

The role of sample collection method and the bias between different standard matrices in the determination of volatile organic compounds in air

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Abstract This study was undertaken to assess the relative bias between two types of sampling methods for volatile organic compounds (VOCs), i.e., sorbent tube vs. bag sampling methods and between different standard phases. For the purpose of this comparative study, gaseous standards containing three major aromatic VOCs (benzene, toluene, and xylene—commonly called BTX) were analyzed by thermo-desorption gas chromatography (TD-GC) with flame ionization detector. According to our findings, the relative response of target compounds can be smaller in the bag method than in the tube method. Although the relative bias varies with the sample transfer conditions for the TD, the mean slope values of the former are smaller by up to 20% relative to the latter, possibly due to sorptive loss on the bag sampler. In addition, the effects of different standard matrices (i.e. liquid and gas phases) were also examined using the sorbent tube method. The results indicated that the slope values of the gas-phase standard were smaller by half (about 43–56%) than the liquid-phase standard. Consequently, information concerning the extent

of relative bias between sampling methods (e.g., bag and tube) or standard matrices (e.g., gas and liquid) should be considered as one of the key factors in TD applications.

Keywords Volatile organic compounds · Thermal desorption · Calibration · Tube sampling · Tedlar bag

Introduction

At present, gas chromatography (GC) is the most commonly used technique for the quantitative analysis of volatile organic compounds (VOC) [1–3]. The GC method offers a combination of high selectivity, precision, separation between compounds, and a wide linear dynamic range. However, unless the VOC samples are representative of very strong source environments (like industrial areas or landfills), they cannot be quantified without the modification of an analytical technique such as the employment of additional setups like the thermal desorber (TD) or the microextraction technique [4–6]. These alterations of the instrumental system, however, cannot be validated without considering the subsequent changes in the analytical properties.

The most common approaches used for the collection of VOC samples generally involve either whole air sampling (such as glass bulbs, canister bags, polymer bags, and Tedlar film bags) or preconcentration method (i.e., the use of tube sampler filled up with sorbent materials or solid phase microextraction (SPME)). The advantages and disadvantages involved in these sampling approaches are relatively well known [7–11]. The use of the former is effective for repetitive analysis but can suffer from low recoveries of polar compounds. In contrast, the latter approaches can be limited in terms of the reproducibility, artifact formation, or water sorption problems. Because of

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the diverse features involved in different sampling options, the choice of a sampling method is often tied to analytical options or the level of performance [7]. For instance, the analytical results of the cryofocusing (CF) method can differ depending on the selected pathway of sample transfer into the CF system, i.e., either directly from the Tedlar bag (bag method) or after the initial desorption of sorbent tube in TD (tube method).

As the type of sampling approaches can ultimately affect the quality of the chemometric analysis, a better knowledge on the type and nature of bias between different sampling methods is a valuable asset in the analysis of VOC. In an effort to explore the fundamental aspects of sampling bias, a comparative analysis was designed to systematically diagnose the differences between the bag and tube sampling. To this end, a series of laboratory calibration experiments were conducted by analyzing the identical gaseous VOC standards through the application of two collection methods on a parallel basis. In addition, consideration was also given to examine the effect of sample matrix type (between gas and liquid) in the application of the sorbent tube method. As gaseous samples are collected on sorbent packed in tube, their quantification based on gas phase standard is the most reliable option. However, if the calibration is conducted by loading liquid phase standard on the tube, the resulting quantification can yield a significant underestimation of data due to the enhanced sensitivity of such standard [12]. The discrepancy caused by standards of different phases on sorbent tube method is hence tested and discussed based on ancillary experimental data.

Experimental

Experimental approaches for comparative sampling methods

In this study, a comparative analysis was made to accurately assess the relative properties of the bag and tube methods in the analysis of VOC. To this end, three major aromatic VOCs including benzene, toluene, and p-xylene (commonly called, BTX) were selected as the target components. The basic physicochemical properties (e.g., molecular formula, molecular weight, and chemical structure) of these target compounds are shown in Table S1 (Electronic Supporting Material: ESM). The analysis of VOC was made by the gas chromatograph with a flame ionization detector (FID) (DS 6200 model, Donam Instruments, Korea) and a thermal desorber with an air server (AS) unit (UNITY model, Markes, Ltd., UK).

