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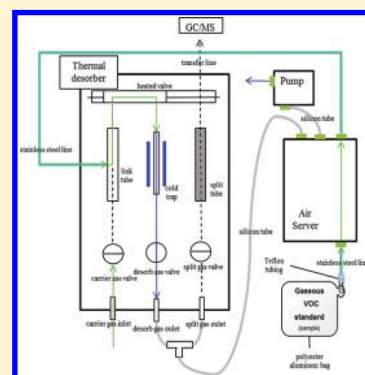
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# Novel Approach to Test the Relative Recovery of Liquid-Phase Standard in Sorbent-Tube Analysis of Gaseous Volatile Organic Compounds

Yong-Hyun Kim and Ki-Hyun Kim\*

Department of Environment and Energy, Sejong University, Seoul 143-747, Korea

**ABSTRACT:** Sorbent tubes (STs) are highly efficient and versatile tools for collecting gaseous samples of volatile organic compounds (VOCs). In order to assess the experimental bias in their application, the relative recovery (RR) of 19 VOCs (acetaldehyde, propionaldehyde, butyraldehyde, isovaleraldehyde, valeraldehyde, benzene, toluene, *m*-xylene, *p*-xylene, *o*-xylene, styrene, methyl ethyl ketone, methyl isobutyl ketone, isobutyl alcohol, butyl acetate, propionic acid, butyric acid, isovaleric acid, and *n*-valeric acid) was evaluated in accordance to three different sorbent tube types: (1) Tenax (Te), (2) Carboxen 1000 (X), and (3) Tenax + Carboxen B + Carboxen 1000 (TBC). Calibration was initially made by direct injection of the liquid working standard (L-WS) into the link tube (LT) of the thermal desorption (TD) system. The LT was modified to optimize the transfer of all the VOCs to the focusing trap of the TD. Three different types of ST were then loaded with the same L-WS using (1) direct injection (DI) to tube and (2) injection to tube via vaporization (VAP). The results of the two ST/TD methods (DI and VAP) were normalized to those of the LT/TD to derive RR. The mean RR values of all target VOCs were 62.6 (X), 83.9 (Te), and 82.8% (TBC) for the DI and 76.5, 75.8, and 81.0% for the VAP. Although the results using TBC and Te tubes exhibited better recovery in DI than in VAP, those of X tubes had the reverse trend. As such, the relative affinity of each sorbent material can be affected by the mode of introduction of the standard. The practicality of the LT/TD, especially as a reference for the ST/TD, was also validated from some environmental samples in an ancillary experiment. As such, we were able to demonstrate the usefulness of the LT/TD method to evaluate analyte recovery from spiked sorbent tubes.



Sources of volatile organic compounds (VOCs) encountered in daily life are diverse, including indoor facilities, automobile tailpipes, and industrial chimneys.<sup>1–3</sup> Many countries have developed and established regulatory guidelines for VOCs in air, because they can pose a significant public health threat.<sup>3</sup> Accurate measurement of VOCs in air requires that the sampling method be tailored to the compounds of interest and to the sensitivity of the analytical method. The sampling approaches for VOC have been developed to include several options. A whole-air sampling using containers (such as canisters and bags) can be selected commonly for the repetitive analysis. On the other hand, others prefer the use of sorbent material of which analysis is carried out by either thermal desorption (TD) or solvent extraction.<sup>4,5</sup> Each of these methods has its own advantages and disadvantages. For example, the capacity of sample containers used for whole-air sampling can be limited both physically (by the sample size) and chemically (by sorptive loss or artifact formation). Although solvent extraction simplifies the sample delivery to the detection system (after extraction), it can be subject to significant analytical bias due to incomplete and irreproducible extraction efficiency. TD-based analysis of sorbent tubes (ST) is robust and repeatable by comparison. Although the ST/TD method has been well documented for a wide range of compounds, it can have one-off approaches, depending on the capabilities of the analytical system selected.<sup>6</sup>

In order to quantify VOCs collected by sorbent tubes, one needs to rely on gas chromatography (GC), typically with flame ionization detection (FID) or mass spectrometry (MS) detection, both of which are commonly interfaced to TD systems.<sup>7,8</sup> The experimental accuracy of trace-level VOC analysis is thus affected by several basic variables including the properties of target compounds, the type of sorbent materials used, and the performance of the analytical system.<sup>9</sup>

In this study, the relative recovery (RR) of VOCs during TD/GC/MS analysis is evaluated by comparing the results from spiked sorbent tubes with vapor-phase standard injected directly into the TD-GC analytical system. A new approach to introducing vaporized standard directly into the TD/GC/MS was developed for this study by modifying the link tube (LT) component of the TD. This LT/TD comprises heated (150 °C), inert-coated, narrow-bore tubing and is used to transfer desorbed analytes into the cold trap of the thermal desorber, without loss or bias, for subsequent GC/MS analysis. The use of LT/TD makes it the ideal mechanism for introducing standards to use as a reference. Results from standards introduced directly into the TD/GC/MS analytical system in this way (LT/TD) were compared with results for ST loaded

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**Table 1.** List of 19 Target VOCs Selected for the Relative Recovery of Liquid-Phase Standard between Different Treatment Types

order	group	compounds	abbreviation	MW (g mol <sup>-1</sup> )	density (g cm <sup>-3</sup> )	boiling point (°C)	formula	CAS number
1	aldehyde	acetaldehyde	AA	44.1	0.785	20.2	C <sub>2</sub> H <sub>4</sub> O	75-07-0
2		propionaldehyde	PA	58.1	0.798	46–50	C <sub>3</sub> H <sub>6</sub> O	123-38-6
3		butyraldehyde	BA	72.1	0.805	74.800	C <sub>4</sub> H <sub>8</sub> O	123-72-8
4		isovaleraldehyde	IA	86.1	0.797	90–93	C <sub>5</sub> H <sub>10</sub> O	590-86-3
5		valeraldehyde	VA	86.1	0.81	102–103	C <sub>5</sub> H <sub>10</sub> O	110-62-3
6	aromatic	benzene	B	78.11	0.87	80.1	C <sub>6</sub> H <sub>6</sub>	71-43-2
7		toluene	T	92.14	0.865	111	C <sub>7</sub> H <sub>8</sub>	108-88-3
8		styrene	S	104.2	0.909	145	C <sub>8</sub> H <sub>8</sub>	100-42-5
9		<i>p</i> -xylene	<i>p</i> -X	106.2	0.864	138	C <sub>8</sub> H <sub>10</sub>	106-42-3
10		<i>m</i> -xylene	<i>m</i> -X	106.2	0.864	139	C <sub>8</sub> H <sub>10</sub>	108-38-3
11		<i>o</i> -xylene	<i>o</i> -X	106.2	0.861	144	C <sub>8</sub> H <sub>10</sub>	95-47-6
12	ketone	methyl ethyl ketone	MEK	72.11	0.805	79.64	C <sub>4</sub> H <sub>8</sub> O	78-93-3
13		methyl isobutyl ketone	MIBK	100.2	0.8	117–118	C <sub>6</sub> H <sub>12</sub> O	108-10-1
14	alcohol	isobutyl alcohol	i-BuAl	74.12	0.802	108	C <sub>4</sub> H <sub>10</sub> O	78-83-1
15	ester	butyl acetate	BuAc	116.2	0.88	126	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	123-86-4
16	carboxyl	propionic acid	PPA	74.1	0.99	141	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	79-09-4
17		<i>n</i> -butyric acid	BTA	88.1	0.96	163.5	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	107-92-6
18		isovaleric acid	IVA	102	0.925	175–177	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	503-74-2
19		<i>n</i> -valeric acid	VLA	102	0.93	186–187	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	109-52-4

either using direct injection of liquid standards or by introducing vaporized liquid standards. The performance of LT/TD was also evaluated against three different sorbent tube types, specifically (1) Tenax TA (Tube code: Te), (2) Carboxen 1000 (X), and (3) a Tenax TA + Carboxen B + Carboxen 1000 (TBC) multitubed system. The results of this analysis were used to learn more about the relationship between compound property, sorbent material type, and the sorbent tube loading method.

## MATERIALS AND METHODS

**Preparation of Working Standards.** In this study, the recovery of VOCs was estimated principally by comparing the results of the ST method obtained by both direct injection of liquid standard and its transfer after vaporization with those obtained by introducing the vaporized liquid standard directly into the GC/MS system via the LT/TD. The standard used contained 19 VOCs, many of which are odorous. The compounds selected fell into 3 main groups: (1) toluene (T), *p*-xylene (*p*-X), *m*-xylene (*m*-X), *o*-xylene (*o*-X), styrene (S), methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), isobutyl alcohol (i-BuAl), and butyl acetate (BuAc) and one reference (benzene), (2) (carbonyls) acetaldehyde (AA), propionaldehyde (PA), butyraldehyde (BA), isovaleraldehyde (IA), and valeraldehyde (VA), and (3) (volatile fatty acids) propionic acid (PPA), butyric acid (BTA), isovaleric acid (IVA), and *n*-valeric acid (VLA) (Table 1).

