

The effects of sampling materials selection in the collection of reduced sulfur compounds in air

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Received 9 July 2005; received in revised form 12 August 2005; accepted 12 August 2005

Available online 16 September 2005

Abstract

In this study, the analytical bias in the measurements of reduced sulfur compounds (RSC) was investigated in terms of sorptive loss caused by the materials selected for the sample introduction. For the purpose of this study, three vacuum samplers made in the combination of different vacuuming efficiencies (e.g., rapid versus slow sampling) and different materials (i.e., Teflon versus stainless steel (SS)) were tested to evaluate the sampling recovery rate (RR) for five RSCs: H₂S, CH₃SH, DMS, CS₂ and DMDs. To make a parallel comparison of RR, the RSC standard samples contained in one bag were transferred to another bag using each sampling system. Their relative contents between, before, and after the transfer were then evaluated between different samplers to assess the sampling bias caused by the interaction between RSC and the sampling material. In the case of the most reactive compound, H₂S, the sampling loss from the SS inlet line amounted to as high as 45%, while that for the Teflon counterpart was almost insignificant. When the sampling time was arbitrarily elongated (i.e., use of a slow sampler), the sampling loss rate of the SS inlet sampler became more significant with the RR values dropping down from 55 to 70%, across different RSCs. The overall results of our comparative study indicate that the sampling system for the reactive gaseous compounds should be checked for the material feasibility to guarantee sufficient analytical reliability.

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Keywords: Reduced sulfur compounds; GC/PFPD; Sampler; Material; Recovery rate; Removal rate

1. Introduction

In light of the complicated nature of malodor and nuisance, the odor-associated subjects are often considered and treated as one of the most sensitive environmental issues in the modern society [1–3]. The significance of such issues has been recognized broadly from many nations in the world. If residential areas are allocated in the proximity of strong source areas (e.g., land-fill, industrial region, etc.), such issues tend to be dealt more seriously with the rise of major public complaints. Hence, it is often found that the debates remain open to determine the responsibility. However, in fact, as malodor is a sensory pollution, there are also many occasions, when the accused cannot

fully accept the court order or legal decision against the cause of malodor release.

The definition of malodor can be different from culture to culture or between countries. Nonetheless, it generally implies the presence of a stimulating odor (such as H₂S) at concentration levels high enough to disturb humans' sense of smell. It is considered to be a highly delicate task to specifically characterize a broad spectrum of diverse malodor components and to confine their contribution to a given nuisance. Hence, many uncertainties still remain not only in assessing the common nature of malodor but in establishing the tactics for its control.

In an effort to assess the fundamental nature of the malodor phenomenon, numerous study groups have continuously worked on a variety of projects to accurately measure and detect odorous compounds contained in diverse media (e.g., [4–6]). In the early stage of our study, we have developed a GC technique for reduced sulfur compound (RSC) analysis over a wide

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concentration range with the application of a dual analytical system (e.g., [7–10]). The fundamental properties of such system were attested in various manners. For instance, the sorptive loss of analytes within the sample container (e.g., Tedlar bag) was evaluated by combining the calibration data obtained by different standard storage media and among different RSCs [11]. As a continuation of such efforts, the analytical bias associated with the sample collecting technique was examined further in the present study by quantifying the sample loss rate and/or recovery rates (RR) due to the selection of sampling materials through a number of laboratory and field studies. The analytical bias involved in the sampling system (or procedure) was carefully evaluated to place limits on the measurement errors for odorous S compounds.

2. Materials and methods

2.1. Experimental design for the comparison of sampling system

In the present study, the analyte loss (or addition) that can occur in the vacuum sampling system was examined by means of comparing the RSC concentrations in air samples between prior to and after the sample transfer. A number of vacuum-driven bag sampling system were designed and employed for a series of comparative tests (Table 1). To check for analytical

Table 1
Characteristics of RSC sampler types used to compare recovery rate in this study

Sampler type	Sampling inlet line material	Sampling time ^a (min)	Reference
A	Teflon	<1	ACEN (AVS-550)
B	Stainless steel	<1	ACEN (AVS-550B)
C	Stainless steel	5–10	Manually produced

^a Assuming the sample volume of 10 l.

