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Analysis of low concentration reduced sulfur compounds (RSCs) in air: Storage issues and measurement by gas chromatography with sulfur chemiluminescence detection

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ABSTRACT

Reduced sulfur compounds (RSCs) were measured at low concentrations in small volume air samples using a cryo-trapping inlet system and gas chromatograph outfitted with a sulfur chemiluminescence detector (GC-SCD). The relative sensitivity of the system to the RSCs follows the sequence $H_2S < CH_3SH < OCS \sim DMS < CS_2$. The analytical system achieves a detection limit of 120 ppt in a 100 mL air sample, which is suitable for measuring reactive RSCs (e.g., H_2S and CH_3SH) at ambient or near ambient atmospheric concentrations. The inlet system allows for replicate sampling from a stored air sample (sub-sampling), thereby improving estimates of instrumental precision and demonstrating the reproducibility of the analytical method. Although the SCD theoretically provides linear responses equivalent to the sulfur mass injected, we found that the response properties for each RSC differed. At concentrations below 2 ppb, the compounds H_2S and CH_3SH have diminished responses, leading to larger measurement uncertainties. Two generations of commercially available SilcoCan canisters were tested to evaluate the relative RSC loss due to storage in the canister and loss of inertness because of coating age. The older generation canister (>6 years from initial coating) saw significant loss of H_2S and CH_3SH within 2 days, while the more recent generation canister (<1 year from initial coating) yielded percent recoveries of RSCs in the range of 85% (H_2S and CH_3SH) to 95% (OCS, DMS and CS_2) after 7 days of storage, suggesting that these canisters may be suitable for the short-term storage of low level RSCs. The development of this low concentration, low sample volume method is well suited for measuring RSC gas fluxes from natural soils in laboratory incubations and in field flux chamber studies.

1. Introduction

Interest in the trace analysis of reduced sulfur compounds (RSCs) in air has grown considerably because of their significant role in atmospheric pollution and global climate change [1,2]. Various approaches have been employed to determine the quantitative analysis of RSCs such as hydrogen sulfide (H_2S), methane thiol (CH_3SH), carbonyl sulfide (OCS), dimethyl sulfide ($(CH_3)_2S$, DMS), carbon disulfide (CS_2), and dimethyl disulfide ($C_2H_6S_2$, DMDS) in the atmosphere [3]. Gas chromatographic analyses with different detection devices such as the sulfur chemiluminescence detector (SCD), the atomic emission detector (AED), the pulsed flame photometric detector (PFPD) and the mass spectrometer (MS) are now established techniques for detecting atmospheric sulfur compounds [2–4]. Among the detectors, the SCD has a number of advantages for low concentration sulfur gas analysis, including a wide linear range, equimolar response for all sulfur compounds and very good sensitivity and selectivity [2,5,6]. At high concentrations, the RSCs have been analyzed successfully from whole air collected in sample loops and directly injected into the GC or with a thermal desorption (TD) unit connected to the GC [3,7,8]. However, at concentrations below a few ppb (parts per billion), most GC detectors are not sensitive enough for the accurate detection of RSCs [3].

In ambient air, RSCs are present at very low concentration levels; thus, a pre-concentration step is required for collecting sufficient masses of analytes, lowering the detection limit and reducing potential interferences in GC analyses [4]. Different types of pre-concentration techniques, namely (i) sorption on certain metal surfaces (e.g., gold, palladium and platinum), (ii) sorption on solid adsorbents (e.g., silica gel, activated carbon, molecular sieve, porous polymers and graphitized carbon black), and (iii) cryogenic trapping have been established for detecting RSCs in ambient air [2]. Sorption on metal surface/solid adsorbent does not give satisfactory results for the reactive volatile sulfur gases due to interferences, low response and/or inconsistent recoveries [9]. Cryo-trapping methods are inconvenient for field collection due to the difficulty of storing and transporting samples [10]. Drawing air into canisters or PTFE-lined bags is the most direct method for collection and storage

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of ambient air samples. However, RSCs are reactive and trace levels can undergo irreversible adsorption, catalytic rearrangement by contact with different materials and/or reactions with substances with which they have been sampled [11]. Because of the lower stability, Tedlar® bags and electropolished stainless steel canisters are not suitable for collecting and storing low-level (ppb) sulfur compounds [12,13]. Using stainless steel canisters whose interior surfaces are coated with chemical vapor deposited amorphous silicon may significantly enhance the stability of very low levels (1–20 ppbv) of sulfur compounds under dry or humid storage conditions [14]. For the canisters used in this study (SilcoCans, Restek, Bellefonte, PA, USA), the coatings were performed by a chemical vapor deposition (CVD) process at elevated temperature to deposit amorphous silicon. The inner surface of this material was then functionalized via hydrosilylation (to react with remaining Si–H moieties) to create a highly inert surface on the stainless steel substrate (D. Smith, Restek, Pers. Comm.).

