Use of solid phase microextraction (SPME) in the analysis of the reduced sulfur compounds (RSC) and its experimental limitations

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A B S T R A C T

In this study, techniques based on solid-phase microextraction (SPME) with gas chromatography (GC)–pulsed flame photometric detection (PFPD) were evaluated for its application toward a list of reduced sulfur compounds (RSCs) such as hydrogen sulfide (H_2S), methanethiol (CH_3SH), dimethyl sulfide (DMS), carbon disulfide (CS_2), and dimethyl disulfide (DMDS). Its performance was tested against direct injection (DI) and thermal desorber (TD) approaches. Although the SPME-based calibration of RSCs showed good linearity ($r^2 > 0.9$) like other methods, it was more prone to analytical bias for the lighter molecular weight (MW) RSCs (especially H_2S) due to distinctively reduced sensitivity relative to the heavier MW compounds. As such, the detections limits (DL) of SPME vary by more than an order of magnitude for the lighter and heavier MW RSCs (DL = 16.9 ng for H_2S and 1.46 ng for DMS). Evidence collected from an extended reproducibility test further supports that the experimental reliability of SPME approach is fairly low, especially with respect to H_2S. The quality of SPME-based analysis thus needs more cautious validation in the study of odor and air pollution, as the lighter RSCs like H_2S (or CH_3SH) are often identified as the key components under various settings.

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1. Introduction

The environmental interests in reduced sulfur compounds (RSCs) have increased steadily due to their unique properties, e.g., offensive odor, toxicity, and potential corrosivity [1]. It is very important to quantify these compounds accurately and precisely for the proper assessment of their potent role in each environmental setting. There are several methods for the detection of RSCs such as gas chromatography (GC), spectrophotometry, polarography, fluorescence, coulometry, potentiometry, and impregnated filter tapes [2]. However, due to the combined effects of several factors (e.g., lack of sensitivity, complexity of methodology, unreliability of calibration, and the occurrence of interfering compounds), many of these methods are found to be implausible in the application toward ambient air samples [3]. Moreover, some of these methods suffer from high expenses, longer time to setup (or to operate), more analytical skills, more logistic needs (such as combination with thermal desorber), or the license of radioactive material treatment. For their ambient-level detection, GC with sulfur selective detection has been preferred over other options because of its excellent separation capability and high detectability [2,4,5].

A number of GC techniques have been introduced for sulfur gas analysis such as pulsed flame photometric detection (PFPD), sulfur chemiluminescence detection (SCD), and atomic emission detection (AED) [6]. Most of these detection methods have been sensitive enough to detect sulfur components at much reduced detection limits [7,8]. However, the analysis of ambient air samples still requires the enhancement of their detectability with the aid of preconcentration tools, e.g., cryofocusing (CF) and thermal desorption (TD) techniques [7]. Our study group has been involved in developing GC-based analytical techniques with or without the aid of TD to precisely quantify RSCs in ambient air [9–14].

The most common difficulties one encounters in the detection of RSCs include the variable range of concentrations, high reactivity, and the complexity of matrices [15]. To resolve problems associated with the limited detectability of the instruments, their detection for environmental samples (e.g., ambient air) is inevitably aided by the use of preconcentration tools like solid adsorbents or cryogenic trapping [15–17]. To induce adsorption of analytes, air is first pumped through a solid sorbent. The collected analytes are then released in the next stage desorptive analysis with the aid of TD. As an alternative to solid sorbent enrichment methods, solid-phase microextraction (SPME) has been investigated intensively. Being an inexpensive solvent-free enrichment method, SPME allows the combining of sampling and preconcentration of analytes in a single step [18]. In fact, in a number of studies, SPME has been employed to determine RSCs in many different matrices including liquid, solid, and air samples [19–22]. Among many fiber coatings, the Carboxen–polydimethylsiloxane (CAR–PDMS) fiber has repeatedly been demonstrated as a superior choice for the quantification of sulfur compounds [23–27]. In

this study, we investigated the relative performance of the combined setups between CAR–PDMS SPME fiber and GC–PFPD in comparison to other GC-based approaches. This SPME-based method is also applied to the analysis of a few real samples for further evaluation of analytical reliability against other common approaches like TD or direct injection (DI).

2. Materials and methods

2.1. Chemicals and material

Gaseous standard mixtures of RSCs contained in a cylinder were purchased at equimolar concentrations ($10\ \mu mol\ mol^{-1}$ with $\pm 5\%$ accuracy) for five target sulfur gases (e.g., H_2S, CH_3SH, DMS, CS_2, and DMDS) from Ri Gas, Corp. (Dae Jeon, Korea). This cylinder standard was used as primary standard (PS) to produce working standard (WS) for the actual calibration analysis discussed in this study. The SPME device and $75\ \mu m$ CAR–PDMS-coated fiber used in this study were purchased from Supelco (Bellefonte, PA, USA). Prior to use, the fiber was conditioned at 250 °C for 1 h in the GC inlet. The basic properties (e.g., chemical formula, structural formula, molecular weight, CAS number, etc.) of all these compounds are summarized briefly in Table 1.