uncertainties associated with the selection of sampling materials, the vacuum sampling systems built with different material types were tested against each other. In order to explain the basic properties of different sampler types used in this study, their pictures are also presented in Fig. 1. Depending on the sampling materials and sampling durations, three different samplers were classified into the types A, B and C (refer to Fig. 1(A) for their schematics). Hence, these three samplers can be comparatively tested against each other to diagnose the sampling efficiency and/or bias in the RSC measurements. The type A and B samplers were purchased from a manufacturer (AVS-550 model, ACEN Co., Korea). On the other hand, the type C sampler was built manually in the laboratory. Both A and B samplers were equipped with a high-speed vacuum pump to shorten sampling duration (e.g., approximately 30 s for a 5 l bag). Hence, these two sampler types can be used for the fast collection of samples to allow monitoring of rapid changes in odor occurrences.

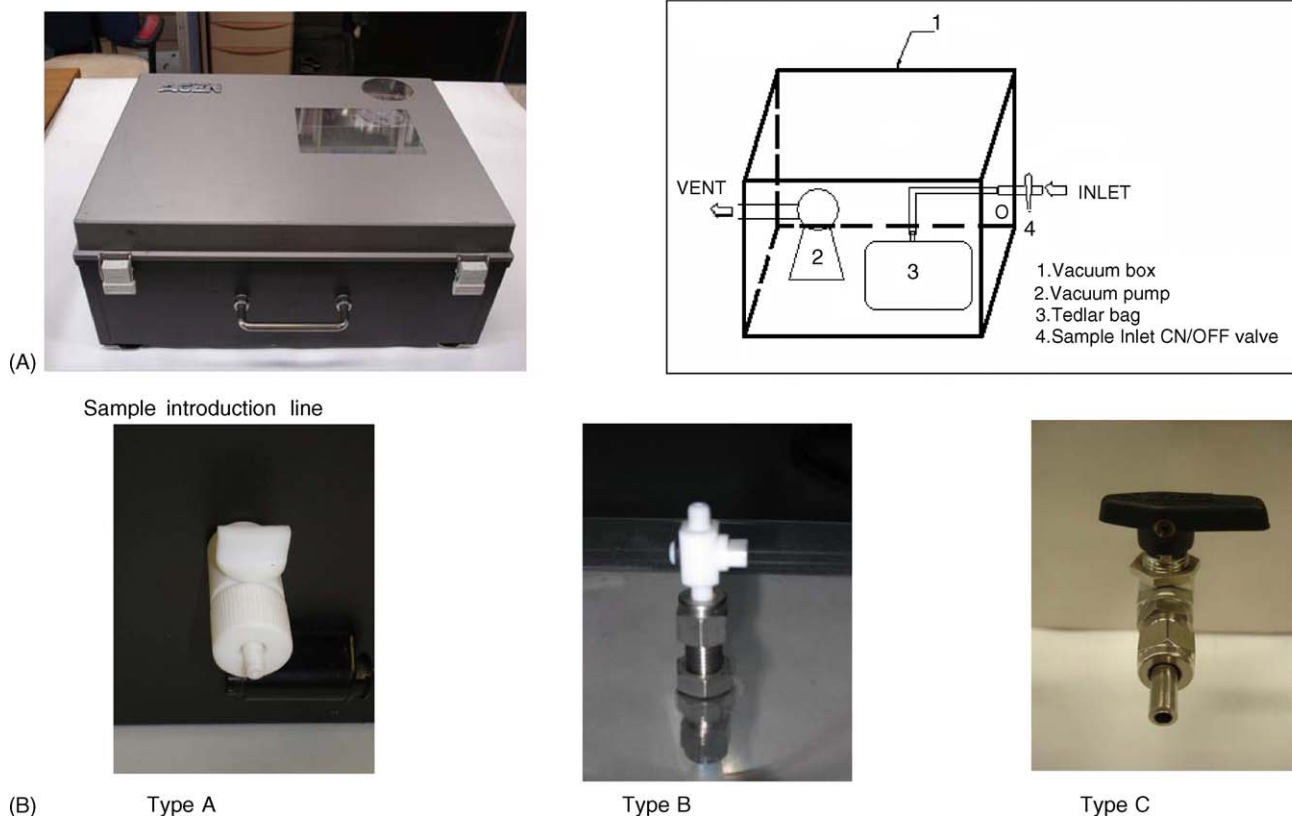


Fig. 1. Pictures of three different vacuum sampler types used for sampling RSC samples: (A) sampler type A (the main body) and the basic structure of samplers used in this study and (B) comparison of sample introduction lines of types A, B, and C.

