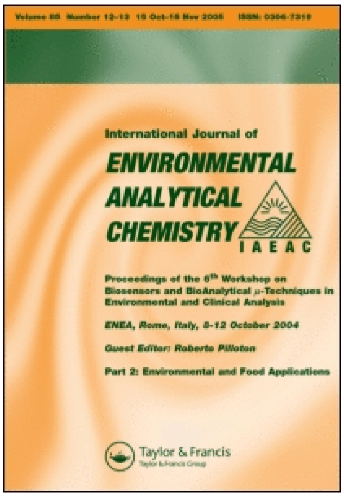

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Kim, Ki-Hyun(2006) 'A dual-mode GC analysis of reduced sulphur compounds in air over a wide concentration range', International Journal of Environmental Analytical Chemistry, 86: 11, 805 — 817
To link to this Article: DOI: 10.1080/03067310600583832
URL: http://dx.doi.org/10.1080/03067310600583832

Intern. J. Environ. Anal. Chem.
Vol. 86, No. 11, 15 September 2006, 805–817

A dual-mode GC analysis of reduced sulphur compounds in air over a wide concentration range

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(*Received 3 October 2005; in final form 22 December 2005*)

In this study, the general requirements of the GC/PFPD analysis have been investigated in the measurements of reduced sulphur compounds (RSC) (hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH), dimethylsulphide (DMS), and dimethyldisulphide (DMDS)) in air over a wide concentration range. To cover samples collected under various environmental conditions, a dual-mode analytical system was developed for both low (i.e. combination of a Peltier cooling (PC) and thermal desorption (TD) method) and high concentration detection settings (i.e. the direct loop injection (LI) method). They were combined to measure both lower- (ambient air samples in ppt level) and upper-bound concentrations (source-affected samples in ppb or ppm level) without the modulation of samples (e.g. dilution of samples). Their relative performance was evaluated in terms of differences in the analytical sensitivity by comparing both the calibration slope ratios and detection limits. According to this comparison, the result from the high mode setting exhibited a generally enhanced sensitivity relative to the low mode setting; such a difference can be explained in part in that the two analytical modes are calibrated under each respective set-up. Nonetheless, their relative detection characteristics were found to be highly consistent in various respects. The sensitivity of different S compounds tends to increase on the order of H_2S, CH_3SH, DMS, and DMDS (with two S atoms), regardless of the selected analytical mode. Based on the comparative analysis of the two GC settings, it is concluded that the versatile application of the GC/PFPD technique can be used effectively for the accurate quantification of S gases in various environmental samples.

Keywords: GC/PFPD detection; High mode; Low mode; Detection characteristics; Malodor; Hydrogen sulphide

1. Introduction

There have been continuous improvements in the analytical techniques for detecting various pollutants. As a result, we are now able to measure and quantify various trace components, some of which were once considered to be non-existent or undetectable. In line with such advances in analytical skills and techniques, developments accomplished in the field of S gas analysis are astonishing. Although various instrumental settings have been involved in such a task (e.g. flame photometric detection (FPD), pulsed UV

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International Journal of Environmental and Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online © 2006 Taylor & Francis
DOI: 10.1080/03067310600583832

fluorescence (PUVF), lead acetate tape (LAT), etc.) [1], changes made in gas chromatographic (GC) techniques have attracted special interests [2]. Whereas most GC-based analysis of S compounds heavily rely on a classical FPD method [3], more selections are available to date with the introduction of such upgraded techniques as pulsed-FPD (PFPD), sulphur chemoluminescence detection (SCD), and atomic emission detection (AED) [4–6].

Due to the many improvements made in GC methods, one can detect a series of reduced sulphur compounds (RSC) at around a few picograms using a technique such as GC/PFPD [7, 8]. However, the direct application of such a method is not yet able to determine the concentrations of ambient air samples. For instance, to directly measure air samples of DMS at 10 ppt concentrations (i.e. ~0.025 pg per 1 mL air), any detection method should have a DL below 0.01 pg (assuming a maximum volume of GC injection as 0.5 mL). Consequently, the application of the preconcentration method (e.g. cryofocusing and thermal desorption: CF/TD) is considered the most desirable alternative because it allows the analyte to accumulate sufficiently prior to the GC detection. However, it should be noted that such a modification can inevitably induce changes in the analytical performance such as the alteration of GC response behaviour (e.g. changes in retention time, reproducibility, etc.) or the absolute degradation of sensitivity (e.g. because of the destruction or loss within the analytical line).

