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## Automated *in situ* analysis of volatile sulfur gases using a Sulfur Gas Analyser (SUGAR) based on cryogenic trapping and gas-chromatographic separation

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Based on the technique of cryogenic trapping, gas-chromatographic separation, and flame-photometric detection, we designed an instrument for the analysis of reduced sulfur compounds. The fully automated Sulfur Gas Analyser (SUGAR) consists of a dual sampling system, an electrically cooled cryotrap, and a newly devised small gas chromatograph, which is integrated mechanically and in terms of system control. The system incorporates microprocessor control and provides significant ease of operation. All operational parameters necessary for a complete sampling audit trail are logged on non-volatile memory. SUGAR achieves adequate sensitivity for measuring reduced sulfur gases at typical atmospheric concentrations. Applications under laboratory conditions and in the field demonstrate the versatility of the automated system. Field deployment proved the capability of continuous operation over a period of several weeks. The potential for further improvements of sensitivity and portability by use of different sulfur specific GC detectors is discussed.

**Keywords:** sulfur gases; gas chromatography; automation

### 1. Introduction

Volatile sulfur compounds in the environment have received much attention because of their role in pollution and global climate change [1]. The most important reduced sulfur compounds found in the atmosphere are dimethyl sulfide (DMS), carbonyl sulfide (COS), hydrogen sulfide (H<sub>2</sub>S), carbon disulfide (CS<sub>2</sub>), and methanethiol (CH<sub>3</sub>SH). With the exception of COS, these compounds are rapidly oxidized in the atmosphere and lead to the formation of sulfate aerosol, which damages human health [2] and causes environmental harm because of its acidity [3,4]. Sulfate aerosol also plays an important role in the Earth's radiation budget and in climate forcing by directly scattering incoming solar radiation and by modifying cloud properties [5,7].

A considerable amount of sulfur is released from anthropogenic sources, mainly in the form of SO<sub>2</sub>. However, natural sources including volcanoes (SO<sub>2</sub>, H<sub>2</sub>S, COS and CS<sub>2</sub>) and

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biogenic emissions (oceans: DMS, COS, CS<sub>2</sub>, H<sub>2</sub>S and CH<sub>3</sub>SH; anoxic soils/wetlands: H<sub>2</sub>S, DMS, COS, CS<sub>2</sub> and CH<sub>3</sub>SH; land vegetation: H<sub>2</sub>S, CH<sub>3</sub>SH and DMS) also make a significant contribution to the global budget of atmospheric sulfur. COS plays a special role [8], because it is chemically more stable than the other reduced sulfur gases and comparatively inert to oxidation by the OH radical in the troposphere. It has a tropospheric lifetime of about 4 years [9], and is transported into the stratosphere, where the strong UV radiation and oxygen radicals can oxidise it more efficiently. COS as a source of stratospheric aerosol [10], which affects the amount of incoming solar radiation reaching the Earth's surface [11] and heterogeneous ozone chemistry [12], has been subject to debate [13] but has recently received renewed support [14].

Increasing interest in the various sulfur species in the atmosphere and their natural and anthropogenic sources has led to extensive efforts to measure these compounds in different environments. An instrument operated in the field should be sufficiently mobile, robust, and easy to use, in addition to having good accuracy and precision, adequate time resolution, and the ability to measure several compounds simultaneously. Although other techniques have been applied for various compounds, including tuneable diode laser spectroscopy for COS [15], or mass spectrometric techniques for COS [16] and DMS [17], gas chromatography–flame photometric detection has most often been the method of choice for simultaneous measurement of reduced sulfur compounds [18]. The wide range of specific applications and the many innovations made to this technique over the past decades have been reviewed by Wardencki [19,20]. In recent years, compact and portable sulfur analysis systems have been developed [21], and some off-the-shelf instruments have become available. However, the detection limit of these sulfur analysers mostly falls into the low ppb range or higher. While this is sufficient for applications such as direct emission control or natural gas analysis, much lower concentrations need to be detected in applications in the fields of atmospheric chemistry and biogeochemistry.

With our Sulfur Gas Analyser (SUGAR), we present a state-of-the-art gas-chromatographic system capable of measuring background concentrations of reduced sulfur compounds under field conditions. With the aim of maximising portability, automation, and long-term maintenance-free operation without compromising sensitivity and the range of applications, all analytical components and the calibration source are directly integrated into a 'one box' sampling system and controlled by a single custom-made microprocessor. This includes a low-cost easy-to-build compact gas chromatograph designed for a wide range of applications.

We have used SUGAR successfully for laboratory and field measurements of COS, CH<sub>3</sub>SH, and CS<sub>2</sub> at typical ambient concentrations (~500 ppt for COS, 5–40 ppt for CH<sub>3</sub>SH and CS<sub>2</sub>). This set-up can be used to measure DMS, dimethyl disulfide (DMDS) and, with some easy alterations, H<sub>2</sub>S. With modifications to the chromatography and detection components, the SUGAR sampling system could be useful for a range of other environmentally relevant species.