In addition to storage issues, sample integrity for RSCs can be compromised when air samples flow through sampling or analytical apparatus and contact parts that are not composed of glass, Teflon or silanized steel [13]. Thus, the inlet system (e.g., tubing, connecting materials) must also be inert enough to reduce adsorption loss. Sample loss can be minimized in the inlet system using chemical vapor deposited amorphous silicon coated tubing and connections throughout the ‘wetted’ parts. We have developed such an inlet system which includes a cryogenic trap coupled with GC-SCD and is designed to measure replicate subsamples of an air sample stored at ambient pressure in a SilcoCan canister. In this study, a series of calibration experiments were conducted to describe the ability of the inlet system to accurately quantify RSCs at ambient and near ambient concentrations. The suitability of SilcoCan canisters for storing ppb to ppt level RSCs in air was also tested over various time intervals.

2. Instrumental

RSCs were quantified using an Agilent 7890A Gas Chromatograph interfaced with an Agilent 355 Sulfur Chemiluminescence Detector. A custom-built cryo-trapping and sample introduction system (Fig. 1) was developed for the analysis of low volume (10–400 mL) air samples. At one end of the inlet system, an evacuated 1 L end volume connected to a calibrated pressure transducer (Paroscientific Inc., Redmond, WA, USA) was used to draw air from an air sample canister through a 6-port Valco valve (VICI, Valco Instrument, Houston, TX, USA) with Sulfinert treatment (Restek, Bellefonte, PA, USA) and a small trap consisting of an 1/8 in. O.D. Silcosteel tube (Restek, Bellefonte, PA, USA) filled with glass beads (Sigma–Aldrich, St. Louis, MO, USA) and immersed in liquid nitrogen. The cryo-trapping step enhanced chromatographic resolution, providing sharper peaks that were easier to integrate. The sampling valve switched between the load position (sample introduction onto the trap) and the inject position (sample injection onto the GC column). When the valve was switched to the inject position, the helium carrier gas was directed through the trap into the gas chromatograph. The trap was then heated at 100 °C under helium flow to desorb the analytes onto GC column.

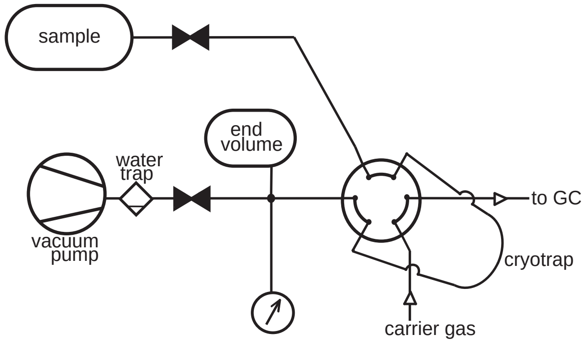

Fig. 1. Schematic of the inlet system.

For chromatographic separation, a DB-1 capillary column (30 m × 0.32 mm ID, 5 μm film thickness, J&W Scientific) was used with each running cycle ending at 16 min intervals. The initial column temperature was 30 °C held for 5 min, ramped up to 150 °C over 8 min (15 °C min^{-1}) and then held at 150 °C for 3 min. Helium carrier gas was kept at a constant pressure of 5 psi, which provided a flow rate of 2.53 and 1.45 mL min^{-1} at 30 °C and 150 °C, respectively.

Separated analytes entered a furnace (800 °C), where the compounds were reduced in hydrogen (45 mL min^{-1}) and air (55 mL min^{-1}) to generate sulfur monoxide. The sulfur monoxide reacted with ozone within the SCD, producing sulfur dioxide and light. The light generated was detected by a photomultiplier tube, with the resultant signal linearly proportional to the amount of sulfur in the sample. The data integration system for quantifying peak area, height and width was performed using Agilent Chemstation software (Agilent Technologies, Palo Alto, CA, USA).

Prior to calibration, analytical breakthrough tests were performed to determine the maximum sample volume and flow that could be drawn through the cryo-trap. Several incubation chamber air samples with ambient room air mixed with aliquots of the RSC standard were conducted and found no co-elution of RSCs with CO_2 and other volatiles. Nitrogen blank tests were performed after running high concentration samples and did not find any sample carryover between consecutive runs.

