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Generation of Sub-Part-per-Billion Gaseous Volatile Organic Compounds at Ambient Temperature by Headspace Diffusion of Aqueous Standards through Decoupling between Ideal and Nonideal Henry's Law Behavior

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S *Supporting Information*

ABSTRACT: In the analysis of volatile organic compounds in air, the preparation of their gaseous standards at low (sub-ppb) concentration levels with high reliability is quite difficult. In this study, a simple dynamic headspace-based approach was evaluated as a means of generating vapor-phase volatile organic compounds from a liquid standard in an impinger at ambient temperature (25 °C). For a given sampling time, volatile organic compound vapor formed in the headspace was swept by bypassing the sweep gas through the impinger and collected four times in quick succession in separate sorbent tubes. In each experiment, a fresh liquid sample was used for each of the four sampling times (5, 10, 20, and 30 min) at a steady flow rate of 50 mL min^{-1}. The air–water partitioning at the most dynamic (earliest) sweeping stage was established initially in accord with ideal Henry's law, which was then followed by considerably reduced partitioning in a steady-state equilibrium (non-ideal Henry's law). The concentrations of gaseous volatile organic compounds, collected after the steady-state equilibrium, reached fairly constant values: for instance, the mole fraction of toluene measured at a sweeping interval of 10 and 30 min averaged 1.10 and 0.99 nmol mol^{-1}, respectively (after the initial 10 min sampling). In the second stage of our experiment, the effect of increasing the concentrations of liquid spiking standard was also examined by collecting sweep gas samples from two consecutive 10 min runs. The volatile organic compounds, collected in the first and second 10 min sweep gas samples, exhibited ideal and nonideal Henry's law behavior, respectively. From this observation, we established numerical relationships to predict the mole fraction (or mixing ratio) of each volatile organic compound in steady-state equilibrium in relation to the concentration of standard spiked into the system. This experimental approach can thus be used to produce sub-ppb levels of gaseous volatile organic compounds in a constant and predictable manner.
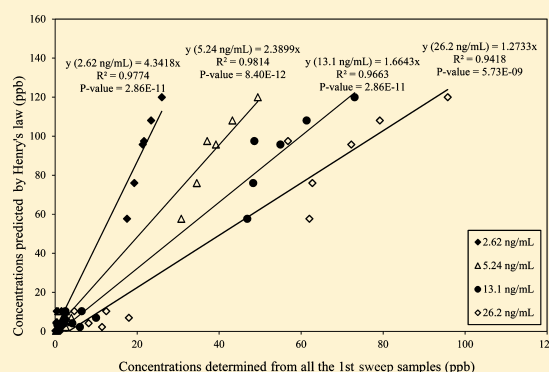
I n order to analyze volatile organic compounds (VOCs) in air, diverse analytical methods have been used by several researchers. Basically, gas chromatographs (GC), equipped with either a flame ionization detector (FID) or mass spectrometer (MS) as a detector, have been most commonly used for the analysis of diverse VOCs in air.[1−5] Liquid- or gas-phase standards are a fundamental requirement for the quantitative analysis of VOCs in gaseous media, especially air. Although liquid standards offer the advantages, such as low expense and easy handling compared to gaseous standards, they are more prone to matrix effects than gaseous standards.[6,7]

In general, the use of a gaseous standard for quantitative analysis of gaseous samples is advantageous, as it can reduce experimental biases associated with matrix effects. However, the preparation and handling of gaseous standards are much more complicated than those of liquid standards. Moreover, it may be much difficult to store the diverse kinds of VOCs in gas relative to liquid counterparts, especially if the required VOC concentrations are at or near ambient air levels, e.g., below

the sub-ppb level.[8,9] For these reasons, the use of liquid standard is as common as or may be more frequent than that of the gaseous counterpart in the practical quantitation of VOCs.[6]

Enormous efforts have been made to eliminate or reduce matrix effects in the application of liquid standards for quantitative analysis of the gaseous VOC sample. As part of such efforts, the development of vaporization approaches through which a liquid standard is converted into a gaseous standard has gained a great deal of attention (i.e., thermal vaporization or the use of the diffusion, e.g., using membrane permeation).[10−12] However, the reliability of these methods can be limited by a number of factors. As such systems are generally built to diffuse high amounts of target compounds, a modified application is needed to produce standards at low concentration levels.[12−14] The reproducibility or accuracy of