## 2. Experimental

### 2.1 System setup

An overview of SUGAR is given in Figure 1. The system is designed to allow consecutive sampling from two different sources, which is necessary for applications such as gradient

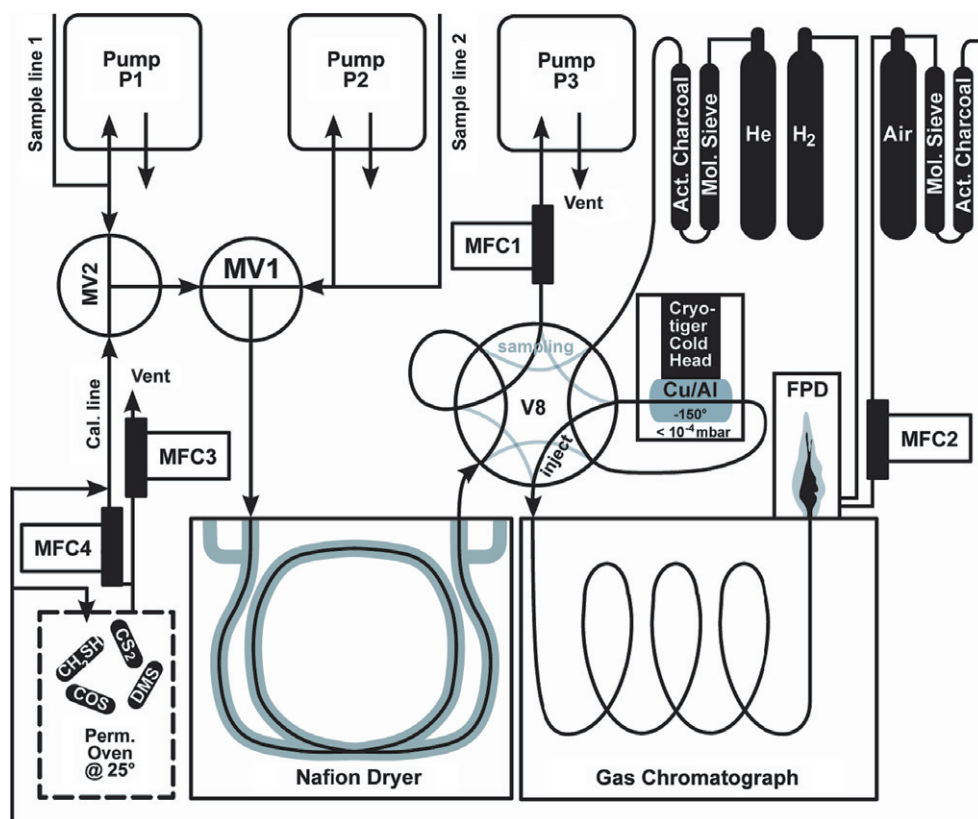


Figure 1. Schematic of SUGAR. MFC: mass flow controller; MV: magnetic three-way valve; V8: automatic eight-port valve; FPD: flame photometric detector. The functions of the different parts and the sampling procedure are explained in the text.

measurements or trace gas exchange measurements. For example, with the dynamic enclosure method, air samples need to be collected at the inlet and outlet of an enclosure, or at the outlets of a sample enclosure and an empty reference enclosure. Both sample lines (1/4" or 3/8" tubing) are continuously purged with sample air at a flow rate of  $10 \text{ dm}^3 \text{ min}^{-1}$  to eliminate any carryover from the previous sample using the small diaphragm pumps **P1** and **P2** (N811KNDC, KNF Neuberger, Freiburg, Germany). The sample air flow can be regulated by restriction or a flow controller. For atmospheric measurements of the short-lived sulfur gases ( $\text{H}_2\text{S}$ , DMS,  $\text{CH}_3\text{SH}$ , and  $\text{CS}_2$ ), a cotton scrubber is placed inside the entrance of the sampling line to remove radicals such as ozone that could react with the analytes [21]. Because the sampling of reduced sulfur compounds may be affected by ad- and desorption effects on surface materials, all tubes, fittings and connecting blocks are made of inert Teflon (FEP or PFA). The use of polytetrafluoroethylene (PTFE) in the pump head of either **P1** or **P2** allows for the sampling of an enclosed headspace (e.g. a static chamber or a seawater equilibrator) without contamination of the sample. A third pump **P3** of the same type as **P1** and **P2** draws a sample out of either sampling line 1 or 2, depending on the position of the three-way-magnetic valve **MV1** (Fluoroware, Bad Rappenau, Germany). The subsample is first

passed through a Nafion Dryer (Perma Pure, Farmingdale, NJ), which has been shown to efficiently remove moisture without influencing the sulfur gas measurement [22]. The gas stream is then drawn through the cryotrap (see below). The actual sample volume is determined by the flow rate at STP measured by a mass flow controller MFC1 (Tylan, Eching, Germany) and the time that the eight-port valve V8 (Valco, Houston, TX) is in the 'sampling' position. When valve V8 is switched to the 'inject' position (1/4 turn), the helium carrier gas is directed through the trap into the gas chromatograph. A 1/8" diameter tubing is used to connect MV1 to V8 via the Nafion Dryer, V8 to MFC1 and V8 to the gas chromatograph.