The liquid-phase standard was prepared gravimetrically. Primary-grade chemicals were purchased at a purity of 97% (for PA, IA, and VA), 99.5% (for B, T, and MIBK), and 99% for the rest (Sigma-Aldrich, USA). The primary standards (PSs) were prepared using these chemicals, while the liquid-phase working standards were prepared by a two-step gravimetric dilution of the PS using methanol (Table 2). The concentration of each VOC in the liquid working standard (L-WS) was adjusted to a similar level, except for AA. The concentration of AA was set 3 times higher than the others due to its lower sensitivity.<sup>10</sup> For preparation of the primary standard, 300  $\mu$ L aliquots of each VOC (900  $\mu$ L in the case of AA) were mixed

with methanol (Burdick & Jackson, USA) to make a final volume of 20 mL with a mean concentration of each VOC at 12.8  $\mu$ g  $\mu$ L<sup>-1</sup> (except AA). Twenty milliliters of working standards was then prepared using a two-step gravimetric dilution. In step 1, the primary standard was diluted by a factor of 10 to create the first L-WS with a mean concentration of 1,279 ng  $\mu$ L<sup>-1</sup> for all VOCs except AA. In step 2, this first L-WS was diluted further to create the lower-level standards needed for the 4-point calibrations; these contained 6.39, 12.8, 25.6, and 63.9 ng  $\mu$ L<sup>-1</sup> of each VOC, respectively (except AA). The analytical system was then calibrated by direct injection of each of these lower-level standards into the TD/GC/MS analytical system via the link tube.

### Sorbent Material Types for the Sorbent Tube Method.

The three types of sorbent tubes were then loaded with these lower-level standards using liquid injection and the introduction of the standard in the vapor phase. The recovery of each VOC was then determined on each of the three different sorbent materials and for each of the two different loading methods using data from the direct standard injection (without ST) to the TD/GC/MS via the link tube as the reference. The Tenax (Te) tubes were tried first (Table 3a). A traditional porous polymer, Te, is one of the most widely used adsorbents for the preconcentration of VOCs.<sup>11,12</sup> Although it has a relatively low adsorption capacity, it allows relatively high boiling compounds to be desorbed and recovered easily.<sup>13</sup> Tubes packed with sorbent X were used next. Carboxen X has a significantly greater adsorption capacity than Tenax, consequently making complete desorption and recovery of less volatile organics relatively difficult.<sup>14</sup> The 3-bed TBC tubes containing Tenax TA, Carboxen B, and Carboxen 1000 were tried last. As these sorbents have different adsorptive capacities, this modified form of tube can be used to capture and release a wide range of VOCs in a convenient manner.

**Instrumental System.** All the analyses in this study were carried out using a GC-2100 (Shimadzu, Japan) equipped with a QP2010 MS (Shimadzu, Japan) and a UNITY thermal desorber (Markes International, Ltd., UK) equipped with an Air Server Accessory. The TD focusing trap was packed with

Table 2. Preparation of Liquid-Phase VOC Standard for the Analysis by the TD/GC/MS System

(a) Preparation of Liquid-Phase Standard for 19 VOCs																		
compounds	methanol	AA	PA	BA	IA	VA	B	T	S	p-X	m-X	o-X	MEK	MIBK	i-BuAl	BuAc	PPA	BTA
primary-grade chemical																		
concentration (%)		99.0	97.0	97.0	97.0	97.0	99.5	99.5	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0
volume (μL)		900	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300
concentration (ng μL <sup>-1</sup> )		34,972	11,611	11,954	11,596	11,786	12,985	12,910	13,499	12,830	12,830	12,786	11,954	11,940	11,910	13,068	14,702	14,256
first L-WS <sup>b</sup>	18	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
concentration (ng μL <sup>-1</sup> )		3,497	1,161	1,195	1,160	1,179	1,298	1,291	1,350	1,283	1,283	1,279	1,195	1,194	1,191	1,307	1,470	1,426
(b) Preparation of Second L-WS for 4 Point Calibration: Absolute Mass (ng) of VOCs Loaded on the Tube Sampler																		
concentration <sup>c</sup> (ng μL <sup>-1</sup> )																		
mixing volume (μL)	methanol	AA	PA	BA	IA	VA	B	T	S	p-X	m-X	o-X	MEK	MIBK	i-BuAl	BuAc	PPA	BTA
order	first L-WS																	
1	7.5	1492.5	17.5	5.81	5.80	5.89	6.49	6.46	6.75	6.42	6.42	6.39	5.98	5.97	5.95	6.53	7.35	7.13
2	15	1485	35.0	11.6	11.8	11.6	13.0	12.9	13.5	12.8	12.8	12.8	12.0	11.9	11.9	13.1	14.7	14.3
3	30	1470	69.9	23.2	23.2	23.6	26.0	25.8	27.0	25.7	25.7	25.6	23.9	23.9	23.8	26.1	29.4	28.5
4	75	1425	175	58.1	58.0	58.9	64.9	64.6	67.5	64.2	64.2	63.9	59.8	59.7	59.5	65.3	73.5	71.3

<sup>a</sup>PS: Dilution of pure chemical (primary grade chemical) to make a 20 mL solution. <sup>b</sup>First L-WS: Dilution of PS to make a 20 mL solution. <sup>c</sup>Analysis volume: 1 μL.

Table 3. Information of Adsorbent Tube Materials Used for VOC Sampling and Operational Conditions of TD/GC/MS

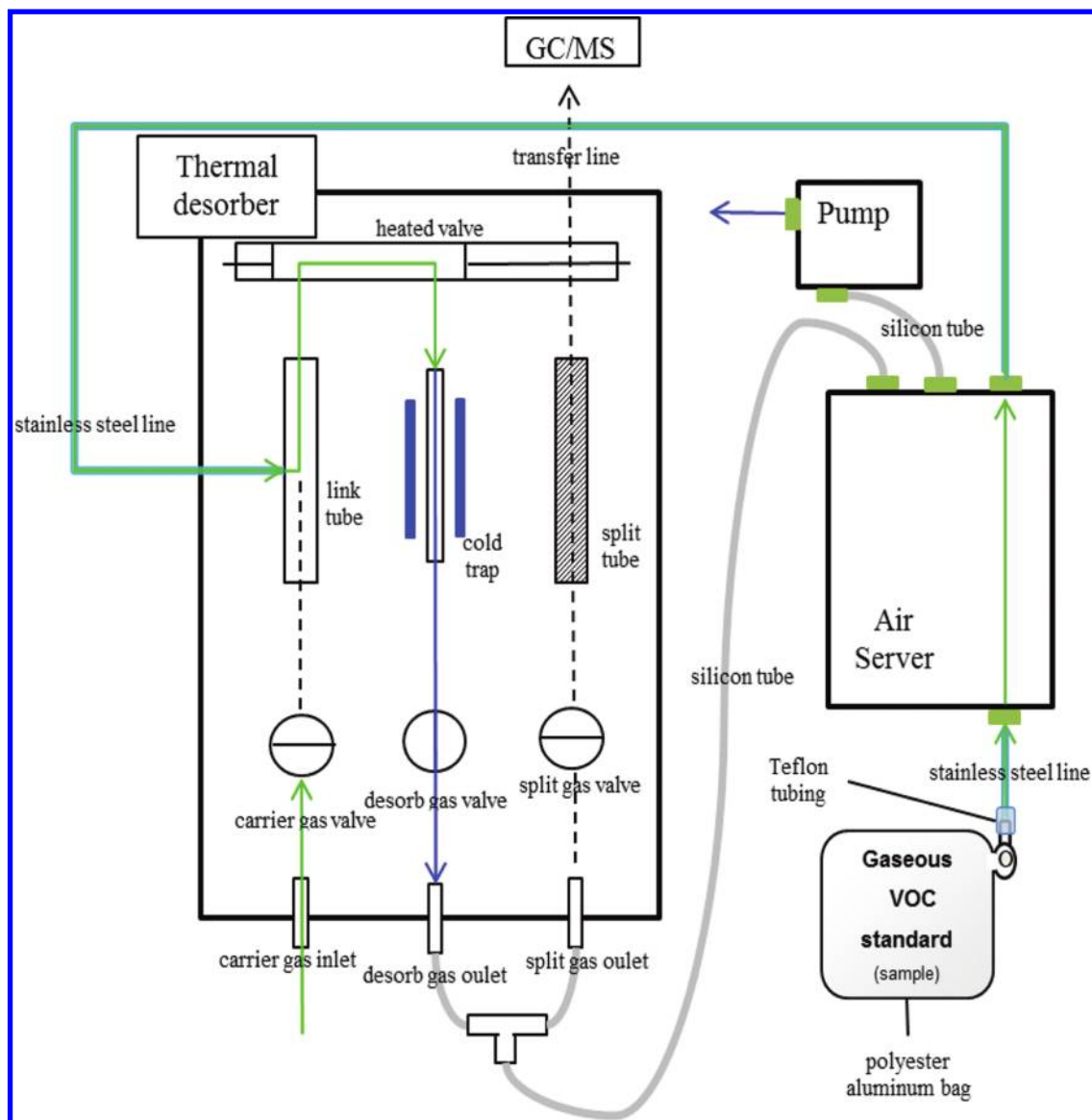
(a) Information of Adsorbent Tube Materials				
order	tube code	adsorbent type	surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	manufacturer
1	Te	Tenax TA (60/80 mesh) 200 mg	35	Alltech (USA)
2	X	Carbopack X (40/60 mesh) 300 mg	250	Supelco (USA)
		Tenax TA (60/80 mesh) 100 mg	35	Alltech (USA)
3	TBC	+ Carbopack B (60/80 mesh) 100 mg	100	Supelco (USA)
		+ Carboxen 1000 (60/80 mesh) 100 mg	1200	Supelco (USA)
b. Operational Condition of TD/GC/MS <sup>b</sup> System for the Comparative Analysis of 19 Target VOCs				
GC (SHIMADZU GC-2010, JAPAN), MS (SHIMADZU GCMS-QP2010, JAPAN)				
column: CP wax (diameter: 0.25 mm; length: 60 m; film thickness: 0.25 μm)				
oven setting		detector setting		
oven temp:	40 °C (5 min)	ionization mode:	EI (70 eV)	
oven rate:	10 °C min <sup>-1</sup>	ion source temp.:	200 °C	
max oven temp:	200 °C (4 min)	interface temp.:	200 °C	
total time:	25 min	TIC scan range:	35–250 m/z	
carrier gas:	He (99.999%)	threshold:	100	
	thermal desorber (Unity, Markes, UK)			
cold trap:	Carbopack B + Tenax TA			
split ratio:	1:5	trap low:	−10 °C	
split flow:	5 mL min <sup>-1</sup>	trap high:	320 °C	
trap hold time:	20 min	flow path temp:	150 °C	
sampling tube				
desorb flow:	50 mL min <sup>-1</sup>			
desorb time:	5 min	temp:	300 °C	
<sup>a</sup> Manufacturer data. <sup>b</sup> TD (UNITY, Markes International, Ltd., UK).				