To evaluate the sampling loss rate of RSC in the use of bag sampler, a series of lab experiments were conducted. In the course of the laboratory experiments, sampling loss rates of RSC were evaluated in a stepwise manner as follows: (1) a number of RSC working standards were prepared and stored in each Tedlar bag and used as the source samples for this comparison test. (2) To initiate this experiment, a Tedlar bag filled with the source samples (i.e., working standard) at given concentrations was connected to each of three samplers (types A–C) with an empty Tedlar bag (to collect target samples) inserted. (3) After securing the connection, a vacuum pump was turned on to start the transfer of RSC standard samples in the source bag (bag 1) to the empty sampling bag (bag 2). This sample transferring process ceased, after approximately one-half of the source samples was transferred to the target bags inserted in the sampler. Both bags were then retrieved and analyzed to measure differences and ratios of RSC contents (i.e., target/source concentration ratios). The analysis of the two Tedlar bags was made on the basis of the GC/PFPD technique as described below.

2.2. Instrumental set-up for the RSC analysis

To compare sampling loss rate of RSC between different sampler types, an analysis of all RSC was made by the gas chromatography (GC). For the analysis of RSC, the GC system (Model DS 6200, Donam Instruments, Korea) was interfaced with a pulsed flame photometric detector (PFPD) (Model 5380, O.I. Co.). Detailed information concerning the GC/PFPD application to the RSC analysis has been described elsewhere [7]. To measure RSC samples over a wide concentration range, a dual injection system was built that can switch in between low (cryo-focusing (CF) via thermal desorption (TD) unit) and high concentration ranges (via direct loop injection onto GC column) [10]. In the present study, the GC system was operated at both injection modes depending on the RSC concentration levels tested. The temperature (T) conditions for the system were set as follows: (1) T (initial): 100 °C for 2 min; (2) T (ramping): 6 °C min⁻¹ rate; (3) T (final): 210 °C at 2 min. To acquire a good resolution between different RSCs, a BP-1 column (60 m × 0.32 mm i.d., 5 μm film thickness, SGE) was used at a column flow rate of 1.2 ml min⁻¹ (N₂ 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.), gases were provided at the following flow rate: H₂ = 11.5, Air 1 (wall gas) = 10 and Air 2 (combustor) = 14 ml min⁻¹. In addition, to allow a 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. The use of the SR function efficiently masks the SR response of the detector (i.e., due to the conversion of S atoms to an S₂ complex). Hence, the calibration procedure of the PFPD system can be facilitated, as if one handles a simple first-order equation. The fundamental analytical parameters covering the analytical performance of the GC/PFPD system is summarized in Table 2.

In this study, RSC standard samples with varying concentration levels were prepared by diluting the primary standard (10 ppm equimolar concentrations of five RSC: Ri Gas, Korea)

Table 2
Analytical performance of the GC/PFPD system used in this study

	DL ^a		Precision ^b (%)
	pg	ppt	
H ₂ S	29.3	25.9	3.00
CH ₃ SH	27.6	17.3	4.90
DMS	12.2	5.87	1.59
CS ₂	4.03	1.59	2.70
DMDS	5.87	1.87	0.57

^a DL values are given in both absolute contents of detectable amounts of analyte (pg = 10⁻¹² g) and mixing ratio terms (ppt = 10⁻¹²). For the latter term, maximum sampling volume of 800 ml was assumed.

