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# A Review of Methods for the Determination of Reduced Sulfur Compounds (RSCs) in Air

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The importance of reduced sulfur compounds (RSCs) in air is well-known for its significant effect on global atmospheric chemistry and malodor and quality of life. In this review, methodological approaches commonly employed for the analysis of RSCs such as hydrogen sulfide, methane thiol, dimethyl sulfide, carbon disulfide, and dimethyl disulfide in air are described. To this end, we focus on gas chromatography (GC) because it is the most feasible, frequently used, and widely accepted approach for the analysis of RSC in air. The advantages and possible limitations related to sampling and/or preconcentration methods are also discussed. The relative performance of different GC-based detection methodologies is evaluated in terms of basic quality assurance. Some alternative methods (i.e., other than GC) that deal with the determination of RSCs in air matrices are also discussed briefly. Finally, this review addresses the methodological developments of RSC analysis by highlighting current limitations and future developments.

## Introduction

Considerable efforts have sought the precise determination of reduced sulfur compounds (RSCs) or volatile sulfur compounds (VSCs) in air because of their potent role in the global atmospheric chemistry (1). The most abundant RSCs in the environment include hydrogen sulfide ( $\text{H}_2\text{S}$ ), carbonyl sulfide (COS), methane thiol (MeSH), dimethyl sulfide (DMS), carbon disulfide ( $\text{CS}_2$ ), and dimethyl disulfide (DMDS) (2). The dominant fractions of RSCs originate from natural and/or biogenic sources (3–7). As most RSCs (exception for COS) have a strong potential to be oxidized (e.g., formation of sulfate aerosols), they are often designated to exert influences on the Earth's radiation budget and climate forcing (8).

RSCs are normally present at very low concentration levels (i.e., below ppb levels). If present in excess quantities, these RSCs can also cause social and health problems (9). A number of RSCs are present in various matrices and exhibit large concentration differences (e.g., several orders of magnitude) among different species and/or different environments (10). It has been a challenge to measure RSCs in ambient air without bias from reactivity (e.g., absorption, adsorption, and photo oxidation 11–13) or instrumental instability (2).

In this review, we focus on the developments of methodological approaches commonly available for the analysis of the most common RSCs in air (such as  $\text{H}_2\text{S}$ , MeSH, DMS,  $\text{CS}_2$ , and DMDS (Table 1)), with a special focus on gas chromatographic (GC) methods. In the course of this review,

we also discuss techniques most commonly applied for sampling and detection of RSCs from gaseous matrices with an aid of preconcentration or isolation methods. In addition, the analytical performance of different methodologies is discussed in terms of basic quality assurance (QA) criteria.

## Background of Reduced Sulfur Analysis in Air

In the analysis of RSCs in air matrices, the gas chromatography technique has been and is the most common methodology because of its excellent separation capability and quantitative recovery (14, 15). The GC-based analysis commonly involves a sample collection stage, injection, and separation on a chromatographic column. The final detection can then be carried out through various sulfur-selective (or universal) detectors.

Direct chromatographic analysis or direct injection (DI) of RSCs into a GC injector is highly recommended when the concentration of samples is in the detectable range of a given GC-setup. The use of the DI method can reduce possible loss (or gain) due to contact with different surface types and analysis time by eliminating time-consuming procedures such as supplementary sample treatment by which contamination or loss of analytes can occur (16–18). However, the application of the DI approach is often limited, as most detectors of the GC method are not sensitive enough to cover ambient samples that are typically below a few ppb in concentration. Therefore, research has sought to improve and develop GC methods based on sulfur-specific detectors. As a result, a number of choices are currently available for detector types which include electron capture detector (ECD), flame photometric detector (FPD), pulsed flame photometric detector (PFPD), sulfur chemiluminescence detector (SCD), atomic emission detection (AED), Hall electrical conductivity detector (HECD), and photo ionization detector (PID). Combined application of a mass spectrometer (MS) and GC system has also been reported by numerous authors (19–22). However, these detectors vary in detection characteristics in terms of operation mode and relative response properties to individual sulfur compounds.

To allow the analysis of increasingly smaller quantities of target compound(s), the range of instrumental detectability needs to be improved. As a means to extend the detectability of a given GC system, one can increase the total amount of analytes injected by adopting some preconcentration (or sample enrichment) stages: (1) sorption on certain metal surfaces such as gold, palladium, and platinum (23–25), (2) sorption on solid adsorbents such as activated charcoal, silica gel, aluminum oxide, graphitized carbon black, molecular sieves, and porous polymers (26–28), and (3) cryogenic trapping (18, 22, 29, 30). However, the analysis of low level

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**TABLE 1. Brief Description of the Reduced Sulfur Compounds (RSCs) Reviewed in This Study**