Our study group has been involved in a number of projects aimed toward the evaluation of sampling/analytical biases in the RSC measurements [9–12] and toward their analysis from various source areas (industrial regions and landfill sites) [13, 14]. Although a number of options are available for the GC method to measure RSC at varying concentration ranges, the most common approaches involve the application of the CF/TD type to accommodate samples in a low concentration range. However, the application of such a complicated analytical setting can introduce various types of errors in the analysis of high concentration samples, as it requires the additional modification of samples (e.g. stepwise dilution) [12]. Hence, for the accurate analysis of S gases at varying concentration ranges, we developed and employed a dual-mode GC/PFPD system. This dual-mode system was built to interchange between a high mode setting with direct loop injection (LI) and a low-mode setting with the CF/TD system. Hence it can be used separately to measure samples with both high (above ppb or ppm concentration levels) and low concentration ranges (ambient samples at ppt levels). Here, we present the results of the comparative study to characterize the relative performance of the dual-mode GC/PFPD setting in the analysis of atmospheric RSC. Based on this study, the fundamental aspects of the PFPD application between the two independent (high and low) detection modes are explored on a parallel basis with respect to its sensitivity to four different S compounds.

2. Experimental

2.1 *Configuration of a dual-mode analytical setting for S gas detection*

In our laboratory, we intended to measure RSC over a broad concentration range so a GC setting for S gas measurements was configured with either a high or low mode setup depending on the target range of the analyte concentrations and/or the analyte delivery

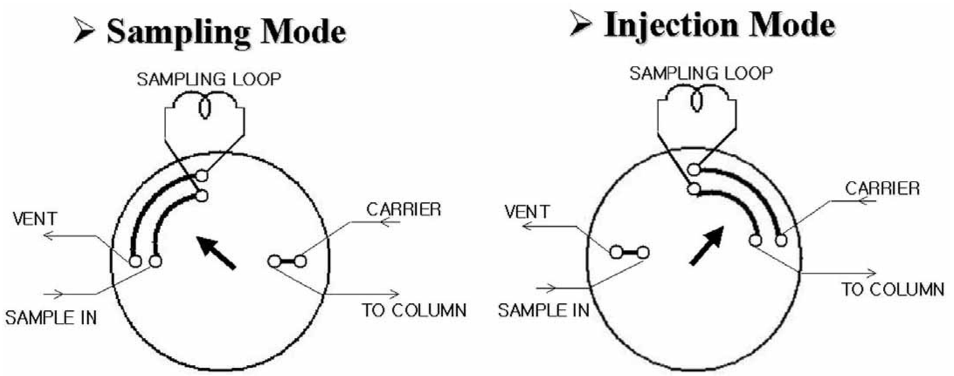

Figure 1. Schematic diagram of the high mode setting (a direct loop-injection system) for S gas analysis in this study.

mode (LI or CF/TD type). For detection of the S compounds, our GC system (Model DS 6200, Donam Instruments, Korea) was interfaced with a PFPD (Model 5380, O.I. Co.). The high mode setting with the LI system was built with a six-way switching valve to switch between sample loading (onto the loop at the load position) and injection (onto the GC column at inject position) (figure 1). Taking into account the varying concentration range of environmental samples, a number of loops made of stainless steel with different volume capacities of 10, 50, 100, 250, and 500 µL (all at an identical i.d. of 1/16 inch (1.59 mm)) were used interchangeably by connecting each with the switching valve. For instance, a loop with the smallest capacity (10 µL) was used for samples of a few tens ppb or above, while that with the largest capacity (500 µL) was used for those around a few parts per billion. In the inject mode, samples or standards are loaded onto the loop, and their excess amount is ventilated via a Teflon tubing placed in a water-filled vessel (visible checkup of by-pass through the formation of gas bubbles). Once loading is confirmed, it is switched to the inject mode so that the samples or standards are transferred to the GC system. The performance characteristics of this high mode setting have been described in detail elsewhere [12], and its applicability was verified as successful from our field measurement studies in the landfill area [13, 14].

The low mode setting with the CF/TD system was operated in the following steps. First, samples or standards with low S concentrations were brought into the TD unit, and target analytes were preconcentrated during the CF stage. This CF step was performed using the cold trap, consisting of two different adsorbents (silica gel and carbotrab B) with the aid of the Peltier cooling (PC) unit, which helps maintain the temperature condition of the PC stage at −15°C. As the PC stage was completed, desorption of S compounds was induced by heating the TD unit at 350°C. (To describe both general and specific facets of the preconcentration method, the abbreviation terms of PC or CF were used interchangeably from here.) Finally, the analyte components were transferred to the GC system for the gas-chromatographic quantification of the S compounds.