Table 1. Basic Information of the 14 Target VOCs Investigated in This Research

order	group	compounds	short name	MW (g mol^{-1})	density (g cm^{-3})	boiling point (°C)	formula	CAS number	mass spectrum[a] (m/z)
1		benzene	B	78.11	0.878	80.1	C_6H_6	71-43-2	78
2		toluene	T	92.14	0.866	111	C_7H_8	108-88-3	91, 92
3	aromatic	p-xylene	p-X	106.2	0.865	138	C_8H_{10}	106-42-3	91, 106
4		m-xylene	m-X	106.2	0.865	139	C_8H_{10}	108-38-3	91, 106
5		o-xylene	o-X	106.2	0.88	144	C_8H_{10}	95-47-6	91, 106
6		styrene	S	104.2	0.906	145	C_8H_8	100-42-5	78, 103, 104
7		propionaldehyde	PA	58.1	0.798	46−50	C_3H_6O	123-38-6	58
8	aldehyde	butyraldehyde	BA	72.1	0.805	74.8	C_4H_8O	123-72-8	39, 41, 43, 72
9		isovaleraldehyde	IA	86.1	0.797	90−93	$C_5H_{10}O$	590-86-3	39, 41, 43, 58, 71
10		n-valeraldehyde	VA	86.1	0.81	102−103	$C_5H_{10}O$	110-62-3	39, 41, 43, 58
11	ketone	methyl ethyl ketone	MEK	72.11	0.805	79.64	C_4H_8O	78-93-3	43, 72
12		methyl isobutyl ketone	MIBK	100.2	0.802	117−118	$C_6H_{12}O$	108-10-1	43, 58
13	ester	n-butyl acetate	BuAc	116.2	0.881	126	$C_6H_{12}O_2$	123-86-4	43, 56
14	alcohol	isobutyl alcohol	i-BuAl	74.12	0.801	108	$C_4H_{10}O$	78-83-1	42, 43

[a]Mass spectrum selected for the EIC-base analysis.

Table 2. Preparation Procedures of Liquid Phase VOC Standard Used for the Analysis by the TD-GC-TOF MS System in Both Exp Stages 1 and 2

		(A) preparation of liquid phase standard for 14 target VOCs selected in this research														
	compounds	methanol	B	T	p-X	m-X	o-X	S	PA	BA	IA	VA	MEK	MIBK	BuAc	i-BuAl
primary grade chemical	concentration (%)		99.5	99.5	99.0	99.0	97.0	99.0	97.0	99.0	97.0	97.0	99.0	99.5	99.5	99.0
PS[a]	volume (μL)	16 640	240	240	240	240	240	240	240	240	240	240	240	240	240	240
	concentration (ng μL^{-1})		10 483	10 340	10 276	10 276	10 243	10 763	9 289	9 563	9 277	9 428	9 563	9 576	10 519	9 516
1st WS[b]	volume (μL)	19 750	250	250	250	250	250	250	250	250	250	250	250	250	250	250
	concentration (ng μL^{-1})		131	129	128	128	128	135	116	120	116	118	120	120	131	119

			(B) preparation of liquid-WS (L-WS) for sorbent tube (ST)-based calibration													
	mixing volume (μL)		concentration[c] (ng μL^{-1})													
order	1st L-WS	methanol	B	T	p-X	m-X	o-X	S	PA	BA	IA	VA	MEK	MIBK	BuAc	i-BuAl
1	30	1 470	2.62	2.59	2.57	2.57	2.56	2.69	2.32	2.39	2.32	2.36	2.39	2.39	2.63	2.38
2	75	1 425	6.55	6.46	6.42	6.42	6.40	6.73	5.81	5.98	5.80	5.89	5.98	5.98	6.57	5.95
3	150	1 350	13.1	12.9	12.8	12.8	12.8	13.5	11.6	12.0	11.6	11.8	12.0	12.0	13.1	11.9
4	300	1 200	26.2	25.9	25.7	25.7	25.6	26.9	23.2	23.9	23.2	23.6	23.9	23.9	26.3	23.8
5	750	750	65.5	64.6	64.2	64.2	64.0	67.3	58.1	59.8	58.0	58.9	59.8	59.8	65.7	59.5