<sup>a</sup>Manufacturer data. <sup>b</sup>TD (UNITY, Markes International, Ltd., UK).

Tenax TA and Carbopack B in a 1:1 volume ratio (inner diameter 2 mm and total sorbent bed length = 50 mm). The target VOCs separated on a CP-Wax column (diameter = 0.25 mm, length = 60 m, and film thickness = 0.25 μm) using a 25 min running cycle (Table 3b).

**Choice of Sample Loading Approaches for TD Analysis.** By varying the sorbent(s) used in the TD sample tube and the method of sample introduction (pumped or diffusive sampling), TD can be applied to a diverse range of target VOCs. Note that the thermal desorber used for this study was equipped with an Air Server accessory, which also allows the analysis of whole air or gas samples (e.g., in canisters) and gas-phase standards without using sorbent tubes (Figure 1). For a series of comparative analyses, the general TD setup was changed to a number of different configurations during this study. The configuration used for direct introduction of the standard via the TD link tube is shown in Figure 2 (LT/TD mode). Figure 3 shows schematics of the two modes of loading liquid standards into the sorbent tubes.

**Link Tube/Thermal Desorber (LT/TD) Approach as a Reference Method.** The recovery of VOCs from liquid standards introduced to sorbent tubes is influenced by several factors, primarily the strength (sorbent capacity) of the sorbents and the efficiency/performance of the thermal desorption system. Other factors include the type of solvent, the injection



**Figure 1.** Normal TD setup for the analysis of gaseous VOCs with the aid of AS (AS/TD mode).

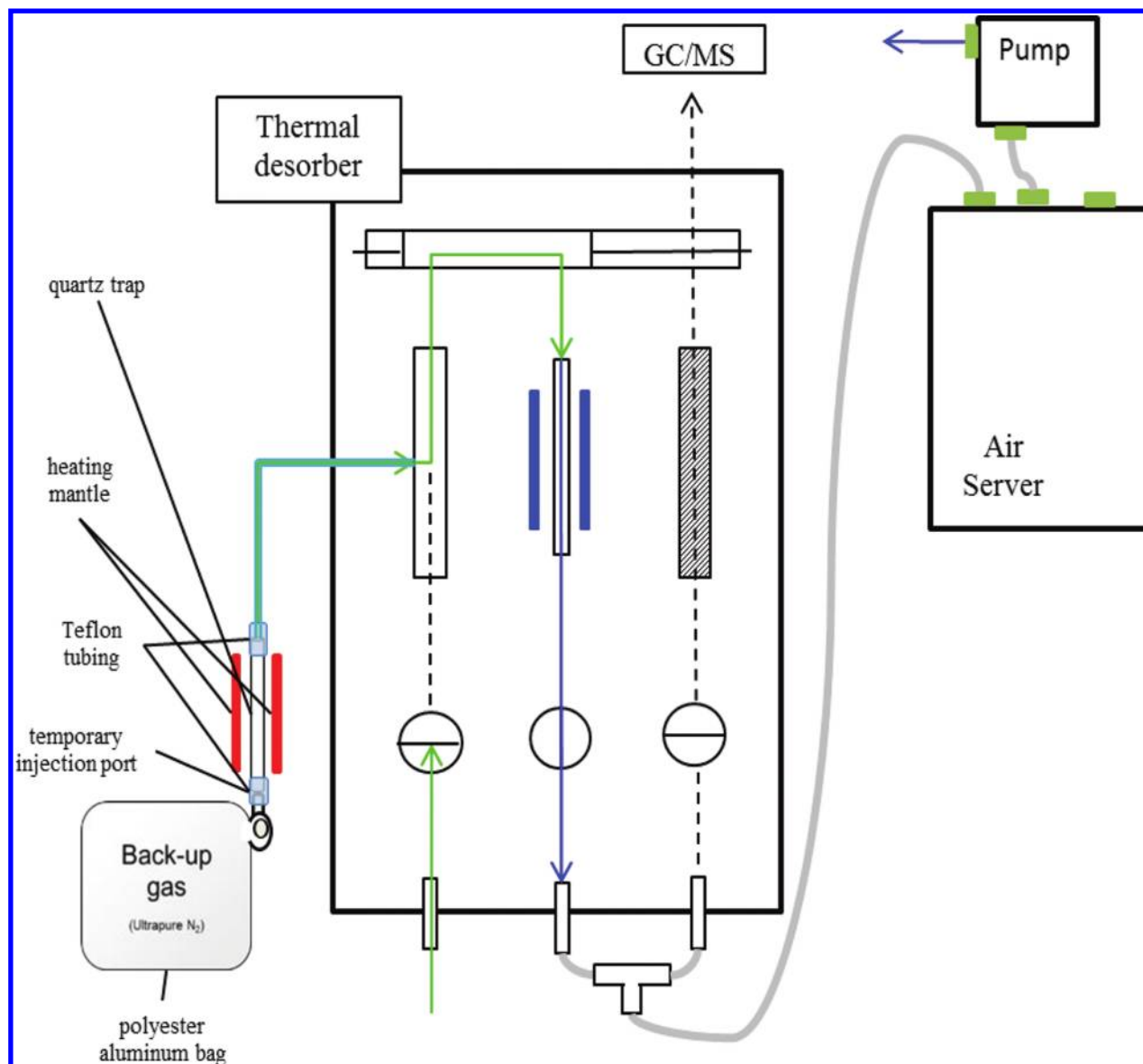
volume, the analytical conditions (particularly desorption split flows), and whether or not it is possible to selectively purge the solvent from the sorbent tube or from the focusing trap (partially or completely) prior to analysis. Microliters of liquid solvent will become milliliters of vapor when the sorbent tube is heated, leading to potential split discrimination and other chromatographic interferences (masking, quenching, etc.) if the mass of retained solvent is not kept to a minimum.

Direct introduction of the vaporized liquid-standard to the focusing trap of the thermal desorber via the TD link tube eliminates the sorbent tube variable and allows the standard to be transferred into the system via the simplest (or shortest) sample transfer track. To enable this, the TD system, combined with the Air Server accessory including the electronic mass flow controller (MFC), was modified to allow the liquid standard to be vaporized and transferred directly into the TD focusing trap through the link tube (Figure 2). For convenience, we refer to this mode of introducing vaporized liquid standard directly to the TD as the LT/TD method. To eliminate any possible bias that can stem from the amount of solvent retained by the CT, an ancillary experiment was conducted to compare

the recovery of analytes in relation to solvent volume (at 1, 2, 5, and 10  $\mu\text{L}$ ) loaded for the LT/TD method. The results of this ancillary test confirmed that such an effect was not apparent up to the injection volume of 2  $\mu\text{L}$ , as there were no significant differences in RF values derived between 1 and 2  $\mu\text{L}$ . In contrast, the magnitude of RF values began to drop noticeably with limited linearity ranges after solvent volume beyond 5  $\mu\text{L}$ . As all of our comparative analysis was made using 1  $\mu\text{L}$  of standard solution, we can exclude the possible sources of bias associated with the solvent retention in the CT. Likewise, we found an excellent agreement in the relative recovery of several VOCs between the gas and liquid-phase standard when the analysis of the latter (1  $\mu\text{L}$ ) was made by an ST/TD method identical to that employed in this study.<sup>9</sup> The agreement in relative recovery between different standard phases thus indirectly supports the idea that the extent of solvent retention in this research did not actually affect the performance of CT.