Whatever the sources of S transfer to the GC line may be (e.g. either LI or CF/TD), operation of the GC system was set to proceed in the following sequence. As the analytes are introduced into the GC column, separation of different RSCs was carried out under the following conditions. The temperature (T) programme was initiated so that the oven temperature was maintained as: (1) T (initial): 100°C for 2 min; (2) T (ramping rate), 6°C min^{-1} rate; and (3) T (final): 210°C at 2 min. To acquire an optimum resolution between different S components, we used a BP-1 column (60 m × 0.32 mm, 1.8 mm i.d.) at a column flow rate of 1.2 mL min^{-1} (N_2 as carrier gas) with each running cycle ending at 20 min intervals. To provide pulsed flames in the combustor (15 mm length and 2 mm i.d.), the detector was maintained at 220°C, and gases were supplied as: $H_2 = 11.5$, Air1 (wall gas) = 10, and Air2 (combustor) = 10 mL min^{-1}. In addition, in the case of the low mode setting, the PC/TD system was controlled as follows: a cold trap was set to run from the low end at −15°C to the high end of 300°C via thermal desorption with 5 min holding at the flow path with T at 80°C. In the present study, the performance of both high and low analytical modes was tested without the application of sample splitting in the analytical lines. It should, therefore, be noted that the performance and configurations for both analytical modes in the present study are clearly distinguished from those introduced in our recent study [10] of the PC/TD recovery rate test in which we were able to demonstrate a fairly excellent recovery rate of the PC/TD system by loading identical standards in a compatible manner; in that study, an instrumental set-up (a GC injector interfaced with a PFPD (Model 3800, Varian Technology)) different from the present set-ups was used under highly controlled conditions (i.e. the application of identical split ratios to both the GC injector and PC/TD system). However, both high- and low-mode settings for the present study were operated without any splitting options.

In order 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. because of the conversion of S atoms to an S_2 complex), the whole calibration procedure can be facilitated by handling a simple first-order equation. Because the noise level of blank was efficiently low enough, calibration curves obtained from three (or four) points calibration typically showed an excellent linearity; correlation coefficients above 0.99 were commonly achieved, even when their offset value was forced to pass the zero point on both the x- and y-axis.

2.2 *Preparation of standards and their calibration*

Primary standards contained in a cylinder were purchased at equimolar concentrations (10 ppm) of four target S gases that included H_2S, CH_3SH, DMS, and DMDS (prepared by the ISO 6142 method and certified at ±5% accuracy: Ri Gas, Corp., Korea). To obtain calibration curves for the high-mode operation, we used a syringe-dilution (SD) technique for standards as introduced in our previous work [2, 12]. This method is basically set to modulate the volume of standards in a 10 mL gas-tight syringe. At first, a volume (a few hundred millilitres) of primary standards (10 ppm) was transferred to a small-capacity Tedlar bag (e.g. 1 or 2 L). A certain portion of the standard was then drawn into the syringe and mixed with the outdoor air (i.e. zero blank values) to the desired concentrations. For instance, for the preparation of the 2000 ppb concentration standard, the syringe served as a mixing chamber for the primary standards (2 mL drawn initially) and the outdoor air (8 mL drawn additionally). However, for the standards of the smallest concentration range used, a double-stage dilution proceeded in a stepwise manner. Upon loading samples into the loop system (at load mode), the loop system was then checked for the fill-up status via gas-bubble formation. It was found that when both single- and double-stage dilutions were used to draw one calibration curve at the same time, a strong compatibility was observed consistently between low (a double-stage dilution) and high standard concentration points (a single stage dilution) with an excellent correlation coefficient [2]. This suggests that the use of a gas-tight syringe as a mixing chamber and of a syringe-based multi-step dilution should be reasonable enough to quantify the S gases at their upper-bound concentrations. On the other hand, calibration of the low-mode setting was performed using a bag-to-bag dilution (BD) technique. For instance, a working standard of 10 ppb concentration was obtained by mixing the primary standard (10 ppm equimolar concentration) with ultrapure air at a 1 : 1000 ratio. Because of contact with extra surface, the BD technique can involve more uncertainties relative to the SD technique [9]. Hence, investigation of the analytical uncertainties involved in the low-mode (BD-based) analysis relative to the high-mode (SD-based) analysis constitutes a highly desirable subject [9].

3. Results and discussion

3.1 *Detection characteristics of the high mode analytical setting*

As the starting-point of this study, the fundamental aspects of the high mode setting were examined in several respects. First of all, this setting was tested by examining the GC/PFPD sensitivity as a function of loop-size capacity (e.g. 10, 50, 100, 250, and 500 µL). For this purpose, calibration curves for each loop size were made by filling up the standard gases of five different concentrations (100, 500, 1000, 5000, and 10,000 ppb) into the selected loop. Figure 2 illustrates the four calibration curves for each of the four compounds obtained using an identical loop-injection system with a 10 µL loop capacity. The results of this analysis indicate the strongest sensitivity of DMDS with the two-S-atom structure. If this type of comparative analysis is extended

