similar amounts of OCS were also injected using a syringe injection system developed previously (Hattori et al.,

30 2015). Comparisons of OCS concentrations and δ and Δ values are depicted in Figure 4. Although the observed OCS isotopic compositions using 3 nmol OCS with the developed method were scattered (1σ: 1.0 ‰, 1.0 ‰,, and 0.5 ‰, respectively, for δ^{33}S, δ^{34}S, and Δ^{33}S values), the reproducibilities at the 6 nmol level were sufficient (1σ: 0.4 ‰, 0.2 ‰,, and 0.4 ‰, respectively,

for $\delta^{33}S$, $\delta^{34}S$, and $\Delta^{33}S$ values) and were similar to those obtained with the conventional syringe injection system for Hattori et al. (2015) (Figure 4). Consequently, this system better accommodates OCS samples over 6 nmol, indicating the necessity for collection of ambient air in amounts greater than 300 L.

5   Furthermore, to test possible sulfur isotopic fractionations during sampling/purification processes, which might change the measurement accuracy, we compared the developed sampling/purification system with the conventional syringe injection system using 8 nmol of the in-house synthesized OCS (samples B, C, D, and E) with triplicates injections. In Figure 5, the $\delta^{34}S(OCS)$ values measured using the developed sampling/purification system were 0.2 ‰ lower (sample B) but 0.8 ‰, 0.4 ‰, and 0.6 ‰ higher (samples C, D, and E, respectively) than those measured using the syringe injection system of Hattori et al. (2015) (Table 2). This phenomenon was observed similarly for the $\delta^{33}S$ values (Figure 5c), indicating that this process is

10 not isotopic fractionation but that rather suggests contamination during the sampling processes. Indeed, if possible OCS blank comes from the atmosphere, which presumably has the same δ values as the ambient observation ((10.5 ± 0.4) ‰ for $\delta^{34}S(OCS)$ value, see section 3.4), with (0.30 ± 0.16) nmol OCS (approx. 5 % for 8 nmol OCS samples), then the $\delta^{34}S(OCS)$ values measured using the developed sampling/purification system are consistent with those measured using a conventional syringe injection system (Hattori et al., 2015). Therefore, we conclude that differences observed between the developed

15 sampling/purification system and the conventional syringe injection system (Hattori et al., 2015) derive from OCS blanks during sampling. Therefore, the changes are not needed for corrections for the atmospheric samples described in a later section. From experimentation, the precision values (1σ) of this sampling/purification system were estimated as 0.4 ‰, 0.2 ‰, and 0.4 ‰, respectively, for $\delta^{33}S$, $\delta^{34}S$, and $\Delta^{33}S$ values adapted from those observed for sample B measurements (Table 2).

3.3 Sulfur isotopic composition for atmospheric OCS

20 Four ambient air samples were collected at the Suzukakedai campus of Tokyo Institute of Technology located in Yokohama, Japan (35.5°N, 139.5°W, 27 m height) during 23–25 April 2018 every 12 h (sampling times were 23 April 2018 12:00, 24 April 2018 00:00, 24 April 2018 12:00, and 25 April 2018 00:00). The sampling volume was 500 L (i.e. 100 min with a pump flow of 5 L min^{-1}). Measurements of OCS concentrations and sulfur isotopic compositions were carried out within an hour after the sampling. The OCS concentrations and $\delta^{34}S(OCS)$ values observed for ambient air are presented in Figure 6.

25   In contrast to the $\delta^{34}S(OCS)$ value, the $\delta^{33}S(OCS)$ value in air was not determined because of the unexpected peak (approx. 40 mV height) observed for m/z: 33, which slightly overlapped the OCS peak of the chromatogram (Figure 7). We notably didn't observe any interferences on m/z: 32 and m/z: 34. The interfering compound could have not yet been identified. Known fragments interfering on m/z: 33 are CH_5O^+ originating from the protonation of methanol and/or the reaction of CH_3^+ with H_2O, as well as CH_2F^+ that is indicative hydrofluorocarbons. To measure m/z: 33 of OCS without interferences, further

30 improvement of peak separation of OCS with interferences is required by changing parameter of the separation in the system and/or data processing. For example, custom made MATLAB routine, which can extrapolate the peak tail of interference via

an exponentially decaying function to distinguish the two gaseous species as described in Zuiderweg et al. (2013), would enable us to analyze m/z: 33 in addition to the standard ISODAT software used for isotope ratio measurements.

The observed OCS concentrations ranged from 447 to 520 pmol mol^{-1} (Figure 6a), averaging (492 ± 34) pmol mol^{-1}. This OCS concentration observed at Suzukakedai campus shows good agreement with the OCS concentrations observed at

5   similar latitude in U.S.A. (e.g. 400–550 pmol mol^{-1}; Montzka et al., 2007). The observed δ^{34}S(OCS) values of four atmospheric samples were in the range of 10.4–10.7 ‰ (Figure 6b) and averaged (10.5 ± 0.4) ‰. They showed no clear diurnal variation (Figure 6b).

