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The evaluation of recovery rate associated with the use of thermal desorption systems for the analysis of atmospheric reduced sulfur compounds (RSC) using the GC/PFPD method

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Abstract

In this work, the recovery rate (RR) of preconcentration technique was examined using a combination of the Peltier cooling (PC) and thermal desorption (TD) system for the gas chromatographic (GC) analysis of reduced sulfur compounds (RSC) in air. The possible loss or gain of analytes resulting from the use of the PC/TD system was estimated by analyzing equimolar standards (10 ppm) of four S compounds including H_2S, CH_3SH, DMS, and DMDS in two different manners: (1) by injecting directly the four S compounds into the GC via injector and (2) by introducing them through the PC/TD system. When a series of tests were conducted on different types of gas media (ultrapure air versus N_2) and across varying relative humidity (RH), it was found that the RR values for the four S compounds vary from 80 to 110% range. The overall results of our study thus indicate that the RR for the PC/TD system is fairly good and that subtle differences in their RR values may reflect the combined effects of different factors investigated in this study such as types of gas media, RH change, and properties of target analytes (e.g., recovery rate of the least (H_2S) versus the highest compound (DMDS)).

Keywords: GC/PFPD; Reduced sulfur compound (RSC); Hydrogen sulfide; Recovery rate; Peltier; Thermal desorption

1. Introduction

In the analysis of environmental samples, reduced S compounds (RSC) belong to a group of compounds that require most skillful approaches due to the complexities involved in their detection, as they have dramatically variable concentration ranges, from a few ppt to a few hundreds ppm [1,2]. In reality, however, the analysis of RSC contained in environmental samples is confronted most frequently with a technical difficulty in detecting lower-bound concentrations such as ambient air samples with a small ppt range (e.g., [1]). Until recently, the combination of gas chromatography (GC) and FPD has been one of the most common methods for S detection [3,4]. Hence, introduction of improved techniques like sulfur chemiluminescence detection (SCD) or pulsed flame photometric detection (PFPD) helped us extend our capability to monitor both absolute and relative response behavior of RSC against GC techniques, e.g., lowering detectabilities by two to three orders of magnitude in comparison with those of FPD [5–8]. However, despite such improvement, the analysis of ambient air samples still requires preconcentration tools, e.g., cryofocusing (CF) and thermal desorption (TD) technique [9].

Most preconcentration tasks have previously been conducted by a laboratory-based or hand-made TD system. However, there has been a gradual shift from manual systems to a commercialized automatic TD system; this modified system can efficiently facilitate the TD process with an electronically regulated desorption stage and the Peltier cooling

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(PC) (i.e., eliminating the inconvenient use of liquid N_2). Although application of these improved systems allows RSC measurements at low concentration ranges, many uncertainties still remain concerning the possible introduction of bias due to the additional analytical system (i.e., PC/TD system).

Our research team has been involved in developing GC/PFPD techniques for RSC analysis by means of a dual system equipped with a loop injection (LI) system (high concentration mode for samples above 10 ppb concentration range) and a PC/TD system (low concentration mode below 10 ppb concentration range) [10]. The results of this study indicated that relative detection properties of different S compounds are maintained in a highly consistent manner between the two different analytical settings. The main purpose of this study is to examine the extent of bias in the GC/PFPD performance due to the use of a PC/TD system in measuring samples with significantly low RSC concentrations. To evaluate the performance of the system, we attempted to measure recovery rates of GC/PFPD by comparing the GC responses for the same amount of four different sulfur compounds between high (i.e., via GC injector to GC column) and low mode settings (i.e., transfer of analytes into GC via a PC/TD system). The results of our preliminary work on TD applicability are presented in this paper.