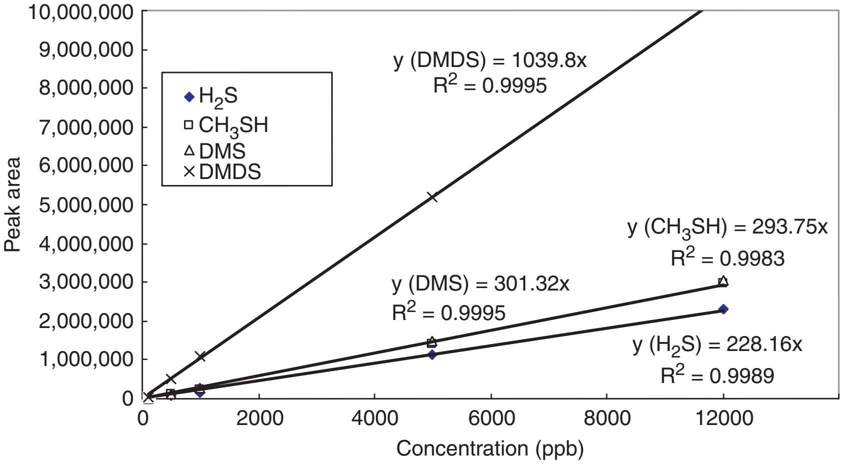

Figure 2. Comparison of calibration curves obtained using a loop-injection system with a 10 µL capacity. Calibration curves were measured by injecting equimolar standards of four S gases prepared at five different concentration points of 100, 500, 1000, 5000, and 10,000 ppb. (The DMDS result at 10,000 ppb is omitted because of an off-scale value.)

further by comparing the results from loops with large capacities, it is found that many S compounds experienced notable deflections in their calibration linearities at the 10 ppm level; the most sensitive component (like DMDS) already suffered from such problem at the 5 ppm level. In fact, the occurrence of inflexion points, when the calibration of RSC is performed over a wide concentration range, has been recognized commonly [e.g. 15]. The detailed properties of PFPD inflexion behaviour have also been described in our recent study of its performance characteristics [2]; in that study, a loop-based calibration of RSC standards was made to cover 10 concentration points (50–3200 ppb concentration range). The points of calibration-associated inflexion were then found to be affected most effectively by such factors as the inherent chemical reactivity and/or stability. The inflexion points of RSC calibration were thus found to occur on the order of decreasing sensitivity such as DMDS, DMS, CH_3SH, and H_2S.

The calibration results derived for all different loop capacities can be compared for each RSC in terms of the magnitude of slope values; in this respect, the absolute contents of each S gas are compared against the molar quantity of S compounds to facilitate inter-compound relationships on the same quantity basis (figure 3). The analysis of the relative calibration patterns in fact indicates several fundamental principles of S gas quantification by the GC/PFPD approach. First of all, all four RSCs tend to exhibit a strong consistency in their relative calibration patterns such that slope values increase with decreasing reactivity [2, 9]: $H_2S < CH_3SH \sim DMS < DMDS$. Second, the system seems to experience a significant enhancement in sensitivity with a decrease in loop capacity. Finally, such a loop-size effect, when it occurs, is found to be effective for all S compounds, regardless of the concentration ranges selected for the investigation.

It is interesting to evaluate the results shown in figure 3 from some other aspects of loop-size effects. First, the pattern for such effects differs greatly across different loop capacities, when the results are compared for each individual compound. For instance, it is found that H_2S exhibits a twofold increase in slope values (2.43×10^5 at a 250 μL loop to 5.58×10^5 at a 10 μL loop), while DMDS experiences a threefold enhancement for the respective loop capacities (7.56×10^5 to 2.54×10^6). As a result, the most remarkable sensitivity for each S compound is acquired consistently from the smallest loop capacity of 10 μL size, regardless of S speciation. As illustrated in figure 4, a comparison of slope values obtained across different loop sizes indicates the presence of systematic and exponential changes in the GC/PFPD sensitivity; it is found that such enhancement in sensitivity occurs rather dynamically with a decrease in loop size. The observed improvement in sensitivity is most likely to come from the combination of both the matrix effect and sorptive loss phenomenon. With the decrease in injection volume (and loop size), the matrix effect will be less significant so that it can help increase the sensitivity of RSC detection. It is also plausible to expect that the sorptive loss of RSCs occurs in the inner surface of loop made of the stainless steel material (i.e. because of a proportional decrease in loop volume, i.e. a maximum of 250 to a minimum of 10 μL, with an inner surface area at a fixed inner diameter of 1.59 mm in this study). It should be noted that there is a preferential loss of light RSCs (H_2S and CH_3SH) with this type of material, while it is almost negligible with heavy RSCs (DMS and DMDS) [11]. Hence, in compliance with these general expectations, the slope value of DMDS at the 10 μL loop is approximately 4.6 times larger than that of H_2S, whereas their difference at the 250 μL loop is about 3.1 times (figure 3).