Sample losses on the interior surface of the container were investigated using two generations of SilcoCan canisters: “older generation” canisters were manufactured between July 2004 and December 2004; “newer generation” canisters were manufactured in 2010. Although amorphous silicon material was bonded to the inner surface of electropolished stainless steel for both generations, the thicker coating (100–250 nm) of the newer SilcoCan purportedly improved the inertness and stability of the canister surface [14].

To quantify the extent of RSC loss in the canisters, a series of experiments were conducted over time intervals of up to 10 days to evaluate the canister sampling method with respect to the analytical bias occurring from the collection and storage of RSCs. The results of these measurements were taken as base for the calculation of the recoveries of RSCs over time in two different types of vessels. Each air canister was measured at least three times each sampling day to evaluate the repeatability of the method.

To investigate the analytical performance of the instrument in terms of relative sensitivity of RSCs using a GC-SCD and custom-built inlet system, a series of working standards at different concentration levels were passed through the cryogenic trap at different sample volumes to derive calibration curves for each of the standards. The calibration results of RSCs were compared with each other to determine the relative sensitivity of the sulfur compounds in terms of instrumental response factors. The response factors for each RSC were calculated in terms of picograms sulfur per unit peak area, with higher response factors indicating lower detector sensitivity for a particular compound. The analytical detection limit in units of picogram sulfur per second (pg S s^{-1}) was determined from the analysis of standard samples in a given matrix containing the analyte.

$$\text{analytical detection limit}(DL) = \frac{0.66 \times M \times N}{W_{1/2ht} \times H}$$

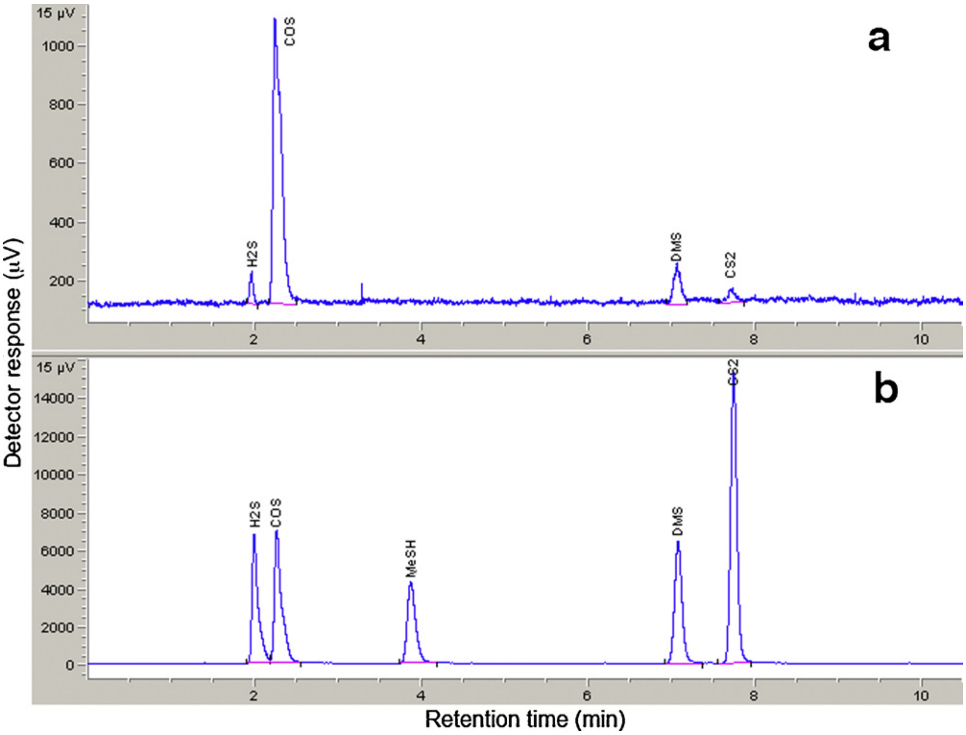

Fig. 2. Chromatograms of (a) ambient air collected near a salt marsh, Fremont, CA (~150 mL sample) and (b) Matheson gas standard of the RSCs (~22 pmoles of each compound).

where M is the mass of sulfur in pg that reaches to the detector; N is the peak to peak noise (in µV); $W_{1/2\text{ht}}$ is the width of the peak at half height (in seconds); H is the height of the peak (in µV). The constant, 0.66 was used in the calculation using an analytical DL signal to noise ratio of 3.29 [15].