To facilitate the comparison between the two types of calibration experiments (based on the bag and tube sampling methods), they were named as Exp-B (bag) and

Exp-T (tube), respectively (Fig. 1). To scrutinize the detection properties of different VOC species in relation to different sampling approaches, the performance of both approaches were evaluated on a parallel basis. For both experiments, the gaseous standards (GS) were prepared using a 10 L Tedlar bag with single polypropylene septum fitting (Product code: 232-08, SKC, Eighty Four, PA, US). The primary standard (PS) gases containing the three target compounds of BTX were purchased to have an equimolar concentration of BTX at $20 \mu\text{mol mol}^{-1}$ level (Ri gas Co., Korea). To conduct each calibration in relation to each sampling method, the GS of BTX were prepared at equimolar quantities to cover a total of 4 concentration ranges (20, 50, 100, and $200 \text{ nmol mol}^{-1}$). The preparation of the WS was accomplished by a one-step dilution of the PS transferred to a 1 L Tedlar bag with ultra pure N_2 gas with the aid of a gas-tight syringe.

For both Exp-B and -T, the analysis of VOCs was made to draw 4-point calibration curves by combining the experimental results from each of all 4 WS concentrations prepared in 4 separate bags. In Exp-B, the analysis of gaseous VOC standards prepared in each Tedlar bag was conducted, as if unknown samples were collected by the bag sampling method. The bag-based analysis of BTX was initiated by transferring VOC standard representing 4 concentration levels with the aid of AS unit to the CF system at the duration of 0.4, 1, 2, and 4 min at a fixed flow rate of 50 mL min^{-1} . For tube method, a stainless steel tube (5 mm id, 6.3 mm od, and 9 cm length) was packed with Tenax TA sorbent (60/80 mesh, porous organic polymers with specific surface area of $35 \text{ m}^2 \text{ g}^{-1}$). To reduce the source of bias in the treatment of standard for both Exp-B and -T, the GS left over in the same Tedlar bag (after Exp-B) were again tested in Exp-T. However, as the sample loading in Exp-T was made externally (i.e., out of AS/TD line), the physical conditions for the sample loading on the tube was carried out to mimic those of AS unit for Exp-B as much as possible. To initiate the sample loadings for Exp-T, the sampling inlet (in septum fitting body) of the Tedlar bag containing each standard is connected to tube sampler. This tube is then connected to the vacuum pump (Shibata, Japan), and samples in the bag are transferred into the tube in the loading condition set identically to those of Exp-B (i.e., the duration of 0.4, 1, 2, and 4 min at a fixed flow rate of 50 mL min^{-1}). These tube samplers are then detached from the external loading system and connected to the thermal desorber to allow cryofocusing in the CT unit. In addition to the comparative analysis of bag and tube method, we also made an ancillary test to examine the matrix effect of standard phase on tube methods. To this end, liquid standards (LS) of BTX were prepared at 1, 5, 10, and $25 \text{ ng } \mu\text{L}^{-1}$. Then, $3 \mu\text{L}$ of each standard was loaded onto tube and analyzed in the analogous manner as those of GS.