## 2.2 Cryogenic trapping

The method used for cryogenically trapping the analytes out of the sampling stream is described in detail in von Hobe *et al.* [23] The trap itself is a silanized glass-lined steel tube (SILCOSTEEL, L 20 cm, OD 3.2 mm, i.d. 2.2 mm, Restek, Bellefonte, PA) filled with acid-washed dimethyldichlorosilane (DMCS) treated mesh 45/60 Chromosorb W that offers a good trapping efficiency because of its large surface area. The tube is cooled by a Cryotiger (APD Cryogenics, Allentown, PA) refrigerator. The interface between the trap and the cold end of the refrigerator is made of copper and aluminium to ensure a fast heat transfer, while its mass buffers the heat pulse. A thin layer of silicon tape (0.3 mm) electrically isolates the trap from the copper and the cold head. All contact surfaces are covered with small amounts of silicon grease (Dow Corning, Midland, MI) to ensure uniform heat transfer. Trap and cold head are placed inside a vacuum chamber at a pressure of less than  $10^{-4}$  mbar, as is needed to operate the Cryotiger. The trap ends are secured to the chamber walls through short pieces of PTFE tubing (OD 6.4 mm, i.d. 4.0 mm) tightened using steel screw connectors (Swagelok, Frankfurt, Germany). The PTFE ensures electrical isolation from the vacuum chamber. Temperatures at the copper block and the aluminium tube are around  $-170^{\circ}\text{C}$  and  $-150^{\circ}\text{C}$ , respectively, measured using chromel alumel thermocouples. To elute the analytes, the trap is heated by a 1-s pulse of electrical current (200 A at 1.5 V), which almost instantaneously raises the temperature inside the trap to over  $100^{\circ}\text{C}$ .

## 2.3 Gas chromatography

In order to miniaturize the instrument for maximum mobility, a simple and small oven was designed (Figure 2), which is capable of heating and cooling the column rapidly. The housing and lid of the cylindrical oven (12 cm i.d.  $\times$  10 cm) are made of thin aluminium sheets filled with glass wool for insulation ( $\sim 16$  mm thick). The oven is suspended underneath an aluminium base plate (25 cm  $\times$  25 cm  $\times$  8 mm) with the lid resting on an electromagnetic actuator for opening and closing. The oven temperature is regulated to  $\pm 1^{\circ}\text{C}$  between ambient temperature and about  $200^{\circ}\text{C}$  by a pulsed wire heating element (0.6 m  $\times$  1 mm stainless steel, Thermocoax, Athis de l'Orne, France) and a chromel–alumel thermocouple connected through the base plate. Heating rates of up to  $80^{\circ}\text{C min}^{-1}$  can be achieved. A propeller in the centre of the oven, driven by a 24-V motor mounted on top of the plate, mixes the air volume, ensuring a homogeneous temperature inside the GC and rapid exchange with the outside air for cooling when the lid is open. Placing a second propeller at a  $90^{\circ}$  angle to the GC wall next to the gap between the wall and the lid can

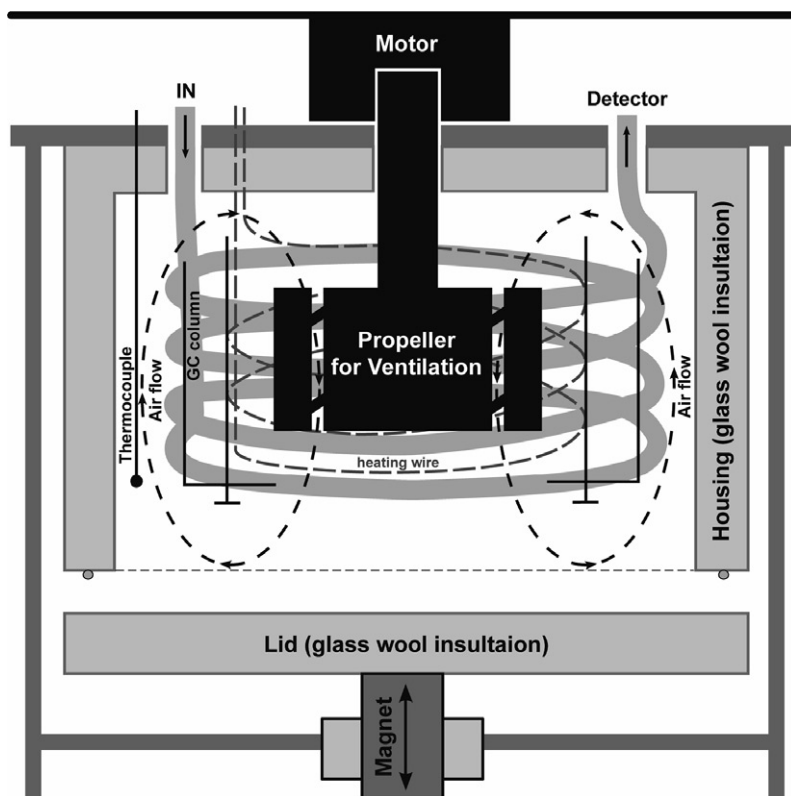


Figure 2. Schematic of the GC incorporated in SUGAR.

