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Some Insights into the Gas Chromatographic Determination of Reduced Sulfur Compounds (RSCs) in Air

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The analytical properties of four reduced sulfur compounds (RSCs), including hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS), were investigated to improve the techniques for their measurements at sub-part-per-billion (sub-ppb) concentration levels. For this purpose, a gas chromatographic (GC) system with a pulsed-flame photometric detector (PFPD) was interfaced with a thermal desorption (TD) unit for the collection and analysis of RSCs in ambient air. The calibration results obtained by working standards of equimolar concentrations (prepared at five different concentrations of 5, 10, 20, 50, and 100 ppb) were evaluated to properly describe the detection characteristics of the GC/PFPD setting and of different RSCs. It was observed that the absolute magnitude of calibration slopes changed among different S compounds in a consistent manner (e.g., enhanced sensitivity toward the compound of heavy molecular weight and/or high sulfur contents), while their full scales of linearity range varied in an opposite pattern. The absolute magnitude of the H_2S calibration slope values was remarkably sensitive to the initial standard concentrations, while such effects were not so evident from other RSCs. The overall results of this study suggest that the GC detection of H_2S by means of the bag sampling technique can suffer from the strongest variability due to the dynamic change of its calibration in accord with its initial concentration.

1. Introduction

It is well-known that a broad spectrum of reduced sulfur compounds (RSCs) exists in ambient air (1). In recognition of their importance in global atmospheric chemistry, a number of analytical approaches have been developed to measure these compounds, including spectrophotometry, polarography, fluorescence, coulometry, potentiometry, impregnated filter tapes, etc. (2). Despite great efforts devoted to the improvement of such technology, the application of those methods to actual environmental samples suffers from such limitations as the lack of detectability, interfering substances, procedural complexity, and weak reproducibility. Sensitivity is generally found to be the most serious issue given the low abundance in most environmental samples. There is, in fact, a line of evidence suggesting that many previous studies suffered most significantly from the quantification of such a compound as H_2S due to both its chemical instability and limited sensitivity (e.g., 3).

As the most practical means to measure these RSCs in a quantitative sense, the combination of the S-specific gas

chromatographic (GC) detection method (e.g., flame photometric detection (FPD)) and the thermal desorption (TD) unit has been used most extensively (4–6); this setup may be considered a prerequisite to sufficiently preconcentrate and analyze S gases above their detection limit (DL). In fact, this analytical system can be used to detect S gases in amounts as little as sub-nanogram level, which enabled the detection of a few to a few tens of part-per-trillion (ppt) concentration with the total sample volume of air at a few liters or more (7, 8). However, as each individual S gas has its own physicochemical properties, their analytical detection can be distinguished not only by different retention times but also by different response characteristics (e.g., maximum range of linearity) (9).

In the present study, efforts were directed to (1) the assessment of the analytical properties of important RSCs (including hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS)) against the combination of the GC and pulsed flame photometric detector (PFPD) systems and to (2) the evaluation of such setup for the usability in RSC analysis at sub-ppb concentration levels. The detectability of different S gases was therefore examined in terms of their calibration properties using the RSC standards in environmental concentration levels. On the basis of this study, some important aspects of S gas quantification at the sub-ppb concentration range are discussed.

2. Materials and Methods

To examine the detection properties of the four RSCs in both an absolute (e.g., maximum linearity) and a relative sense (e.g., inter-compound relationships), a high-concentration standard was obtained to contain all four S compounds at an equimolar concentration of 10 parts-per-million (ppm); this standard gas was prepared gravimetrically using a concentration of 5% (by ISO 6142 method: Ri gas, Korea). This 10 ppm standard was then mixed with ultrapure dry air (purchased at 99.999% purity and a moisture content of less than 5 ppm) to produce working standards at five different concentrations (5, 10, 20, 50, and 100 ppb). For all of the S standards, minimum moisture levels were maintained as the content of the moisture itself is a variable affecting the test results. All of the experiments were conducted under laboratory conditions, and the samples were analyzed immediately after preparation.