			(C) preparation of spiking standard (SS)-based calibration of VOC using impinger approach (Exp stage 2)													
	mixing volume (μL)		concentration[d] (ng mL^{-1})													
order	L-WS (3rd)[e]	distilled water	B	T	p-X	m-X	o-X	S	PA	BA	IA	VA	MEK	MIBK	BuAc	i-BuAl
1	10	49 990	2.62	2.59	2.57	2.57	2.56	2.69	2.32	2.39	2.32	2.36	2.39	2.39	2.63	2.38
2	20	49 980	5.24	5.17	5.14	5.14	5.12	5.38	4.64	4.78	4.64	4.71	4.78	4.79	5.26	4.76
3	50	49 950	13.1	12.9	12.8	12.8	12.8	13.5	11.6	12.0	11.6	11.8	12.0	12.0	13.1	11.9
4	100	49 900	26.2	25.9	25.7	25.7	25.6	26.9	23.2	23.9	23.2	23.6	23.9	23.9	26.3	23.8

[a]PS: Dilution of pure chemical (primary grade chemical) to make 20 mL of solution. [b]1st WS: Dilution of PS to make 20 mL solution. [c]Analysis (injection) volume for the ST loading: 1 μL. [d]Total volume of water contained in impinger: 50 mL. [e]For this impinger-based analysis, the third calibration point of L-WS for ST-based calibration (B = 13.1 ng μL^{-1}) was used: a single spiking volume of 10 μL in exp stage 1 and four spiking volumes of 10−100 μL in exp stage 2.

such adaptations may be compromised further by significant experimental effects such as sorptive loss on storage container surfaces during sample transfer. This generally implies that the production of low concentration gaseous standards is less reliable technically than that of their high counterparts or liquid standards. Moreover, an extended storage of such low concentration standards should be generally more vulnerable in terms of stability.[15,16]

In an effort to accurately produce gaseous VOC standards, we investigated a simple vaporization approach. Our method is partly based on the concept of the "dynamic headspace saturation" technique used to create a representative vapor
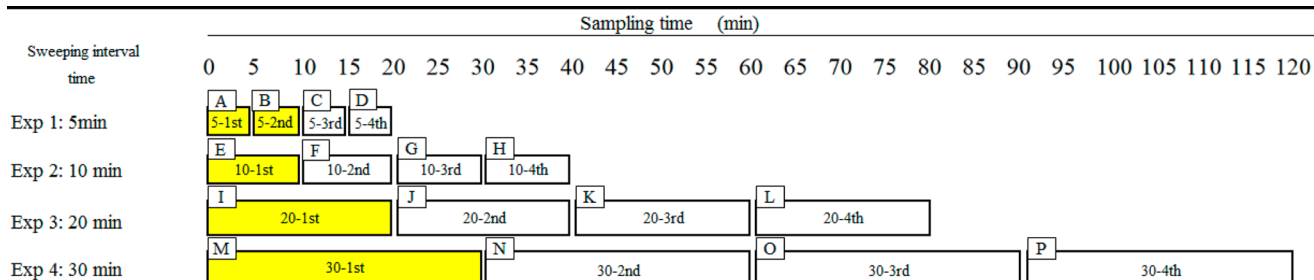
Figure 1. Experimental scheme of vaporized VOC analysis in the Exp stage 1 (fixed spiking solution concentration: 10 μL addition of 13.1 ng μL^{-1} L-WS into 50 mL of solution to make the final concentration of 2.62 ng mL^{-1} (in the case of benzene)).

mixture for substances that are mixtures of multiple compounds.[17−19] To this end, the vaporization properties of VOCs were evaluated through a series of calibration experiments with the aid of an impinger device as the sweep gas generation platform. To summarize, liquid VOC standards were spiked into the distilled water inside the impinger. Nitrogen (N$_2$) was then swept through the impinger to vaporize the VOCs. The swept gas samples were collected on a sorbent tube (ST) sampler and analyzed to characterize the vapor concentration of each individual VOC produced under the physicochemical conditions employed in the experimental system. On the basis of this study, we introduce a simple and reliable approach to the generation of low concentration gaseous VOC standards.