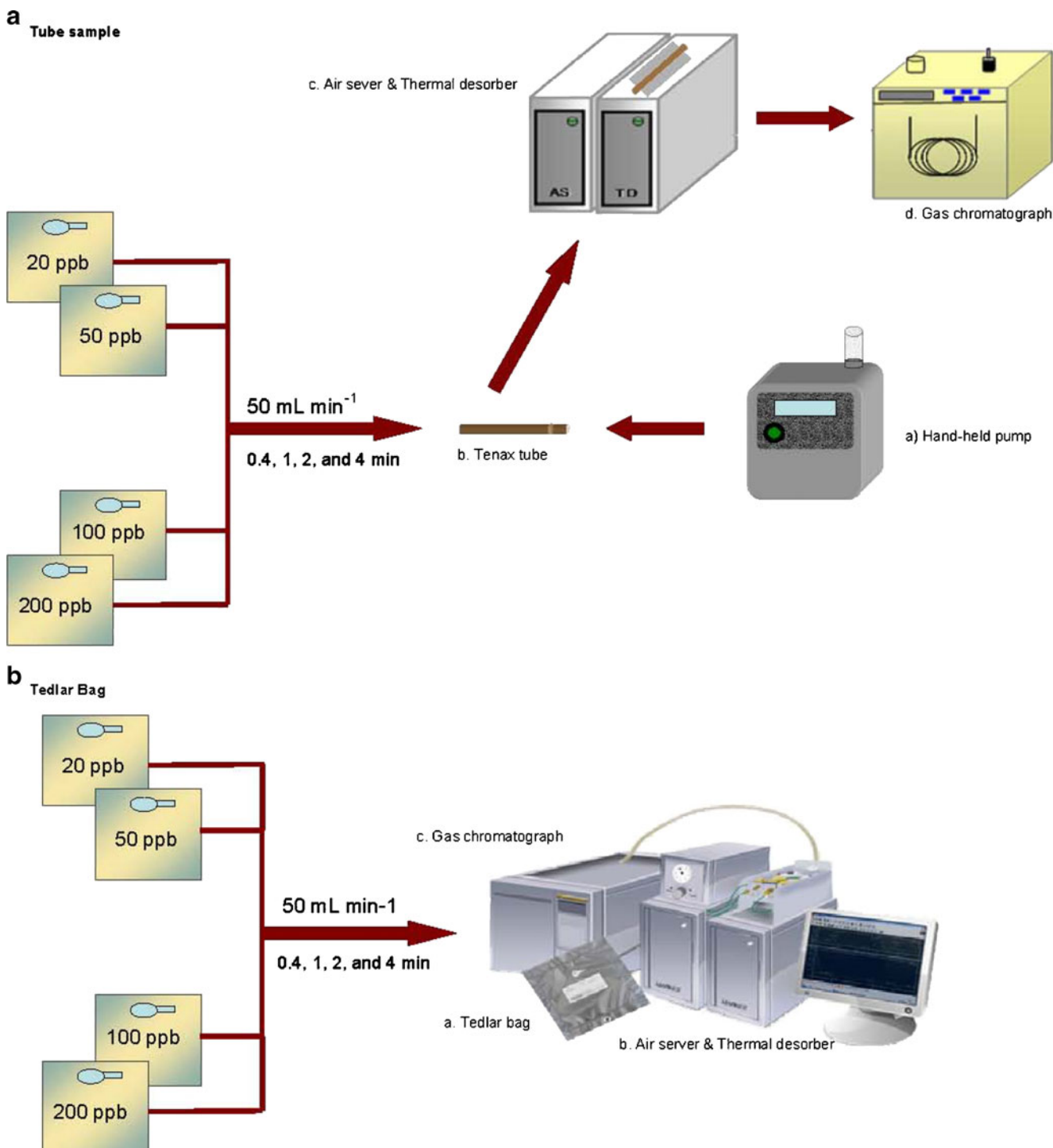


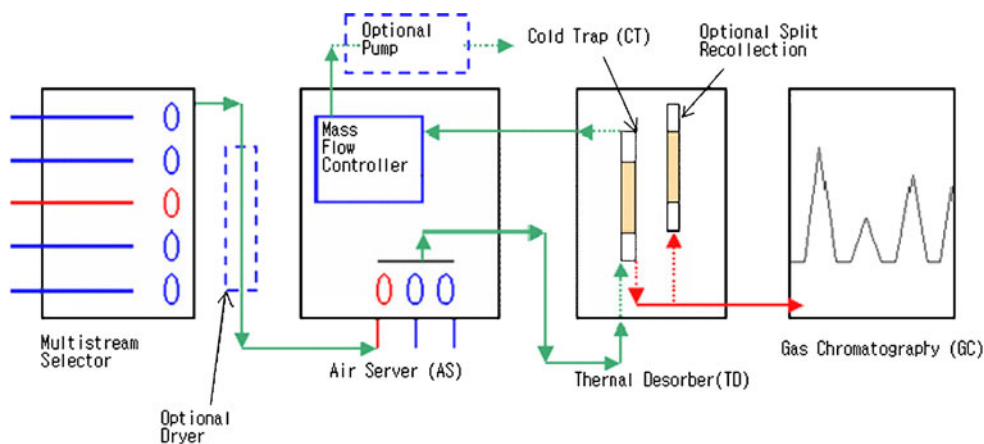
Fig. 1 Schematic of the two sampling approaches (bag and sorbent tube method) for volatile organic compounds adopted in the study