The LT/TD-mode for standard introduction is described in detail as follows. An empty quartz tube was placed between the TD link and a 10 L polyester aluminum (PEA) bag filled with ultrapure nitrogen (> 99.999%) using pieces of Teflon tubing





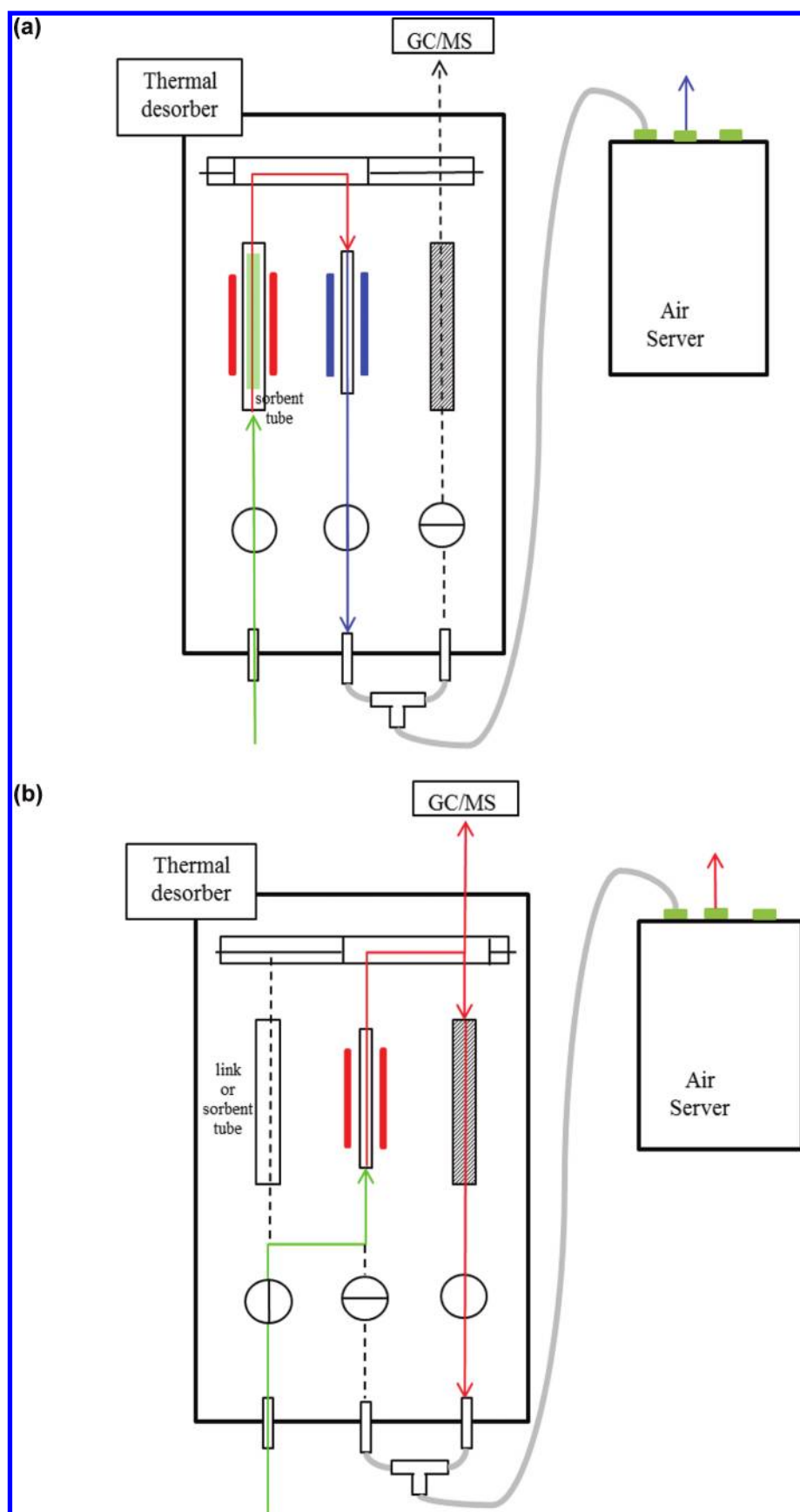
**Figure 2.** Modification of TD setup for the analysis of L-WS via vaporization with the link tube (LT/TD mode).

(Figure 2). The binding between Teflon tubing and each unit of the LT application was aided by silicon tubing to prevent leakage of the vaporized standard. The aliquot of L-WS was withdrawn from a standard vial by a microsyringe and injected into the quartz tube through the Teflon tubing (Figure 2). The temperature of the quartz tube was raised to 90 °C using a heating mantle (TC200P (Pt), Korea) and maintained for 10 min to vaporize VOCs in the L-WS. An external vacuum pump was used to pull the pure nitrogen from the bag, through the heated quartz tube and into the TD link tube at 50 mL min<sup>-1</sup>. The vaporized L-WS was then captured by the TD focusing trap, thermally desorbed, and transferred to the GC column for separation and detection. The sample transfer and desorption stage of LT/TD method is shown in Figures 2 and 3b, respectively.

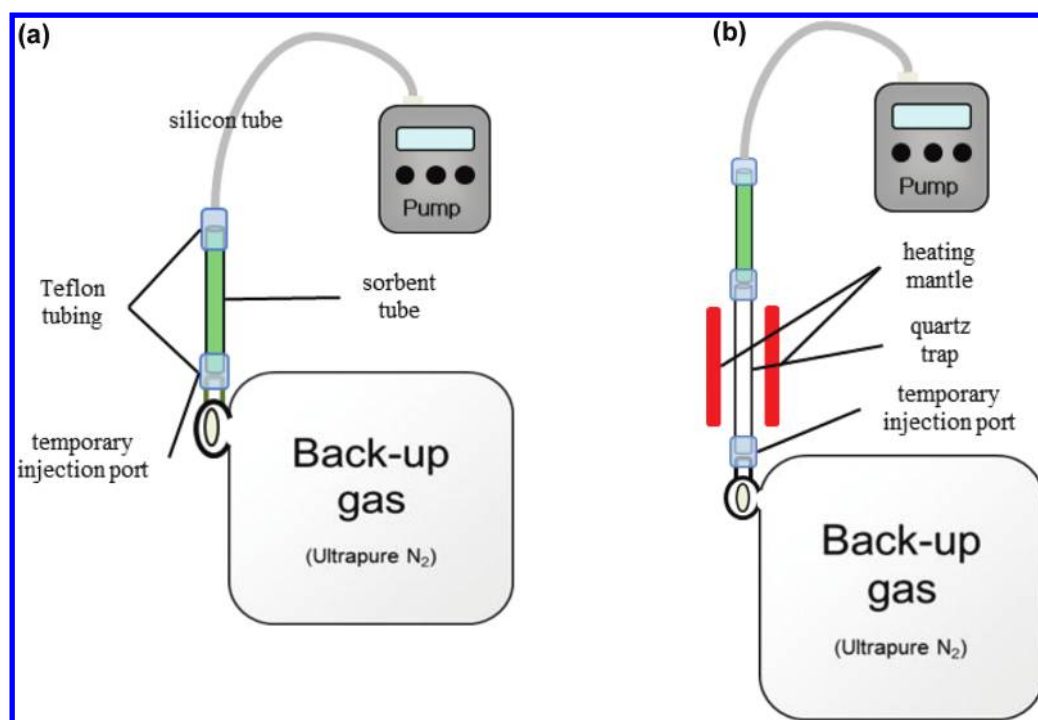
**Sorbent Tube Approach Based on Direct Injection (DI) of L-WS.** Liquid standards are commonly injected directly into the sampling end of sorbent tubes under a flow of inert gas using a microsyringe. In these experiments, direct injection was achieved by connecting the sampling end of the sorbent tube to

a PEA bag filled with reservoir of ultrapure nitrogen. The other end of the tube was connected to a mini-pump interfaced with MFC (Shibata ΣMP-30, Japan) (Figure 4a). As mentioned above, the connections between Teflon tubing and each compartment was made with the aid of silicon tubing. Liquid standard was injected into the sorbent tube through the Teflon tubing by a microsyringe, as described above. In the meantime, nitrogen was pulled from the reservoir and through the tube at a rate of 50 mL min<sup>-1</sup> for 10 min. The sorbent tube was then placed into the TD system (in the same location as had been used for the link tube for leak testing, purging, and primary desorption, as depicted in Figure 3a). Desorbed organics were then recaptured by the TD focusing trap and redesorbed inside the TD system for final detection by the GC/MS system (Figure 3b).

**Sorbent Tube Approach Based on Vaporization (VAP) of L-WS.** Quantitative recovery of analytes using direct injection has not been validated for all analytes on all possible sorbents under all possible conditions. The results of our recent study indicate that the reliability of direct liquid injection for the



**Figure 3.** TD setup for the analysis of the sorbent tube (ST) method by the two-stage desorption (for both DI and VAP approach). (a) Primary desorption of VOCs collected in the sorbent tube. (b) Secondary desorption of VOCs collected in the cold trap.