An ambient air sample was collected and analyzed to confirm the measurement capability of RSCs in a natural gas matrix. Ambient air was collected from a salt marsh ecosystem (Coyote Hills Regional Park, Fremont, CA, USA) with a 1 L newer generation canister. After 2 days of storage, sub-samples of air (~150 mL) were analyzed on the GC-SCD.

A primary standard containing 5 sulfur components at nearly equimolar concentration (1 ppm H_2S, OCS, DMS, CH_3SH, CS_2 with ±5% accuracy) (Scott Specialty Gases, Plumsteadville, PA, USA or Matheson Tri-Gas, Inc., Newark, CA, USA) was diluted using a separately constructed gas dilution line to prepare working standards over a wide range of concentrations (120 ppt, 760 ppt, 1.6 ppb, 3.8 ppb, 9.0 ppb, 20.2 ppb, and 50.4 ppb). The primary standard of sulfur compounds was mixed with ultrapure nitrogen (grade 5.0) to produce the first working standard (50.4 ppb) in a new generation SilcoCan. The other working standards were prepared by successive manometric dilutions. It should be noted that each calibration data set for each working standard was obtained on a continuous run basis within a day after preparation.

3. Results and discussion

3.1. Detection characteristics of the analytical system

The analytical methods showed excellent peak separation and shapes for the five RSCs of interest (Fig. 2b), along with a later eluting sixth component identified as dimethyl disulfide (DMDS, not shown). A typical sampling of 100 mL yields a detectable concentration for RSCs of about 120 ppt. Consequently, the GC-SCD offered improved detection limits compared with the GC-FPD [16] and GC-PFPD [17]. The detection of RSCs from low concentration standard sample as well as ambient air sample (Fig. 2a) with low sample volume confirms that the analytical approach would be suitable for measuring RSC gas fluxes from natural soils in laboratory incubations and in field flux chamber studies.

The detector linearity for the RSCs was investigated by analyzing 7 different working standards (0.12, 0.76, 1.6, 3.8, 9.0, 20.2, and 50.4 ppb) at comparable sample volumes (100–150 mL) (Fig. 3). A linear regression analysis of peak areas versus standard concentrations showed excellent correlations with r^2 values greater than 0.99 for all of the RSCs. The slope values indicate the analytical responses to equimolar injections of the individual RSCs, and they follow the sequence: $H_2S < CH_3SH < OCS \sim DMS < CS_2$. If the

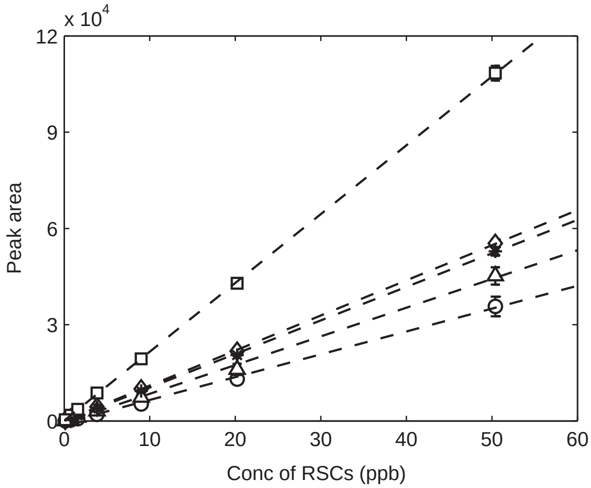

Fig. 3. Detection characteristics of each RSC at different sulfur standard concentrations. Circles (○) represent H_2S; triangles (△) represent CH_3SH; asterisks (*) represent DMS; diamonds (◇) represent OCS; squares (□) represent CS_2. Peak areas are in 15 µV s.

analytical response were linear to the number of sulfur atoms per mole of analyte, then the CS_2 response would be twice the response of other compounds (i.e., the ratio of slopes = 2). Indeed, this is what is observed when comparing CS_2 to OCS (1.96) and DMS (2.06). However, the ratio is higher for CH_3SH (2.44) and H_2S (3.09). Deviations from expected results are not believed to be due to different conversion rates of RSCs to sulfur monoxide or due to detector nonlinearity with time, but rather due to loss of the more volatile sulfur gases (CH_3SH and H_2S) before the analytes reached the detector.