The analysis of VOC in relation to each sampling method and different standard matrix

Although the analysis of the bag and tube samples is made by the combined setup of AS-TD, the flowpath lines of sample gas differ moderately between the bag and tube samples (Fig. 2). For the analysis of the bag samples, the

supply rate of GS was regulated electronically by the mass flow controller (MFC) installed within the AS system. The standard sample passed through a Nafion dryer (Perma Pure, US) before entering the CF system in the TD. The TD was then operated to place samples onto Peltier-based cold trap (CT), to thermally desorb analytes, and to transfer them into the GC for chromatographic separation and subsequent

Fig. 2 Schematic diagram of an instrumental set-up for the air server (AS) and thermal desorber (TD) unit for the analysis of volatile organic compounds



detection. The analytes were then separated on a DB-VRX column ($60\text{ m} \times 0.32\text{ mm} \times 1.8\text{ }\mu\text{m}$) and detected by the FID detector. Ultra pure N_2 was used as a carrier gas at a constant flow rate of 2 mL min^{-1} . The GC/FID system was operated at flow rates of $30\text{ (N}_2\text{ and H}_2\text{)}$ and 300 mL min^{-1} (Air). The oven temperature was maintained at 50°C for 5 min and then programmed to ramp at 5°C min^{-1} to 230°C . The detector temperature was set at 240°C .

To carry out the analysis of tube samplers, the TD unit was operated without the support of the AS unit in the following sequence: (1) the initial thermal desorption of tube by controlling the TD; (2) focusing of analytes on a CT at 5°C ; (3) thermal desorption of CT at 300°C for 5 min; and (4) subsequent delivery of analytes into the GC system. Consequently, the essential difference in the detection stage between the bag and tube method arises from the fact that the latter requires an extra thermal desorption stage to initiate the sample transfer between the sorbent tube and CT. In contrast, the sample transfer of the former proceeds with the aid of additional flowpath line of the AS unit (but without extra-desorption). The use of the same standard materials contained in the Tedlar bag for both Exp-B and -T, however, allows the elimination of one of the main sources of bias between Exp-B and -T. For instance, the effect of sorptive loss of BTX within the Tedlar bag system is balanced, if the sample supply of both Exp-T and -B is based on the identical Tedlar bags for the matching data pairs.

The basic quality assurance (QA) information regarding our analytical method was evaluated in detail with respect to the sorbent tube method. The precision of the analysis was quantified in terms of the relative standard error (RSE (%)) of triplicate analyses for each species by the sorbent tube. The RSE values of each species varied in the range of 2 to 5%, regardless of sampling methods. The detection limits (DL) for the three compounds, when assessed by 7 replicates of the minimum quantities loaded on the sorbent tube, were commonly achieved in the range of 0.6 (benzene) and 1.2 ng (xylene). However, as discussed

below, the detectability of the bag method is slightly poorer than that of the tube method due to the reduced sensitivity. The basic QA results obtained for the BTX compounds generally appeared to be comparable to each other.

Experimental procedure and interpretation of calibration data

In order to describe the effects of sampling methods and standard matrix differences on the analytical performance, the calibration results derived by both bag and tube methods were examined from a number of respects. As shown in Table 1, the TD-based calibration of GS was designed to cover BTX standard gases of 4 concentration levels (20, 50, 100, and 200 nmol mol^{-1}) at four sample loading volumes (20, 50, 100, and 200 mL). To obtain comparative calibration data sets, the analysis of BTX proceeded in the order of Exp-T and -B. Upon completion of Exp-B, a part of Exp-T was conducted again to confirm the reproducibility of the tube experiment just after the bag experiment using gaseous working standards of BTX. For a given standard concentration, each tube sampler was loaded incrementally with increases in gaseous sample loading volume. Likewise, calibration data for each concentration can be derived by combining the calibration results of each loading volume of gaseous standards.