**Figure 4.** Illustration of two sampling approaches of DI and VAP mode injection of liquid-phase standard (L-WS) of VOCs using the two contrasting ST methods. (a) Direct injection (DI) approach. (b) Injection via vaporization (VAP) approach.

quantitation of unknown gas samples is highly compound- and sorbent-specific.<sup>9</sup> Although differences between liquid- and gas-phase standards were found to be negligible for certain species (e.g., benzene and MIBK), this was not the case for other species (i-BuAl and BuAc) introduced at the same time.<sup>9</sup> The following factors have all been reported to potentially impact the validity of liquid standard calibration of air/gas-phase monitoring methods using sorbent tubes: target compounds, solvent choice, tube sorbent(s), volume of liquid standard injected and potential for selective purging of same predesorption, potential for water retention during sampling and for selective purging of the sample (dry-purging), analytical TD split conditions (split ratio during tube desorption (if applicable) and during trap desorption (if applicable)), and focusing trap conditions (temperature, sorbents, and opportunity for selective purging). Guidelines are also available for minimizing the risk of analytical discrimination, which could otherwise potentially result from these factors (e.g., HSL report and TDTS75 from Markes). However, in cases where this guidance cannot be applied, steps should be taken to validate the use of liquid standards to calibrate sorbent tube-based methods for air/gas monitoring. In order to simulate the collection condition of gas-phase samples by the ST method, a heated quartz tube was inserted in the apparatus before the sorbent tube in order to ensure all target analytes were in the vapor phase before reaching the sorbent (Figure 4b). Liquid standard was injected into the quartz trap via the Teflon tubing, while ultrapure nitrogen was pumped through the tube from the reservoir at a rate of 50 mL min<sup>-1</sup> for 10 min. After this, the quartz tube was heated at 90 °C for 10 min to vaporize all target components (Figure 4b). The loaded sorbent tube was then analyzed by thermal desorption as described above (Figure 3a,b). Note that the vaporization step used in this approach to loading the tubes is identical to that used for direct introduction of standard to the thermal desorber via the link tube, the only difference being the sorbent tube.

## RESULTS

**The Analysis of VOC Based on the Link Tube (LT) Method (as a Reference Method).** The results obtained from direct introduction of liquid standard via the TD link were used to examine the relative recovery (RR) of analytes using the two different methods of loading the sorbent tubes (DI and VAP). In Table 4, the calibration results of VOCs derived by the LT/TD method are provided for 19 target VOC analytes in terms of (1) response factor (RF), (2) coefficient of determination ( $R^2$ ), and (3) relative standard error (RSE: %), along with those derived from sorbent tubes loaded by the two methods described. The RF values of each target VOC in the LT/TD method are consistently higher than those of the two ST methods except for two carbonyls (AA and PA). The LT/TD results of the two carbonyls were fairly stable, with  $R^2$  values above 0.9 and RSE below 5%. However, their results were excluded from the comparative analysis, due to their unusual recovery patterns relative to higher boiling carbonyls and the other VOCs studied. The cause of the significantly biased results of these two light carbonyls is suspected to come from the lack of their feasibility with our focusing system. As a result, they were excluded from further consideration in this study.

The results of a 4-point calibration produced using the LT/TD method yielded fairly stable patterns for all the 17 remaining target VOCs, as shown in Table 4. The RF values of BTSX were relatively high (mean RF values (BTSX) = 215,552 ± 22,690), while those of the VFAs showed relatively low values (mean RF values (VFA) = 81,059 ± 30,090%). The selected target VOCs had a fairly good linearity ( $R^2 > 0.99$ ) and reproducibility (RSE below 4%). In the case of heavy CCs (BA, IA, and VA), a very low mean RSE value of 0.65 ± 0.07% was obtained, while VFAs (PPA, BTA, IVA, and VLA) had a relatively high mean RSE of 2.73 ± 0.46%.

**The Basic QA of the Sorbent Tube-Based Methods (DI and VAP) and Their Relative Recovery.** Differences in



Table 4. Comparison of Response Factor (RF) Values for Liquid-Phase VOC Standards between Different Sorption Procedures

injection type	tube code	compound																							
		AA	PA	BA	IA	VA	B	T	S	p-X	m-X	o-X	MEK	MIBK	i-BuAl	BuAc	PPA	BTA	IVA	VLA					
LT	TBC	Te	X	TBC	Te	X	R <sup>F</sup>																		
							1,541	12,635	91,827	130,007	113,566	172,391	216,541	213,420	225,561	235,657	229,740	96,598	159,598	128,926	149,074	38,464	85,648	108,969	91,155
							1,854	16,117	78,028	102,217	88,556	150,195	174,890	174,387	181,334	189,687	186,614	77,073	128,964	103,277	117,034	33,179	75,843	96,561	83,371
							621	10,391	72,407	100,865	94,110	145,821	177,662	173,033	179,317	190,322	190,339	86,974	130,276	103,674	117,120	33,584	76,308	100,444	88,100
							2,620	11,469	63,476	101,182	82,782	145,049	190,374	131,799	137,435	158,261	146,908	75,298	128,936	95,289	113,553	20,188	25,970	17,067	10,255
VAP	TBC	Te	X	TBC	Te	X	R <sup>2</sup>																		
							1,554	16,367	77,368	104,644	87,718	150,453	174,098	173,872	183,932	195,129	191,619	76,817	130,358	106,132	118,758	31,716	69,442	85,527	66,330
							537	23,420	68,908	93,792	76,008	134,711	163,382	167,124	174,209	185,840	186,213	79,020	131,624	94,935	109,215	28,363	62,411	82,354	66,337
							1,814	16,731	70,387	108,418	91,430	149,335	192,561	167,260	174,969	192,252	185,091	82,798	137,570	105,654	124,402	30,945	47,968	49,808	42,399
							R <sup>2</sup>																		
LT	TBC	Te	X	TBC	Te	X	R <sup>2</sup>																		
							0.9392	0.998	0.9991	0.9973	0.9983	0.9995	0.9978	0.9953	0.9982	0.9962	0.9966	0.9944	0.9998	0.9998	0.9993	0.9931	0.9945	0.9968	0.9943
							-22.94	0.9985	0.9992	0.9978	0.9972	0.9883	0.991	0.9942	0.9961	0.9944	0.9961	0.9921	0.9986	0.9991	0.9999	0.9914	0.9941	0.9973	0.9918
							-153.6	0.6146	0.9993	0.9992	0.994	0.9984	0.9903	0.9977	0.9977	0.9957	0.999	0.9969	0.9977	0.9934	0.9952	0.9977	0.9891	0.9936	0.9932
							-10.04	0.9992	0.9978	0.9976	0.9936	0.9997	0.9918	0.9976	0.9958	0.9962	0.9969	0.9915	0.9988	0.9895	0.9859	0.9063	0.9168	0.9513	0.9569
VAP	TBC	Te	X	TBC	Te	X	R <sup>2</sup>																		
							-0.248	0.9935	0.9992	0.9988	0.9990	0.9856	0.9978	0.9968	0.9983	0.998	0.9987	0.9955	0.9995	0.9984	0.9975	0.9922	0.9949	0.9937	0.9902
							-41.14	0.9967	0.9986	0.9955	0.998	0.9942	0.9906	0.9915	0.9929	0.9899	0.994	0.9863	0.9986	0.9993	0.9996	0.9868	0.9895	0.9942	0.9889
							-0.818	0.9831	0.9975	0.9999	0.9976	0.9972	0.9923	0.9975	0.9965	0.9963	0.9969	0.9894	0.9976	0.9915	0.9868	0.9067	0.9509	0.9881	0.9808
							RSE (%)																		
LT	TBC	Te	X	TBC	Te	X	RSE (%)																		
							4.05	1.11	0.58	0.72	0.65	1.57	1.75	1.10	1.53	1.37	1.24	1.29	1.99	0.54	1.00	3.22	2.17	2.56	2.98
							6.56	1.61	1.15	1.65	1.89	0.78	2.02	1.84	1.44	1.38	1.41	0.94	1.71	1.29	1.31	2.59	1.13	2.59	2.78
							2.66	9.69	3.05	3.42	4.39	2.30	2.62	3.13	3.07	2.61	3.43	2.75	3.04	2.96	3.76	4.49	3.55	4.93	4.82
							6.14	2.09	2.11	1.31	2.69	0.72	0.96	0.76	1.05	0.71	0.65	1.49	1.20	0.85	1.41	9.72	6.33	8.47	14.23
VAP	TBC	Te	X	TBC	Te	X	RSE (%)																		
							4.98	1.92	1.94	1.46	2.48	1.99	1.77	2.22	2.03	1.55	1.59	1.96	1.68	1.38	2.28	0.75	2.79	0.72	2.81
							10.1	3.63	2.80	2.23	2.97	2.08	2.18	1.54	1.42	1.13	1.44	1.91	3.28	1.65	1.70	3.28	4.00	3.66	4.34
							8.43	1.05	1.87	1.93	2.50	2.09	2.45	3.98	4.27	4.13	3.88	1.68	2.26	2.59	3.32	3.60	4.67	3.94	2.98