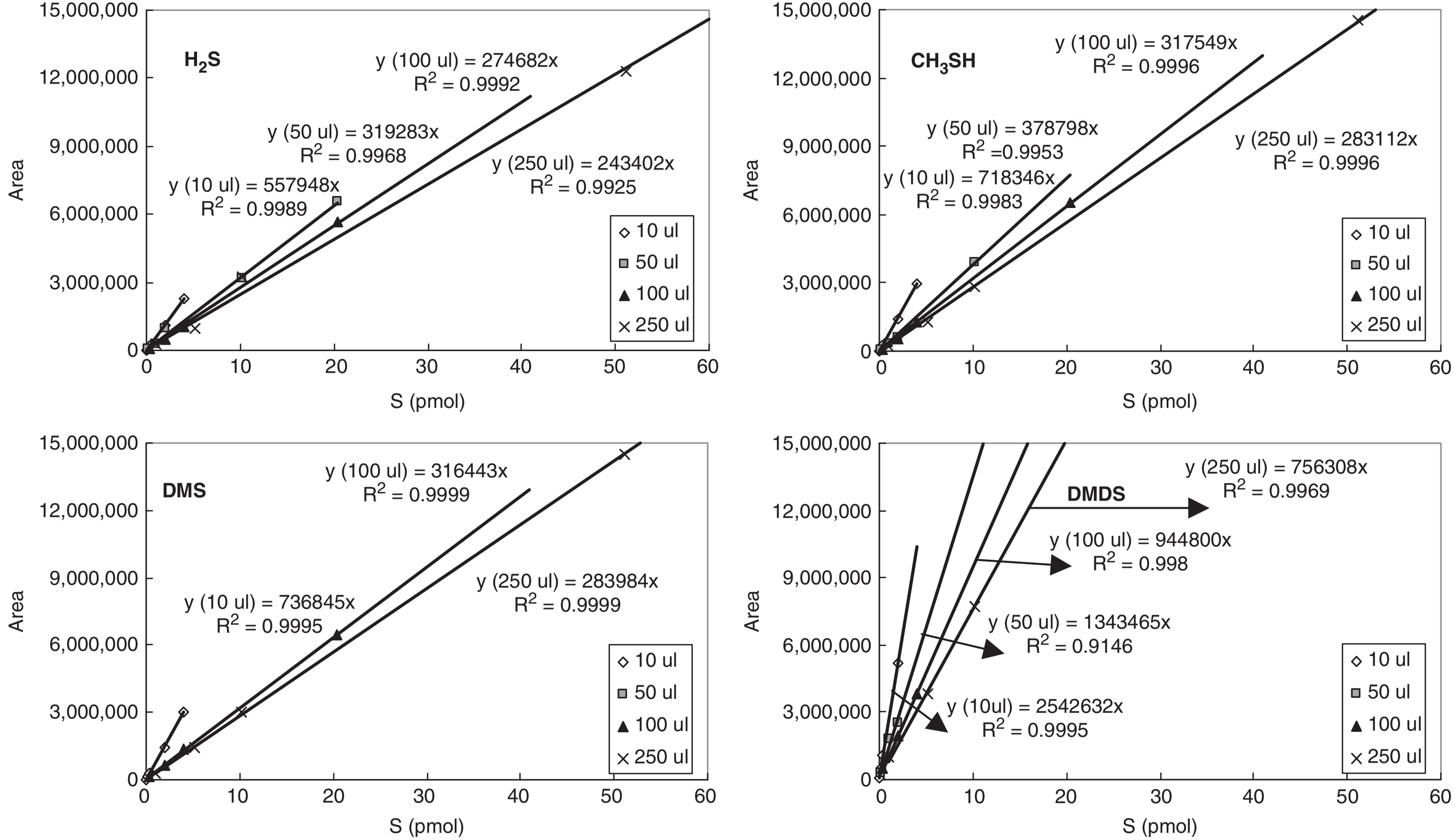

Figure 3. Changes in GC/PFPD calibration slopes as a function of loop size capacity. All data obtained for calibration (e.g. the results shown in figure 2) were modified to compare the patterns as a function of loop size. In all cases, relationships were compared between absolute S injected (pmol) and integrated area. DMS data for a 50 µL loop system were lost due to the system failure.