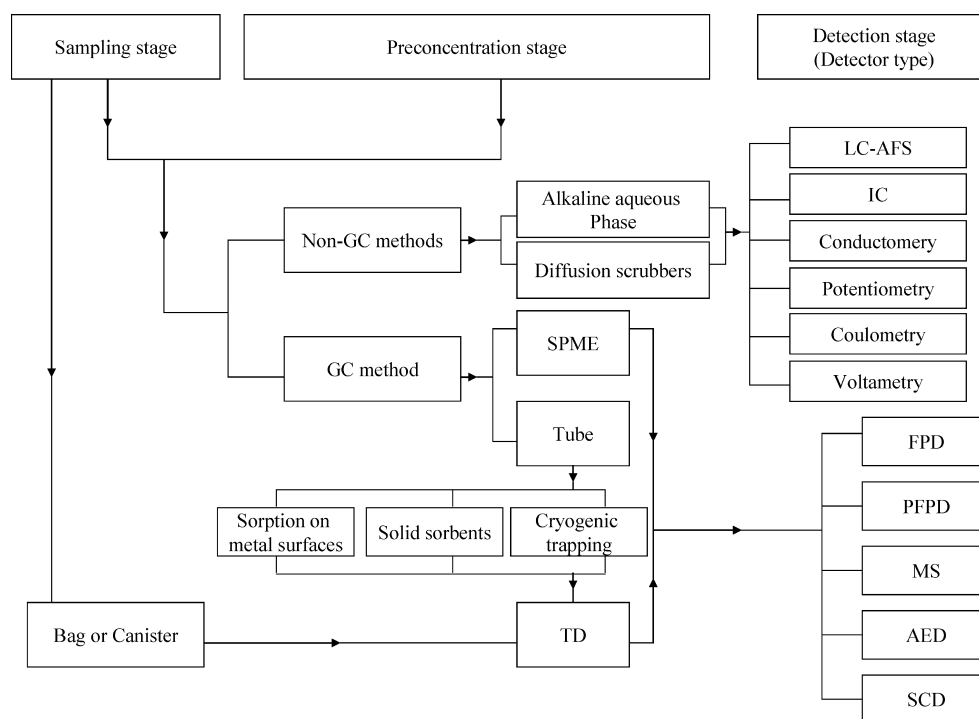
order	RSCs	acronym	CAS no.	chemical formula	molar mass (g mole <sup>-1</sup> )
[A] RSCs most frequently referred in this study					
1	hydrogen sulfide	H <sub>2</sub> S	7783-06-4	H <sub>2</sub> S	34.1
2	methane thiol	MeSH	74-93-1	CH <sub>3</sub> SH	48.1
3	dimethyl sulfide	DMS	75-18-3	(CH <sub>3</sub> ) <sub>2</sub> S	62.1
4	carbon disulfide	CS <sub>2</sub>	75-15-0	CS <sub>2</sub>	76.1
5	dimethyl disulfide	DMDS	624-92-0	(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>	94.2
[B] Other RSCs					
6	carbonyl sulfide	COS	463-58-1	OCS	60.1
7	ethane thiol	EtSH	75-08-1	CH <sub>3</sub> CH <sub>2</sub> SH	62.1
8	propane thiol	PrSH	107-03-9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> SH	76.2
9	pentane thiol	PeSH	110-66-7	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> SH	104
10	iso-propane thiol	i-PrSH	107-03-9	CH <sub>3</sub> (CH) <sub>2</sub> SH	76.2
11	iso-butane thiol	i-BuSH	109-79-5	CH(CH <sub>3</sub> ) <sub>3</sub> SH	90.2

sulfur species through such modifications can be subject to positive blank (e.g., memory effect) or sorptive loss in the chromatographic system (31, 32). A general outline of the analytical protocols commonly employed in RSC analysis is illustrated in Figure 1.

### GC-Based Analysis

**Sampling and Preconcentration Strategies.** RSCs from air matrices can be collected in vessels such as glass bulbs, canister bags, polymer bags, and Tedlar film bags. Considering the highly reactive nature of sulfur compounds, the sampling vessels should be inert enough to reduce adsorptive loss. Moreover, careful attention should be given to tubing and connecting materials used for sampling of sulfur compounds. This is because certain materials can act as significant sources of bias in the determination of RSC concentrations (33). For instance, the storage ability of different sampling containers (i.e., standard Tedlar sample bags, black/clear layered Tedlar sample bags, and Silcosteel sample cylinders) was investigated using a gaseous multi-

component standard (MeSH, EtSH, DMS, ethyl methyl sulfide, 2-PrSH, 1-PrSH, 2-BuSH, diethyl sulfide, and 1-BuSH) prepared at a concentration of 1 mg m<sup>-3</sup> (for each compound) in nitrogen (31). The study revealed that RSC concentrations in the black/clear layered Tedlar sample bags decreased noticeably (e.g., up to 10% for MeSH) after 2 days of storage, whereas those in Silcosteel sample cylinders were stable. However, the RSC recoveries of the latter exceeded 100%, especially for compounds with higher boiling point. These authors later identified that silicone tubing used to transfer RSCs into a standard Tedlar sample bag was the source of the artifact (32). As the sorptive loss of the heavier RSCs (on such tubing material) proceeded less effectively than the lighter ones, the results of the former were overestimated in their early study (31). In continuation of these efforts, the loss patterns of four RSCs (H<sub>2</sub>S, MT, DMS, and DMDS) were investigated against five different tubing materials (stainless steel, silicone, PTFE Teflon, tygon, and copper) (12). The results indicated that the loss patterns of RSCs are distinct