It is noteworthy that the δ^{34}S(OCS) values of four atmospheric samples were clearly distinct from our earlier observed δ^{34}S(OCS) value of (4.9 ± 0.3) ‰ obtained from sample G (Hattori et al., 2015), that was postulated as a global representative

10   δ^{34}S(OCS) value in the atmosphere. In fact, the OCS concentrations in the commercial cylinders F, G and H were significantly lower than typical atmospheric OCS concentrations of approx. 500 nmol mol^{-1}. Ascertaining the δ^{34}S(OCS) value in sample G using the current sampling/purification system yielded a δ^{34}S(OCS) value of (6.1 ± 0.2) ‰ being slightly higher than the previous value of $((4.9 \pm 0.3)$ ‰; Hattori et al., 2015). The causes for the OCS losses in the commercial pressurized air cylinders could not be investigated here. Indeed, as reported by Kamezaki et al. (2016), OCS is decomposed by hydrolysis, which

15   increases the δ^{34}S(OCS) value. Additionally, observation of OCS loss caused by adsorption to walls in the canister was reported by Khan et al. (2012). The compressed air of samples F and G might be affected by anthropogenic OCS sources at the sampling site and/or during the compressing processes. All in all, the δ^{34}S(OCS) value of sample G is no longer considered as a representative of atmospheric OCS. The δ^{34}S(OCS) values observed for four atmospheric samples $((10.5 \pm 0.4)$ ‰) are reasonable signals in terms of global representative values.

20   ## 3. 4   Atmospheric implications

We earlier discussed the balance equation described in Leung et al. (2002) and Hattori et al. (2015), with expected δ^{34}S values for SSA of −3.4 ‰ to 2.7 ‰ according to δ^{34}S(OCS) value of atmospheric background and isotopic fractionations during decomposition in the stratosphere (Hattori et al., 2011; Schmidt et al., 2013). The estimation of δ^{34}S values for SSA is also revised by change of the δ^{34}S value of atmospheric background OCS from 4.9 ‰ to 10.5 ‰. The calculated δ^{34}S values for

25   SSA of 2.3–9.0 ‰ show good agreement with the earlier observed δ^{34}S value of background SSA $((2.6 \pm 0.3)$ ‰; Castleman et al., 1974).

Another atmospheric implication is that the δ^{34}S(OCS) value of (10.5 ± 0.4) ‰ is generally consistent with earlier estimation by Newman et al. (1991). As described in that report, the authors estimated the δ^{34}S values of OCS based on the flux of proportional to the organic matter produced by photosynthesis (roughly the same for ocean (18 ‰) and continents

30   (3 ‰)); then the mean δ^{34}S(OCS) value is 11 ‰ (Newman et al., 1991). Contributions from plants in freshwater and saline reservoirs were omitted from this mass balance calculation because their extent is minor and their mean δ^{34}S value is 11 ‰. This estimation is based on older information, but current measurements of atmospheric DMS and DMSP are similar to 20 ‰

(Said-Ahmad and Amrani, 2013; Amrani et al., 2013; Oduro et al., 2012); continental sulfur sources also show approx. 0–5 ‰ (Tcherkez and Tea, 2013). It is noteworthy that sulfur isotopic fractionations for the troposphere (OH radical, Schmidt et al., 2011) and decomposition by soil microorganisms (Kamezaki et al., 2016; Ogawa et al., 2017) are expected to cause changes in atmospheric $\delta^{34}S(OCS)$ values. Future studies must be conducted to estimate the dynamics of atmospheric $\delta^{34}S(OCS)$ values.

5   In addition to stratospheric chemistry and tropospheric OCS sources, OCS have some potential as tracers of net ecosystem exchange into gross primary production (GPP) on land (Campbell et al., 2008). Based on our earlier experiments, to elucidate OCS in the troposphere and its relation to biochemical activity by plant and soil microorganisms, OCS sulfur isotope analysis provides a new tool to investigate soil OCS sinks in the troposphere. To date, we have determined the isotopic fractionation constants for OCS undergoing bacterial OCS degradation and its enzyme (Kamezaki et al., 2016; Ogawa et al.,

10 2017). Similarly, additional studies that include specific examination of isotopic fractionation by plant uptake, another major sink of atmospheric OCS, are indispensable for distinguishing the respective OCS fluxes of soil and plants. By coupling isotopic fractionations by soil and plant with atmospheric observations of $\delta^{34}S(OCS)$ values using our newly developed method, the atmospheric observations of $\delta^{34}S(OCS)$ values are expected to help refine estimates of biological activities of plant and soil microorganisms and their respective contributions to OCS degradation in the troposphere.

15 **3.5 Preservation of the OCS in the adsorption tube**

As described above, we measured OCS concentration and sulfur isotopic compositions of atmospheric samples within one hour after sampling, and the OCS concentrations are consistent with the observed OCS concentrations in the same latitude. However, after the development of the system, we realized that 50 % of OCS was decomposed during preservation in the adsorption tube after we have measured the samples at 14 days after sampling. In fact, it is known that OCS reacts with the

20 surface of stainless steel (Khan et al., 2012) and is hydrolyzed by water (e.g. Kamezaki et al., 2016). For future use, this requires appropriate ways of preservation of OCS during transportation from field sampling sites to laboratory till analysis. As a first step, we modified the adsorption tube by replacing stainless steel tube and valves by a sulfinert® treated tube and sulfinert® treated valves. Also, according to Bahlmann et al. (2011), we investigated the preservation of OCS on the adsorption tube at −80 °C.

25   For first tests OCS from sample H ((200 ± 7) pmol mol^{-1} of OCS in a cylinder) was concentrated with a pump flow at 5 L min^{-1} for 100 min (i.e. approx. 3 nmol of OCS). The concentrated samples were then transferred to the adsorption tube, and the adsorption tube were stored at −80 °C until the measurement. After each storage period, the samples were analyzed as described in section 2.3 and 2.4.1. When the sulfinert® treated adsorption tube was kept at −80 °C, OCS was preserved for least 7 days (Figure 8). Thus, for field application, it is possible to preserve OCS by storing under cold temperature. Further

30 investigation of preservation of OCS concentrations and isotopic integrity during the storage of the adsorption tubes with respect to storage temperature and materials of the adsorption tube are currently underway.