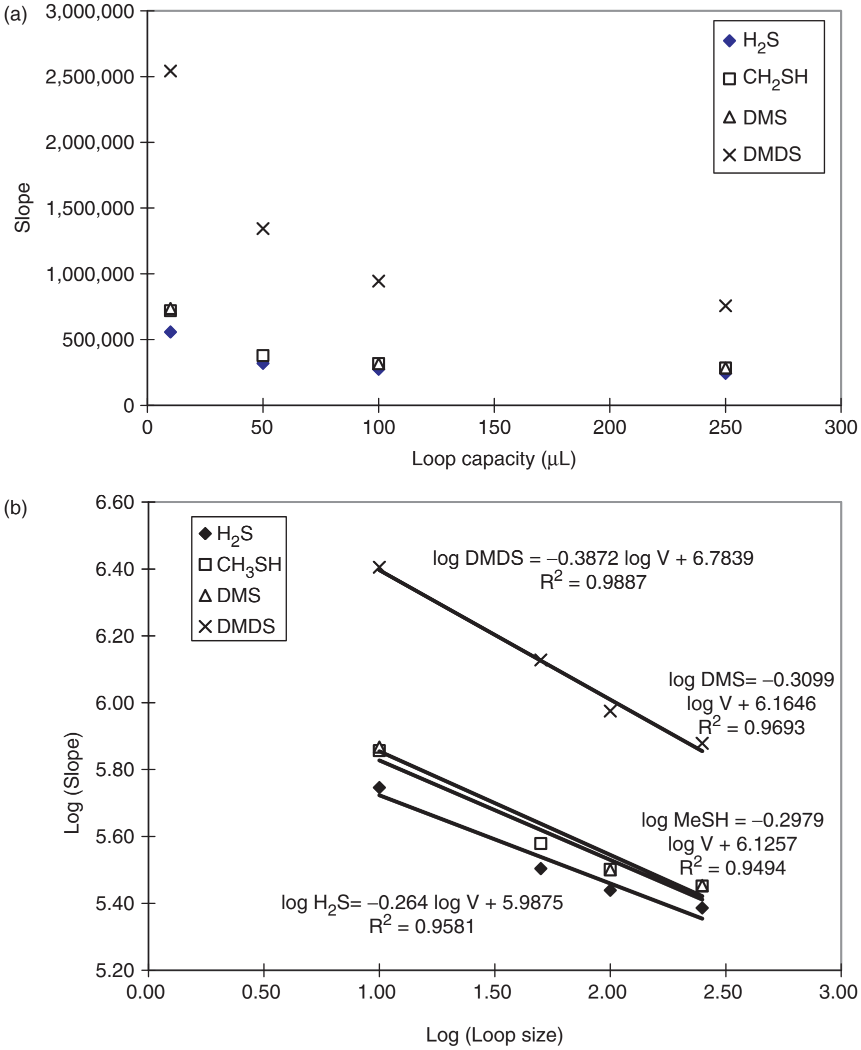

Figure 4. Changes in the GC/PFPD sensitivity as a function of the loop size (V in μL) selected for the high-mode analysis. (a) Normal scale; (b) Same as (a), but in a log–log relationship.

According to the high mode analysis in the present study, it is clearly noted that the dependence of the calibration slope values with the loop size coincides with the maintenance of relative calibration patterns between different RSCs. These unique patterns of loop-injection method seem to suggest a number of important factors involved in RSC analysis. First of all, it should be mentioned that changes in relative calibration patterns of RSCs occur moderately across different loop sizes. However, as seen in our previous study [10], the relative distinction between RSCs becomes negligible if analysed by direct injection into the GC system. Hence, it may be possible to infer that differences in absolute slope values across different loop sizes may be affected more sensitively by injection-related, rather than detector-related, variables. In addition, it should also be addressed that the GC system seems to experience the sensitivity change in a highly systematic manner. The enhancement in slope values, which occurs systematically with the decreasing injection volume, is most likely to be attributed to the reduced disturbance of the GC system because of the decreasing matrix effect.

3.2 *Detection characteristics of the low mode analytical setting*

The evaluation of the high mode setting helped us broaden our understanding on the fundamental aspects of GC/PFPD performance with respect to S gas detection. Although the analytical performance of PFPD shares many similarities to that of FPD [2], the former seems to take advantage of a highly improved sensitivity to a large extent in that its detectability can be extended significantly in the low concentration range (e.g. below the picogram range). As shown above, it was an intriguing subject to assess the inherent analytical properties of GC/PFPD in the S gas detection at the high-mode analytical setting. However, it may also be very important to describe the GC/PFPD performance characteristics for environmental samples at substantially low concentration ranges (e.g. ambient air at the ppt concentration level). Because the GC/PFPD analysis of the low-mode setting is basically performed with the aid of the PC/TD (or CF/TD) technique, modification of its performance characteristics may be inevitable to a certain extent between the two different analytical modes [9]. Hence, in this section, such an aspect of GC/PFPD performance is discussed in relation with those of a high mode setting, especially with respect to differences in absolute sensitivities between the two modes.

A direct comparison of calibration slope values is made in figure 5 using the calibration data sets obtained by each individual analytical mode on 5 September 2004. The results of this comparison indicate that the calibration curves of the low-analytical mode system (i.e. the use of a PC/TD set-up) experienced a significant drop in its sensitivity relative to the calibration results obtained by the high mode system (i.e. the use of a loop-injection system with a 500 µL loop). If the high/low (H/L) mode ratio of calibration slopes is computed using the calibration data shown in figure 5 for that specific period (5 September), the differences in their ratios are large across four S compounds; H_2S is computed to have the biggest H/L ratio of 51.0, while that of DMDS has the smallest ratio of 14.4. In table 1, the same type of comparison based on the H/L ratio is extended further to the same loop size with the different date (27 August) or to the data obtained by the other loop sizes (10 µL). Although H/L ratios for the most sensitive loop size range (i.e. 10 µL) are generally higher than those of the least sensitive size (i.e. 500 µL), such differences differ noticeably among different S compounds. It can be seen that the H/L values for H_2S and DMDS exhibit a notable increase from 500 to 10 µL loop size, while those of DMS do not. A comparison of these H/L ratios thus demonstrates a number of factors; [1] the high mode settings can experience a sensitivity change with the loop size change, and [2] such changing patterns are rather complicated across different loop sizes and between different S compounds. A detailed inspection of figure 5 results thus confirms that, despite such notable changes in sensitivity between the two different modes, the relative order in the slope values among different RSCs is maintained in a highly consistent manner such that $H_2S < CH_3SH <$ DMS < DMDS. In addition, it should be mentioned that the presence of generally high H/L ratio values in the present study should be distinguished