The detection limits for each compound relate to the minimum required mass of injected analyte, which is a function of sample concentration and volume. By minimizing loss of analytes on the internal coatings of the inlet system and quantitative cryotrapping of samples, the current analytical system detects RSCs in low concentration and low volume samples. Previous studies measuring ppb-level sulfur concentrations required total sample volumes of a few liters or more [3,7,18–20], but with this system required <100 mL. The absolute detection limit of the analytical system ranged from 0.1 pg S s^{-1} (for OCS, DMS and CS_2) to 0.3 pg S s^{-1} (for H_2S and CH_3SH), which is much lower than previously achieved [8,16,17,20]. The absolute detection limit for the detector is likely lower than this for the reactive RSCs, as some degradation may occur during the pre-concentration step, when analytes are in prolonged contact with inner surfaces of the inlet system. However, the pre-concentration step is required for better chromatographic separation than can be achieved with direct air injections of whole air samples. The instrumental precision based on replicate analysis ($n \geq 5$) was 2% (OCS, DMS and CS_2) to 7% (H_2S and CH_3SH). The poorer instrumental precision for lighter RSCs (H_2S and CH_3SH) with low molecular mass and high reactivity were possibly a result of less efficient recoveries with the inlet system and sample canisters at low concentrations.

3.2. Study of sample losses in the canister

Any loss of analytes within the container and inlet system can reduce the accuracy of quantification of the sulfur samples and yield a negative bias (i.e., systematically low estimated concentrations) for sulfur compounds [11]. Thus the extent of loss in different types of sampling canisters was monitored over time utilizing 10 ppb synthetic air standards. Fig. 4 shows the comparative percent recoveries of the sulfur samples in two generations of SilcoCan canisters over different storage times.

The stability of H_2S and CH_3SH is very poor in the older generation of SilcoCan canister: within 1 day, more than 50% of both compounds are degraded, while the concentrations of OCS, DMS and CS_2 remained practically constant over the remaining 10 day period (Fig. 4a). The manufacturer of the SilcoCan (Restek Bellefonte, PA, USA) stated that conditioning of the canister might prevent adsorption loss of H_2S and CH_3SH in SilcoCan. Thus the canister was conditioned 3 times by evacuation (<10 mTorr) followed by filling with humidified nitrogen and heating at 80 °C. There was no significant improvement of the recoveries of H_2S and CH_3SH after conditioning the canister (Fig. 4b). It is possible that cracks in the coating of the inner surface of the canister occurred owing to extensive prior usage of canisters in field sampling under different environmental conditions. Surprisingly, DMDS was simultaneously produced in the canister with decreasing H_2S and CH_3SH over the storage time interval. Extracting and summing individual chromatogram peak areas for all RSCs gave nearly constant values over different storage time intervals, suggesting a quantitative conversion of reactive light sulfur compounds (e.g., H_2S and CH_3SH) to a more stable configuration as DMDS.

Significant improvements of the stability of all RSCs were found in the new generation SilcoCan (Fig. 4c). More than 97% of RSCs were recovered after 3 days of sample storage. Even after 7 days, >96% of OCS, DMS, CS_2 and >85% of H_2S and CH_3SH were recovered. Assuming that the reduced recovery was from loss of analytes rather than reduced detector sensitivity over time and that loss rates were steady in these new generation canisters, the potential loss rates in the canisters were 0.09, 0.05, 0.01, 0.004 and 0.006 ppb day^{-1} for H_2S, CH_3SH, DMS, OCS and CS_2, respectively.

3.3. RSC calibration pattern and response factor

In the calibration experiment, a series of standards at varying concentrations and volumes were stored for <1 day in a new generation SilcoCan, cryofocused on the custom inlet system and injected onto the GC-SCD. The calibration curves of RSCs for a range of concentrations are shown in Fig. 5. With the exception of high inputs of CS_2, linear signal responses with increasing sample volumes and sample concentrations were found for all experiments. Nonlinear-