2.2. Preparation of working standards and real samples

The WS of RSCs were prepared at eight concentration ranges (5, 10, 20, 40, 80, 200, 500, and 1000 ppb) by mixing the primary standards with ultrapure nitrogen in 1-L Tedlar bags for SPME injection. This mixing stage was completed by a single-step dilution of the primary standard gas to the desired concentration with the aid of a gas-tight syringe. For instance, for the preparation of a 10 ppb concentration standard, 10 mL of PS gas was drawn by a gas-tight syringe and mixed with 990 mL ultrapure nitrogen in the Tedlar bag to make the final volume of 1 L.

2.3. GC–PFPD analysis

A Varian CP-3800 gas chromatograph (Varian, Walnut Creek, CA, USA) equipped with a pulsed flame photometric detector (PFPD) was used for this study. Chromatographic separation of RSCs was done by BP-1 column (60 m × 0.32 mm i.d. and 5 μm film thickness (SGE Ltd., Melbourne, Australia)) at a column flow rate of 2 mL min^{-1} (ultrapure
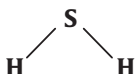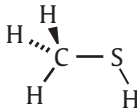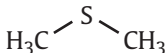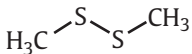
N_2 carrier gas). Each running cycle was programmed to end at 20 min intervals. The detector was heated at 250 °C with the constant gas supply of 14 (H_2), 17 (air 1), and 10 mL min^{-1} (air 2). Other detector settings include: photo multiplier voltage (550 V), gate delay (6 ms), gate width (20 ms), gain factor (20), and trigger level (200 mV). Details of experimental setups are provided in Table 2.

The air–hydrogen needle valve controlling the ratio of wall flow to combustor flow in the PFPD system was optimized to ensure the operation of detector close to tick-tock mode. The tick-tock sound occurs, when the combustible mixture ignites in the ignitor chamber. The detector response signals were integrated using computer software (Star Workstation 6.2, Varian). For analyzing the WS of RSCs, the SPME fiber was inserted into the Tedlar bag. After 15 min of adsorption, the fiber was retracted and immediately inserted into the inlet of GC injection port to induce thermal desorption at 150 °C for 5 min.

To assess relative performance of our SPME methods, a series of ancillary calibration experiments were also conducted. To understand the adsorptive properties between different RSCs, adsorption was induced repetitively for all RSCs over 4 consecutive times (in a row) all by exposing the SPME fiber into the same WS bags with different concentration levels. Moreover, we also examined the compatibility of SPME with other types of sample loading methods such as DI and TD method. The calibration curves of the DI method were obtained by "fixed standard concentration (FSC)" approach [12]. Our DI-based calibration experiment was conducted at six injection volumes (i.e., 10, 20, 40, 80, 200, and 400 μL) using 10 ppm PS. The calibration data were combined together to derive response factor (RF) values across varying injection volumes.

To build up the basis for comparison between different pretreatment approaches, we also derived RF values based on TD method with the aid of an air server (AS) unit for the control of sample or standard gas flow. TD based analysis of RSCs was eventually completed by GC (Model DS 6200, Donam Instruments, Korea) equipped with a PFPD (Model 5380, O.I. Co., USA). The details of the analytical performance of the AS/TD settings have been described in a series of articles made from our laboratory [9]. Our GC system with AS/TD setup was operated at the following temperature (T) conditions: (1) T (initial): 80 °C for 4.5 min; (2) T (ramping): 20 °C min^{-1}; and (3) T (final): 200 °C at 9.5 min. To acquire an optimum resolution between different sulfur components, we used a BP-1 column (60 m × 0.32 mm, 5.0 μm, SGE) for 20 min cycles. To provide pulsed flames into the combustor (15 mm length and 2 mm ID), gases were provided as: $H_2 = 11.5$, air1

Table 1
The basic properties of target reduced sulfur compounds (RSC) investigated in this study.

Full name	Short name	Chemical formula	Chemical structure	CAS number	Molecular weight (g mole^{-1})
Hydrogen sulfide	H_2S	H_2S		7783-06-4	34.1
Methanethiol	CH_3SH	CH_3SH		74-93-1	48.
Dimethyl sulfide	DMS	$(CH_3)_2S$		75-18-3	62.1
Carbon disulfide	CS_2	CS_2		75-15-0	76.1
Dimethyl disulfide	DMDS	$(CH_3)_2S_2$		624-92-0	94.2