**FIGURE 1. General protocols of reduced sulfur compounds (RSCs) analysis in air matrices. The abbreviations used in figure are as follows: LC-AFS = liquid chromatography-atomic fluorescence spectrometer, IC = ion-chromatography, SPME = solid phase microextraction, FPD = flame photometric detector, PFPD = pulsed flame photometric detector, MS = mass spectrometer, AED = atomic emission detector, SCD = sulfur chemiluminescence detector, and TD = thermal desorber.**

**TABLE 2. Summary of Preconcentration Methods Commonly Employed for the Analysis of RSC in Ambient Air Samples**

method	RSC type	collection media	source
(i) sorptive metals	DMS	gold-coated glass wool	Curran et al. (48)
	DMS	gold coated glass beads	Braman et al. (24)
	DMS	gold plated sand	Braman et al. (24)
	total sulfur	metal foils	Farwell et al. (47)
(ii) sorption on solid sorbent	DMS	activated charcoal	Lewis et al. (52)
	COS, DMS	molecular sieve	Wylie et al. (53), Davison et al. (45), Bruyn et al. (54)
	DMS	Tenax TA	Pio et al. (55)
	EtSH, DMS, CS <sub>2</sub> , PrSH, DMDS, and PeSH	Tenax TA	Rosa Ras et al. (22)
	DMS	Tenax TA	Bruyn et al. (54)
(iii) cryogenic trapping	H <sub>2</sub> S, MeSH, DMS, CS <sub>2</sub> , and DMDS	cryofocusing on cold trap packed with silica gel + carbopack B	Kim (30), Pandey and Kim (18)
	DMS and CS <sub>2</sub>	cryogenic trap	Ivey and Swan (51)
	COS, MeSH, and CS <sub>2</sub>	silanized glass-lined steel tube filled with chromosorb W	Hobe et al. (8)
(iv) solid phase microextraction (SPME)	H <sub>2</sub> S, MeSH, EtSH, DMS, and DMDS	100 $\mu$ m PDMS, 65 $\mu$ m DVB-PDMS, and 75 $\mu$ m CAR-PDMS fibers in a Tedlar bag	Lestremau et al. (82)
	MeSH, BuSH, i-PrSH, and i-BuSH	100 $\mu$ m PDMS and 75 $\mu$ m carboxen-PDMS fibers from permeation tubes	Haberhauer-Troyer et al. (81)
(v) other methods (non-GC)	RSC (Not specified)	PTFE tubes	Dincer et al. (20)
	H <sub>2</sub> S, MeSH, EtSH, and PrSH	trapping/ preconcentration in alkaline aqueous phase	Bramanti et al. (106)
	sulfide, methanethiolate, sulfite, and sulfate	collection on diffusion scrubbers	Ohira and Toda (105)

among different tubing types due to the unique loss mechanisms of each RSC against those tubings.

A major difficulty in sampling of RSCs is interference caused by atmospheric oxidants such as SO<sub>2</sub>, O<sub>3</sub>, and NO<sub>x</sub> which are common in ambient air. To help overcome these problems, many substances were developed as scrubbers including PTFE, Tygon, glass fiber filters, chromosorb, anakrom, and glass beads with a coating of Na<sub>2</sub>CO<sub>3</sub> or MnO<sub>2</sub> (24). The Na<sub>2</sub>CO<sub>3</sub> based scrubbers were successfully used, showing reliable results in field applications (34, 35). KOH or NaOH-based filters were also used as oxidant removing materials by impregnation on a prefilter device (36, 37). Some studies have also evaluated the scrubbing efficiency of the aforementioned materials. For instance, Saltzman and Cooper (38) reported that a carbonate-based Anakrom scrubber was superior to KOH filter. In another intercomparison study, a KI/glycerol/Vitex filter was found to be superior to filter scrubbers with Na<sub>2</sub>CO<sub>3</sub> and KOH/NaOH (39). Furthermore, Na<sub>2</sub>CO<sub>3</sub>, FeSO<sub>4</sub>·7H<sub>2</sub>O, KI, and KBr were ineffective for oxidant removal in moderately polluted air, if applied as either pure salts or coated on Anacom P (40). Inomata et al. (28) used ascorbic acid as a potent scrubbing agent to remove atmospheric oxidants for the simultaneous analysis of five RSCs (COS, H<sub>2</sub>S, CS<sub>2</sub>, MeSH, and DMS) with flame photometric detection (FPD).