**Table 5. Comparison of the Relative Recovery (RR: %) of 17 VOCs between Different Sorbent Tube (DI and VAP) Methods against Link Tube and Thermal Desorption (LT/TD) Approach**

order	compound <sup>a</sup>	RR (DI)			RR (VAP)			PD <sup>b</sup>		
		TBC	Te	X	TBC	Te	X	TBC	Te	X
1	BA	85.0	78.9	69.1	84.3	75.0	76.7	0.85	4.83	−10.9
2	IA	78.6	77.6	77.8	80.5	72.1	83.4	−2.37	7.01	−7.15
3	VA	78.0	82.9	72.9	77.2	66.9	80.5	0.95	19.2	−10.4
4	B	87.1	84.6	84.1	87.3	78.1	86.6	−0.17	7.62	−2.95
5	T	80.8	82.0	87.9	80.4	75.5	88.9	0.45	8.04	−1.15
6	S	81.7	81.1	61.8	81.5	78.3	78.4	0.30	3.41	−26.9
7	p-X	80.4	79.5	60.9	81.5	77.2	77.6	−1.43	2.85	−27.3
8	m-X	80.5	80.8	67.2	82.8	78.9	81.6	−2.87	2.35	−21.5
9	o-X	81.2	82.8	63.9	83.4	81.1	80.6	−2.68	2.17	−26.0
10	MEK	79.8	90.0	77.9	79.5	81.8	85.7	0.33	9.15	−9.96
11	MIBK	80.8	81.6	80.8	81.7	82.5	86.2	−1.08	−1.03	−6.70
12	i-BuAl	80.1	80.4	73.9	82.3	73.6	81.9	−2.76	8.43	−10.9
13	BuAc	78.5	78.6	76.2	79.7	73.3	83.4	−1.47	6.75	−9.55
14	PPA	86.3	87.3	52.5	82.5	73.7	80.5	4.41	15.5	−53.3
15	BTA	88.6	89.1	30.3	81.1	72.9	56.0	8.44	18.2	−84.7
16	IVA	88.6	92.2	15.7	78.5	75.6	45.7	11.4	18.0	−192
17	VLA	91.5	96.6	11.3	72.8	72.8	46.5	20.4	24.7	−313
	average	82.8	83.9	62.6	81.0	75.8	76.5	1.93	9.25	−47.9
	SD	4.15	5.37	22.9	3.13	4.01	13.5	6.19	7.29	82.6
	CV <sup>c</sup>	5.01	6.40	36.5	3.86	5.29	17.6	321	78.7	−172

<sup>a</sup>AA and PA are excluded from this comparison, as explained in the text. <sup>b</sup>Percent difference (PD) = [RF(DI) − RF(VAP) × 100/RF (DI)]. <sup>c</sup>CV (coefficient of variation) = SD/mean × 100.

analyte responses between the three types of sorbent tubes (Te, X, and TBC) were evaluated using both direct injection and vaporization injection of the liquid standard. As shown in Table 4, the compatibility of RF values between the DI and VAP approaches differ greatly between compounds.

As a simple means to assess the VOC recovery patterns for each of the two ST methods, the calibration data of each ST method were normalized against those of the LT/TD method. The results shown in Table 5 indicate that the mean RR of the DI method (after normalization) is low for the X tube ( $X = 62.6 \pm 22.9\%$ ) relative to the other tube types (TBC =  $82.8 \pm 4.15\%$  and T =  $83.9 \pm 5.37\%$ ). It should be noted that the magnitudes of the RR values for most VOCs with relatively short retention time (Rt) are similar across all ST materials. In contrast, the RR values for species with relatively long Rt (such as some aromatics (p-X, m-X, o-X, and S) and VFA (PPA, BTA, IVA, and VLA)) tend to be significantly different between sorbent types. These complicated patterns are likely to reflect the effect of competitive adsorption and analyte displacement. The results of the X tube are much smaller for most of the long-Rt species than those of the Te and TBC tubes (mean relative recovery: TBC =  $84.8 \pm 4.40\%$ , T =  $86.2 \pm 6.17\%$ , and X =  $45.4 \pm 22.9\%$ ). The RR patterns of each VOC derived by the DI approach are plotted in Figure 5a. All target compounds on the x-axis are placed by their relative ordering of retention time (Rt) determined in this study. In the case of the X tube, the RR values of the DI approach decreased gradually with increasing Rt from p-X to VLA. In particular, compounds such as IVA and VLA seem to have rather low RR (below 20%), due possibly to their strong sorptivity.

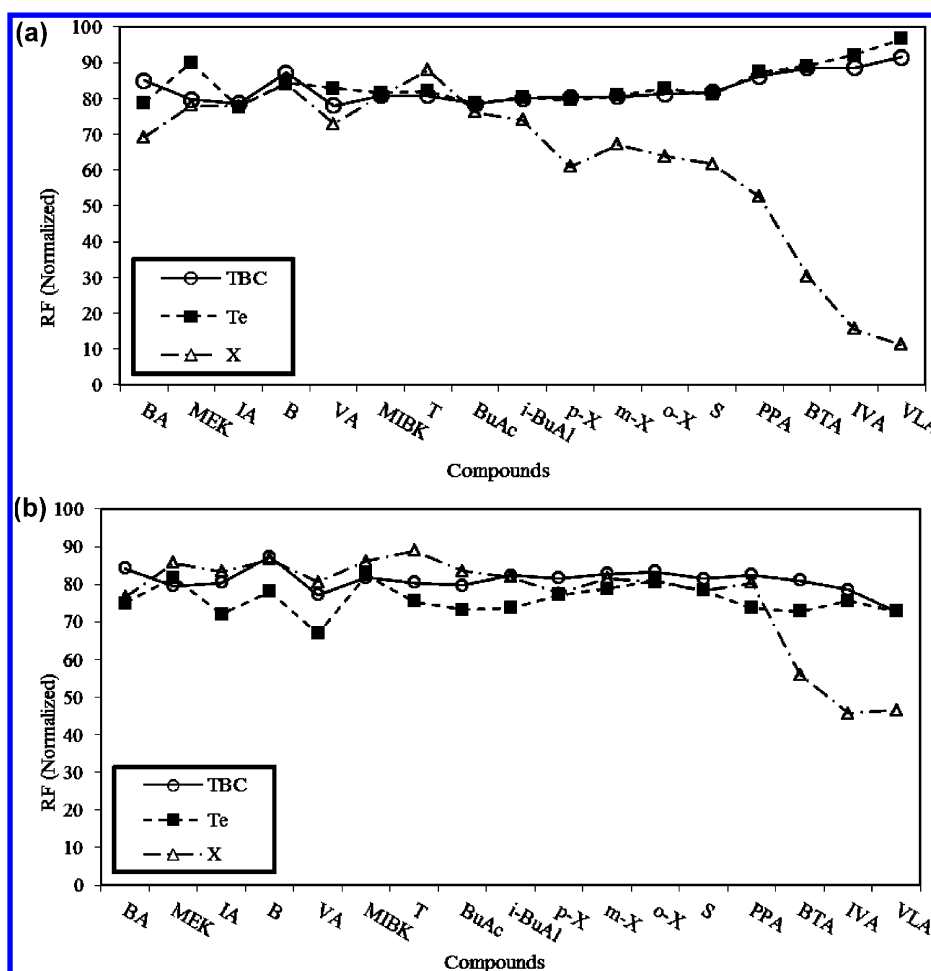
The reliability of the LT/TD method has been assessed in relation to some basic QA parameters. The linearity of VOCs derived from all three ST materials (except VFA on the X tube) is generally very significant with the  $R^2$  values of above 0.99.

In addition, the reproducibility of the LT/TD method can be compared briefly against those of the two sorbent-based methods (DI and VAP) in terms of RSE values of the response factor (Table 4). The results of the former appear to be superior over the latter two methods (using the mean of the three sorbent materials for each method) from 17 and 18 out of all 19 compounds, respectively. In fact, compilation of the reproducibility data shows that the RSE values of all VOCs are generally less than 5% with a few exceptions like VLA. As such, the observed results suggest that the LT/TD method investigated in this research should yield analytical precision far better than the common criteria (e.g., like less than 20%) recommended for the analysis of duplicate pairs of VOC by TO-17 of the US EPA.<sup>15</sup>

As shown in Table 5, the mean RR values of the VAP approach are generally higher for TBC ( $81.0 \pm 3.13\%$ ) than the others (T =  $75.8 \pm 4.01\%$  and X =  $76.5 \pm 13.5\%$ ). The mean RR values of Te and X tubes are similar, but the values for the individual species vary to a certain degree. For species with relatively long Rt (p-X to PPA), the results of all sorbent materials exhibit similar RR, with mean values of  $82.3 \pm 0.83\%$  (TBC),  $77.8 \pm 2.68\%$  (Te), and  $79.7 \pm 1.67\%$  (X). In contrast, the results derived for other species exhibit strongly contrasting trends. In the case of short-Rt species (BA to i-BuAl), the RR of the VAP method is higher in the X tube than in the Te tube (Figure 5). The mean RR values of the VAP method show significantly large gaps in BTA, IVA, and VLA between X ( $49.4 \pm 5.73\%$ ) and the others (TBC =  $77.4 \pm 4.25\%$  and Te =  $73.7 \pm 1.59\%$ ).

## DISCUSSION

**Comparison of Calibration Results between the Two ST Methods: Direct Injection vs Vaporization.** The results of our VOC analysis indicate that recovery by the ST method is



**Figure 5.** Comparison of the relative recovery (i.e., LT/TD-normalized RF values) of 17 VOCs between three sorbent tube types. (a) Direct injection (DI) of liquid-phase VOC standard into the ST. (b) Injection of liquid-phase VOC standard via vaporization (VAP).

strongly dependent on variables such as compound type, sorbent material type, and injection approach. The results summarized in Table 5 provide the RR values of target VOCs derived from each ST method against the LT/TD method. In addition, the difference in the VOC recovery between the two ST methods can also be assessed directly in terms of percent difference (PD).