enhance cooling by accelerating the exchange with outside air. The maximum cooling rate is somewhat dependent on how long the GC is held at high temperatures, but in the course of our experiments it never took more than 3.5 min to cool the GC from 120°C to 50°C.

The GC is equipped with a fluorinated ethylene propylene (FEP) column (1.8 m long, i.d. 1.6 mm) packed with 60/80 mesh Carbopack B/1.5% XE 60/1.0% H<sub>3</sub>PO<sub>4</sub> (Supelco) that has been shown to efficiently separate reduced sulfur gases [22]. Separation of COS, CH<sub>3</sub>SH, DMS, and CS<sub>2</sub> (Figure 3) is achieved by a three-stage temperature programme (1.8 min at 50°C; 30°C min<sup>-1</sup>; 2 min at 85°C; 30°C min<sup>-1</sup>; 2.5 min at 120°C). We have not performed laboratory or field measurements of H<sub>2</sub>S with SUGAR. Should H<sub>2</sub>S determination be desired, a cooling device must be installed in the oven to allow a temperature step at -15°C [22], because separation of H<sub>2</sub>S from CO<sub>2</sub> is poor at higher temperatures (Figure 3).

The flow rate of the He carrier gas is 20 cm<sup>3</sup> min<sup>-1</sup> at STP. The sampling line is attached to the column inlet via a Swagelock<sup>®</sup> connector (BEST, Aschheim, Germany) placed in the base plate. The column outlet is connected to a flame-photometric detector (FPD) (Hewlett Packard, Palo Alto, CA) also mounted on the base plate. The detector is held at a constant temperature of 160°C, and the flame is sustained by a mixture of

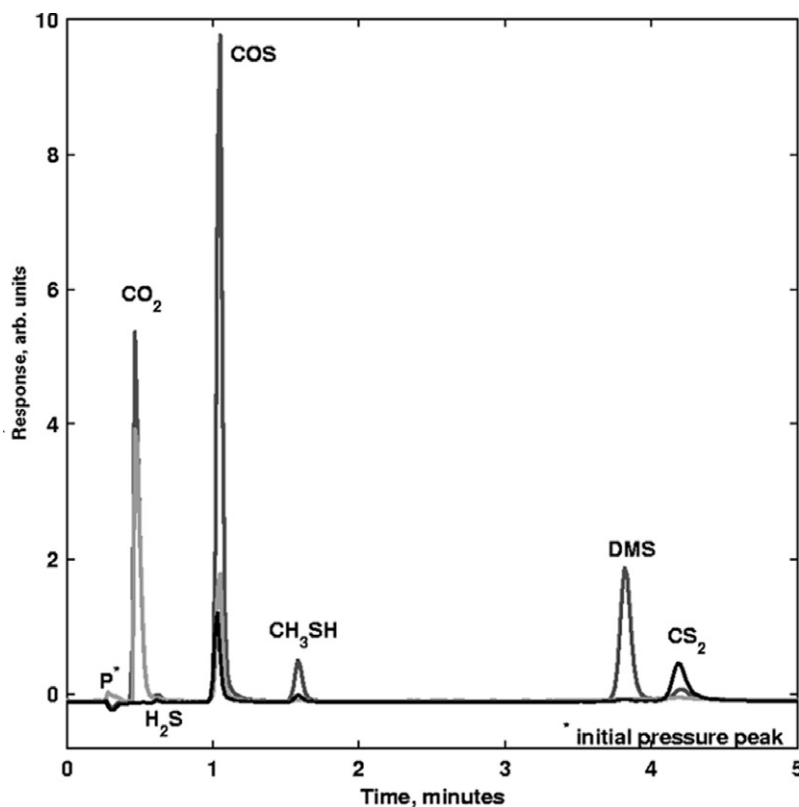


Figure 3. Chromatograms obtained with SUGAR for ambient air (light grey), a sample from a seawater equilibrator (dark grey), and a calibration standard containing H<sub>2</sub>S, COS, CH<sub>3</sub>SH, and CS<sub>2</sub> (black).

hydrogen and synthetic air at flow rates of 130 and 110 cm<sup>3</sup> min<sup>-1</sup> at STP, respectively. The air flow rate is regulated by MFC2. Alternative detectors that may be used instead of the FPD, which could further augment SUGAR's portability and/or analytical performance, are discussed in Sections 2.6 and 3.1.