For the efficient collection and preconcentration of RSCs, a multi-functioned TD system equipped with an air server unit (UNITY model, Markes International Ltd., U.K.) was operated at the beginning stage to selectively cryofocus S compounds contained in working standard gas. The details of the TD setting, introduced previously in our recent publication (11), can be summarized as follows. Equipped with an internal vacuum pump and mass flow controller (MFC), the air server unit of the TD can pull up any type of gas mixtures (standard gas or air samples) contained in various container types (e.g., Tedlar bag in our study) at varying flow rates (i.e., between 5 and 100 mL min^{-1}) for a variable duration (i.e., between 0.1 and 999.9 min); this TD system consists of a cold trap (a mixture of silica gel and Carbotrap B) allowing cryofocusing of the S gases via electronic cooling (-15°C by Peltier cooler, PC), as the preconcentration efficiency of cold trap is found to be optimized at or below this temperature.

The preconcentrated S compounds were released from the TD and analyzed with a GC equipped with a pulsed flame photometric detector (PFPD; O. I. Co., model 5380). Chromatographic separation of different RSCs was done via BP-1

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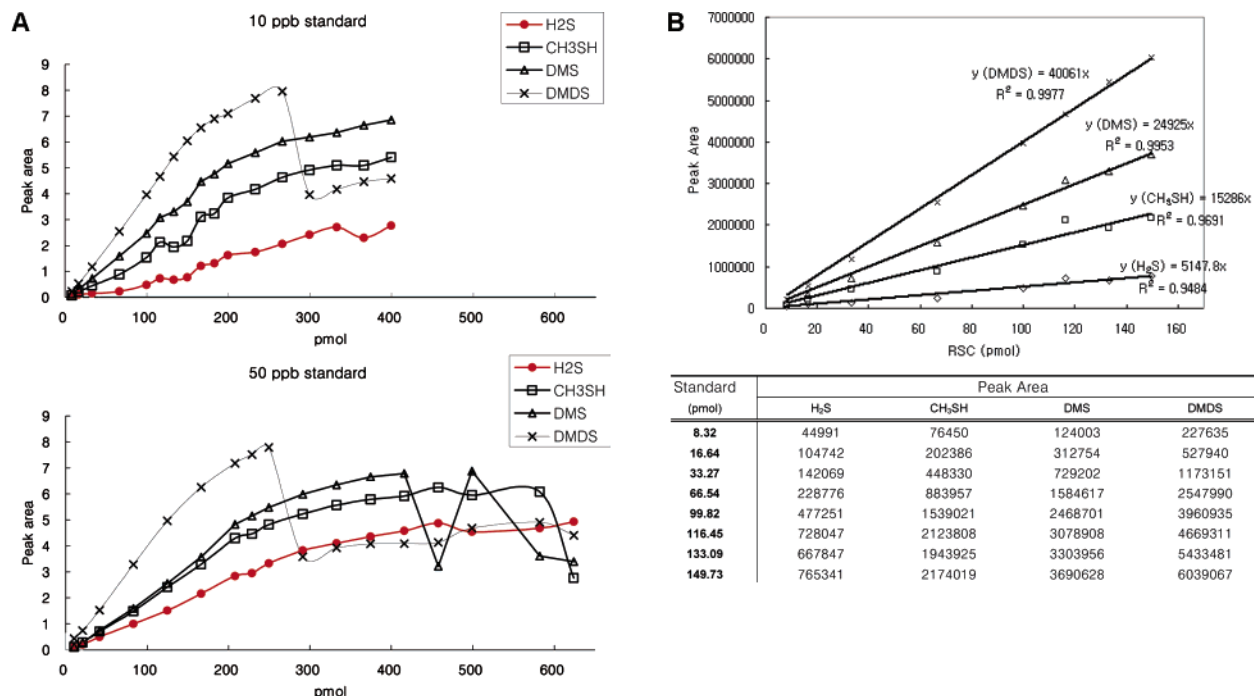


FIGURE 1. (A) Comparison of linearity performance of the GC/PFPD method: the test is made by two types of S gas standards containing equimolar concentrations at 10 (upper) and 50 ppb (lower). Peak areas were adjusted arbitrarily by multiplying 10^{-6} . Two experiments were performed on February 4 and 9, 2004. (B) Comparison of calibration curves obtained using the data sets of a 10-ppb equimolar standard (up to 150 pmol concentration range). Calibration curves are drawn by the identical data shown in the upper part of A (i.e., 10-ppb calibration results).

column (60 m \times 0.32 mm, 5.0 μ m, SGE) for 20-min cycles. Other conditions for the GC analysis can be summarized as follows: detector temp of PFPD 220 $^{\circ}$ C; flow rate mL min⁻¹ air(1) = 10, air(2) = 10, H₂ = 11.5; carrier gas, N₂, 1.2 mL min⁻¹ (20 psi) cold trap, low = -15 $^{\circ}$ C, high = 250 $^{\circ}$ C, hold time = 5.0 min; outlet split, 5.0 mL min⁻¹ (5:1 split ratio); flow path temp 80 $^{\circ}$ C.

