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The fundamental properties of the direct injection method in the analysis of gaseous reduced sulfur by gas chromatography with a pulsed flame photometric detector

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ABSTRACT

In this study, the fundamental aspects of gas chromatography with a pulsed flame photometric detector were investigated through the calibration of gaseous reduced sulfur compounds based on the direct injection method. Gaseous standards of five reduced sulfur compounds (hydrogen sulfide, methane thiol, dimethyl sulfide, carbon disulfide, and dimethyl disulfide) were calibrated as a function of injection volume and concentration level. The results were evaluated by means of two contrasting calibration approaches: fixed standard concentration method (variable volumetric injection of standard gases prepared at a given concentration) and fixed standard volume method (injection of multiple standards with varying concentrations at a given volume). The optimum detection limit values of reduced sulfur compounds, when estimated at $100\,\mu L$ of injection volume, ranged from $2.37\,pg$ (carbon disulfide) to $4.89\,pg$ (dimethyl sulfide). Although these detection limit values improved gradually with decreasing injection volume, the minimum detectable concentration (e.g., in $nmol\,mol^{-1}$ scale) remained constant due to a balance by the sample volume reduction. The linearity property of pulsed flame photometric detector also appeared to vary dynamically with changes in its sensitivity. According to this study, the performance of pulsed flame photometric detector, when tested by direct injection method, is highly reliable to precisely describe the behavior of reduced sulfur compounds above $\sim 20\,nmol\,mol^{-1}$.

1. Introduction

The environmental significance of sulfur compounds is well-recognized because of their potent role in acid deposition, rapid acidification of lakes, the loss of forests, the corrosion of metal structures and historical monuments, and the production of oxidized pollutants (e.g., sulfuric acid) [1]. The socio-environmental concerns related to unpleasant odors have led to the quantification of many odorous sulfur compounds which include: hydrogen sulfide (H_2S), methane thiol (MT: CH_3SH), dimethylsulfide (DMS: $(CH_3)_2S$), and dimethyldisulfide (DMDS: $(CH_3)_2S_2$) [2]. These malodors have been called volatile sulfur compounds (VSC) or reduced sulfur compounds (RSCs) [3]. In contrast to the oxidized form of sulfur species (e.g., SO_2), RSCs predominantly originate from natural sources (e.g., marine, terrestrial biogenic, volcanic, biomass burning, etc.) [4].

In light of RSC's potential for malodor [5,6], accurate acquisition of their concentration levels is often considered as a basic means of odor control [7]. The determination of

RSCs contained in environmental samples has been achieved most commonly by gas chromatography (GC) interfaced with several detection systems, e.g., flame photometric detection (FPD), pulse flame photometric detection (PFPD), sulfur chemiluminescence detection (SCD), and atomic emission detection (AED) [8]. Although most of these detectors have proven to be valuable in sulfur analysis, the PFPD provides certain advantages such as price (e.g., relative to SCD and AED), sensitivity and selectivity (e.g., relative to FPD), and reproducibility [9].

Our research group has been investigating the GC-PFPD detection techniques for diverse RSCs in both clean and polluted air samples. In an earlier study, the performance of GC-PFPD was tested with the loop-based injecting method against four RSCs (H$_2$S, MT, DMS, and DMDS) over a wide concentration range (0.1–10 μmol mol^{-1}) [10]. The properties of calibration error in the determination of RSCs were assessed by employing two contrasting calibration approaches (i.e., fixed standard concentration (FSC) and fixed standard volume (FSV)) based on the identical loop-based injection method [11]. In a good analogue to our previous efforts, Catalan et al. also examined the loop-based injection method to estimate the detection properties of GC-PFPD for the sulfur compounds in various respects [8].