■ MATERIALS AND METHODS

Preparation of Liquid VOC Standards and Instrumental Setups. A total of 14 VOCs were selected as the target analytes in this study: (1) aromatic hydrocarbon, benzene (B), toluene (T), *p*-xylene (p-X), *m*-xylene (m-X), *o*-xylene (o-X), and styrene (S); (2) aldehyde, propionaldehyde (PA), butyraldehyde (BA), isovaleraldehyde (IA), and *n*-valeraldehyde (VA); (3) ketone, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK), and (4) others, *n*-butyl acetate (BuAc) and isobutyl alcohol (i-BuAl) (Table 1). The selection of these targets was made, as differences in their physicochemical properties, while most of them are well-known as strong odorants, they offer unique opportunities to evaluate the relative response properties of different VOC functional groups in the thermal desorber (TD)/GC/MS analysis.[7,12] Note that the use of the chemical acronyms (given in the parentheses) is confined to tables and figures for simplicity. Liquid working standards of these VOCs were prepared: (1) for the generation of a vaporized VOC standard sample through spiking into distilled water and (2) for direct introduction into a ST to assess the recovery rate of the spiking standard (SS).

The liquid working standard (L-WS) was prepared by a two-step gravimetric dilution of the primary standard (PS) using methanol (Table 2). For the quantitative analysis of the vaporized VOC collected via sweep gas, we used a combination of a sorbent tube (ST) and a TD (UNITY model, Markes International, Ltd., U.K.). The ST was prepared as a three-bed type (100 mg of Tenax TA, Carbopack B, and Carboxen 1000)[12] and analyzed using a GC 7890A (Agilent) equipped with a Bench TOF-dx MS (Almsco, U.K.). The TD focusing trap was packed with Tenax TA and Carbopack B (Table 1S in the Supporting Information). The results were initially examined in total ion chromatographic (TIC) mode over

(mass range, 35−350 amu). Extracted ion chromatographic (EIC) mode was also applied to eliminate the influence of the potential interferences (Table 1). The details of preparation procedures for standards and instrumental setups are described in the Supporting Information.

Experimental Approach. *Direct Analysis of Liquid Working Standard by ST.* The liquid working standard used for the production of vaporized VOC was initially analyzed by directly loading it (via syringe) onto ST. These ST-based calibration results were then used as a reference to assess the relative recovery of vapor-phase standard generated when the spiking standard was used in the impinger. The liquid standard was injected directly into the ST and then analyzed by the TD-GC-time-of-flight (TOF) MS system. The method used for this ST-analysis of liquid working standard was described in detail in our previous study.[12] In short, the inlet and outlet of the ST were connected to a 10 L polyester aluminum (PEA) bag filled with back-up gas (ultrapure nitrogen >99.999%) and the vacuum pump interfaced with mass flow controller (Sibata ΣMP-30, Japan), respectively. The liquid working standard was injected onto the ST via a temporary injection port made from the Teflon tube that connected the inlet of the ST and the PEA bag,[12] while the back-up gas flowed from the PEA bag to the ST (flow rate = 100 mL min^{-1} for 5 min). The VOC loaded on the ST was then thermally desorbed, separated, and detected by the TOF MS (Table 2S in the Supporting Information).

Analysis of Vaporized VOCs Released via Sweep Gas from the Spiked Standard. To acquire vapor-phase VOC from liquid working standard, two types of experiments defined as stages 1 and 2 were conducted. In exp stage 1, the impinger (173 mL capacity) was first loaded with 50 mL of deionized water, and 10 μL of the liquid working standard used for the third point ST-based calibration (13.1 ng μL^{-1} in case of benzene) was spiked (added) to make the final concentration of 2.62 ng mL^{-1}. The VOCs vaporized from the spiked standard in the impinger were then swept into the ST by a 50 mL min^{-1} flow of gas (Figure 1S in the Supporting Information). A set of vaporized VOC samples were then collected onto ST using four different sampling periods (5, 10, 20, and 30 min). For each of all four intervals, the collection of VOCs was made in a quick succession, four times, to describe the temporal trend of vaporization from our dynamic vapor generation system. Figure 1 depicts the experimental scheme in this study and the sample code designated for the sampling interval (min) and order. Here, the code of "10-2nd" is used to designate the second ST collected at 10 min sampling interval -"F" in Figure 1.