^b Relative standard error (R.S.E.) was evaluated by five replicate analysis.

with ultrapure N₂ gas. The working standards prepared at three different concentrations (10 ppb, 50 ppb and 2 ppm) were then employed to examine the effects of concentration differences on the RSC loss rate in relation with the characteristics of each sampler type. In the case of 10 and 50 ppb standards, the RSC analysis was made with the aid of a low mode injection system (i.e., analysis of sub-ppb RSC by the combination of the Peltier cooling (PC) and TD system [10]). On the other hand, when a 2 ppm standard was used for comparison, the analysis was made using a high mode loop injection system [10]. In addition to the lab experiment to assess the RSC sampling loss rate, field experiments were also performed. It should however be noted that the acquisition of all RR data sets in the low mode analysis was made based on a single-point analysis (i.e., without replicate analysis of the same sample) to be free from a significant memory effect in the CS₂ analysis and the associated long duration of blanking procedure. As we intended to produce a series of experimental data sets under the consistent performance conditions of the GC/PFPD setting (e.g., acquisition of comparable data sets within a relatively short duration of 24 h), the adoption of the single-point analysis was inevitable. However, as seen from the results of reproducibility test (Table 2), the data sets produced from our GC/PFPD system can be used with a fairly good reliability.

3. Results and discussion

3.1. Comparison under laboratory conditions using working standards

In Table 3, the results of the laboratory test aiming to focus the material effects on the sampling loss are presented. As a first step, to facilitate the comparison of sample loss, changes in RSC quantities (prior to and after the transfer stage) were compared. The absolute quantities of RSC samples transported to the GC system were assessed by considering the volume of samples loaded to the TD system (refer to Table 3(A)). To make a proper evaluation of the sampling loss as part of the transfer process, original working standards contained in bag 1 were first transferred into bag 2 by running all types of vacuum sampling system shown in Fig. 1. The RSC quantities in both bags were then quantified by running the GC/PFPD system in a compatible manner (Table 3). According to the results shown in Table 3(B),

Table 3
Comparison of an experimental plan and the actual experimental results for the recovery rate (RR) test in the laboratory

Exp. no.	Sampler type	Concentration (ppb)	RSC standard gas (ml min ⁻¹) flow rate	Sample loading duration (min)	Absolute amount loaded (pmol) ^a
(A) Experimental plan					
1	A	10	40	1.0	16.6
2	B				
3	C				
4	A	10	40	2.0	33.3
5	B				
6	C				
7	A	10	40	3.0	49.9
8	B				
9	C				
10	A	50	20	0.5	20.8
11	B				
12	C				
13	A	2 ppm standard injected to GC via a 20 µl loop			0.0017
14	B				
15	C				
Exp. no.	H ₂ S	CH ₃ SH	DMS	CS ₂	DMDS
(B) Experimental results					
Absolute amount (pmol) of RSC actually measured from target bag to which the original RSC working standards in source bag are transferred					
1	19.9	15.9	15.2	17.8	15.7
2	16.8	13.9	14.1	15.3	15.3
3	10.3	12.4	15.4	16.1	15.9
4	37.3	35.1	35.4	OS	OS
5	29.5	32.3	38.0	OS	OS
6	18.8	25.0	29.7	31.4	OS
7	62.7	56.9	61.9	OS	OS
8	44.5	48.2	58.5	OS	OS
9	35.1	44.6	61.0	OS	OS
10	16.2	17.9	23.5	20.3	21.1
11	16.5	18.1	23.8	20.8	20.9
12	11.5	13.8	17.5	15.8	16.0
13 ^b	0.0012 ± 6.2E-05	0.0016 ± 1.8E-05	0.0017 ± 1.2E-05	0.0016 ± 1.3E-05	0.0016 ± 3.6E-05
14 ^b	0.0010 ± 1.1E-04	0.0015 ± 4.5E-05	0.0017 ± 2.1E-05	0.0016 ± 2.4E-05	0.0016 ± 2.4E-05
15 ^b	0.0009 ± 2.8E-05	0.0014 ± 1.2E-05	0.0016 ± 3.8E-07	0.0015 ± 1.4E-05	0.0015 ± 6.9E-06
(C) Recovery rate (%) is computed using the RSC quantities of the prior to (A) and after the transfer (B)					
1	119	95.5	91.3	107	94.6
2	101	83.3	85.0	92.2	91.7
3	61.9	74.5	92.6	96.9	95.4
4	112	106	106	OS ^c	OS
5	88.7	97.0	114	OS	OS
6	56.5	75.2	89.1	94.2	OS
7	126	114	124	OS	OS
8	89.2	96.5	117	OS	OS
9	70.3	89.4	122	OS	OS
10	78.0	86.2	113	97.8	102
11	79.2	86.8	115	99.9	100
12	55.1	66.6	84.2	75.9	76.9
13	73.2	95.9	101	98.9	98.9
14	60.9	91.3	99.8	96.6	95.5
15	55.5	86.7	93.9	92.3	88.4