2. Materials and methods

2.1. Configuration of analytical settings

In our laboratory, as we intended to measure S gases over a broad concentration range, a GC setting for S gas measurements was configured to measure samples with both low and high concentration ranges using low and high set-up modes, respectively. The distinction between the two different modes can be made both by the target range of the analyte concentrations and by the analyte delivery mode (LI or PC/TD type) [10,11]. In this study, our evaluation of the recovery rate of the PC/TD system was, however, attempted in a very simplified manner: (1) direct injection of high concentration equimolar standards (200 μl of 10 ppm standards corresponding to about 82 pmol each) of four sulfur compounds through a GC injector and (2) injecting the identical amounts of the analytes in the introductory line of the PC/TD system and checking the GC performance in the same manner. As shown in Table 1, the single dosage (200 μl of 10 ppm standards) was injected repetitively, regardless of system; the high mode analysis was conducted simply as direct injection through a GC injector interfaced with a PFPD (Model 3800, Varian Technology). In a manner analogous to this direct injection, the analysis of RSC was also conducted by the same GC but through a PC/TD system equipped with the UNITY air server model developed by Markes Ltd. (UK). The high mode analysis of the present system relying on the direct injection of samples through the GC injector can be distinguished from that for the dual injection system introduced in our recent study [10]; the latter system was basically built on and operated by a loop injection system which exhibits notable changes in sensitivities as a function of loop capacity.

Table 1
Conditions for the recovery rate test on thermal desorption (TD) system

Major condition			
[A] Information concerning the amount of sample loading at injection split ratio of 13:1			
STD concentration (ppm)	10		
Volume of injection (μl)	200		
Amount of analyte injected (pmol)	81.8		
[B] Computation of response factor (RF) for four S compounds under investigation			
	Integrated area (unitless)[a]		Response factor (area/pmol)
	Mean	S.D.	
H_2S	462272	26092	5651
CH_3SH	489779	34318	5988
DMS	429029	24333	5245
DMDS	860748	117435	10523

[a] Peak area information obtained by triplicate injection of S gas STD (refer to [A]) to the GC system at 13:1 injector split ratio.

To provide a basis to evaluate the recovery rate of this PC/TD system, we established an experimental plan to run a high mode setting (i.e., direct injection via injection port) initially (as a baseline reference for all comparisons) and to run a low mode setting (i.e., through a PC/TD system) under the varying conditions by comparing different gas media (ultrapure N_2 and air) and by varying RH values (0, 60, and 80%). Hence, to begin with, a single point calibration of the high mode setting was performed to derive the response factor (RF) for all four RSC. In order to allow simple comparison of the PFPD 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 S_2 complex), the calibration procedure can be facilitated by handling a simple first-order equation. As a first step of calibration, a fixed amount of standard with equimolar concentration (i.e., 200 μl of 10 ppm or about 82 pmol) was loaded into the GC system via injector. These standard gases were purchased at equimolar concentrations (10 ppm with ±5% accuracy) of four target S gases (Ri Gas, Corp., Korea).

On the other hand, to derive the results for the matching conditions of the low mode setting, the PC/TD system was operated through the following steps. First, the Tedlar bag containing ultrapure gas media with a given RH value was connected to a PC/TD line, and the sample was transferred at flow rate of 50 ml min^{-1} for a duration of 4 min. This step can hence be interpreted to yield a dilution effect of the original 200 μl standard (10 ppm) with 200 ml of mixing media (either pure air or N_2). After the initiation of the transferring stage, the identical amount of standard gas was also injected through a temporary injection port installed in the connection line between the Tedlar bag and PC/TD system using the same gas-tight syringe. Then, the preconcentration was performed by the cold trap consisting of two different adsorbents (silica gel and carbotrab B) and a Peltier cooling unit at −15 °C. After the PC stage was completed, S compounds were desorbed thermally by heating the cold trap at 250 °C. The cold trap was heated rapidly (at 60 °C/s) to allow quick desorption and transfer of S compounds to the analytical column without additional cryofocusing. Finally, the analytical components were detected by the GC/PFPD system for the quantification of the S compounds.

As the S gases were transferred to the GC column, operation of the GC system was set to proceed in the following sequence. Separation of different S compounds was made at the following conditions. Temperature (T) program was initiated so that the oven temperature was maintained as: (1) T (initial): 80 °C for 3 min; (2) T (ramping): 10 °C min^{-1} rate; (3) T (final): 200 °C. To acquire an optimum resolution between different S components, we used a CP-Sil 5CB column (60 m × 0.32 mm, 5 μm i.d.) at column flow rate of 1.8 ml min^{-1} (N_2 as carrier gas) with each running cycle ending at 20 min intervals. To provide pulsed flames into the combustor (15 mm length and 2 mm i.d.), the detector was maintained at 200 °C and gases were supplied with flow rates of H_2 = 14, Air1 (wall gas) = 17, and Air2 (combustor) = 10 ml min^{-1}, respectively. In the case of the low mode setting, control of the PC/TD system was made as follows: cold trap (low end at −15 °C and thermal desorption at 300 °C with 5 min holding), outlet split with the 5:1 ratio at a 5 ml min^{-1} flow, and flow path temperature of 80 °C.