To allow a simple comparison of the PFPD's responses among different S compounds, integration of their peak areas was made in the linear mode with the square root (SR) function on. As the use of the SR function efficiently masks the squared response of the detector (i.e., due to the conversion of S atoms to an S₂ complex), the whole calibration procedure can be facilitated by handling a simple first-order equation. Because the noise level of blank was sufficiently low, calibration curves obtained from three (or four) points calibration typically showed an excellent linearity; correlation coefficients above 0.99 were commonly achieved, even at the offset mode, which forced the curve to pass through zero on both the x and y axes. The use of GC/PFPD setting following the TD preconcentration allowed the determination of RSCs with absolute DL values of \sim 10 (CH₃SH, DMS, and DMDS) to 30 pg (H₂S). If precision is evaluated in terms of the relative standard error (RSE) of the analyses in triplicate, it was found to vary between 1 and 5%. The reproducibility of S gas detection was, however, rather variable with respect to the time and type of the RSC.

3. Results and Discussion

3.1. Effects of Initial Concentration on the Calibration Linearities of RSC. As a first step to investigate the general characteristics of the GC/PFPD detection, the maximum linearity was checked for each RSC by running two independent calibrations with two standards prepared at 10 and 50 ppb (Figure 1). Because of the relatively long duration required for each experiment, there was a five-day break between the two calibrations. Hence, these results may reflect the factors associated with the concentration differences and with the GC performance conditions. Nonetheless, these

results are still valuable enough to diagnose the relative detection characteristics of different RSCs, as they are shown to be consistent for both the upper and lower graphs in Figure 1A. However, the results obtained in both concentrations show that linearity ranges are different for different RSCs, although the lightest compounds such as H₂S are linear within a large concentration range (e.g., 300 pmol), and the heavier ones such as DMDS have much more limited linearity ranges (e.g., 150 pmol). Beyond those limits, the response characteristics of RSCs vary to such an extent to yield highly unpredictable patterns for DMS and DMDS (Figure 1A). Consequently, in the derivation of calibration curves for each RSC, those data falling within the linearity range were sorted out and used (Figure 1B).

In the case of the 10-ppb-based calibration shown in the upper section of Figure 1A, a data set covering 17 different concentration points was obtained. The reproducibility of the calibration procedure was checked after 3 to 4 injections for this series of 17 experiments, and the results were found to be consistent. Noting that the minimum loading time of the TD system is 0.5 min, the amount of standard gases loaded into the TD system was regulated by changing the loading time (e.g., 0.5, 1, 2, 4, ..., 20, 22, and 24 min) at a fixed flow rate of 40 mL min⁻¹. This GC/TD setting allowed the minimum injectible amount of S gas (using 10-ppb standard) to be 8.3 pmol for all four RSCs (or 0.28 ng in the case of H₂S). Hence, the minimum quantity of standard gas to be loaded to the TD system, which is defined as the total TD loading volume (TTLV), corresponds to 20 mL at a flow rate of 40 mL min⁻¹. Likewise, the calibration test beginning with the 50-ppb standard was designed so that the absolute quantities of RSCs could be comparable to each other. Considering the higher sulfur content per unit volume, this 50-ppb standard was loaded at a reduced flow rate of 10 mL min⁻¹.