In the second stage of our experiments, the effect of the concentration of standard spiked into the impinger on the generation of vaporized VOC was also evaluated by sampling twice, consecutively at each liquid standard concentration level, each for a period of 10 min. For this second stage experiment, the same liquid working standard used for exp 1 (13.1 ng μL^{-1} in the case of benzene) was also used, as described in Table 2C. To assess vaporization with the varying concentrations of the initial liquid working standard, 10, 20, 50, and 100 μL of this liquid working standard were spiked into 50 mL of solution to make four different concentrations (2.62−26.2 ng mL^{-1}). Using each of these solutions, the relationship between the mole fraction of vaporized VOC and the concentration of the liquid standard was investigated. The results were then used to derive the equation to predict the mole fraction of vapor that would be generated from the initial liquid standard concentration.

■ RESULTS AND DISCUSSION

Patterns to Generate the Vaporized VOC at Fixed Concentration. Table 3S in the Supporting Information shows the mass (ng) and mole fraction (nmol mol^{-1}) of VOC vaporized from SS at four different intervals of 5, 10, 20, and 30 min in exp stage 1. In addition, on the basis of the quantitation of vaporized VOC, the relative recovery of sweep gas (SG) against spiking standard (SS) was also computed as relative recovery (RR) = SG/SS (%). The mole fractions of vaporized VOCs varied depending on the characteristics of VOC concerned and the vaporization conditions (such as the sampling time and the number of repetitive runs for sampling). For a comparison, the mole fractions of vaporized VOCs derived from these experiments are plotted in Figure 2S in the Supporting Information. The six aromatic VOCs exhibited the highest mole fractions during the first sweep cycle (i.e., the first sweep gas). Then, their mole fractions decreased gradually with the repetition of the sampling (2-4th sweep gas samples) (The mean mole fractions (nmol mol^{-1}) of the six aromatic VOCs in the first sweep gas also decreased significantly with increasing the sampling time: (1) 5 min = 33.8 ± 5.57, (2) 10 min = 21.5 ± 2.99, (3) 20 min = 13.1 ± 2.58, and (4) 30 min = 9.72 ± 2.66). In contrast, the six aromatic VOCs measured from the continuous run (e.g., 2-4th sweep gas samples) had fairly low, but constant, vapor mole fractions below 6 nmol mol^{-1}, regardless of differences in the sampling duration.

The concentrations of methyl ethyl ketone, methyl isobutyl ketone, and n-butyl acetate were also higher in the first sweep gas samples than in the 2nd-4th sweep gas samples. The mean mole fractions (nmol mol^{-1}) of methyl ethyl ketone, methyl isobutyl ketone, and n-butyl acetate in the first sweep gas were (1) 5 min =2.11 ± 0.49, (2) 10 min =1.77 ± 0.48, (3) 20 min =1.51 ± 0.29, and (4) 30 min =1.10 ± 0.16. Their concentrations in the first sweep gas were about 3 times higher than those of the second-fourth sweep gas samples. It should however be noted that such differences were much smaller than those seen from aromatic VOCs. In the case of four aldehydes and isobutyl alcohol, their concentrations were similar between the first and later samples. Although the "5-1st" concentrations of four aldehydes and isobutyl alcohol had higher values, all the subsequent (15) samples generally maintained very stable (similar) concentrations (relative standard error (RSE) of all samples without "5-1st") (1) propionaldehyde = 5.09%, (2) butyraldehyde = 3.54%, (3) isovaleraldehyde = 3.74%, (4) n-valeraldehyde = 2.08%, and (5) isobutyl alcohol = 7.00%.

Hence, in order to generate the vaporized standards from the model system, the vaporization trend of VOCs needs to be defined between the initial (first sweep gas) and near-equilibrium sampling stages (2-4th sweep gas), as described below.

Characteristics of VOC Vaporization at the Initial Dynamic Stage. As soon as liquid standard is added into the impinger, VOCs begin to vaporize. The vaporization of each VOC is affected by the combined effects of several factors (i.e., polarity, molecular weight, boiling point, solubility, etc.). The extent of vaporization tends to peak consistently in the first sweep gas but reduces to a constant level in subsequent runs. The characteristics of the vapor concentration curve for each VOC are initially controlled by air−water partition coefficients (which are in turn controlled by the ideal Henry's law behavior (solubility)) during the first sweep cycle. However, it is then regulated by the steady-state equilibrium stage such as the nonideal Henry's law behavior (ones collected subsequently after the first sweep sample (first sweep gas)). Hence, diffusion of VOC from the liquid to gas phase should be controlled initially by air−water partitioning due to the solubility of VOC (the Henry's law).[20] Although many different forms of the Henry's law have been introduced, one can express it in a simplified form of

$$k_H = p/C$$

where k_H is a constant with the dimensions of pressure divided by concentration.[20] This constant however varies depending on the relationship between solute and the solvent as well as the temperature conditions.