Because of our experimental design, the calibration data derived sequentially by both sampling methods can be described in two different ways. The resulting data can be organized initially to analyze the effect of sample loading volume changes at a given standard concentration; hence, it is defined as fixed standard concentration (FSC) approach. The same data sets can also be arranged to analyze the effect of sample concentration changes at a given loading volume, which can be defined as fixed standard volume (FSV) approach. In our previous studies, these two types of calibration approaches were commonly applied to assess the validity of the sample transfer methods for direct injection or TD method [e.g., 13, 14]. Information concerning both

Table 1 Experimental design for the calibration of gaseous BTX standards with four different concentration levels (20, 50, 100, and 200 nmol mol⁻¹)

Experiment order	Working standard (nmol mol ⁻¹)	Loading duration ^a (min)	Total sample volume (mL)	Amount injected (pmol)
1	20	0.4	20	16.6
2		1	50	41.4
3		2	100	82.9
4		4	200	166
5	50	0.4	20	41.4
6		1	50	104
7		2	100	207
8		4	20	414
9	100	0.4	20	82.9
10		1	50	207
11		2	100	414
12		4	200	829
13	200	0.4	20	166
14		1	50	414
15		2	100	829
16		4	200	1,657

^a Transfer of standard gas to cryofocusing unit (bag method) or its loading on the tube sampler (tube method) was performed similarly by setting the identical loading duration at a fixed flow rate of 50 mL min⁻¹

absolute and relative calibration trends between FSV and FSC has been useful to distinguish some factors involved in calibration characteristics of the analytical system. Although the initial Exp-T was conducted to cover all 4 sample loading volumes, the second Exp-T was done partially (only at the largest loading volume of 200 mL) for the purpose of a simple check-up. In addition, the tube-based calibration of LS was also analyzed in relation to those derived by GS.

Results and discussion

Comparison of calibration results between two different sampling approaches

In light of the experimental design introduced above, all the results acquired from a series of calibration experiments can be evaluated by two different criteria: (1) difference between sample collection media—sorbent tube vs. bag sampling method and (2) difference in standard transfer approaches—FSV and FSC. As shown in Fig. S1 (ESM), the results of benzene are shown to allow comparison in terms of both criteria. In Table 2, the detailed calibration results derived by both methods are presented for the FSV cases. In addition, the results of these calibration experiments are also summarized in terms of both criteria in Table

S2 (ESM). To check for the relative difference induced by the first criterion, the percent difference (PD) is computed by slope values of each compound between the bag and tube method. In case of the FSV data sets, the PD values are about -15% for both benzene and toluene and ~2% for xylene. It thus implies that the analysis made by the bag method can be subject to the loss of benzene and toluene by such proportion (-15%) relative to the tube method. However, unlike the two lighter compounds, the pattern for the heaviest xylene is characterized with a slight gain (~2%) which contrasts with the other compounds. This type of relative loss pattern between different VOCs is in fact more significant in the FSC data sets, because their respective PD values are much larger with -19, -23, and -5%.

To test the reproducibility of the relative sensitivity between the two methods, an ancillary test was conducted for tube method to calibrate BTX (at 200 mL loading volume based on the FSV) just after the bag-based calibration. Differences in the two tube-based experiments (Exp-T(1) and -T(2)), when expressed in PD values, were highly consistent to show moderate differences for each compound such as 10 (B), 1.8 (T), and 2.5% (X). Considering the strong similarity between the two tube experiments conducted before and after the bag experiment, the relative loss of analyte in the bag samples appears to be a systematic, rather than a random, phenomenon. It also confirms that the analyte loss, if occurring, can be pronouncing in the lighter compounds relative to the heavier compounds. In addition, these calibration results further suggest that relative loss of analytes can also be affected by standard concentration levels and sample loading volumes. The results shown in Table S2 (ESM) indicate that the largest PD values tend to occur either at the lowest sample loading volume (20 mL for FSV data) or at the lowest standard concentration (20 nmol mol⁻¹), although such changes tend to occur more systematically in the FSC data sets. Evidence collected in this study (e.g., differences in slope values between the methods and in relative loss of compounds across different molecular weights) thus suggests that the analyte loss may occur most noticeably in the bag method during sample storage or the transfer into the CF unit along the AS flowpath lining [15].