Figure 1A shows the results of the comparative calibration tests made using standards beginning at two different concentrations. A comparison of their calibration patterns shows that they are generally consistent with each other in

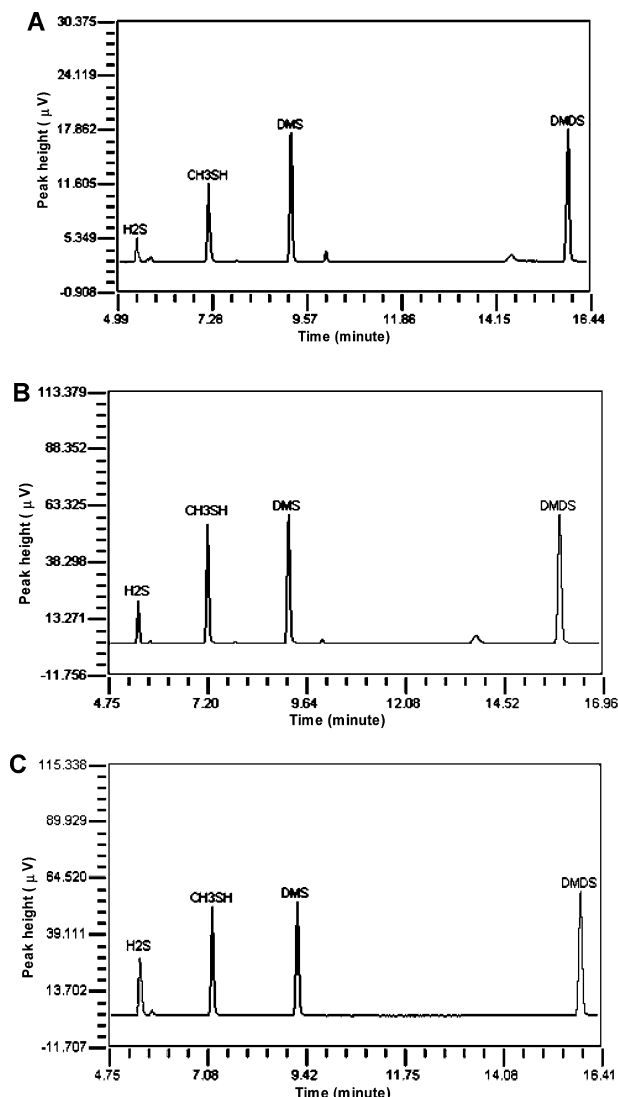


FIGURE 2. Comparison of chromatograms obtained by injecting different contents of sulfur gases into the GC system. All standard gases were prepared as equimolar contents of four sulfur gases including H_2S , CH_3SH , DMS, and DMDS. (A) Absolute amount of S gases injected = 33.3 pmol [TTLV of 160 mL for 5-ppb standard (4-min injection at FR of 40 mL min^{-1})]. (B) Absolute amount of S gases injected = 166.4 pmol [TTLV of 800 mL for 5-ppb standard (20-min injection at FR of 40 mL min^{-1})]. (C) Absolute amount of S gases injected = 166.4 pmol [TTLV of 40 mL for 100-ppb standard (1-min injection at FR of 40 mL min^{-1})].

several respects. First, the relative ordering in slope values between the different RSCs (e.g., $\text{H}_2\text{S} < \text{CH}_3\text{SH} < \text{DMS} < \text{DMDS}$) is maintained at two different standard concentrations. This relative pattern is highly compatible with those seen from an earlier study (9) in which the GC/PFPD detection technique was investigated by injecting the gases of high S content directly into the GC column without the aid of the TD system. Second, the analytical response to the equimolar level S compounds is shown to be well distinguished among different RSCs; more enhanced sensitivities are apparent for the heavier RSCs compared to the lighter RSCs. In addition, the lighter ones with weaker sensitivity have more extended ranges of linearity. The least sensitive compound of H_2S exhibited the most extended linearity range among the studied RSCs up to 300 pmol; however, the values for the most sensitive RSC (DMDS) had a linearity range of 150 pmol which is nearly one-half the value of H_2S . To evaluate the actual calibration patterns for the data sets shown in Figure 1A, linear regression equations are derived using the data

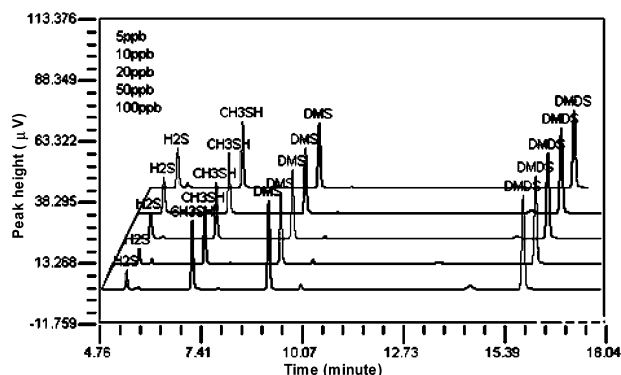


FIGURE 3. Comparison of chromatograms with identical amounts (83.2 pmol) of sulfur gases. Five different chromatograms were obtained by adjusting the injection volume of the standard gases with 5 different concentrations from 5-ppb (total TD loading volume (TTLV) of 400 mL) to 100-ppb mixing ratio (TTLV of 20 mL). The chromatograms are lined up so that the one drawn by the least concentration (5 ppb) comes to the front, while that of the highest one (100 ppb) comes at the back.