4   Conclusions

For this study, we developed a new OCS sampling and purification system. OCS is extracted from 500 L of ambient air was with a collection efficiency of almost over 95 % of OCS. The blank of the sampling and purification system was (0.30 ± 0.16) nmol and memory effects were negligible. By comparison with the previous used syringe injection (Hattori et al., 2015) we proofed that any potential isotopic fractionation during sampling and purification is negligible. The analytical repeatability values (1σ) for δ^{33}S, δ^{34}S, and Δ^{33}S values for OCS with more than 6 nmol were, respectively, 0.4 ‰, 0.2 ‰, and 0.4 ‰. We determined δ^{34}S(OCS) values for four atmospheric samples at Suzukakedai campus of Tokyo Institute of Technology located in Yokohama, Kanagawa, Japan. δ^{33}S(OCS) were not reported because of a small overlapping signal on m/z: 33 in the ambient air samples. The OCS concentrations and δ^{34}S values respectively, were in the range of 447–520 pmol mol^{-1} and 10.4–10.7 ‰. No clear diurnal variation in the δ^{34}S values was observed. Further modification of gas chromatographic techniques and/or data processing must be undertaken to measure δ^{33}S and Δ^{33}S values in future studies.

We earlier proposed a δ^{34}S(OCS) value of (4.9 ± 0.3) ‰ for atmospheric OCS from measurements from a commercially available cylinder of compressed air (sample G in this study) (Hattori et al. 2015). Based on the four atmospheric samples taken in this study we revise this earlier value to (10.5 ± 0.4) ‰ being clearly distinct from the earlier value. The new δ^{34}S(OCS) proposed here is in accordance with the δ^{34}S(OCS) estimates of tropospheric and marine sources of OCS based on the OCS flux (Newman et al., 1991). Furthermore, the estimation of δ^{34}S values for SSA is revised by changing the δ^{34}S value of atmospheric background OCS from 4.9 ‰ to 10.5 ‰. The newly calculated δ^{34}S values for SSA range from 2.3 ‰ to 9.0 ‰ and are still in agreement with the previously observed δ^{34}S value of background SSA ((2.6 ± 0.3) ‰; Castleman et al., 1974). With application of this method, atmospheric observations of δ^{34}S values for OCS will help to refine estimates of biological activities of plant and soil microorganisms and their contributions to OCS degradation in the troposphere. Although OCS decomposition during preservation before the measurements was concerned, we found that no such OCS decomposition has been observed for the modified adsorption tube made by sulfinert® treated tube and valves and preservation at −80 °C at least within 7 days.

Recently, sulfur isotope analysis using multi-collector inductively coupled plasma (MC-ICP)-MS has been used for gaseous sulfur compounds with approx. 20 pmol sulfur compounds (DMS/DMSP, Said-Ahmad and Amrani, 2013; organic sulfur compounds, Said-Ahmad et al., 2017). Our method has some shortcomings in terms of sample amounts, but we emphasize that the fragmentation of OCS also produces CO^{+}, that is useful for carbon and oxygen isotope measurements (Hattori et al., 2015). Results demonstrate that atmospheric observation and application to carbon and oxygen isotopes of OCS can improve the future elucidation of sources and sinks of OCS in the troposphere.

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5   **Table 1: OCS samples used for this study**

Sample	Sample type	Concentration	Comments
A	Commercial cylinder	10.5 %	Balanced with He
B	Commercial cylinder	5.9 µmol mol^{-1}	Balanced with He
C	In-house (CO + S reaction)	100 %	Wako
D	In-house (CO + S reaction)	100 %	Sigma-Aldrich
E	In-house (CO + S reaction)	100 %	Mixture of Wako and Sigma-Aldrich
F	Commercial cylinder	(380 ± 15) pmol mol^{-1}	Compressed air sampled in 25 July 2017
G	Commercial cylinder	(168 ± 7) pmol mol^{-1}	Compressed air sampled in 2 July 2012
H	Commercial cylinder	(200 ± 7) pmol mol^{-1}	Compressed air sampled in 2 Dec 2017

Table 2: Averages and standard deviations (1σ) of sulfur isotopic compositions for OCS measured for this study (newly developed sampling/purification system) and by conventional syringe injection as described by Hattori et al. (2015)

Sample	n	$\delta^{33}S$ (‰)	$\delta^{34}S$ (‰)	$\Delta^{33}S$ (‰)	n	$\delta^{33}S$ (‰)	$\delta^{34}S$ (‰)	$\Delta^{33}S$ (‰)
		This study			Syringe injection (Hattori et al., 2015)			
B	3	6.9 ± 0.4	13.8 ± 0.1	-0.2 ± 0.4	3	7.0 ± 0.1	14.0 ± 0.01	-0.2 ± 0.1
C	3	-2.8 ± 0.2	-5.5 ± 0.2	0.03 ± 0.2	3	-3.3 ± 0.1	-6.3 ± 0.2	-0.06 ± 0.1
D	3	1.5 ± 0.4	2.8 ± 0.7	0.08 ± 0.1	3	1.1 ± 0.2	2.4 ± 0.2	-0.07 ± 0.1
E	3	-0.8 ± 0.6	-1.9 ± 0.6	-0.2 ± 0.3	3	-1.5 ± 0.1	-2.5 ± 0.2	-0.2 ± 0.1