## 2.4 Calibration

SUGAR is calibrated by switching the magnetic valve MV2 (Fluoroware, Bad Rappenau, Germany) from sampling line 1 to the calibration line, thus drawing standards into the system. These are prepared by gas dilution, using stainless steel permeation devices (Vici Metronics, Houston, TX), which emit the analytes (i.e. COS, CS<sub>2</sub>, CH<sub>3</sub>SH and DMS) at known rates. The permeation devices are held in a special oven thermostated to a constant temperature (25.0 ± 0.1°C) and flushed with synthetic air at a constant flow rate. Stainless steel surfaces are electropolished to minimize the wall interaction of the analytes. After passing through the chamber, the flow is split through MFC3 and MFC4 (Tylan, Eching, Germany) so that a known fraction is fed into the calibration line. Ambient air from which sulfur gases have been removed by a molecular sieve (5Å)/activated charcoal scrubber is added up to the flow rate of MFC1. With a fresh scrubber, no signals are

Table 1. SUGAR power requirements.

Vacuum pump	260 W
Cryotiger	460 W
SUGAR GC system (GC oven, FPD, MFCs, etc.)	~100 W
Nafion dryer	20 W
Permeation oven	20 W

detected in blank samples. The changing interval of the scrubber is in the order of several weeks and depends on the scrubber volume, the frequency of calibrations and ambient sulfur gas levels.

### 2.5 System control

The core of the control unit is a custom-made microprocessor unit (described in detail by Kuhn *et al.* [24]) that provides control signals for the operation of all SUGAR components and stores data to a non-volatile memory (PCMCIA flash disk). The applied software is a multitasking, multiprocessing real-time operating system with a built-in Pascal compiler. It allows the setting of sampling times and periods by controlling the operation of sampling valves and mass flow controllers and operates the GC by setting the oven temperature and the heat pulse to eject the sample from the cryotrap. Sampling protocols, including regular calibrations, can be easily custom-programmed to meet the needs of individual applications. A PC can be connected to the unit via an RS-232 interface to allow the downloading of programme settings and the offloading of sampling result reports. Alternatively, a keypad and a small display on the outside the control unit can be used if no PC is available.

### 2.6 Deployment issues

The overall dimensions of the SUGAR instrument are  $0.68 \times 0.48 \times 0.48$  m with a weight of about 65 kg plus the Cryotiger compressor (30 kg). Sampling system, cryotrap, GC and control unit (contained in a 19" rack) are housed in a frame made of  $40 \times 40$  mm aluminium X-profiles. Cover plates can be attached to all sides for transport. The total power requirement is less than 1 kW (Table 1). The duration of maintenance-free operation is limited by the data-storage capacity and the use of compressed gases. For the measurements presented in Section 3.3, a sample rate of 1 sample every 15 min with 8-min acquisition time for each chromatogram was chosen, resulting in 4 MB of data being stored per day. Gas consumption amounts to  $\sim 500 \text{ dm}^3 \text{ day}^{-1}$  at STP for synthetic air (depending on the frequency of calibrations),  $190 \text{ dm}^3 \text{ day}^{-1}$  at STP for hydrogen, and  $30 \text{ dm}^3 \text{ day}^{-1}$  at STP for helium, which means that standard commercial gas cylinders ( $50 \text{ dm}^3$  at 200 bar) last for approximately 2 weeks for air, 7 weeks for hydrogen, and almost a year for helium. Alternatively, a hydrogen generator and chemically dried and purified ambient air may be used.

With a different detector, gas consumption may be significantly reduced. Using a photoionization detector (PID) or an electron capture detector (ECD) could eliminate the need for detector supply gases. The ECD requires a make-up gas unless nitrogen is used as carrier gas, and its sensitivity varies with the electronegativity of the compounds to be



analysed (e.g. it is not very sensitive to DMS). The ECD is also negatively affected by water, and its radioactive source imposes licensing requirements for the operator, and special regulations and precautions during transport and field use. The applicability of the PID depends on the sample matrix and the retention of impurities by the column, as it does not equal the FPD in terms of selectivity for sulfur gases.

The recently developed pulsed flame photometric detector (PFPD) [25,26] has approximately 10 times lower gas usage requirements compared with a standard FPD while also possessing superior sensitivity (cf. Section 3.1) and selectivity towards sulfur compounds. With its reduced gas consumption, several days of continuous operation would be possible by supplying gases from small (1 or 2 dm<sup>3</sup>) cylinders incorporated into the instrument frame.

### 3. Results

#### 3.1 Detection limit

The detection limit depends on the sampling volume, which is determined by the trapping time and the flow rate through the cryotrap, and the absolute detection limit of the FPD detector, which is about 10 pg S/s. A typical sampling routine of 2 min trapping at a flow rate of 200 cm<sup>3</sup> min<sup>-1</sup> at STP yields a detectable concentration for reduced sulfur gases of about 20 ppt (10 ppt for CS<sub>2</sub> because it contains two sulfur atoms).