The loop-based injection technique is useful for moderately increasing the volume capacity of a directly injectable quantity, as the system allows for the transfer of analytes filled in a given loop size [11]. In contrast, such expansion is limited when using direct injection, due to the low flexibilities of control on the injectable volume of the sample (e.g., the build-up of back pressure within the injector line). The direct GC-injection method is however preferred because of its simplicity, reliability, convenience, and throughput for the analysis of various compounds [12–14]. However, since the application cannot be expanded beyond a certain injection volume, there is a lack of information pertaining to its basic properties. Hence, the present study is intended to describe the general aspects of the direct injection method in GC-PFPD application.

In this study, a number of direct injection-based calibrations were conducted for five RSCs (H$_2$S, MT, DMS, carbon disulfide (CS$_2$), and DMDS) by varying the aforementioned variables in different combinations (i.e., using standards of different concentration levels and of different injection volumes within a relatively wide range). The results of all calibration data were then pooled together to evaluate the similarities and differences in terms of the two contrasting calibration approaches. In addition, the absolute and relative detection properties of the PFPD, obtained through direct injection techniques, were evaluated.

2. Materials and methods

2.1. Experimental scheme

The fundamental properties of GC-PFPD were investigated to specifically describe its response characteristics against five RSCs (H$_2$S, MT, DMS, CS$_2$, and DMDS). A series of calibration experiments were designed and conducted to assess the relationship between injection volume and concentration range

of gaseous RSCs standards. The primary standard gas was mixed with ultrapure nitrogen to prepare working standards (WS) at five different calibration points with different concentration levels. As the maximum available concentration of the primary standard was 10 μmol mol^{-1}, these WS gases were prepared at five individual concentration levels (0.5, 1, 2, 5, and 10 μmol mol^{-1}). Hence, our calibration experiments were designed and conducted to cover five concentration levels (0.5–10 μmol mol^{-1}) at five injection volumes (100, 200, 300, 400, and 500 μL) (Table 1). The calibration curves for each injection volume can be drawn by pooling the gaseous standards of all five concentration levels (Table 1); this approach is hence named the fixed standard (injection) volume (FSV) method [11]. All the calibration data examined on the basis of FSV approach can be re-organized as a function of the standard concentration level. Hence, the calibration data for each concentration level can also be combined together to derive calibration curves across varying injection volumes. The procedure used for the latter concept was named as the fixed standard concentration (FSC) approach [11].

For the acquisition of comparative calibration data sets between FSV and FSC, the first round of experiments started with injection at the lowest volume (100 μL) for working standards of all five concentration levels and proceeded consecutively for other injection volumes in the same manner. All the gaseous samples (of 100–500 μL) were introduced into the system by injecting them with a single gas-tight syringe of 500 μL capacity. The second and third rounds of the experiment then proceeded to obtain the replicate calibration data sets. However, during the second round, the calibration started from the highest injection volume (500 μL) and ended with the lowest (400, 300, 200, and 100 μL). After completing the second round, the third round was initiated again in the same manner as the first round (i.e., starting from low to high injection volume). The initiating conditions of calibration were controlled by reversing the order of injection volume or concentration; this was necessary to reduce the possible bias that can stem from the abrupt changes in concentration levels or in volume range of the calibration. The system was checked for blank after each analysis, and a blank run was repeated several times after injecting a large quantity of analytes (e.g., 500 μL) to eliminate the possible memory effect of the system. Although a single round of experiment basically required a minimum of 72 h to complete all three individual rounds of calibration (with an individual run time of 20 min), the mean values were derived and used for the data interpretation after combining all matching replicate data sets obtained from three separate rounds of calibration experiments.

2.2. Preparation of working standards

Primary standards of RSCs contained in a cylinder were purchased at equimolar concentrations (10 μmol mol^{-1} with ±5% accuracy) for five target sulfur gases (Ri Gas, Corp. Dae Jeon, Korea). The working standards of RSCs were prepared at five concentration ranges (0.5, 1, 2, 5, and 10 μmol mol^{-1}) by mixing the primary standards with ultrapure nitrogen in a 1-L Tedlar bags (refer to Table 1). This mixing stage was completed by a single-step dilution of the primary standard gas (i.e., 10 μmol mol^{-1}) to the desired concentration with the aid