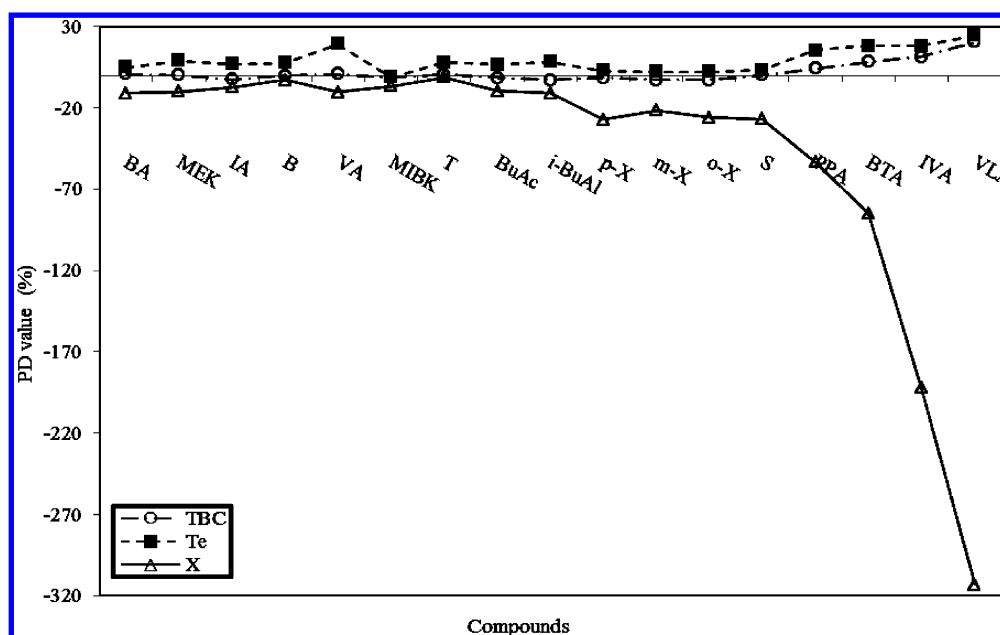
$$\text{PD (\%)} = \frac{(\text{RF (DI)} - \text{RF (VAP)})}{\text{RF (DI)}} \times 100 \quad (1)$$

The PD values of target VOCs derived from each of all three tube types can be compared meaningfully (Table 5). The results of the TBC tube are relatively low ( $1.93 \pm 6.19\%$ ), as all target VOCs other than VFA (PPA, BTA, IVA, and VLA) generally had fairly low PD values (i.e., below 3%). In the case of VFAs, their PD values increased systematically with the increasing molecular weight (MW), i.e., PPA = 4.41, BTA = 8.44, IVA = 11.4, and VLA = 20.4. The percent difference of VOCs between the two ST approaches was generally insignificant in the TBC tube. However, the DI approach yielded higher recovery for VFA than the VAP approach. It can thus be inferred that the VFA with strong physical adsorptivity should suffer more from the sorptive loss, if they are delivered in vaporized form along the transfer line of the TD system (comprising a stainless steel line, quartz trap, link tube, etc.).

In the case of the Te tube, the DI approach yielded higher RF values than the VAP approach, with a few exceptions

(e.g., MIBK) (the mean PD value of all target VOCs =  $9.25 \pm 7.29\%$ ). In particular, the VFA results from Te maintained higher PD values than the other target VOCs (PD values: PPA = 15.5%, BTA = 18.2%, IVA = 18.0%, and VLA = 24.7%). The observed PD patterns of Te thus suggest that its adsorptive reactions should have been induced less efficiently by the VAP than by the DI approach.

It is striking that the patterns of target VOCs, derived by the X tube (which has fairly strong adsorptivity relative to Te, for example), are significantly different from those of the other sorbents. The PD values of the X tube were consistently found to be negative for all target VOCs, implying the enhancement of RF values in the VAP relative to the DI approach (mean PD value =  $-47.9 \pm 82.6\%$ ). The results for VFA exhibited the largest difference in recovery patterns of sorbent materials between the two ST methods. In the case of TBC and Te tubes, the DI approach had higher RF values for VFA than the VAP approach, yielding positive PD values. In contrast, the patterns of the X tube were completely reversed, showing substantially large negative PD values (%) of  $-53.3$  (PPA),  $-84.7$  (BTA),  $-192$  (IVA), and  $-313$  (VLA). This observation thus clearly demonstrates the reduced capture/release efficiency of X tube for more sorptive (and less volatile) species like VFA.<sup>14</sup> In addition, it is also worth noting that the adsorption efficiency of the X tube uniquely shows preferential adsorption of gaseous VFA (VAP) over the liquid phase (DI approach).



**Figure 6.** Comparison of experimental bias (PD (%)) for the vaporization injection (VAP) approach relative to direct injection (DI) into sorbent tube types.

Figure 6 shows the PD values of target VOCs with three different ST material types. In the case of the X tube, the VAP approach appears to produce enhanced RF values more effectively for VFA. However, comparable data derived using the Te and TBC tubes was characterized by high RF values for the DI approach, yielding a positive PD. It is thus concluded that the TBC tube with the largest versatility should experience the least analyte loss of all ST sorbent tubes tested. This superiority of the TBC tube can be accounted for by the synergistic effect of all three sorbents to extend the adsorption capacities of each individual sorbent.

**Relative Recovery of VOCs for the Two Sorbent Tube Approaches.** In the application of the LT/TD method, the minimum loss of VOCs in the L-WS can be attained, as the analytes can be transferred into the CT along the simplest track without the use of the sorbent tube. As such, the LT/TD method is useful to assess the recovery of VOCs relative to the ST methods and between different sorbent materials. Table 4 provides the calibration results of L-WS in terms of the RF,  $R^2$ , and RSE (%) values among all three key analytical methods investigated in this work. The RF values of all 17 target VOCs

in the LT/TD method are consistently higher than those derived by the two ST methods. As shown in Table 5, the relative recovery of the target VOCs can thus be assessed for each of the two ST methods in relation to the LT/TD data. The RR of target VOCs derived by VAP is generally higher in TBC than the other sorbent types. In contrast, the DI-based results showed the largest mean recovery in the Te tube of all three sorbents. The mean RR of DI was computed on the order of Te =  $83.9 \pm 5.37\%$ , TBC =  $82.8 \pm 4.15\%$ , and X =  $62.6 \pm 22.9\%$ , while those of VAP were TBC =  $81.0 \pm 3.13\%$ , X =  $76.5 \pm 13.5\%$ , and Te =  $75.8 \pm 4.01\%$ . The observed difference in VOC recovery patterns with types of sorbent materials, when compared with some previous studies, was in fact different to a certain degree. For instance, Gallego et al.<sup>16</sup> assessed the recovery patterns of two sorbent tube materials ((1) Tenax TA and (2) multibed (Carbotrap + Carboxen 569)) by measuring up to 27 VOCs from both indoor and outdoor samples. These authors evaluated the percent differences in the measured concentration between the two types of sorbent tubes as follows:

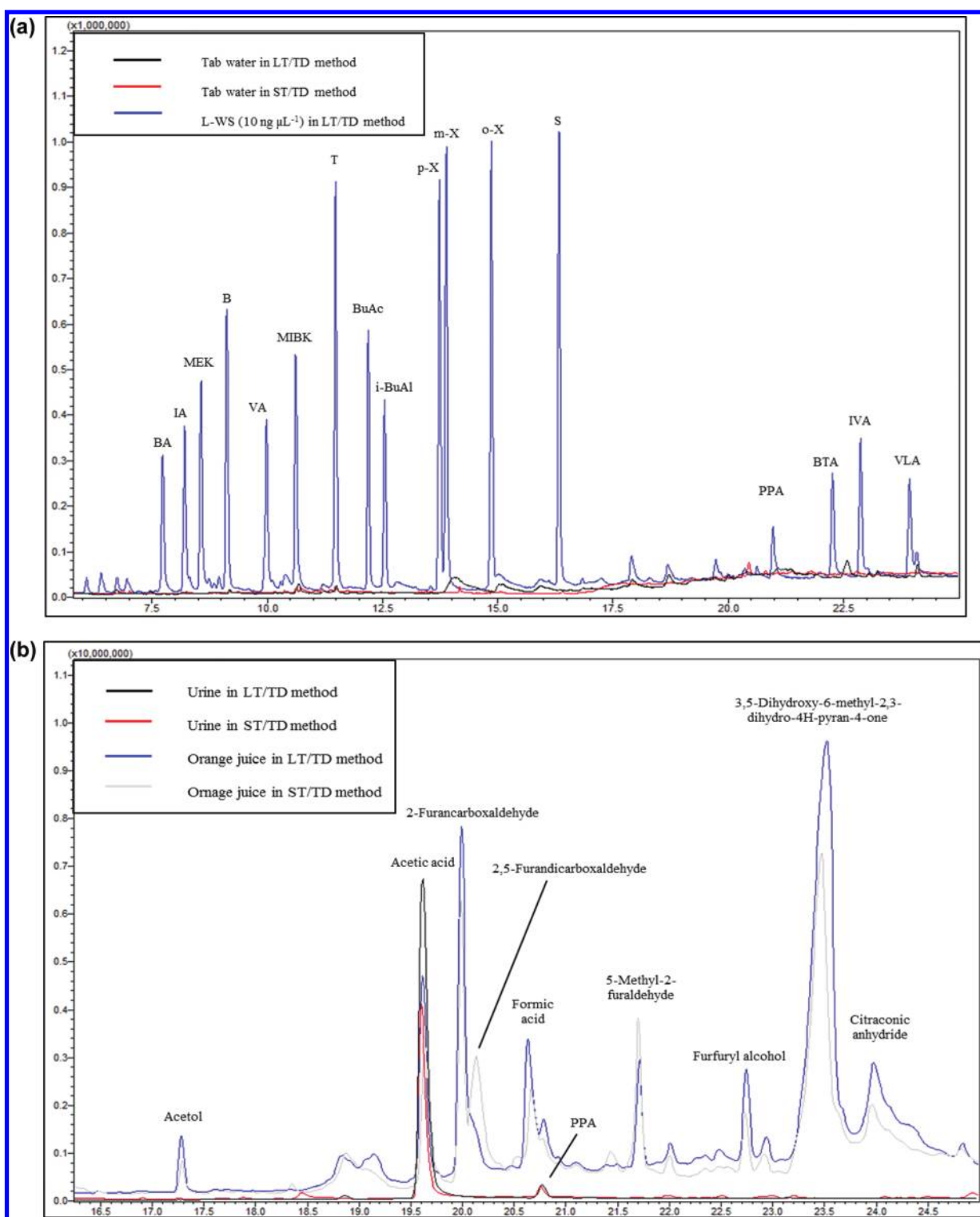
$$\text{PD (\%)} = \frac{(\text{Concentration of multibed tube} - \text{concentration of Te tube})}{\text{concentration of multibed tube}} \times 100 \quad (2)$$