^a The expected absolute quantities of RSC standards prior to bag transfer are compared at varying pre-concentration set-ups for the thermal desorber (TD) unit connected to the GC/PFPD system.

^b All results made as triplicate analyses.

^c OS: off-scale.

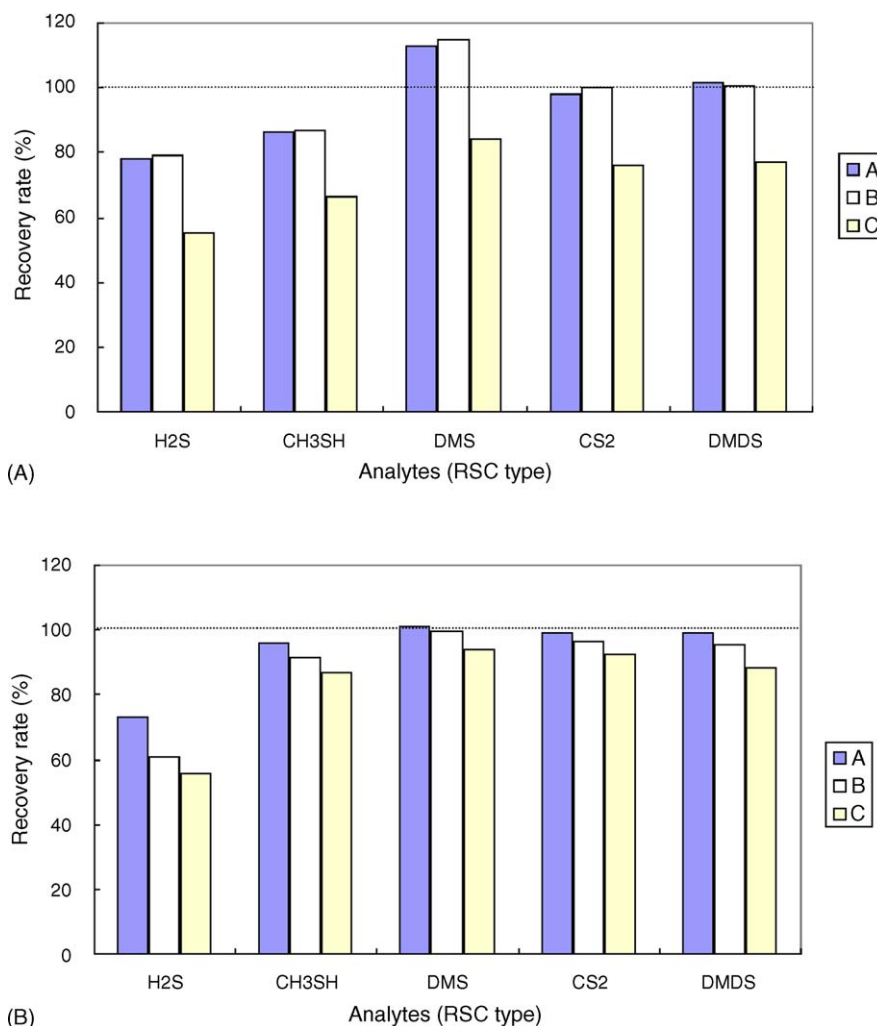


Fig. 2. Comparison of recovery rate test results for different bag sampler types A–C. Results of laboratory experiments computed using both prior to and after transferring: (A) 50 ppb standards and (B) 2 ppm standards.