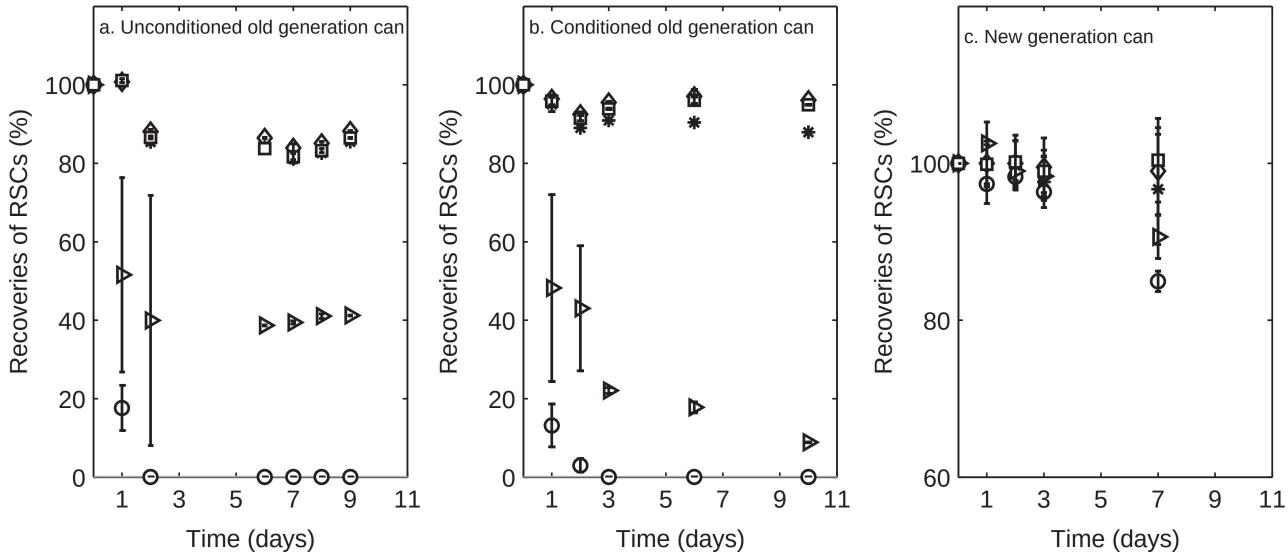

Fig. 4. Sample losses over storage time for (a) unconditioned old generation SilcoCan, (b) conditioned old generation SilcoCan and (c) new generation SilcoCan. Circles (○) represent H_2S; triangles (▷) represent CH_3SH; asterisks (*) represent DMS; diamonds (◊) represent OCS; squares (□) represent CS_2.

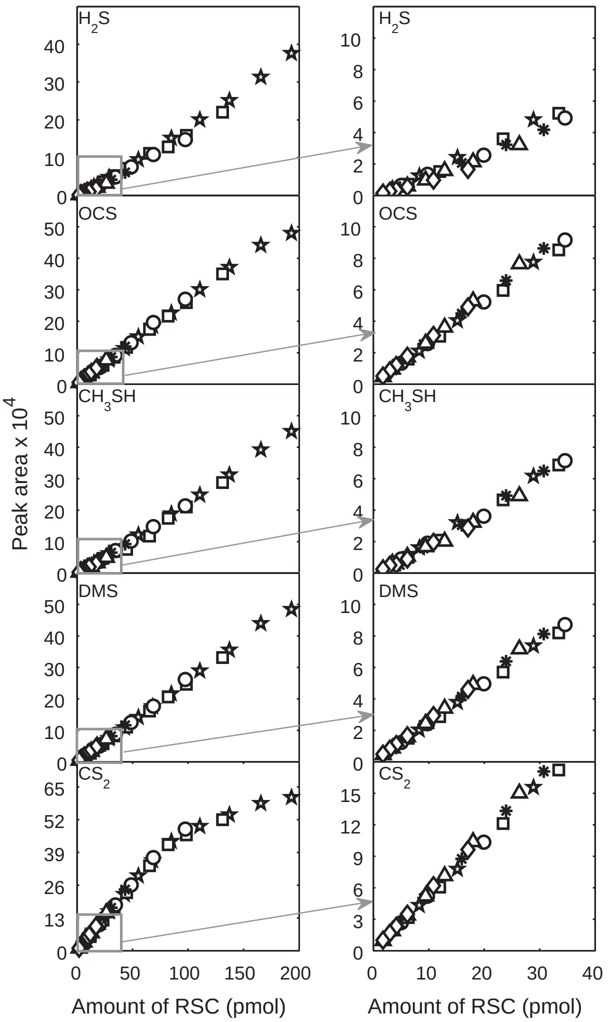

Fig. 5. Calibration curves for different concentrations of RSCs. Open stars (⋆) represent 50.4 ppb; squares (□) represent 20.2 ppb; circles (◯) represent 9.0 ppb; asterisks (*) represent 3.8 ppb; triangles (△) represent 1.6 ppb; diamonds (◊) represent 0.76 ppb. Peak areas are in units of 15 µV s.

ity of CS_2 was noticed in 20 and 50 ppb standards when the sample volumes were higher than 100 and 40 mL, respectively. These calibration curves were used to determine the response factor (pg sulfur per unit area) of individual RSCs for each of the standard concentrations (Table 1).