Obviously, the detection limit crucially depends on the choice of detector. The PID and ECD detectors discussed in Section 2.6 offer improved detection limits compared with the FPD by up to 1 and 4 orders of magnitude, respectively, depending to some extent on the compound to be analysed [27]. The PFPD detector has a detection limit of less than 1 pg S/s [25], ten times more sensitive than the standard FPD. Other commonly used detectors for sulfur compounds include the sulfur chemiluminescence detector (SCD) and the atomic emission detector (AED) with detection limits down to about 0.1 pg S/s and 1 pg S/s, respectively [27].

#### 3.2 Accuracy and precision

Typical calibration curves and error estimates at different concentrations are shown in Figure 4. The FPD response is exponential with

$$PA = 10^A c^B, \quad (1)$$

where PA is the peak area,  $c$  is the analyte concentration, and  $A$  and  $B$  are the fitting parameters of the calibration curve. The standard errors ( $s_c$ ) given in the upper panel of Figure 4 are computed for each sulfur gas from the uncertainties of the fitting parameters  $A$  and  $B$  ( $s_A$  and  $s_B$ ; for the error analysis, the calibration line is shifted in the  $x$ -direction so that the  $y$ -axis intercepts the  $x$ -axis at the mean of  $\log c_{\text{cal}}$  so that  $A$  and  $s_A$  become independent of  $B$  and  $s_B$ ) and the estimated error of the calibration standards using Gaussian rules of error propagation:

$$s_c = \frac{1}{\log e} \sqrt{\left(\frac{\log PA - A}{B^2}\right)^2 s_B^2 + \frac{1}{B^2} s_A^2 + s_{(\log c_{\text{cal}})}^2}. \quad (2)$$

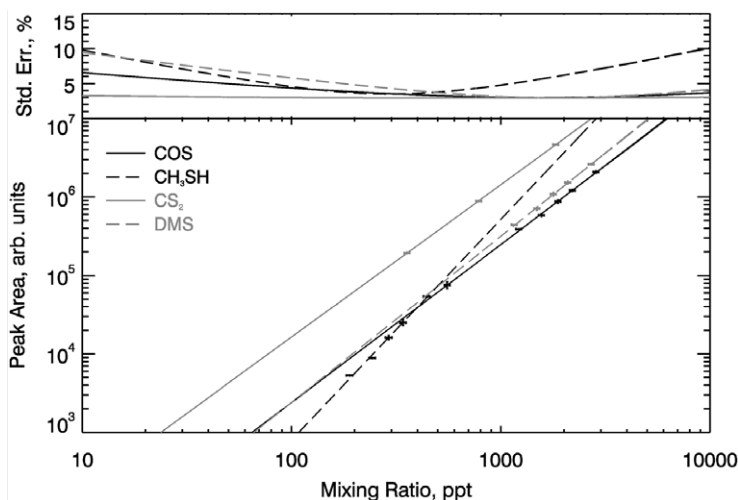


Figure 4. Calibration curves and standard error estimates for COS, CH<sub>3</sub>SH, CS<sub>2</sub>, and DMS. Calibration curves are drawn on a log–log scale because of the non-linear response of the FPD detector. The error minima found at the mean mixing ratios of the calibration standards are 3.0% at 1500 ppt for COS, 3.5% at 300 ppt for CH<sub>3</sub>SH, 2.9% at 800 ppt for CS<sub>2</sub>, and 3.2% at 850 ppt for DMS.

The error in the calibration standards, represented by  $s_{(\log c_{cal})}$ , results from the uncertainties of the gravimetrically determined calibration standard permeation rates (0.6% for COS, CS<sub>2</sub> and DMS, 1.8% for CH<sub>3</sub>SH) and of the flow rates of the MFCs in the calibration system (<2%). It should be noted that accuracy cannot be rigorously established, because the sulfur gas mixtures produced by the SUGAR calibration system do not represent standards of sufficiently well-known and certified composition.

To demonstrate the precision of the sampler, a zero gradient test was performed by repeatedly sampling one common standard gas mixture comprising different reduced sulfur compounds from the permeation oven (Figure 5). A total of 20 samples were taken, switching consecutively between sample line 1 and 2. Mixing ratios calculated from the permeation and flow rates from the calibration system were 632 ppt for COS, 675 ppt for DMS, 202 ppt for CH<sub>3</sub>SH and 471 ppt for CS<sub>2</sub>. The results were  $637 \pm 12$  ppt, corresponding to  $\sigma_{rel} = 1.9\%$  for COS,  $667 \pm 15$  ppt  $\equiv \sigma_{rel} = 2.2\%$  for DMS,  $172 \pm 21$  ppt  $\equiv \sigma_{rel} = 12.4\%$  for CH<sub>3</sub>SH and  $458 \pm 10$  ppt  $\equiv \sigma_{rel} = 2.2\%$  for CS<sub>2</sub>.