The control effect of the Henry's law may be no longer valid, as the steady-state equilibrium stage is established subsequently that does not follow the ideal solubility control. As shown in Table 3S in the Supporting Information, the concentrations of vaporized VOCs in the first sweep gas were much higher than those seen in the 2nd-4th sweep gas. This effect was most significant in the case of nonpolar, aromatic VOCs. The concentration of six aromatic VOCs measured from the"5-1st"sample averaged as 33.7 ± 3.52 ng. If the recovery rate of VOCs is computed as the mass ratio of target compound between sweep gas and spiking standard, the relative recovery value for the aromatic VOCs in "5-1st" averaged 25.7 ± 2.69%. The enhanced vaporization rate was seen in all four sampling periods of the initial sample set relative to the same periods in subsequent sampling sets. It is also noteworthy that the mean RR of six aromatic VOCs in the first sweep gas increased systematically with increasing sweep duration (1) 25.7 ± 2.69% (5-1st), (2) 32.8 ± 2.73% (10-1st), (3) 39.6 ± 3.45% (20-1st), and (4) 43.8 ± 6.78% (30-1st). However, if the recovery is computed in terms of the concentration with the consideration of the sample volume, the RR tend to decrease due to the dilution effect (Table 3S in the Supporting Information).

According to our experimental scheme, the recovery patterns of VOCs released from spiked standards can also be assessed at least partially in terms of the vapor pressure (or polarity) of each VOC. For example, nonpolar aromatic VOCs can be vaporized most effectively upon spiking the liquid standard to record high recoveries. In contrast, compounds with low polarity (e.g., aldehyde, ketone, ester, and alcohol) exhibit low recovery relative to the aromatics. Especially, the RRs of the four aldehydes and isobutyl alcohol were very low: below 1% at "5-1st" (RR: (1) propionaldehyde = 0.46%, (2) butyraldehyde = 0.48%, (3) isovaleraldehyde = 0.64%, (4) n-valeraldehyde =

Table 3. Relationship between Gaseous VOC Concentrations (nmol mol^{-1}) in Sweep Gas (2nd Sample) and Spiking Solution Concentrations (ng mL^{-1}) by Dynamic Vapor Generation System (Exp Stage 2)^a

| | | concentration of SS (ng mL^{-1}) | | | | concentration in sweep gas (nmol mol^{-1}) | | | | predictive equation^b | | |
| | | calibration points | | | | | | | | | | |
order	compounds	1	2	3	4	1	2	3	4	slope	R^2	intercept
1	B	2.62	5.24	13.1	26.2	1.78	2.97	8.08	18.0	0.694	0.9965	−0.4920
2	T	2.59	5.17	12.9	25.9	1.10	1.85	5.85	13.0	0.520	0.9969	−0.6070
3	p-X	2.57	5.14	12.8	25.7	0.46	0.86	3.97	8.96	0.377	0.9963	−0.8002
4	m-X	2.57	5.14	12.8	25.7	0.60	1.17	4.38	9.11	0.375	0.9981	−0.5267
5	o-X	2.56	5.12	12.8	25.6	0.53	1.15	4.45	9.47	0.395	0.9984	−0.6515
6	S	2.69	5.38	13.5	26.9	0.66	1.32	4.71	11.3	0.445	0.9953	−0.8960
7	PA	2.32	4.64	11.6	23.2	0.57	1.36	3.74	8.10	0.360	0.9994	−0.3238
8	BA	2.39	4.78	12.0	23.9	0.29	0.81	2.53	5.45	0.240	0.9998	−0.3193
9	IA	2.32	4.64	11.6	23.2	0.27	0.76	2.54	5.67	0.260	0.9992	−0.4068
10	VA	2.36	4.71	11.8	23.6	0.27	0.66	1.70	3.60	0.156	0.9996	−0.1009
11	MEK	2.39	4.78	12.0	23.9	0.58	1.29	3.66	7.82	0.338	0.9995	−0.2979
12	MIBK	2.39	4.79	12.0	23.9	0.38	0.98	2.97	6.75	0.297	0.9985	−0.4293
13	BuAc	2.63	5.26	13.1	26.3	0.43	1.06	3.06	6.79	0.270	0.9990	−0.3569
14	i-BuAl	2.38	4.76	11.9	23.8	0.05	0.23	0.71	1.41	0.063	0.9977	−0.0792
	mean	2.484	4.968	12.421	24.842	0.569	1.176	3.740	8.238	0.342	0.9981	−0.449
	SD	0.130	0.260	0.649	1.299	0.425	0.643	1.808	4.077	0.154	0.0014	0.235