The response factor values vary by sulfur compound over the tested range of concentrations. By normalizing the response factors of RSCs with the most stable compound, OCS, the relative response factor values (Fig. 6) follow the sequence as $H_2S < CH_3SH < DMS < CS_2$. As expected, the least stability in the response factor was observed for H_2S and CH_3SH, which showed a gradual decrease in response with decreasing standard concentrations. An increase in response factor (i.e., decrease of signal response) was observed for H_2S and CH_3SH at low sample concentrations (<2 ppb). The data for the other RSCs (OCS, DMS and CS_2) show a stable and constant pattern with decreases in concentrations of the standard. In a previous study [3], a twofold decrease in response factor was noted for the highly reactive H_2S at 1 ppb compared to 2 ppb.

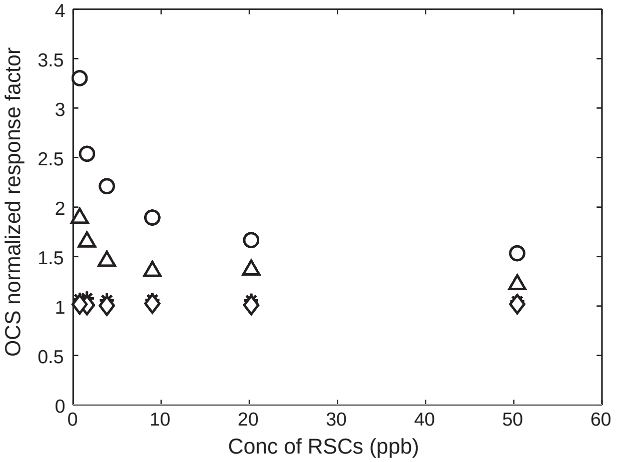

Fig. 6. Comparison of OCS-normalized response factors for different RSCs. Circles (◯) represent H_2S; triangles (△) represent CH_3SH; asterisks (*) represent DMS; diamonds (◊) represent CS_2.

To check the response variability with volume of subsample, the response factors of each RSC were calculated for different subsample volumes for each calibration standard (Fig. 7). Higher response factors (lower sensitivity) were observed at low sample volumes, but injecting higher volumes of sample improved the responses for all the RSCs. Previous studies [21–23] also showed a similar effect of sample volume (passed through a pre-concentration trap) on the sensitivity of GC-detection. Generally, for high sulfur standard concentrations, analyses with low volume subsamples have the possibility of contamination from the analytical line. Low standard concentrations with either low or high volume sampling gave consistent responses in the analytical system.

The lowest response of H_2S and CH_3SH (with high variability) was observed at low concentration of RSCs. Special care should be taken in the treatment of highly reactive sulfur compounds (H_2S and CH_3SH) because variable sample losses inevitably increase analytical uncertainties [24]. As the response factor of the low concentration sulfur sample (H_2S and CH_3SH) is greater than that of higher concentration samples, and the loss of H_2S and CH_3SH in SilcoCans over time is visible for low concentration sulfur samples, calibration standards need to be prepared at least weekly at an appropriate concentration range for measuring atmospheric RSCs accurately. For DMS, OCS and CS_2, there is no significant effect on the response of RSCs in the instrument with changing sample volume injected and sample concentration.

Table 1
Response factor for each RSC standard at different 6 concentrations ($n \geq 5$).

Concentration of RSCs (ppb)	Response factor (pg S/unit area)				
	H_2S	OCS	CH_3SH	DMS	CS_2
50.4	0.0183 ± 0.0016	0.0120 ± 0.0002	0.0146 ± 0.0009	0.0125 ± 0.0003	0.0122 ± 0.0003
20.2	0.0204 ± 0.0012	0.0122 ± 0.0005	0.0167 ± 0.0008	0.0129 ± 0.0006	0.0123 ± 0.0006
9.0	0.0225 ± 0.0006	0.0119 ± 0.0003	0.0161 ± 0.0005	0.0126 ± 0.0003	0.0122 ± 0.0003
3.8	0.0255 ± 0.0006	0.0115 ± 0.0002	0.0168 ± 0.0004	0.0122 ± 0.0002	0.0116 ± 0.0002
1.6	0.0291 ± 0.0005	0.0114 ± 0.0002	0.0189 ± 0.0003	0.0123 ± 0.0002	0.0115 ± 0.0002
0.76	0.0366 ± 0.0002	0.0111 ± 0.0001	0.0210 ± 0.0001	0.0118 ± 0.0001	0.0113 ± 0.0001