### 3.3 Field and laboratory measurements

One of the major limitations in advancing the understanding of the sink/source distribution of sulfur gases and developing strategies for the control of anthropogenic sulfur emissions is the technical ability to accurately measure these compounds. The automated SUGAR system has been used successfully for continuous operation in the laboratory [28,29] and in the field [30]. SUGAR's dual sampling system allows for the investigation of trace gas exchange processes requiring the accurate measurement of small concentration differences. Exemplary results accomplished under controlled laboratory conditions are shown in Figure 6. The COS exchange pattern of a beech tree was

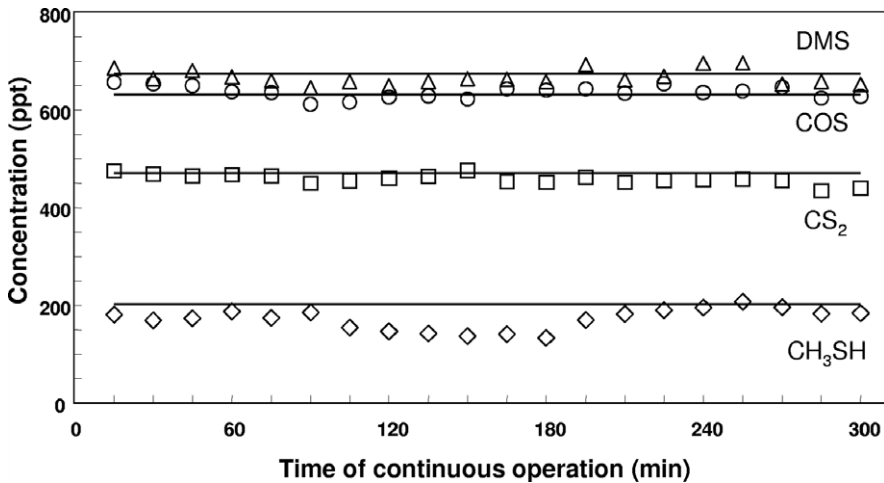


Figure 5. Results of the zero gradient test. The individual determinations are given by the symbols, and the lines represent the mixing ratio calculated from the permeation and flow rates of the calibration system.

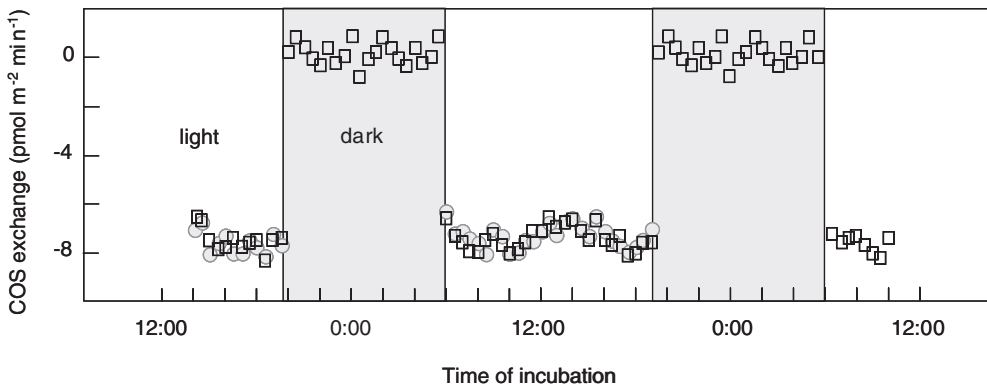


Figure 6. Branch enclosure measurements of the exchange of COS between a beech tree (*Fagus sylvatica* L.) and the atmosphere under controlled laboratory conditions. Uptake of COS (negative values, expressed on a leaf area basis) is observed under daytime conditions and ceases at night (shaded areas). Open squares represent data obtained with the automated SUGAR system, and filled circles are samples collected manually by trapping with glass cryotrap immersed in liquid argon and subsequent gas chromatographic analysis according to Hofmann *et al.* [22].

investigated by means of a dynamic branch enclosure system and used to infer the COS sink strength of plants. The dynamic enclosure method requires that air samples be collected at the inlet and outlet of the enclosure, or preferably at the outlet of a sample enclosure and the outlet of an empty reference enclosure both flushed with the same purging air. Exchange rates ( $\Phi_{\text{COS}}$ ) are calculated from the observed mixing ratios at the inlet  $c_i(\text{COS})$  and the outlet  $c_o(\text{COS})$  of the system, as:

$$\Phi_{\text{COS}} = \frac{F}{A}(c_o(\text{COS}) - c_i(\text{COS})), \quad (3)$$