covering up to 150 pmol range in Figure 1B. Despite the occurrence of a few outlying data points, the results generally show the existence of fairly good correlations for all RSCs, with the smallest r^2 values of around 0.95 for H_2S (Figure 1B).

The results generally indicate the existence of a systematic pattern in RSC calibration results such as a fixed relative order of the slopes. However, if the calibration patterns for each RSC are compared between the two different standard concentrations, the results of H_2S are clearly different from those of other RSCs. The slopes of H_2S are dependent on the initial concentrations of standard gas of 10 and 50 ppb. To learn more about such differences in the calibration pattern, a more deliberate study on RSC calibration patterns was carried out as described in the following section.

3.2. Analytical Limitations of H_2S Calibration and Its Impact. As seen in Figure 1A, the most outstanding results of our analysis are the clear differences found in the absolute slope values of H_2S between two different standard concentrations of 10 and 50 ppb; it was found that the slope value obtained by a 50-ppb standard gas is larger by an order of magnitude than that of a 10-ppb counterpart. To learn more about the possible influence of standard gas concentrations on calibration bias, we extended our test for calibration experiments by adding standard gases at three concentrations of 5, 20, and 100 ppb.

The results of our expanded experiments were first checked by examining the patterns obtained using standards of the two extreme concentration: 5 and 100 ppb. As seen in Figure 2A and B, chromatograms of two different S amounts (i.e., 33.3 and 166.4 pmol for all four RSCs) were obtained by adjusting the TTLV of a 5-ppb standard into 160 and 800 mL, respectively. In Figure 2C, a chromatogram of 166.4 pmol was also obtained by running TTLV of 40 mL for a 100-ppb standard gas. As expected, changes in integrated peak areas of S gases between Figure 2A and B appear to be reasonably proportional for most RSCs. Interestingly, however, rather large differences exist in the H_2S results between Figure 2B and C, despite the fact that they are obtained by loading the identical amounts. Comparison of the H_2S peak area between Figure 2B and C showed a dramatic increase of $\sim 110\%$ (unitless peak areas of 1.14×10^6 to 2.41×10^6). For the readers' reference, those of the three other RSCs were also evaluated; their results are insignificant relative to H_2S (such as -2.6% (CH_3SH), -17% (DMS), and -7.6% (DMDS)). Note-worthy here are the moderately enhanced negative values for DMS and DMDS (relative to CH_3SH). This may suggest that their areas at 166.4 pmol point are already in the linearity limitation range.