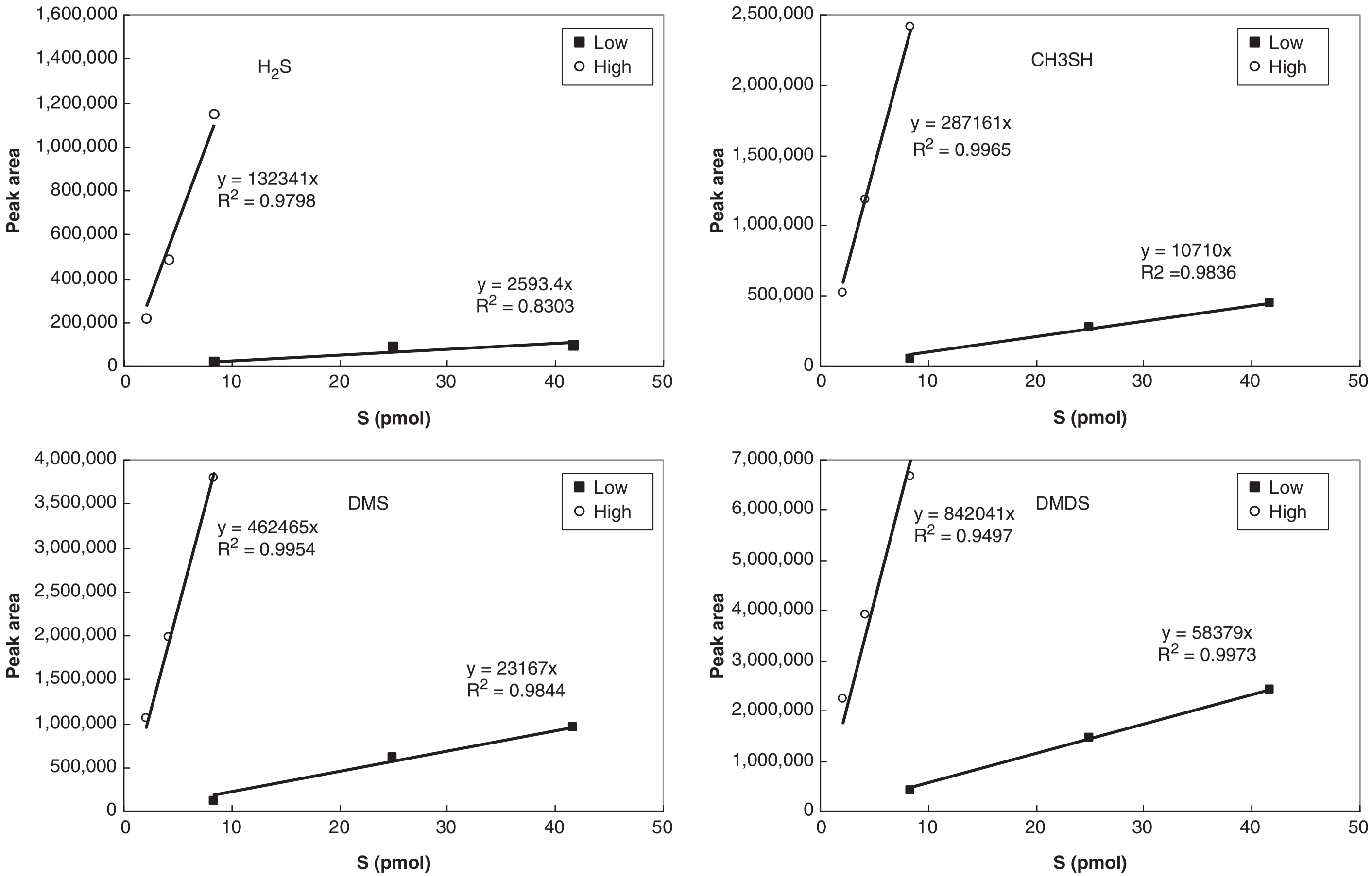

Figure 5. Comparison of GC/PFPD sensitivity made using gaseous RSC standards containing H_2S, CH_3SH, DMS, and DMDS between a high mode, loop (500 µL) injection system and a low mode combination of a Peltier cooling (PC)/thermal desorption (TD) unit. For reference, the calibration slope ratios between the high/low (H/L) mode setting presented in this figure are also shown as the results obtained on 5 September 2004 in table 1.

Table 1. Comparison of RSC calibration slope ratios of the GC/PFPD system was made using the data sets obtained by both high and low (H/L) detection modes.