3. Results and discussion

In this study, the extent of bias in the GC/PFPD performance was examined with respect to the use of a PC/TD system in measuring samples with significantly low RSC concentrations. To account for the factors affecting the recovery rates of the PC/TD system, we conducted a series of laboratory experiments under varying experimental set-ups with RH (0, 60, and 80%) and with different gas media (ultrapure air and N_2). In Table 2, RR values derived using ultrapure N_2 are presented at three different RH values of 0, 60, and 80%. In this Table, RR results for three replicate analyses are shown for each RSC with the basic statistical parameters including mean, S.D., and R.S.E. In Table 3, RR values estimated under the same conditions of RH but with the ultrapure air are also presented. The results of these recovery rate tests are also plotted in Fig. 1 to facilitate direct comparison between the two gas media at varying RH values. According to the results shown in Tables 2 and 3, they generally tend to exhibit strong similarities with some discrepancies. It may be reasonable to expect that the introduction of the additional pathway (like a PC/TD system) in the GC analytical line may cause negative bias (e.g., wall loss), considering strong reactivities of RSC [12]. However, the results of this test indicate that such effect may not be significant and can be limited to a few species. These results seem to fall in a fairly constant and narrow range of RR values, regardless of media types. In the case of ultrapure N_2 media, the RR values in 90–110% range show that the use of the PC/TD system may lead to both positive and negative bias. Particlularly, RR values of H_2S alone were below 100% at RH values other than 0%. According to this finding, it may be possible to infer that the use of the PC/TD system may be more plausible to induce a positive, rather than a negative, bias. In addition, it is also interesting to note that RR values tend to decrease with increasing RH values, although the magnitude of such change is not significantly large. This result suggests that the humidity removal efficiency of the Nafion dryer installed within the PC/TD system tends to decrease with increasing humidities.

As shown in Table 3, it is noted that the results for the ultrapure air are similar to those of ultrapure N_2 to a large extent. Although RR values for most RSC exhibit around 100%

Table 2
Results of TD recovery rate (RR) test at varying relative humidity (RH) values using a purified N_2 gas[a]

RH (%)	Compound	Concentration (pmol)					R.S.E. (%)	RR (%)
		First	Second	Third	Mean	S.D.		
0	H_2S	84.7	86.5	81.2	84	2.7	1.86	103
	CH_3SH	93.9	95.0	90.5	93	2.3	1.44	114
	DMS	97.0	90.1	81.9	90	7.6	4.87	110
	DMDS	95.9	96.4	89.5	94	3.8	2.35	115
60	H_2S	77.1	74.3	88.8	80	7.7	5.58	98
	CH_3SH	85.3	86.9	105.1	92	11.0	6.85	113
	DMS	83.0	84.5	100.0	89	9.4	6.09	109
	DMDS	89.9	82.7	107.8	93	12.9	7.98	114
80	H_2S	71.9	85.8	71.4	76	8.2	6.20	93
	CH_3SH	81.5	100.6	82.4	88	10.8	7.06	108
	DMS	81.7	95.0	85.5	87	6.9	4.54	107
	DMDS	81.6	98.6	85.5	89	8.9	5.81	108

[a] Recovery rates (RR) of a PC/TD system are computed by comparing the RSC concentrations (pmol) determined using response factors of direct GC injection at 81.8 pmol.