it seems that the bag loss rates were influenced by such factors as the initial concentrations of the samples (or standard), sampler types, and the physicochemical properties of chemical compounds. It should also be noted that the physical contact of RSC with the inner surface of bag could have resulted in sample loss (e.g., 10–20% loss depending on RSC type [11]). At this stage, we cannot separate the causes of RSC loss either due to: (1) the sampling loss in the transfer stage and/or (2) the second phase of the wall loss effect simply due to the sample transfer from one to another bag. Consequently, absolute differences in concentration levels, shown as the results of this experiment, cannot be attributed to either one of those two factors. However, RR patterns shown in Table 3(C) are still meaningful, as they reflect the effects of sampling materials in a relative sense; this is because one can assume that the physical loss within the wall surface occur to the similar extent in the same concentration range between the matching sample bags. As such, the relative ordering expressed in terms of RR values can show the effects of the selection of sampling materials.

As an example to explain such variabilities in relative RR patterns, some of those results are also plotted in Fig. 2. If these

results are compared among different RSCs, clear distinctions exist between the two. The results generally show a notable reduction in recovery rates, especially in H₂S and CH₃SH, while other RSCs generally maintain fairly good recovery rates. This type of patterns is distinguished further by the sampler type and/or the initial concentration used for transfer experiment. It is found that the results of sampler C generally exhibit a strongest reduction in RR relative to the other sampler types. If the results are compared after grouping into the initial concentration of the working standard, the patterns of RR reduction are significantly different from the ones compared at high standard concentrations (50 ppb and 2 ppm) relative to the low ones (10 ppb).

Although most heavy RSCs (like DMS, DMDS and CS₂) tend to maintain relatively good RR across varying concentration range, their light counterparts (like H₂S and CH₃SH) are found to be affected more sensitively by the changes in absolute standard concentrations. As such, the results of this test in fact indicate some important aspects of the RSC recovery patterns. It is most interesting to find that the RR values of heavy RSCs are not sensitively affected by the initial concentration of the working standard or by sampler types relative to light RSCs.

In contrast, those unstable or light compounds (like H₂S and CH₃SH) show large variations in their RR. In the case of H₂S, its RR values appear to be the largest in the lowest working standard concentration range of 10 ppb where analytical uncertainties are relatively large. This observation may reflect the fact that the analytical uncertainties increase, while the stability of working standards may decrease due to the reduction in concentration for a certain compound. If one compares the pattern shown in Table 3B, the least RR values are seen from most experiments made by working standards with high RSC concentration (50 ppb and 2 ppm) relative to low concentrations (10 ppb). In some senses, the results of our study are quite compatible with the previous findings of Sulyok et al. [12]. These authors attempted to analyze sorptive losses of RSC in their sampling stage. Although their study did not examine all potential variables causing the RSC loss, they were able to find the material effect on the sampling loss. By comparing a number of tubings with different material types (Teflon, PVC and silicone), they found Teflon to yield the least sorptive loss of RSC. However, they also noticed that a material like silicone can selectively remove heavy RSCs more effectively than light RSCs.

3.2. The evaluation of relative RR using samples collected from the field conditions

To further examine the sampling loss rate under actual field conditions, our measurements were extended to quantify the sampling loss rate under a strongly polluted field condition. A leather processing company was selected for this purpose, as it is well known as a highly potent source for RSC emissions. To explain these field-based RR tests, we undertook an approach that is slightly different from that of standard-based comparison made in the laboratory, which is based on the comparison between the results of different bags (Table 3).

Table 4 presents the results of the field experiments made in a leather processing company. All of field experiments were conducted from three different locations in the leather processing company including: (1) a scrubber (ventilated air), (2) an indoor leather processing unit and (3) inside a sludge container. As this part of experiments was designed to measure RSC concentrations directly under the actual field conditions, they do not have matching data pairs for a parallel comparison as the laboratory data sets (e.g., between bag 1 and 2). Hence, all of these results were explained simply after being normalized against those exhibiting the most stable patterns (type A). The results in fact indicated that the absolute RSC concentration levels could differ greatly among the sampling locations. Acknowledging the fact that many RSC concentrations from both indoor processing units (Exp. nos. 4–9) were not quantified, the data from the scrubber outlet, covering a moderately wide concentration range, were selected (as the most optimal case) to make a meaningful comparison (Exp. nos. 1–3). The scrubber results clearly show that the relative RR values decrease on the following order: A > B > C. For instance, in the case of H₂S, the relative RR values are computed to be A = 100%, B = 68% and C = 48%. Thus, the relative RR of H₂S is approximately two times lower in type