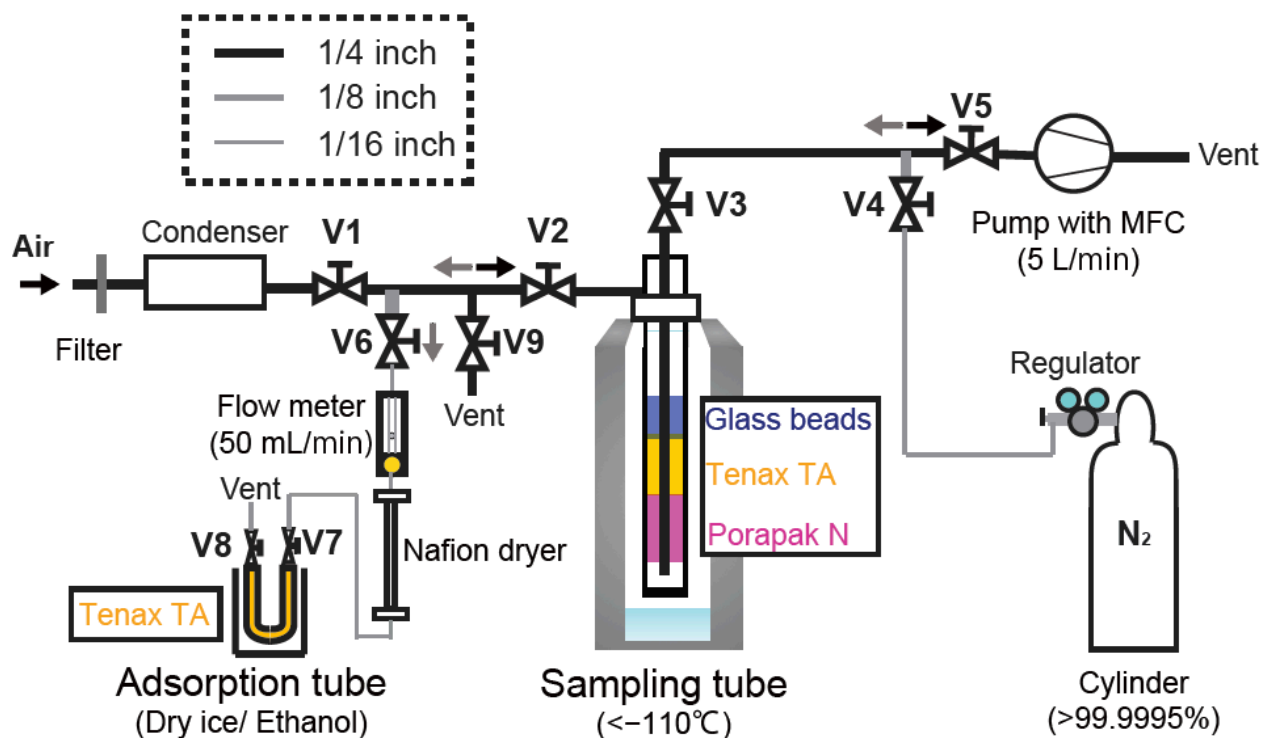



Figure 1: Schematic diagram of the OCS sampling system. System components: V, valve; pump, vacuum pump; MFC, mass flow controller.