^{a}(1) Spiking 10−100 μL of the third point L-WS for the ST-based calibration into 50 mL of water, (2) sweeping gas flow rate = 50 mL min^{-1}, (3) initial sweeping time = 10 min, and (4) sweeping time = 10 min. ^{b}(1) x-axis = concentrations of spiking solution (ng mL^{-1}) and (2) y-axis = concentration of gaseous VOCs (nmol mol^{-1}).

0.51%, and (5) isobutyl alcohol = 0.16%). Their RRs in the first sweep gas did not exceed 2% even at the maximum sampling interval of 30 min (mean RR: (1) 5-1st = 0.45 ± 0.17%, (2) 10-1st = 0.39 ± 0.19%, (3) 20-1st = 0.90 ± 0.40%, and (4) 30-1st = 1.43 ± 0.71%). In comparison to aromatic compounds, the RR values of the four aldehydes and isobutyl alcohol were thus dramatically low, especially in the first sweep gas. The RRs of two ketones and *n*-butyl acetate in the first sweep gas fell in an intermediate range between aromatics and four aldehydes (plus isobutyl alcohol) (mean RR of two ketones and *n*-butyl acetate: (1) 1.63 ± 0.72% (5-1st), (2) 2.74 ± 1.32% (10-1st), (3) 4.64 ± 1.88% (20-1st), and (4) 4.99 ± 1.68% (30-1st)).

Steady-State Equilibrium Characteristics of VOC Vaporization in Sweep Gas. In this research, vapor-phase VOC standard samples were generated from a 50 mL solution spiked with liquid working standard. The equilibrium mole fractions of VOCs in sweep gas were hence assessed by contiguously running the system at varying intervals. In order to assess the stabilized or near-equilibrium concentration in the sweep gas, the collection and analysis of vaporized VOC were made continuously four times (1st, 2nd, 3rd, and 4th sweep gas) by ST at four different intervals of 5, 10, 20, and 30 min (at a constant flow rate of 50 mL min^{-1}). The concentrations and recoveries of vaporized VOCs were thus evaluated in relation to the sampling order of sweep gas samples to determine the steady-state equilibrium concentration of VOC in sweep gas samples. As shown in Tables 3S and 4S in the Supporting Information, the patterns are distinguished rather consistently from all those collected after the first sweep cycle longer than at least 10 min between the initial sweeping stage and the subsequent ones.

On the basis of this observation, we set the major criterion for this grouping at 10 min to distinguish the diffusion of VOC between solubility dominance (ideal Henry's law) and the steady-state equilibrium trend (nonideal Henry's law). Thus, to find the stabilized vapor mole fractions of VOC at each sweep interval, we excluded the five data that were either taken for less

than 10 min (samples A and B in Figure 1) or those including the initial 10 min durations (samples E, I, and M). As shown in Figure 1, 11 out of all 16 vaporized VOC samples (C, D, F, G, H, J, K, L, N, O, and P) or ones excluding five samples of A, B, E, I, and M were thus examined further to analyze the equilibrium mole fractions of sweep gas (Table 4S in the Supporting Information).