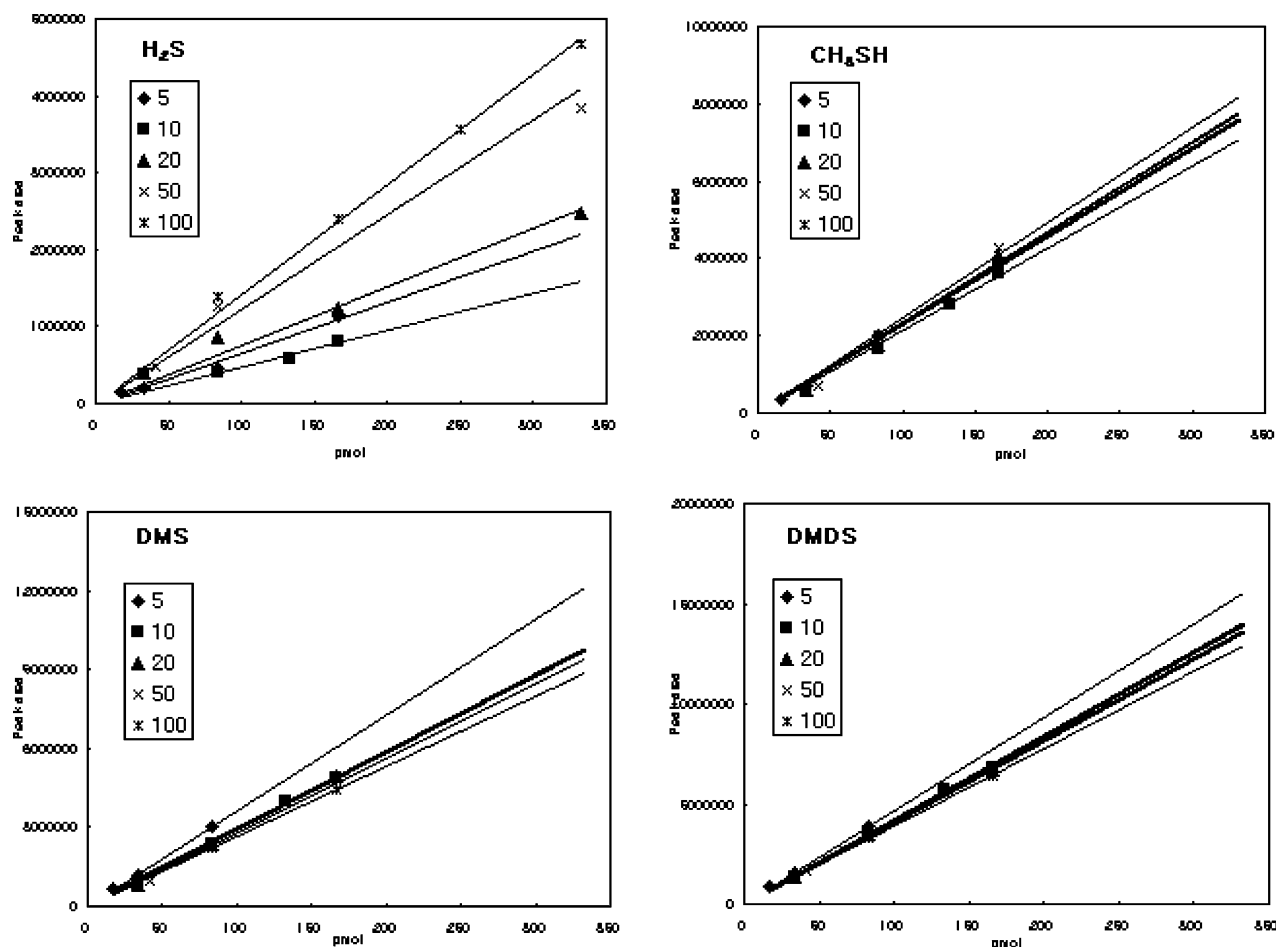


FIGURE 4. Comparison of calibration patterns as a function of analyte concentration using S gas standards prepared at concentration ranges of 5 to 100 ppb (February 16, 2004). Refer to Table 1 for the summary of these calibration data sets.

In Figure 3, the results of this comparative analysis are presented to cover the patterns for all five different standards. To simplify this comparative test, experiments were conducted to produce an individual chromatogram for each standard gas by fixing the absolute quantities of S amounts (i.e., 83.2 pmol) that were to be loaded into the TD system. To this end, the TTLVs were adjusted from as little as 20 mL (100-ppb standard) to the maximum of 400 mL (5-ppb standard). The results shown in Figure 3 consistently indicate that the responses of most RSCs are compatible with each other, while the response of H_2S tends to differ systematically as a function of the initial concentration of standard.

To assess the relative effects of the initial standard gas concentration on the observed slope values among different RSCs, calibration curves were first derived for each RSC using standard gases of different concentrations; for this purpose, the input data for each RSC were screened to include those falling within or near the linearity range. (Refer to Figure 1A for the occurrence pattern of nonlinear data sets beyond the linearity range.) The computed calibration curves for each RSC were put together for a parallel comparison in Figure 4. The calibration results summarized in Table 1 (in terms of slope values) indicate that the patterns contrast quite sharply between H_2S and the others. Although there is a slight exception in the results of a 10-ppb standard, the calibration slopes of the H_2S standard increase generally with the increasing standard concentration. By contrast, the slope values for the other RSCs generally seem to vary less significantly across different calibration results. According to the results shown in Table 1, all slope values except H_2S tend to exhibit fairly excellent agreement in their calibration patterns between the lowest (5-ppb) and the other concen-