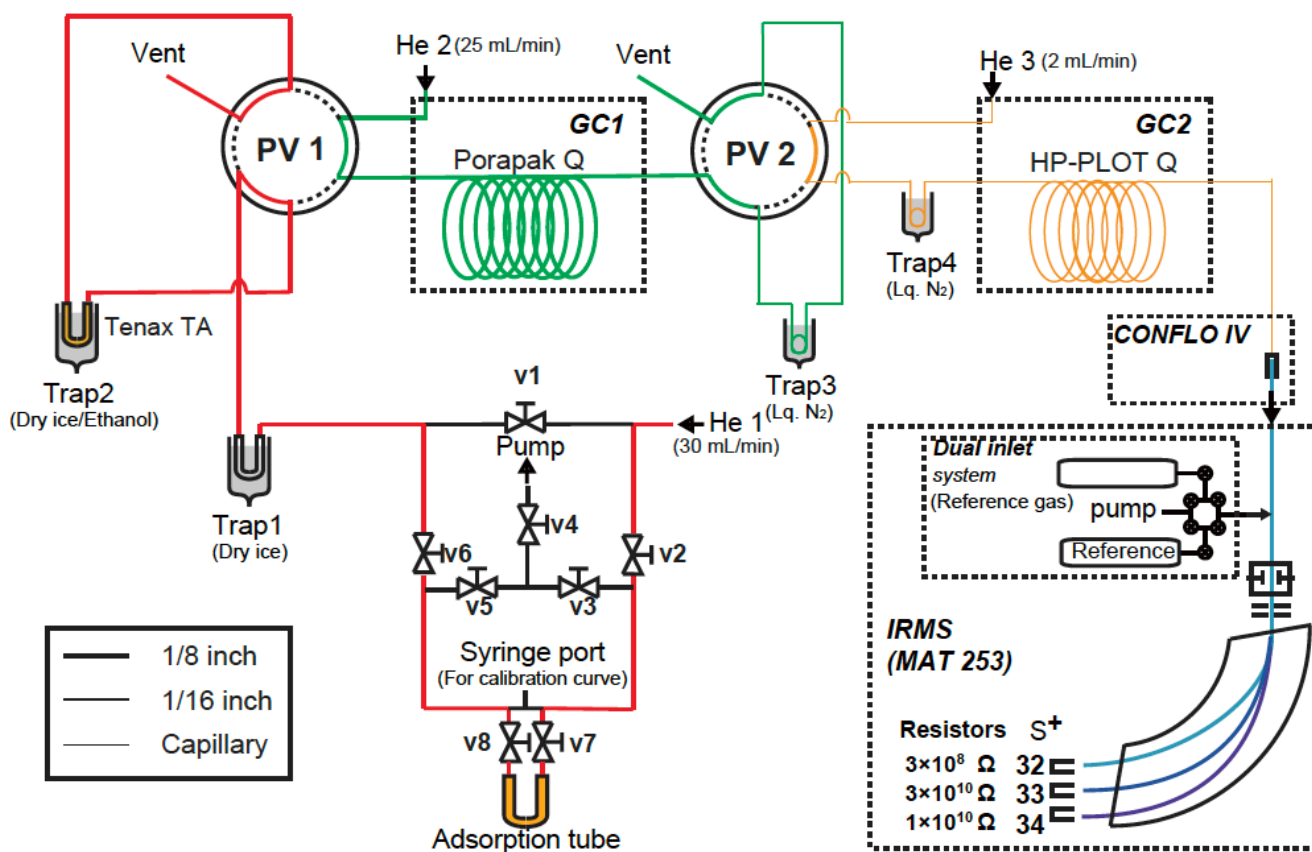



Figure 2: Schematic diagram of the OCS purification system. System components: V, valve; pump, vacuum pump; MFC, mass flow controller.

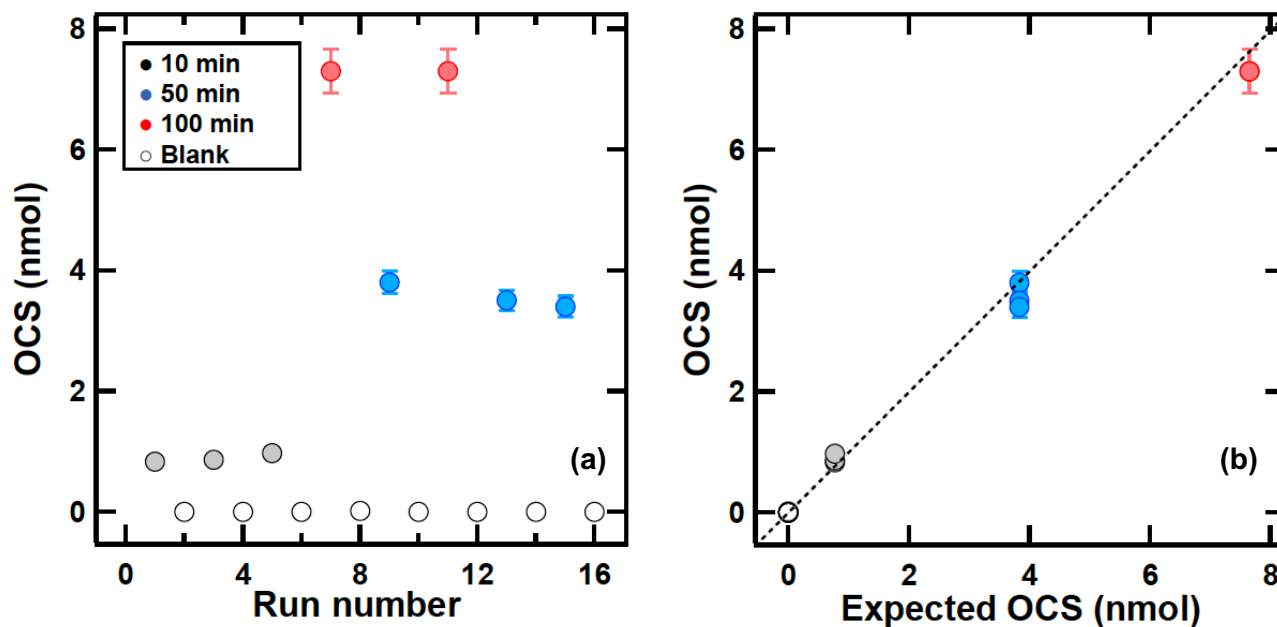



Figure 3: OCS sampling using the sample F ((380 ± 15) pmol mol⁻¹) with different sampling times of blank (0 min), 10 min, 50 min, and 100 min. (a) Collected OCS amounts as a function of run numbers. (b) Observed OCS amounts and OCS amounts calculated using OCS concentration multiplied by the sampling time. The error bar indicates ± 3 % based on residual of measured OCS peak area and calibrated OCS peal area. Dotted line indicates the slope of $x = y$.