Another considerable problem in determining RSCs is relative humidity. This is because water significantly lowers the capacity of adsorbents and can clog cryogenic traps (41). Moreover, it can cause baseline perturbations and retention

time shifts in chromatography to deteriorate detection (41). To overcome the humidity problem, a number of approaches have been attempted. For instance, the use of the drying agent CaCl<sub>2</sub> increased the sampling capacity of Molecular Sieve 5A markedly (42). Commercially available Nafion dryers (Perma-Pure) combined with a cotton oxidant scrubber was tested under laboratory and field conditions. This approach was found to be suitable for the measurements of most RSCs (such as H<sub>2</sub>S, COS, MeSH, DMS, and CS<sub>2</sub>) in the pptv-range in both dry and humid air (43). The applicability of two different types of Nafion membrane dryers (based on counter-current flow and desiccant drying) was tested at ambient concentration levels (1–5 ppbv) in combination with a new ozone scrubbing material (polyphenylene sulfide wool (noXon-S)) for adsorptive sampling of selected VSCs (MeSH, DMS, i-PrSH, and i-BuSH) (41). No analyte losses occurred with either type of dryer at relative humidity (RH) of  $\leq$ 50%, while between 6 and 32% of the thiols tended to be lost at higher RH values ( $>$ 50%) even after conditioning. The combined use of a Nafion membrane dryer and a noXon-S ozone scrubber can thus produce artifact-free sampling for many sulfur compounds (41).

Sample enrichment or the preconcentration step is desirable to analyze samples with low concentration levels (i.e., subppb level) (Table 2). Because many types of enrichment approaches have been tested previously, these issues will be discussed briefly in the following subsections.

**Sorption on Metal Surfaces.** The extent of RSC sorption can be affected greatly by the type of metals (mainly gold,

palladium, and platinum) used for such reaction (23–25, 44). These metallic materials are also found in modified forms such as glass or quartz tubes filled with gold wool, gold-plated sand, or metal foils (24, 40, 45–48). The most common target for these approaches is dimethyl sulfide (DMS). For instance, preconcentration of ambient DMS on gold wool was applied to achieve a lower detection limit of <2 pptv (49). Andreae et al. (50) also used gold wool as a preconcentration means for DMS in maritime air (the east coast of the United States and over the tropical Atlantic near Brazil) for quantification based on GC-FPD. However, the studies have also shown that some losses can occur with gold trapping such as in the case of DMS (e.g., 5%) ((51) and references therein).

**Sorption on Solid Sorbents.** Solid sorbent surfaces are regarded as the most general tools for the preconcentration of volatile species. In this approach, a number of options are also available such as activated charcoal, silica gel, aluminum oxide, graphitized carbon black, molecular sieves, and porous sorbents. A number of them have been tested and found to be useful in collecting volatile sulfur species (45, 52–54). However, porous sorbents such as Tenax have been the most popular choice for sulfur species (22, 54, 55), and they are most extensively used for the absorptive collection of volatile aromatic and aliphatic hydrocarbons, ketones, esters, aldehydes, and alcohol (56, 57). The breakthrough volume of Tenax is not altered by changes in humidity because of its hydrophobic property (58). Its high thermal stability also allows desorption of samples at high temperature. However, the trapping efficiency of Tenax tubes is often limited for organosulfur compounds with low boiling points (e.g., H<sub>2</sub>S, MeSH, etc), if it is used at room temperature (59, 60). The capacity of a sorbent can increase significantly if aided by a cryofocusing system (61).

One of the essential criteria for the selection of a suitable sorptive medium is its adsorption capacity. For this purpose, a number of attempts were made to determine the affinity and/or breakthrough volume of different sorbents (refer to SI Table 1). For instance, the breakthrough volumes of eleven organosulfur compounds including thiols, sulfides, disulfides, and thiophenes were evaluated on different porous polymers such as Chromosorb 102, XAD-2, XAD-4, XAD-7, and Tenax GC (62). According to this study, XAD-4 showed the largest breakthrough volume. However, due to bleeding and efficiency limitations, it was not accepted. Following this attempt, the collection efficiency of 14 solid sorbents was tested for COS and MeSH (63, 64). The study revealed silica gel, Carbotrap, and molecular sieve as optimal choices. Although other important RSCs (such as H<sub>2</sub>S, CS<sub>2</sub>, and DMS) were collected along with COS and MeSH, the collection efficiencies of those compounds were not evaluated. The application of various solid sorbents (i.e., silica gel, molecular sieve, and Carbosieve SIII) has been validated by measurements of RSC concentrations or fluxes under various environmental settings ((65) and references therein).

**Cryogenic Trapping.** Trapping efficiency of adsorbent traps tends to increase exponentially with decrease in temperature (66). Hence, cryogenic trapping is a tool for increasing the capacity of sorptive materials and to facilitate the collection of ultralow concentration samples. Cryogenic preconcentration of volatiles can be accomplished from –150 to –170 °C with the aid of cryogenic fluids (67). However, sampling and chromatographic interferences can occur due to atmospheric water vapor coadsorbed at subambient temperatures (66). Thus, proper caution should be taken to selectively remove or separate water vapor from the sampling path prior to the adsorption stage.