TABLE 1. Comparison of Calibration Slope Values Obtained Using Standards with Varying Mixing Ratios^a

concn (ppb)	H_2S	CH_3SH	DMS	DMDS
5	6624	23228	36345	46659
10	4799	21237	29394	41899
20	7577	23481	29506	40870
50	12280	24654	28259	41604
100	14274	22846	26605	38719
mean	9111	23089	30022	41950
SD	3995	1236	3722	2911
RSE	19.6	2.4	5.5	3.1

^a All of these results are shown as calibration curves of each individual RSC at varying concentration ranges in Figure 4.

tration ranges. The results thus suggest that one can possibly obtain fairly reasonable calibration data sets for most RSCs including CH_3SH , DMS, and DMDS. It is worth mentioning that the slope values for heavier RSCs decrease slightly with increasing standard concentrations. Such patterns are quite evident in the cases of DMS and DMDS, suggesting the fact that the deflection of their slope values occurs more efficiently due to their enhanced sensitivity and/or limited linearity.

To quantitatively assess these concentration effects on the H_2S calibration patterns, the compatibility among different calibration results was evaluated in terms of the relative standard error (RSE) in Table 1. As already seen from a simple comparison of chromatograms (Figures 2 and 3), this computation also indicates clear differences between H_2S and the others. The RSE value for H_2S approaches 20%, while those for all the others are below 5%. Because of the abnormal trend of H_2S , the pattern for its slope changes was also

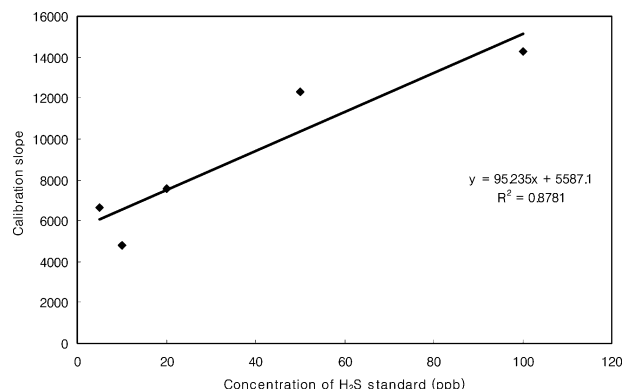


FIGURE 5. Relationship between calibration slope and standard concentration prepared in Tedlar bags.

examined by plotting its slope values against the initial concentrations of each standard gas prepared (Figure 5). The results, shown in Figure 5, clearly indicate that the detectability of our GC/PFPD/TD system is significantly affected by the initial concentration of H₂S standard gas unlike other reduced sulfur gases.

Remarkably, the calibration slopes of H₂S can change with changes in the initial standard gas concentrations. Although the slope values from H₂S calibration are greatly affected by the initial concentrations of RSC standard gases used for calibration, those of others are not so significant. The results suggest several causes and possibilities for such observations. As the RSC standards are prepared by dilution with ultrapure air, more reactive compounds such as H₂S may be destructed more efficiently. Such an effect in fact can be more significant at low concentrations wherein more air is mixed with the small amount of H₂S. In addition, as the standard is contained in a Tedlar bag, it is possible that adsorptive losses occur more efficiently in the case of light RSCs relative to heavy ones (e.g., I₂). Finally, the possibility of the H₂S standard loss inside the analytical line cannot be ruled out, as the H₂S gas is introduced into the GC/PFPD by way of TD systems.

According to our study, it appears to be a highly difficult task to acquire gaseous H₂S standard at significantly low concentrations such as in the sub-ppb concentration range. There appear to be a number of sources to introduce an analytical bias in the gas chromatographic determination of H₂S. For instance, if one analyses H₂S after diluting the initial samples of unknown concentration, the dilution itself can contribute to the propagation of errors. Likewise, if one analyzes the samples of high H₂S concentration by calibration slopes obtained using relatively low-concentration standard gases, the opposite kind of errors can be introduced. Considering the fact that there are a number of different sampling techniques for natural gas compounds (such as

canister, sorbent-based method, solid phase microextraction, etc.), there appears to be a strong need to properly evaluate sampling and the associated analytical biases in the measurements of such a reactive compound as H₂S.

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