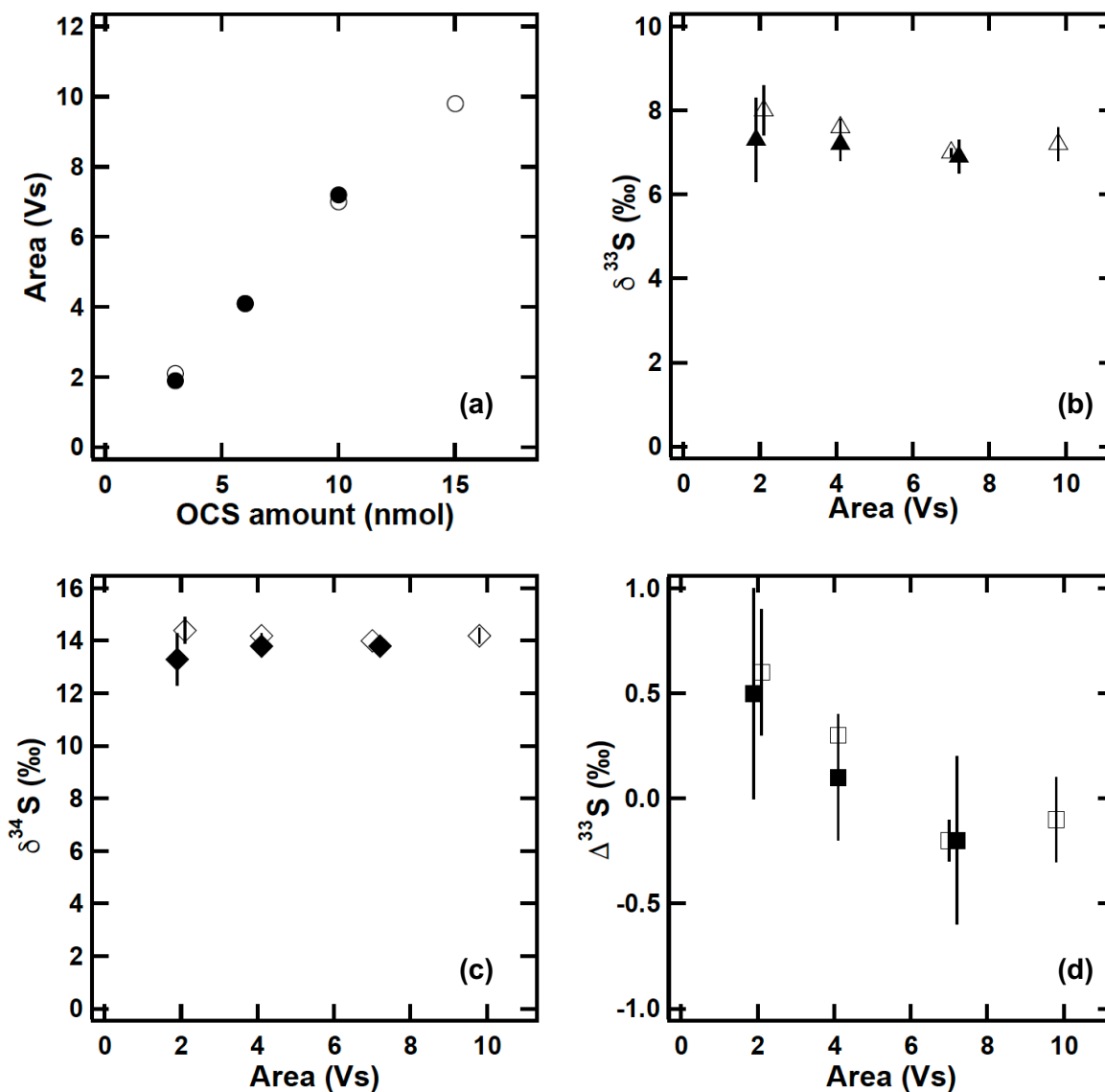



Figure 4: OCS amounts and sulfur isotopic compositions of different amounts of OCS injections ascertained using the developed sampling/purification system and conventional syringe injection system (Hattori et al., 2015): (a) OCS amount; (b) δ^{33}S; (c) δ^{34}S (d) Δ^{33}S; closed symbols: sampling/purification system developed for this study; open symbols, conventional syringe injection system. All sulfur isotopic compositions are relative to VCDT. The error bars are 1σ of
10 **the measurements based on triplicated measurements.**