The cryogenic traps (sampling loops) are generally composed of PTFE, borosilicate glass, and quartz tubes (2). For sampling of RSCs, the cryogenic traps (either straight or

U-shaped) are normally immersed in strong cryogen such as liquid nitrogen or in liquid argon. For instance, the six RSCs (H<sub>2</sub>S, COS, MeSH, DMS, CS<sub>2</sub>, and DMDS) were preconcentrated by pumping air through a U-shaped cryogenic trap cooled with liquid argon (68). Detection limits less than or equal to 10 pg (i.e., when expressed in terms of absolute injected mass of sulfur for 1 L of air) were achieved for individual compounds for GC-FPD based analysis.

Although cryogenic traps can be used as independent systems, they can also be used with a number of sorbents as packing materials to increase sorption efficiency. Commonly used packing materials include glass-fiber wool, glass beads, Tenax, Porapak Q, activated carbon, and carbopack. However, the trapping efficiency of these packing materials differs greatly by such factors as their surface area and the physicochemical properties of the analyte to be sampled. Hobe et al. (69) reported a cryogenic trapping procedure for COS without the use of liquid cryogen at a trapping temperature of –150 °C. The cryotrap was made of a glass-coated steel tube (SILCOSTEEL, L 20 cm, OD 3.2 mm, i.d. 2.2 mm, Restek, Bellefonte, PA) and filled with Chromosorb W adsorbent material (acid-washed dimethyldichlorosilane (DMCS) treated mesh 45/60). Based on a similar cryogenic trapping procedure, the analytical reliability of a fully automated sulfur gas analyzer (SUGAR) was recently tested for the analysis of COS, MeSH, and CS<sub>2</sub> in both laboratory and field settings (8). These authors were able to measure RSCs at typical ambient concentrations (500 ppt for COS, 5–40 ppt for MeSH and CS<sub>2</sub>). They further showed that the SUGAR can also be employed for analysis of DMS and H<sub>2</sub>S at ambient concentration levels.

The application of multibed adsorption tubes, packed in the order of increasing sorbent strength, covers diverse analytes over a broad range of volatility and polarity (70, 71). A three-stage cryogenic trapping preconcentration technique (consisting of glass beads + Tenax TA + capillary focusing trap) was employed to remove excess water (relative humidity (RH) 95%) and carbon dioxide (3.8%) (72). More than 400 mL of the breath sample was preconcentrated to achieve detection limits for MeSH, DMS, and DMDS of 0.13, 0.09, and 0.15 ppbv, respectively. In a recent study, active collection on SilcoSteel multisorbent tubes, packed with Tenax TA and Unicarb, allowed for expansion of air sampling volume to 3000 mL without breakthroughs for EtSH, DMS, CS<sub>2</sub>, PrSH, BuSH, DMDS, and 1-PeSH in a GC-MS-TD application (22). The preconcentration of seven RSCs (H<sub>2</sub>S, COS, MeSH, DMS, CS<sub>2</sub>, DMDS, and dimethyl trisulfide (DMTS)) collected by fused-silica lined canister-based sampling was completed in multistep sorption stages: (1) empty trap, temperature –20 °C, (2) Tenax, temperature –80 °C, and (3) fused silica tube, temperature –150 °C. Here, the traps at each stage were heated sequentially, and the VSCs were eventually retrapped again on cryofocusing trap, which was then rapidly heated to transfer the RSCs into the GC (73).

In recent years, a Peltier cooling (PC) device (e.g., an electrically cooled focusing trap) has proven to be a convenient tool for cryogenic preconcentration (67). The recovery rate (%) of 4 RSCs (H<sub>2</sub>S, MeSH, DMS, and DMDS) was found in a range of 80–110%, when tested with PC-based cryogenic preconcentration in conjunction with the thermal desorption (TD) technique (74). The reproducibility of this PC method was found to be 1–5% when expressed in terms of relative standard error (RSE) for triplicate analyses (30). However, the efficiency of the PC-TD system may change according to the concentration range, loading volume of samples, and sample loading methods (18, 75).

**Solid-Phase Microextraction (SPME).** In recent years, the solid-phase microextraction (SPME) method has received attention as a potential solvent-free sample preparation technique. The convenience of SPME has been demonstrated