Comparison of tube calibration results between different standard matrices

Although the chromatographic method is a highly precise means to measure trace components, its employment under various analytical settings can be subject to numerous sources of analytical bias. For instance, the analysis of gaseous VOC samples collected by the sorbent tube is often carried out by loading the LS to the sorbent tube in a stream

Table 2 Comparison of BTX calibration results (peak area) made by bag and tube sampling approaches on the basis of the FSV approach

Method	Quantity	Standard gas loading volume (mL)											
		Benzene				Toluene				Xylene			
	(pmol)	20	50	100	200	20	50	100	200	20	50	100	200
[A] Tube mode													
	16.6	59,006				61,434				41,265			200
	41.4	85,641	90,721			93,596	105,314			54,863	80,392		
	82.9	150,336		150,932		112,849		184,298		76,499		252,642	
	104		162,296			181,630					125,054		
	166	212,487			277,260	226,541			362,220	189,212			340,298
	207		272,200	304,068		313,197	359,659			247,473	477,285		
	414		553,650	556,086	613,940	582,119	619,933	717,026		514,980	697,938		721,940
	829			1,043,399	1,137,947		1,151,850	1,301,975		954,210			1,202,213
	1,657				2,286,963			2,566,111					2,377,337
[B] Bag mode													
	16.6	–				–				–			
	41.4	–	–			–				–	51,346		
	82.9	86,454		91,817		94,001	112,526			99,036		142,873	
	104		106,347				119,154				123,083		
	166	176,695			195,119	194,462			236,243	198,461			372,231
	207		243,287	235,350			256,849	254,100		266,924	296,532		
	414		478,110	481,810	495,310		515,228	534,897	534,372	527,352	561,633		697,812
	829			991,673	1,022,037		1,053,992	1,097,284		1,097,963			1,206,398
	1,657				2,031,570			2,162,061					2,295,263

of carrier gas [e.g., 12]. However, the choice of the different matrix phases (between standard and samples) can alter the detection properties (e.g., sensitivity) of the target compounds to a large extent. The description of such experimental bias in VOC quantification procedure is not simple, if one considers the inherent variability involved in the split/splitless mode operation. Most importantly, the mass ratio of analyte is not necessarily maintained constantly between the collection (the amount collected on the sorbent tube) and detection stage (the amount determined by the detector) under the split mode operation of GC [12]. This type of variability can be most complicated, if the quantification is performed between different matrix phases across samples and standards.

In Fig. S2 (ESM), the results of tube method derived by two different standard phases (gas and liquid phase) are compared. For this comparison, the calibration results of GS made by both the tube and bag samples with the FSV approach (i.e., 200 mL) are compared for 3 μ L of LS loaded onto the sorbent tube. The LS was prepared at 4 concentration levels, and 3 μ L of each was used to derive their calibration curves (Fig. S2, ESM). The results consistently indicate that the slope values of the GS are systematically smaller than the LS, regardless of the sample loading methods on the sorbent tube. If the slope values of GS are compared to those of LS by the percent difference, the relative deficiencies of the latter are computed as 49 (benzene), 43 (toluene), and 56% (xylene). It thus suggests that the incompatibility of the matrix type can occur in the operation of thermal desorbing system. The occurrence of significantly large biases due to the matrix effect was in fact examined in a highly systematic manner by Demeestere et al. [12]. These authors quantified the sample response factor (SRF) and the relative sample response factor (RSRF) of an internal standard ($[^2\text{H}_8]$ Toluene (Tol- d_8)) and five model compounds which were prepared in both GS and LS. To this end, SRF values of Tol- d_8 standard were determined in five different ways by loading the tube with (1) Tol- d_8 in LS, (2) Tol- d_8 in LS plus stock solution of other VOCs, (3) Tol- d_8 in GS, (4) Tol- d_8 in GS plus other VOCs in gas phase, and (5) Tol- d_8 in GS plus other VOCs in LS. They found that the average SRF values of Tol- d_8 loaded as LS on the sorbent tube are larger by 80% than their GS counterparts which are quite comparable to our toluene data. The subsequent loading of other analytes prepared in either the liquid or gas phase on the same sorbent tube virtually did not affect the SRF of Tol- d_8 . As such, the comparison of the calibration results derived between the present and previous studies indicates the possibility that the performance of the TD method can be affected by the choice of standard matrix (e.g., between LS and GS) for the sorbent tube method, due possibly to differences in their TD-based recovery rates.