On the basis of a comparative analysis of VOCs from those field samples, they reported that the multibed tube had higher mean concentrations of VOCs (42.8% from indoor samples vs 32.1% from outdoor samples) than those of the Tenax tube. Their results for individual species consistently indicate the relative dominance of the multibed tube: B = 86.9%, T = 39%, p- + m-X = 4.05%, and o-X = 8.82%. Note that the concentration of benzene determined by the multibed tube was nearly twice that of the Tenax tube. Although the percent differences of B, T, and X (BTX) for the ST method are comparable between tube types (e.g., TBC and Te), they are significantly different between injection approaches (e.g., VAP

and DI). Although the VAP results consistently yield positive values [B = 10.5%, T = 6.2%, p-X = 5.3%, m-X = 4.8%, and o-X = 2.8%], this is not the case for DI.

$$\text{PD (\%)} = \frac{\{\text{RF (TBC(ST))} - \text{RF (Te(ST))}\}}{\text{RF (TBC(ST))}} \times 100 \quad (3)$$

The difference in BTX recovery between the two tube types is generally much smaller in this study than that found by Gallego et al.<sup>16</sup> However, it is interesting that the difference between sorbent materials decreased greatly with increasing molecular weight of VOCs in both the previous and present studies. The



**Figure 7.** Chromatograms of liquid standard (L-WS) and some environmental samples derived by both LT/TD and VAP-based ST/TD (TBC tube) methods (x-axis: Rt (min) and y-axis: sensitivity (unitless)). (a) Tap water sample and L-WS. (b) Urine and orange juice samples (all from 1  $\mu\text{L}$  samples).

molecular weight dependence of VOC recovery and the associated effect of sorbent types have also been observed.<sup>17</sup> They compared the concentrations of 10 target VOCs in gaseous standards for two types of sorbent tubes: a multibed tube (Tenax-TA + Carbosieve SIII) and a single-bed tube (Tenax TA). The concentration of 10 target VOCs in the multibed tube was consistently higher than the single tube (mean PD values of 10 target VOCs (by eq 2 = 33.5%)). For the low molecular weight

compounds (such as AA and methanol), the PD values were very high (e.g., above 58%), whereas the PD values of heavy species (e.g., toluene, 1,2,4-trimethylbenzene, and hexachlorobutadiene) were below 10%. Although the VOC recovery obtained by sorbent tubes varied with the individual compound, multibed tubes generally gave higher RF values than the Tenax tube.<sup>5</sup>

If the results derived by our reference method (denoted the LT/TD approach) are evaluated on a parallel basis, the loss of



VOCs is found to occur fairly consistently with the use of the ST/TD method. The TBC tube had the highest RR of target VOCs among the ST methods, showing the lowest percent difference between the DI and VAP approaches, e.g.,  $17.2 \pm 4.15\%$  (DI) and  $19.0 \pm 3.13\%$  (VAP). In the case of the X tube, the relative loss of target VOCs was less significant for the VAP approach (76.5%) than for the DI approach (62.6%). The values of  $R^2$  were consistently above 0.99 in all analytical methods (except for the X tube). The RSE values were below 2% in the LT/TD method and the TBC tube and below 4% in the Te and X tubes. In conclusion, the RF values derived by the LT/TD method were consistently the highest of all the analytical methods, with the best reproducibility (and linearity).

**Application of LT/TD and ST/TD Methods to Some Environmental Samples.** As the primary goal of this study, we evaluated the applicability of the LT/TD against the two ST/TD methods by measuring the recovery patterns for a list of target VOCs. In order to examine the extendibility of the LT/TD method, we carried out an ancillary experiment in which the recovery patterns of the ST-VAP approach by TBC were measured from three environmental samples consisting of (1) tap water, (2) orange juice, and (3) urine. The ST-TD analysis of this ancillary experiment was confined to the VAP approach alone since the use of DI can cause the possible contamination of ST by the impurities in the sample matrix.

Figure 7a shows an overlay of the chromatograms of about 10 ng of L-WS (by LT/TD) and 1  $\mu\text{L}$  of tap water with two different analytical methods (LT/TD and ST/TD). The results with tap water in both methods indicate that such samples can be treated as blank samples. In contrast, several compounds were detected from both the orange juice and urine samples (1  $\mu\text{L}$ ). (Figure 7b). However, as only a single compound of PPA from both environmental samples matches a list of target compounds, the direct quantitation of these samples is limited to PPA only. If the PPA concentration in the urine sample is quantified using RF values derived from this study, a value of LT/TD ( $28.5 \text{ ng } \mu\text{L}^{-1}$ ) is obtained, which slightly exceeds that of ST/TD ( $27.6 \text{ ng } \mu\text{L}^{-1}$ ). Although direct quantitation cannot be made for all other species, the compatibility of the two methods can again be assessed by their peak areas as follows:

$$\text{PD (\%)} = \frac{(\text{peak area (LT)} - \text{peak area (ST)})}{\text{peak area (LT)}} \times 100 \quad (4)$$

In the case of the urine sample, the two identified species, acetic acid and PPA, yielded PD values of 36.7 and 16.6%, respectively. The peak areas of the orange juice samples were also consistently higher for the LT/TD method than the ST/TD method except for two compounds (2,5-furandicarboxaldehyde and 5-methyl-2-furaldehyde). Although our test of LT/TD analysis for the real samples has been conducted on a fairly limited scale, the data sets derived from this initial study suggest that the use of such a method can be regarded as a valuable tool to extend the applicability of the TD system.

## CONCLUSIONS

The sorbent tube sampling method is one of the most widespread approaches to collect and analyze gaseous VOCs. In order to quantify VOC samples, many laboratories prefer to use liquid-phase standards rather than gas-phase standards for several practical reasons (e.g., convenience and price). If sorbent tubes are used to analyze VOC samples, loss of VOCs

occurs inevitably in the process of adsorption and desorption during the TD process. Therefore, although the sorbent tube method is fairly useful, its reliability still needs to be validated with respect to its application to the TD system.

In this study, the recovery of all target VOCs in the L-WS was evaluated for two injection approaches by the ST/TD method ((1) DI and (2) VAP), using the LT/TD method as a reference. An ST/TD-based analysis was also made to allow comparison between three types of sorbent tubes ((1) Tenax TA, (2) Carboxen X, and (3) Tenax + Carboxen B + Carboxen 1000). The calibration results derived in terms of RF values were then used to estimate the relative recovery between the two ST methods and three sorbent materials. The recovery of target VOCs by the ST method decreased due to adsorption and desorption for the three sorbent materials examined in this study. The calibration results were consistently higher for the LT/TD method than either of the two ST methods, with the exception of two light carbonyls (AA and PA).

The results of this study confirm that the loss of VOC occurs fairly systematically with the ST method, while such loss patterns vary, depending on the injection approaches employed and with the type of sorbent material. The LT/TD method was highly efficient for allowing the assessment of the relative recovery of the ST methods between different sample loading approaches (DI and VAP). As a result, the calibration of VOCs made by the LT/TD method enabled us to describe the fundamental aspects of VOC recovery by TD/GC/MS, when the ST/TD analysis was made by the diverse sorbent material types. In addition, the results of preliminary tests on some environmental samples suggest that the applicability of the LT/TD method can be expanded to various sample types. The overall results of our study confirm that the LT/TD method is a powerful tool to evaluate the various aspects of VOC analysis by the ST method. Hence, if one considers that there had been no specific tools to assess the relative recovery in the TD-based analysis of volatile species by the sorbent collection method, the introduction of the LT/TD approach can offer some insights into the development of the tactics for narrowing the uncertainties in their determination.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: khkim@sejong.ac.kr. Tel: 82-2-3408-3233. Fax: 82-2-3408-4320.

### Notes

The authors declare no competing financial interest.

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