**TABLE 3. Summary of Main Detection Methods for Reduced Sulfur Compounds in Air**

method	target RSCs	analytical condition	source
FID	DMS	[A] GC-methods field (natural)	Lewis et al. (52)
FPD	DMS	field (natural)	Davison et al. (45), Wylie et al. (53), Bruyn et al. (54), Pio et al. (55)
	H <sub>2</sub> S, MeSH, DMS, and DMDS COS, MeSH, and CS <sub>2</sub>	laboratory laboratory + field (natural)	EPA (100) Hobe et al. (8)
PFPD	H <sub>2</sub> S, MeSH, DMS, CS <sub>2</sub> , and DMDS	laboratory	Pandey and Kim (17)
	H <sub>2</sub> S, MeSH, DMS, CS <sub>2</sub> , COS, SO <sub>2</sub> , and DMDS	laboratory	Kim (16, 29, 30), Catalan et al. (86)
	H <sub>2</sub> S, MeSH, DMS, CS <sub>2</sub> , and DMDS	laboratory	Kim (30), Pandey and Kim (18)
	H <sub>2</sub> S, MeSH, EtSH, DMS, and DMDS	laboratory + field (industrial samples)	Lestremau et al. (82)
SCD	dimethyl sulfide and carbon disulfide	field (natural)	Ivey and Swan (51)
	H <sub>2</sub> S, MeSH, EtSH, 1-PrSH, 2-PrSH, DMS, CS <sub>2</sub> , DMS, COS, and SO <sub>2</sub>	laboratory	SCAQMD (101)
AED	MeSH, BuSH, i-PrSH, and i-BuSH	laboratory	Haberhauer-Troyer et al. (81)
MS	not specified EtSH, DMS, CS <sub>2</sub> , PrSH, DMDS, 1-PeSH	field (bioindustry)	Dincer et al. (20) RosaRas et al. (22)
ASD	not specified		Perkin-Elmer (87)
SCS	H <sub>2</sub> S, MeSH, and DMS	oral malodor measurement	Hanada et al. (108)
LC-AFS	H <sub>2</sub> S, MeSH, EtSH, and PrSH	[B] methods other than GC field (industrial)	Bramanti et al. (106)
IC	sulfide, methanethiolate, sulfite, and sulfate	field (natural)	Ohira and Toda (105)

both in the laboratory and for on-site monitoring, as it allows a single step treatment for sampling, isolation, and enrichment (67, 76–78). For air matrices, the SPME fiber can be used to extract analytes either by direct exposure to raw samples or by use of the headspace method on pretreated samples (77, 79, 80).

The SPME method was tested using the 75- $\mu$ m Carboxen–polydimethylsiloxane (CAR-PDMS) fiber coating (at 22 °C for 20 min) with GC-MS for quantification of nine volatile sulfur compounds at a biogas-production plant and a sewage treatment plant (10): Detection limits (ppbv (v/v)) of RSC fell in the range between 0.001 (CS<sub>2</sub>) and 0.47 (H<sub>2</sub>S). The 75  $\mu$ m CAR-PDMS fiber was superior to 100  $\mu$ m PDMS fiber when tested for air samples spiked with standard gaseous mixture in a 500 mL mixing chamber (81). Optimization of the former (e.g., extraction time = 20 min and desorption at 250 °C for 100 s) recorded detection limits (ppt (v/v)) of DMS, MeSH, i-PrSH, and i-BuSH at 3–4, 3–4, 5–7, and 40–60, respectively. In a study by Lestremau et al. (82), the efficacy of three different SPME-fiber types (such as PDMS, CAR-PDMS, and divinyl benzene (DVB)-PDMS) were evaluated for H<sub>2</sub>S, MeSH, EtSH, DMS, and DMDS. The results showed that CAR-PDMS, when analyzed with a GC-PFPD, can achieve the best sensitivity for most RSCs at subppb levels (below the human perception level). The reliability of SPME approach was tested on a real gaseous sample through comparison between different calibration approaches. Both external and standard-addition based calibration methods were feasible for the higher-molecular-mass compounds

(EtSH, DMS, and DMDS). However, for more volatile sulfur compounds (i.e., H<sub>2</sub>S and MeSH), standard additions had to be performed because of significant biases involved in external calibration (82).

Despite the practical applicability of SPME to sampling and analysis of organosulfur compounds, artifacts can be observed due to such factors as matrix effect, low storage stability, RH dependence of extraction efficiency, etc. (10, 81). Moreover, the production of quantitative data can be restricted further by such factors as competitive sorption/reverse diffusion of certain compounds (82–84) and transformation between compounds during analysis (81, 82, 85). As the most specific instance of the latter case, the stainless steel part of the SPME device can catalyze the oxidative conversion of MeSH into DMDS.

### Comparison of Analytical Performance Among Different GC-Based Detection Systems

The determination of RSCs contained in environmental samples has been achieved most commonly through gas chromatography (GC) interfaced with one of several selectable detection systems, e.g., flame photometric detection (FPD), pulse flame photometric detection (PFPD), sulfur chemiluminescence detection (SCD), atomic emission detection (AED) (86), and amperometric sulfur detection (87) (Table 3).

Flame photometric detection (FPD) is the most frequently applied sulfur selective detector in environmental sulfur

analysis because of low cost, robust nature, and broad applicability ((2) and references therein). Disadvantages of the FPD include its nonlinear (exponential) response (to sulfur compounds) and compound-specific response characteristics. Its application in the determination of sulfur-containing compounds is also biased by the sulfur emission quenching of coeluting nonsulfur organic compounds ((88) and references therein). The pulsed flame photometric detector (PFPD), characterized by the addition of time dependence information of pulsed flame emission, has shown certain advantages over the FPD ((89) and references therein). The possible (temporal) separation of the signals from unwanted hydrocarbon emissions improves its selectivity for sulfur with a total discrimination against hydrocarbon compounds. The lower degree of hydrocarbon-induced quenching of sulfur due to hotter post pulsed flame conditions and uniform (equimolar) sulfur response are other advantageous features of PFPD.