Conclusions

In order to elucidate the effect of sampling methods on the quality of VOC analysis, relative bias between the bag and tube sampling method was examined using three aromatic VOCs (BTX) through a series of calibration experiments. If the compatibility of the two sampling methods is tested by simulating their sample loading conditions to the TD system, the loss of analyte proceeded more prominently in the bag sampling method than in the tube method. To examine the relative response properties of GC-TD in relation to the matrix type containing target analytes, the performance of the sorbent tube method was examined using BTX standards prepared in both gas- and liquid-phase. The findings of considerably reduced sensitivity with gas-phase standard indicate that the matrix effect can be a potential source of bias in the sorbent tube method. As the preparation and storage of gaseous standard often involve delicate procedures, the matrix phases selected between sample and standard do not necessarily match with the techniques involving complicated treatments. Hence, the results of this study suggest that experimental bias due to such mismatch can occur rather commonly, unless one distinguishes the potential bias stemming from such factor. Because our experiments were merely able to find the existence of such bias, it is yet difficult to explain the actual cause(s) of such phenomenon. It can however be addressed that such experimental biases can be ascribable to a number of possible causes associated with either gaseous standards (e.g., less efficient sorption of gaseous analytes by a selected sorbent material) or liquid standards (e.g., preferential loss of solvent relative to analyte). Although the use of an internal standard is suggested as a good alternative to reduce the bias of the sorbent tube method, its application is yet restricted to quantitatively assess the cause of such phenomenon. Hence, more comprehensive and deliberate efforts are desirable in the future study to precisely describe the cause of such problem and to reduce such experimental biases.

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References

1. Helmig D (1999) Air analysis by gas chromatography. *J Chromatogr A* 843:129
2. Demeestere K, Dewulf J, Witte BD, Langenhove HV (2007) Sample preparation for the analysis of volatile organic compounds in air and water matrices. *J Chromatogr A* 1153:130

3. Pandey SK, Kim K-H (2009) A review of methods for the determination of reduced sulfur compounds (RSCs) in air. *Environ Sci & Tech* 29:3020
4. Ras MR, Borrull F, Marce RM (2009) Sampling and preconcentration techniques for determination of volatile organic compounds in air samples. *Trends Analyt Chem* 28:347
5. Matysik S, Matysik F-M (2009) Microextraction by packed sorbent coupled with gas chromatography—mass spectrometry: application to the determination of metabolites of monoterpenes in small volumes of human urine. *Microchim Acta* 166:109
6. Bocchini P, Monaco DD, Pozzi R, Pinelli F, Galletti GC (2009) Solid-phase microextraction coupled to gas chromatography with flame ionization detection for monitoring of organic solvents in working areas. *Microchim Acta* 165:271
7. Traube SL, Scoggin KD, Li H, Burns R, Xin H (2009) Field sampling method for quantifying odorants in humid environments. *Environ Sci & Tech* 42:3745
8. Ouyang G, Pawliszyn J (2006) Recent developments in SPME for on-site analysis and monitoring. *Trends Anal Chem* 25:692
9. Ouyang G, Pawliszyn J (2006) SPME in environmental analysis. *Ana BioAnal Chem* 386:1059
10. Xiong G, Cheng Y, Pawliszyn J (2003) On-site calibration method based on stepwise solid-phase microextraction. *J Chromatogr A* 999:43
11. Li K, Santilli A, Goldthorp M, Whiticar S, Lambert P, Fingas M (2001) Solvent vapour monitoring in work space by solid phase micro extraction. *J Hazard Mater* 83:83
12. Demeestere K, Dewulf J, De Roo K, Langenhove HV (2008) Quality control in quantification of volatile organic compounds analysed by thermal desorption—gas chromatography—mass spectrometry. *J Chromatogr A* 1186:348
13. Kim K-H (2006) The properties of calibration errors in the analysis of reduced sulfur compounds by the combination of a loop injection system and gas chromatography with pulsed flame photometric detection. *Anal Chim Acta* 566:75
14. Pandey SK, Kim K-H (2009) Comparison of different calibration approaches in the application of thermal desorption technique: a test on gaseous reduced sulfur compounds. *Microchem J* 91:40
15. Air Server/MCS User Manual (2006) <http://www.markes.com>