Table 3
Results of TD recovery rate (RR) test at varying relative humidity (RH) conditions using a purified air[a]

RH (%)	Compound	Concentration (pmol)					R.S.E. (%)	RR (%)
		First	Second	Third	Mean	S.D.		
0	H_2S	70.3	69.6	66.3	69	2.1	1.78	84
	CH_3SH	84.8	82.2	87.3	85	2.6	1.75	104
	DMS	76.0	70.1	80.8	76	5.4	4.09	92
	DMDS	92.0	87.2	88.6	89	2.5	1.63	109
60	H_2S	68.8	70.4	69.5	70	0.8	0.68	85
	CH_3SH	83.6	84.6	84.2	84	0.5	0.34	103
	DMS	72.8	75.6	73.8	74	1.4	1.10	91
	DMDS	82.6	86.2	85.0	85	1.8	1.24	103
80	H_2S	68.8	71.4	70.2	70	1.3	1.09	86
	CH_3SH	84.2	82.2	87.5	85	2.7	1.85	103
	DMS	76.2	73.6	76.2	75	1.5	1.14	92
	DMDS	84.3	82.7	84.3	84	0.9	0.63	102

[a] The same approaches applied as introduced in Table 2.

in this case, they tend to be systematically lower than those seen from experiments using ultrapure N_2. The compounds such as H_2S and DMS seem to show the most noticeable reduction in RR values. For instance, RR values of H_2S at 80% range suggest some interesting possibilities; as the large amount of oxygen is introduced into the system in the case of ultrapure air experiments, it may lead to a loss type of oxidative destruction for reactive species like H_2S. However, such results for DMS may not necessarily imply similar effects in other gases, as all the results for the ultrapure air are reduced systematically relative to ultrapure N_2.

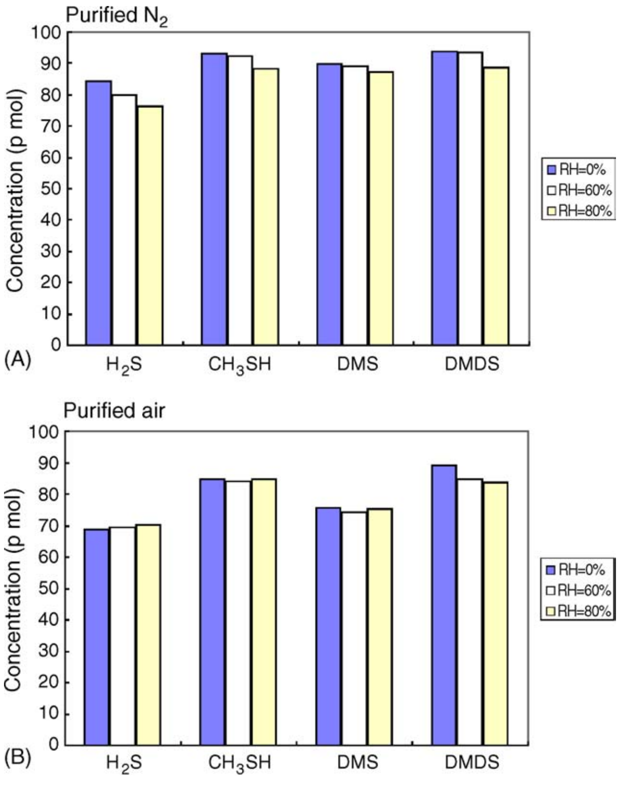

Fig. 1. Comparison of TD recovery rate patterns between different reduced sulfur compounds.The absolute amounts of RSC detected after loading equimolar amounts of four sulfur compounds (i.e., 82 pmol) are compared. For this comparison, tests were conducted by varying relative humidity values of 0, 60, and 80% between purified N_2 and air.

4. Conclusion

In this work, we investigated the recovery rate of the PC/TD system used for the analysis of S gases at a significantly low concentration range. To learn more about the factors affecting recovery rates, a series of laboratory experiments were conducted under varying RH conditions and between different gas media. Our experiments comparing GC performance with direct injection and with the use of PC/TD system indicated that the use of the latter system can introduce both positive and negative bias; however, the magnitude of such bias falls into a fairly narrow range. In addition, there is evidence that the occurrence of those biases is affected by many different factors including changes in RH, types of gas media, and properties of analytes. In light of the bias patterns observed in our RR tests, it may be reasonable to conclude that the use of PC/TD system generally helps maintain the fundamental characteristics of GC performance in the detection of important RSC including H_2S, CH_3SH, DMS, and DMDS.

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