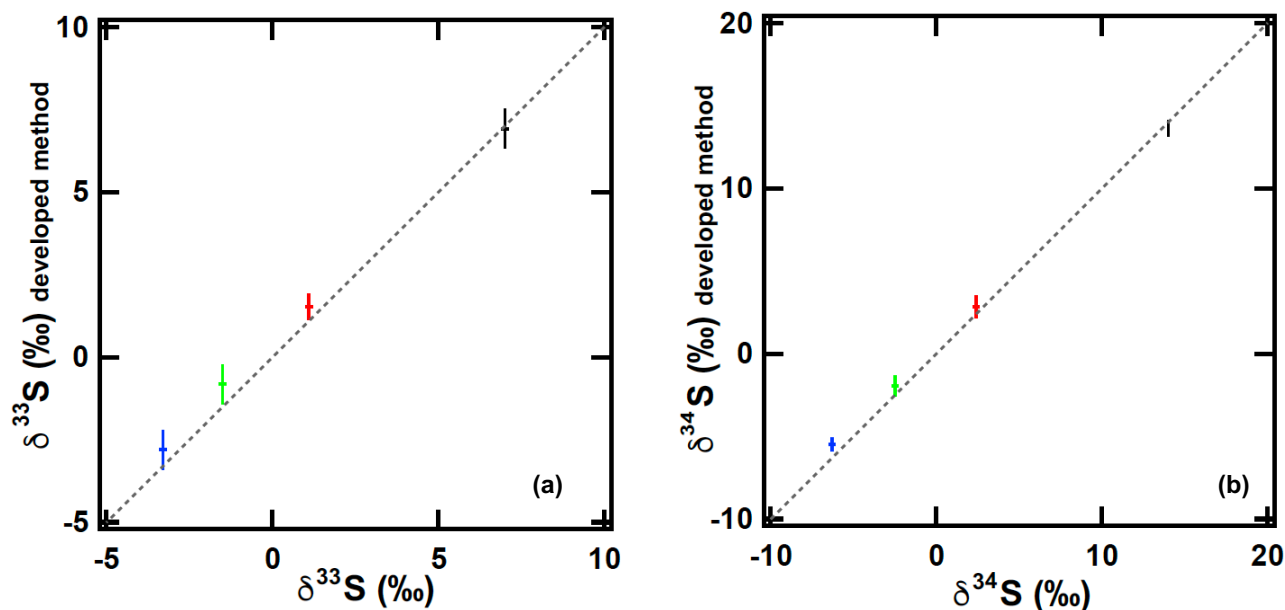



Figure 5: Sulfur isotopic compositions ((a) δ³³S and (b) δ³⁴S) ascertained from the developed sampling/purification system (*y*-axis) and conventional syringe injection system (Hattori et al., 2015) (*x*-axis). OCS sample amounts are 8 nmol. Different colours represent different samples: black, sample B; red, sample C; green, sample D; blue, sample E.
10 **Dotted line indicates the slope *x* = *y*. The error bar is 1σ of each amount of triplicated OCS injection.**

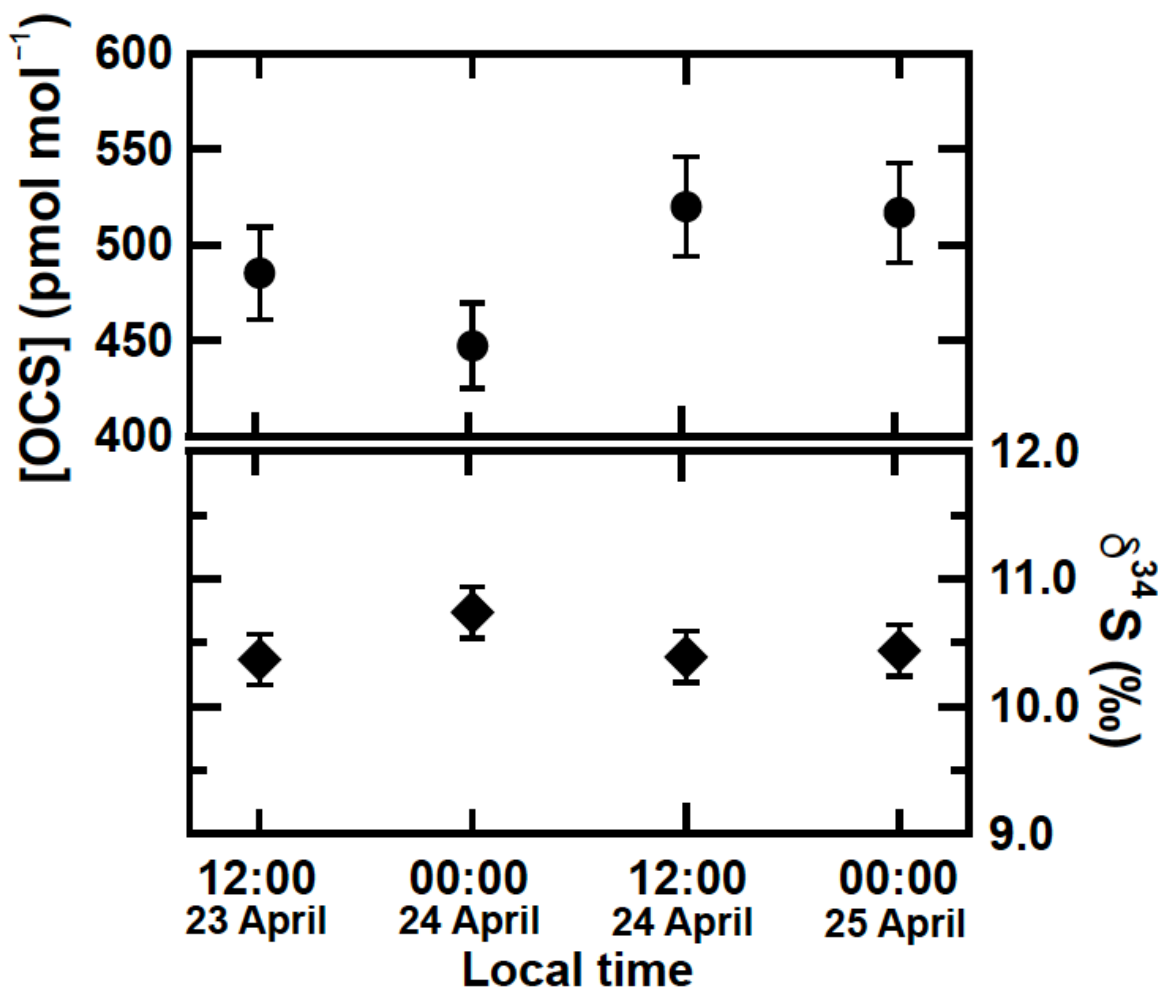
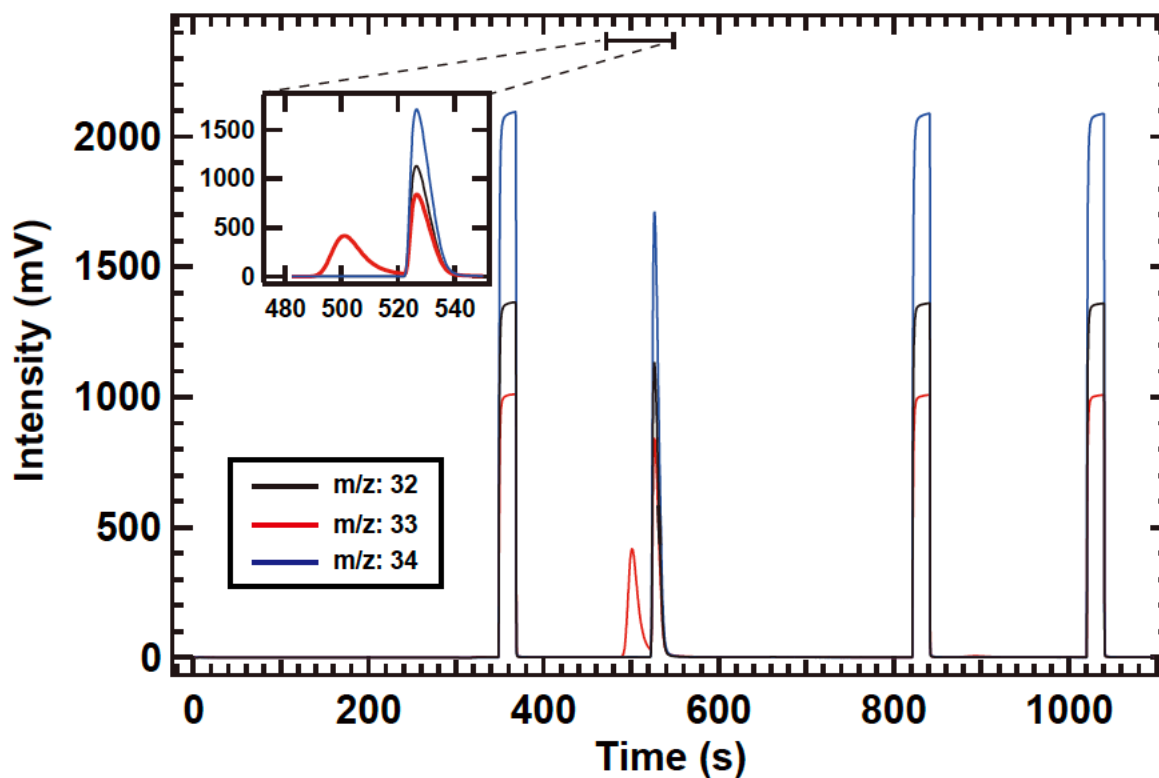