Experimental date	H_2S	CH_3SH	DMS	DMDS
A. H/L ratios[a] with the high-mode loop capacity of a 500 µL size				
27 August 2004	36.8	23.6	16.9	22.6
5 September 2004[b]	51.0	26.8	20.0	14.4
Average	43.9	25.2	18.5	18.5
SD	10.1	2.29	2.14	5.80
B. H/L ratios with the high-mode loop capacity of a 10 µL size				
9 January 2004	58.4	29.6	15.1	27.9
8 May 2004	63.1	28.8	23.2	55.8
23 September 2004	57.1	33.5	21.4	38.4
Average	59.5	30.6	19.9	40.7
SD	3.14	2.52	4.27	14.1

[a] The H/L ratios are computed using the high-mode loop sizes of the most (10 µL) and least sensitive results (500 µL). For the derivation of H/L ratios, calibration for a given day was made by running the two different modes continuously for a short time period.

[b] The results of 5 September 2004 are also shown with the respective calibration slopes of both high and low mode settings in figure 5.

Table 2. Comparison of the GC/PFPD instrumental detection limits (evaluated in terms of absolute mass of the compound in picograms) between both high and low detection modes.

Experimental date	H_2S	CH_3SH	DMS	DMDS
A. DL values for a low-mode GC/PFPD setting				
30 April 2004	58.4	13.4	12.7	13.1
9 May 2004	46.5	10.5	10.5	10.8
2 June 2004	18.1	9.30	9.35	8.85
14 June 2004	10.2	5.44	4.53	4.03
23 July 2004	10.2	6.64	6.37	7.21
6 August 2004	28.1	17.7	19.2	20.5
18 August 2004	21.8	11.8	11.7	11.3
5 September 2004	21.9	15.3	11.5	10.9
Average	26.9	11.3	10.7	10.8
SD	17.2	4.18	4.43	4.81
B. DL values for a high-mode GC/PFPD setting (10 µL loop results)				
20 January 2004	0.27	0.17	0.16	0.17
8 May 2004	4.14	0.93	0.94	0.97
Average	2.20	0.55	0.55	0.57
SD	2.74	0.54	0.55	0.56

from the results of our recent study in which recovery rates of the PC/TD system were demonstrated to approximate those of the direct injection system [10]. Note that the analytical results in the previous study were obtained using a more sophisticated GC instrumental setting and standards prepared in an identical manner with the application of the identical split ratio (5:1) for both the GC injector and the PC/TD system; however, the present study was made by the different GC instrumental set up without the application of the split mode for both modes. In addition, the RSC standards used in the present study are prepared independently between high- (SD) and low-mode (BD) analysis; the use of the latter preparation method can introduce analytical bias relative to the former [12].

To provide an extended basis for comparing absolute performance between the two different analytical modes, their detection limits can also be quantified by three times the SD values of minimum signals distinguished from noise (refer to table 2). As measurements were commonly made in the low mode setting, more DL data are available for it. In addition, as the computation of H/L ratios was done on a random basis, the experimental dates for tables 1 and 2 differ in many cases. The results of this comparison, however, confirm the fact that there are also large differences (e.g. 10–20 times depending on S compounds) in their absolute performance with respect to the detection limits.

4. Conclusion

In order to systematically compare the analytical properties of S compounds in high- (source-affected) and low-concentration (ambient air) samples, the detection characteristics of the GC/PFPD have been investigated using a dual-mode GC/PFPD detection system with four different S compounds: H_2S, CH_3SH, DMS, and DMDS. For the purpose of this study, this dual-mode system with high and low analytical settings was tested by calibrating RSC standards at varying concentration ranges. According to the present study, different S compounds maintain a good consistency in their relative calibration patterns between the two contrasting analytical modes. When the high mode setting was tested, it was found that there were large differences in sensitivities among different RSCs. The relative enhancement in GC/PFPD sensitivity across different S compounds (such as $H_2S < CH_3SH \sim DMS < DMDS$) may reflect differences in their physicochemical properties (e.g. different number of S atoms for a given molecule) and instrumental response. The high mode setting for the analysis, designated for air samples above a few tens of ppb concentration range, was found to experience a significant enhancement in its absolute sensitivities (e.g. depending on loop size) relative to the low mode setting. Despite large differences in their absolute detection properties between the two modes, their relative detection properties were found to be quite consistent among different S species.

The results of our study suggest a number of interesting aspects in the S gas detections or RSC measurements from various types of environmental samples. In light of variable concentration ranges of RSC in environment samples, it is recommended that a multiple analytical mode for S analysis be developed, as introduced in this study; this may then help reduce the analytical uncertainties arising from the changes in the concentration ranges (especially in the case of H_2S) for a group of samples collected under the mixed environmental conditions. In addition to the complexities associated with the collection of GC/PFPD responses over varying concentration ranges, one should recall that the authentic differences in physicochemical properties between different S gases can be incorporated with GC/PFPD responses in a highly unique manner.

Acknowledgements

This work was supported by a Korea Research Foundation Grant (KRF2005-201-C00045). Analytical support provided by Ms Y.J. Choi and Mr S.I. Oh during this study is greatly appreciated.

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