Table 4

Comparison of recovery rate (RR) test under the field conditions (in a leather-manufacturing factory)

(A) Sampling conditions of the field experiments					
Exp.	Sampler type	Sampling site			
1	A	Ventilated samples from scrubber			
2	B				
3	C				
4	A	Indoor operation unit			
5	B				
6	C				
7	A	Indoor air in sludge reservoir unit			
8	B				
9	C				
(B) Results of recovery rate test					
Exp. no.	H ₂ S	CH ₃ SH	DMS	CS ₂	DMDS
RSC concentrations (ppb)					
1	48157	66.9	2.48	5.94	0.25
2	32773	59.5	1.72	5.41	0.21
3	23311	53.7	1.26	3.89	0.17
4	640	1.60	ND	0.85	0.02
5	467	ND	ND	0.70	0.02
6	134	0.80	ND	ND	ND
7	227	22.6	0.08	OS	0.90
8	113	11.7	ND	ND	ND
9	93.8	5.62	0.03	34.8	0.42
Relative recovery rates (RR)					
1	100	100	100	100	100
2	68.1	89.0	69.2	91.0	85.3
3	48.4	80.4	50.9	65.5	70.6
4	100	100	–	100	100
5	73.0	–	–	81.4	67.8
6	20.9	50.3	–	–	–
7	100	100	100	–	100
8	50.0	51.8	–	–	–
9	41.4	24.9	36.9	–	46.2

The results obtained from the actual field samples are compared directly. ND: not detected; OS: off-scale. RR values computed by normalizing all values from B and C sampler types to those of type A.

C than in type A. Similar patterns were also seen in the case of CH₃SH. In contrast, the relative RR values of heavy RSCs were not so different across different sampler types. Hence, in some senses, the observed relative RR patterns show some compatibilities between laboratory and field experiments. Note that recovery rate of light RSCs reduced significantly relative to heavy RSCs. If one acknowledges the fact that the significantly high RSC levels prevailed in the field conditions, the findings of a notable reduction in recovery rates of field data, especially with the light RSCs may be a common pattern at the high standard concentrations (e.g., as seen from the laboratory test). The observed RR values of H₂S in the indoor unit drop down to 21% (Exp. no. 6); this suggests the possibility that the tubing material of stainless steel (SS) can cause the potential loss of RSC under many circumstances, especially when it is exposed to high RSC concentrations.

4. Conclusions

In this study, the sampling loss rate of RSC was investigated in terms of analytical bias involved in the selection of sampling material types and the concentration levels used for the test. In order to examine the potential effects of sampling parameters (e.g., sampling duration, vacuuming capacities, initial concentrations, etc.), we attempted to evaluate such analytical biases in various respects. According to the comparative tests made both under laboratory and field conditions, several patterns in relative RR were derived. If the RR results are compared among different sampler types, the most reliable results were seen from those made of Teflon for rapid sampling (type A sampler). If a comparison is made among different RSCs, the most stable results were seen from heavy RSCs (DMS, CS₂ and DMDS). However, the lighter ones exhibit a contrasting pattern in that the patterns are persistent with the sampler built by inert sample lining materials (e.g., type A sampler using Teflon).

The results of the RR test based on different sampling materials indicate that the samplers built using metal materials (SS) can suffer more significantly than others, particularly from the light RSC (like H₂S). In addition, when one uses the SS-based sampler under the field conditions, the reduction in RR can be more significant with the elongation of contact duration (e.g., comparison of our results made between the sampler types B and C). Because of the effect of such complicated conditions, the relative RR values for less inert material (like stainless steel) can cause significant bias in the RSC measurements under the

field conditions. The results of this study thus suggest that the selection of sampling materials in the sampling stage is one of the essential factors, while the RSC levels in the surrounding environment may also exert important controls on the relative RR pattern.

Acknowledgement

This work was supported by the Korea Research Foundation Grant (KRF-2005-201-C00045) funded by the Korean Government (MOEHRD).

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