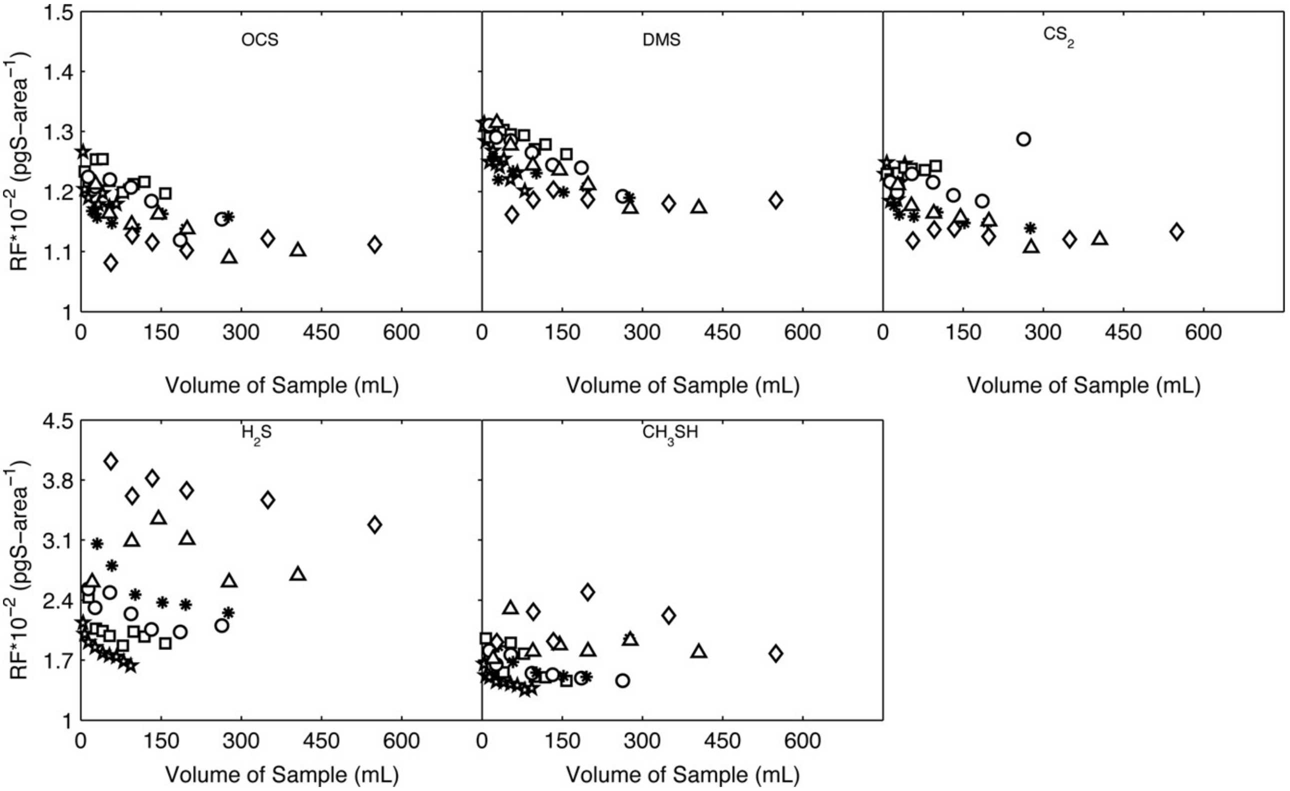

Fig. 7. Response factors at different volumes of standard sample for (top panels) OCS, DMS and CS_2, and (bottom panels) H_2S and CH_3SH. Open stars (⋆) represent 50.4 ppb; squares (□) represent 20.2 ppb; circles (○) represent 9.0 ppb; asterisks (*) represent 3.8 ppb; triangles (△) represent 1.6 ppb; diamonds (◊) represent 0.76 ppb. Note the different vertical scales for the lower panels.

4. Conclusion

The analytical methodology of storing air samples in SilcoCan canisters, cryotrapping subsamples on a custom inlet system, and quantifying analytes using a GC-SCD was shown to be well suited for the quantification of RSCs at near ambient concentrations. The improvement of the stability of RSCs in recently coated SilcoCan canisters is sufficient for preserving low concentration of RSCs sample analysis for up to 1 week, although some corrections may be necessary to account for loss of the more reactive analytes. The detection limit of the analytical system was found to be ~0.3 pg S s^{-1} (for H_2S and CH_3SH) down to ~0.1 pg S s^{-1} (for DMS, OCS and CS_2). The response factors for H_2S and CH_3SH showed significant variability when the concentrations of RSCs were below 2 ppb. The precision of the analytical method was found to be 2–7%. An increase in the sample loading volume and the concentration of RSCs can lead to enhanced sensitivity, but system nonlinearity can occur when injections exceed 200 pmol sulfur, providing an upper range for the expected linear response.

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