Figure 6: OCS concentrations and δ³⁴S(OCS) values for atmospheric samples collected at Suzukakedai campus of Tokyo Institute of Technology located in Yokohama, Japan. The error bar is 6 % for OCS concentration based on the precisions of syringe injection and flow rate of the diaphragm pump in the sampling system. The precision of δ³⁴S is estimated from 1σ of reproducibilities using sample B.

5   **Figure 7: IRMS chromatogram of atmospheric samples collected at the Suzukakedai campus of Tokyo Institute of Technology. Liquid N_2 removal from trap 4 occurred at 0 s in the purification system. Reference OCS was injected three times starting at 350 s, 825 s, and 1025 s for 20 s.**

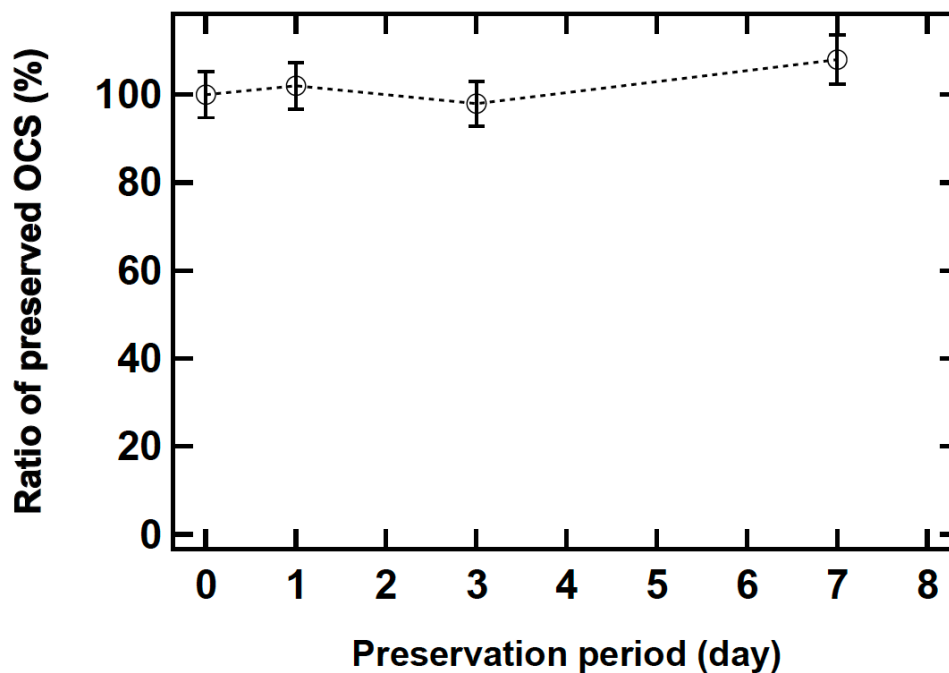



Figure 8: Changes in OCS concentrations preserved in the OCS storage test in sulfinert® treated tube and sulfinert® treated valves at −80 °C. Error bar indicates the 6 % for OCS concentration based on the precisions of syringe injection and flow rate of the diaphragm pump in the sampling system