SCD provides an alternative for analyzing sulfur in terms of detectability, selectability, linearity, and uniform sulfur response (90). SCD developed in flameless mode was proven to be more sensitive (e.g., 1 order of magnitude) than conventional SCD (91). AED is also attractive, as it allows for multielement detection, as the analysis can be made concurrently for sulfur, nitrogen, carbon, phosphorus, etc. (92, 93). However, application of AED is narrowed to simultaneously accommodate several factors such as limited selectivity against carbon, low sensitivity for some nonmetallic elements, discharge tube erosion, high maintenance cost, and complexity in the selection of operation parameters (94–96). AED is also disadvantageous, as it is one of the most expensive detectors for GC because of a plasma excitation source and parallel multiwavelength optical detection equipment (89).

To compare the relative performance of different detection methods, the basic quality assurance parameters such as detection limit (DL) values and precision (expressed either in terms of relative standard deviation (RSD) or relative standard error (RSE) of replicate analysis) achieved in previous studies have been compiled (refer to SI Table 2). There are various approaches to determine the DL values of each RSC for a given experimental method, as described by Catalan (86) and references therein. However, the method detection limit (MDL) defined by the US Environmental Protection Agency (97), i.e., “minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte” is still the most justifiable method to express the detectability of an analytical system. Nevertheless, the MDL defined by the EPA procedure is commonly expressed in units of concentration (e.g., parts per billion (ppbv)), whereas researchers reported the detection limit in units of pg/s (e.g., 68, 98, 99). Hence, we have tried to compare the DL values both in terms of absolute mass (pg) and concentration or mixing ratio (ppbv) for parallel comparison. However, the expression of DL values in terms of mixing ratio is rather limited, unless information concerning actual sampling/or injection volume is given. The DL values from different studies are summarized for each individual RSC, as they tend to exhibit different intercompound relationships for different instrumentations (refer to SI Table 2).

The DL values for a given compound fall in a highly variable range depending on the detection techniques. In terms of absolute mass, the PFPD technique showed considerably improved DL values relative to the conventional GC-FPD technique. For instance, the minimum DL values (pg) achieved with the PFPD were 1.70 ( $\text{H}_2\text{S}$ ), 0.55 (MeSH), 0.55 (DMS), and 0.57 (DMDS) (16, 29). These DL values were

lower by more than 2 orders of magnitude than those obtained with FPD (28, 98) or SCD-based detections (101). The DL values also varied considerably in relation to the type of sample transfer approaches employed in each study. For instance, the DL values (in absolute terms), obtained through cryofocusing and subsequent thermal desorption on similar types of GC-PFPD systems, were moderately high relative to direct injection methods (102, 103). Previous studies have also shown that the alteration of the GC-system (e.g., PC/TD) results in a reduction in absolute sensitivity (18, 74). However, the expandibility of the sample loading volume for a TD-system ultimately improves GC detectability by several orders of magnitude relative to direct injection methods, if compared in terms of minimum detectable concentration (or mixing ratio) instead of absolute mass (ng or pg).

To offer practical comparisons for detectability, the DL values recorded with different analytical systems were also compiled in terms of mixing ratios (ppbv) (refer to SI Table 2). The DL values produced through PFPD are superior to those of FPD or SCD-based detection, when the results derived through direct injection methods are compared. The absolute mass (pg) quantifiable with the aid of PC/TD is moderately higher than that of the direct injection methods (by gas syringe or loop). However, the minimum detectable concentration of the PC/TD system is considerably lower (e.g., subppbv level) due to its expandibility of sampling volume. For instance, the DL values achieved through PFPD analysis with PC/TD were lower by more than 2 orders of magnitude (e.g., subppbv level (in 0.002–0.03 ppbv range; (13)). The other detectors such as AED or MS also showed performance comparable to PFPD, when applied in combination with either TD or other preconcentration methods (such as SPME) (22, 81). If the DL values for a given detection method are compared between individual RSCs, the detectability can improve with molecular mass and number of sulfur atoms. For instance, in the case of GC-PFPD-TD-based analysis, the DL values (i.e., 2 pptv) for both disulfur compounds ( $\text{CS}_2$  and DMDS) were lower by an order of magnitude than single sulfur compounds ( $\text{H}_2\text{S}$  (i.e., 30 pptv) or MeSH (17 pptv)). This is because the PFPD has shown higher sensitivity toward the disulfur compounds relative to the monosulfur species (30). Moreover, lighter RSCs (with low molecular mass and high reactivity) can be subject to less efficient recovery with TD systems (e.g., transfer line loss of sample in the TD system) (30). Because direct injection methods are free from such loss, their application confirms moderate differences in DL values due to differences in PFPD response characteristics between different compounds.

The linear dynamic range of commonly used sulfur sensitive GC-detectors is generally in the range of  $10^2$ – $10^3$  (FPD and PFPD),  $10^3$ – $10^4$  (AED), and  $10^5$  (SCD and MS) (2, 17, 75). If one considers such variable linearity range of GC detectors and differences in their sensitivities, nonlinear response properties of certain detectors (e.g., FPD) can be a critical problem under certain circumstances. Hence, in order to minimize the biases associated with the detection properties of the GC method, calibration curves should be drawn to match the concentration of standard gaseous mixtures with those of target air samples in a comparable range.