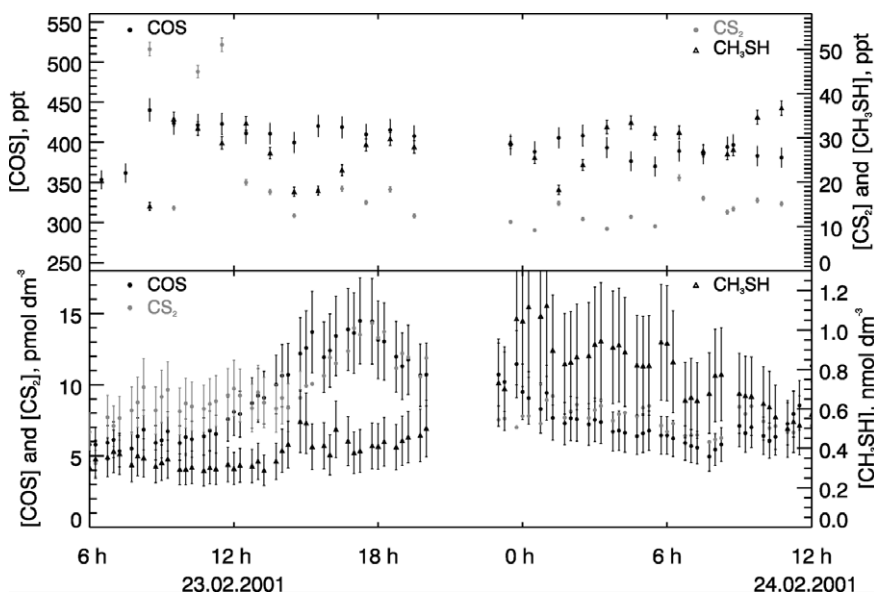


Figure 7. COS, CH<sub>3</sub>SH, and CS<sub>2</sub> data measured with SUGAR during the Poseidon 269 cruise. The upper panel shows atmospheric mixing ratios, the lower panel concentrations in seawater. The larger error bars for the seawater concentrations result from an additional uncertainty of about 10% in the Henry's law constants.

where  $F$  is the air flow through the chamber, and  $A$  is the single-sided leaf area of the investigated plant. A critical limitation in quantifying exchange rates is that the mixing ratios in both the inlet and outlet are high, but the relative differences to be resolved are small, and so there is a need for high precision in the sampling and analytical systems, respectively.

In Figure 6, the performance of the automated system during daytime operation was compared with a conventional cryotrap sample collection system operated manually, with subsequent gas chromatographic analysis according to Hofmann *et al.* [22]. The data derived by both systems were in perfect agreement, i.e. did not show any bias within the uncertainty of the analytical system.

Figure 7 shows field data from a ship cruise in the Canary Island region in February 2001, during which the partitioning and transfer of COS, CH<sub>3</sub>SH, and CS<sub>2</sub> between open ocean water and the atmosphere were investigated. Consecutive measurements of ambient air mixing ratios and seawater concentrations were carried out to investigate the source strength/sink activity of the open ocean in relation to the dissolved organic matter content and the occurrence of phytoplankton blooms [30]. Determination of seawater concentrations was carried out by measuring headspace mixing ratios in a continuously pumped Weiss Equilibrator, as described by Butler *et al.* [31] but made of polyvinylidene fluoride, and converting these to dissolved concentrations (in pmol dm<sup>-3</sup>) using Henry's law constants. Both atmospheric mixing ratios and dissolved concentrations are in the same range as previous observations, and the typical diel cycling in seawater can be clearly seen: maximum concentrations occur in the afternoon for the photoproduct species COS and CS<sub>2</sub>, and in the early morning for CH<sub>3</sub>SH, which photodissociates. The fully automated

system was operated continuously for several days without maintenance, thus proving the reliability of the automated system.

#### 4. Conclusions

SUGAR is a comparatively inexpensive, flexible, fully automated system for measuring reduced sulfur species at low concentrations with good reproducibility. The instrument requires only electrical power and the compressed gases helium, hydrogen, and synthetic air for operation. In particular, no expendable cryogenes are needed in the preconcentration step. Because the design is a portable quick-to-set-up one-box system, in which the sampling system and a novel small gas chromatograph are integrated, SUGAR is a useful instrument for continuous laboratory and field measurements. Because of the complete automation, including calibrations, SUGAR can be pre-programmed for long-term autonomous operation. The analytical performance (sensitivity and selectivity) and portability (lower gas consumption) could be enhanced further by using the novel PFPD detector. For applications where PID and ECD offer sufficient selectivity and sensitivity, the need for a gas supply to the detector may be eliminated.

One advantage over smaller and more portable off-the-shelf systems is the flexibility and wide applicability owed to the modular design of an instrument like SUGAR. The integration into an open frame allows for an easy exchange of the components of both the sampling system and the gas chromatograph to fulfil the specific needs of the user. The trapping temperature of the cold trap may be adjusted between  $-200^{\circ}\text{C}$  and  $0^{\circ}\text{C}$ , with the choice of a different adsorbent further extending the range of possible applications. Both the column and the detector of the GC can be easily replaced, and the temperature programme can be adjusted within the limits described in Section 2.3. Thus, the design of SUGAR may be applied to the analysis of any volatile compounds that can be measured by cryogenic preconcentration and gas chromatographic analysis.

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