Among all sulfur detectors that can be interfaced with GC, the use of the FPD and PFPD has most commonly been reported in combination with a number of sample introduction approaches. A number of publications have shown that the PFPD is superior to conventional FPD in terms of sensitivity, stability, and reproducibility. In recent years, MS-based determination of RSCs has also gained momentum because of its high sensitivity. Although the

accurate quantification of RSCs is also affected by calibration procedures, the bias produced by these factors has gained little attention. The relative humidity of samples and the presence of atmospheric oxidants are also major issues for the future study. As a result, future research should be directed toward the aforementioned aspects: a thorough evaluation of calibration procedures adopted for a given method, proper handling of humidity and oxidant problems, and a more comprehensive evaluation of breakthrough capacity for commonly available sorbents.

### Alternative Methods for RSC Analysis Other than GC

Although GC-based detection is the most common choice for the analysis of RSCs in air, there are also a number of reports that deal with other experimental approaches for quantifying RSC. For instance, for the simultaneous determination of H<sub>2</sub>S with other sulfur species (such as SO<sub>2</sub> and S<sub>8</sub><sup>0</sup>) in volcanic gases, the employment of the ion chromatography (IC) method was introduced (104). The emission gases were sampled using pre-evacuated thorion-tapped vials with purified 0.15 M Cd(OH)<sub>2</sub> in 4 M NaOH. The precipitation of CdS was induced by the reaction between Cd<sup>2+</sup> and H<sub>2</sub>S, and the solid residue of CdS was dissolved for the application of IC. In a similar report, a dual detector ion chromatograph system was applied for the analysis of sulfur gases like H<sub>2</sub>S, MeSH, and SO<sub>2</sub> (105). H<sub>2</sub>S and SO<sub>2</sub> were measured after collection via a single scrubber with 0.1 M NaOH, whereas MeSH was collected with a dual-scrubber system (first scrubber: 5 mM H<sub>2</sub>O<sub>2</sub> + 10  $\mu$ M HCl and second scrubber: 0.3 M NaOH).

Determination of H<sub>2</sub>S and volatile thiols (MeSH, EtSH, and PrSH) in air samples was also attempted through mercury probe derivatization coupled with liquid chromatography (LC)—atomic fluorescence spectrometry (AFS) (106). These authors suggested a sampling procedure based on the trapping/preconcentration of the RSCs in an alkaline aqueous solution with an organic mercurial probe *p*-hydroxymercurybenzoate (HO—Hg—C<sub>6</sub>H<sub>4</sub>—COO: PHMB). In the aqueous phase, the RSCs were induced to form stable PHMB complexes. Then, PHMB complexes were separated on a reverse-phase column (C18) and finally quantified by LC coupled with sequential nonselective UV—vis (DAD) and mercury-specific online detectors (chemical vapor (generation) atomic fluorescence spectrometry, CVAFS). DL values of 9.7, 13.7, 17.7, and 21.7  $\mu$ g L<sup>-1</sup> were achieved for H<sub>2</sub>S, MeSH, EtSH, and PrSH, respectively, through CVAFS detection. The relative standard deviation (RSD) values for this analysis ranged between 1.0 and 1.5% with linear dynamic range (LDR) lying between 10 and 9700  $\mu$ g L<sup>-1</sup>. Conventional UV absorbance detectors tuned at 254 nm can also be employed with comparable RSD and LDR. However, their DL values were higher than the AFS detector by more than 1 order of magnitude. The aforementioned method was applied to quantify sulfur compounds in gas samples (biogas and air samples of a plant for fractional distillation of crude oil).

In another study, electrochemical sensors composed of a ceramic—metallic (cermet) solid electrolyte were employed for the detection of gaseous sulfur compounds. The samples consisted of 11 toxic industrial chemical (TIC) compounds including SO<sub>2</sub>, H<sub>2</sub>S, and CS<sub>2</sub> (107). The study employed a sensor array containing four cermet sensors varying in electrode—electrolyte composition. This sensor array was driven by a cyclic voltammetry producing a current—voltage profile for each analyte. These authors were able to demonstrate the detection of RSCs with other compounds at ppm levels. Some researchers also indicated that supercritical fluid chromatography has some advantages

over the GC method, if combined with SCD for the analysis of thermally unstable and relatively nonvolatile compounds, because relatively mild temperatures (30–100 °C) can be used for SFC-SCD (90).

Besides GC methods, there are some alternative methods which include LC, IC, and sensor-based methods. The reliability of these alternative methods for practical application of real environmental samples has not been sufficiently researched. However, methodologies for online monitoring at ambient concentration levels, especially with respect to portable devices such as sensors (e.g., (108)) would help overcome the time-consuming and tedious processes of sampling, enrichment, and offline analytical protocols in the laboratory.

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### Supporting Information Available

Tables 1 and 2 of detailed information on comparative data related to breakthrough volume of different sorbents and basic quality assurance (detection limit and precision) of different analytical systems. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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