In Table 4S in the Supporting Information, the results of the 11 samples collected with the least effect of the dynamic conditions in each sampling duration are presented in terms of the mass (ng), concentration (nmol mol^{-1}), standard deviation, RSE (%), recovery (%), and mass flow rate (ng min^{-1}). If we increase such stability (data grouping) criterion from 10 min to 20, 30, and 40 min, the number of the samples to examine the steady-state equilibrium concentration systematically decreased to 8 (G, H, J, K, L, N, O, and P), 6 (H, K, L, N, O, and P), and 4 (K, L, O, and P), respectively. The efficiency of VOC vaporization decreased gradually with the increasing time of sweeping interval (T_{SI}) to show moderate changes in the mean mole fractions (nmol mol^{-1}) of 14 target VOCs in sweep gas: (1) $T_{SI} \geq 10$ min = 0.601 ± 0.449 (n = 11), (2) $T_{SI} \geq 20$ min = 0.570 ± 0.401 (n = 8), (3) $T_{SI} \geq 30$ min = 0.557 ± 0.395 (n = 6), and (4) $T_{SI} \geq 40$ min = 0.539 ± 0.381 (n = 4). As such, if the means for mole fraction values are compared between $T_{SI} \geq$ 10 min and $T_{SI} \geq 40$ min, their difference was fairly insignificant at about 10%. If the compatibility of these measured values was examined in terms of relative standard error (RSE, %), their average RSE values were generally small but decreased gradually with increasing intervals such as 4.49% (n = 11) at $T_{SI} \geq 10$ min to 1.93% (n = 4) at $T_{SI} \geq 40$ min. Although the aromatic VOCs had high RSE values (ranging from 5.20 to 7.67%) at $T_{SI} \geq 10$ min relative to other target VOCs, most VOC groups generally maintained stable concentrations at $T_{SI} \geq 10$ min.

Characteristics of Vapor-Phase VOC Standard Generation against the Spiking Solution Concentration. In this section, the characteristics of VOC vapor generated in

sweep gas during both dynamic and steady-state equilibrium stages were evaluated based on the data obtained in the second experiment stage. As aforementioned, all experiments in stage 1 were conducted using the standards of the identical concentration (concentration of benzene = 13.1 ng μL^{-1}). In stage 2, a modification was made for spiking by preparing liquid working standard at four different concentration levels (in the case of benzene = 2.62, 5.24, 13.1, and 26.2 ng mL^{-1}). The effect of the standard spiking in both the dynamic stage and in the steady-state equilibrium stage was then evaluated using the same apparatus. All these experiments were carried out in a simplified mode using a steady sweep gas flow rate of 50 mL min^{-1} for two consecutive 10 min runs and by comparing the data with the results obtained from the first experiment stage. Hence, two consecutive runs were made, and their results were taken to represent the initial dynamic condition (of the first 10 min) and steady-state (kinetic) equilibrium condition (of the second 10 min). The data from this second stage of the experiment were used to assess the predictive relationship between the vapor-phase VOC mole fractions and that in the liquid standard under a given set of experimental conditions.

Table 3 shows the concentration (nmol mol^{-1}) of VOC in the vapor phase after steady-state equilibrium and the various liquid standard. The equations to predict the concentration of vaporized VOC at steady-state from the initial SS concentration are also derived for each VOC. In Table 3, all VOCs had slopes (mean slope (n = 14) = 0.342 ± 0.154 (nmol mol^{-1}/ng mL^{-1})) with a mean R^2 above 0.99. Hence, there is a direct linear relationship in concentrations between the generated vapor and the liquid standard for each VOC. The six nonpolar aromatic VOCs with high partition coefficients had high mean slopes of 0.468 ± 0.124 nmol mol^{-1}/ng mL^{-1}, while the other eight more polar VOCs with higher partition coefficients had reduced values of 0.248 ± 0.097 nmol mol^{-1}/ng mL^{-1}.

In order to assess the characteristics of VOCs vaporized in sweep gas in various aspects, the relationship between the liquid standard concentrations and steady-state vapor concentration of VOC, as described in Steady-State Equilibrium Characteristics of VOC Vaporization in Sweep Gas, was evaluated in greater detail using the data sets of the first experiment stage. In Figure 3S in the Supporting Information, the y-axis is the ratio (or slope) of the vapor-phase VOC mole fractions against those in the SS (sweep gas (nmol mol^{-1})/SS (ng mL^{-1})). The x-axis is the ratio of cumulative VOC mass and the cumulative sampling volume (mass (ng)/volume (L)) at 10 min sampling intervals (sample code: 10-1st, 2nd, 3rd, and 4th). The relationship between the two different parameters for the generation of vapor-phase VOC standard showed a strong correlation with R^2 = 0.8973 (P-value = 2.77 × 10^{-7}). As such, a gaseous VOC standard with stable concentrations can be obtained by controlling the concentration level or sampling volume of sweep gas from a sweep gas generation platform.

Relationship between Vaporization Characteristics and Henry's Law of VOCs. The overall results of our experimental study clearly confirmed the existence of different patterns in the generation of the vaporized VOC between the 1st sweep gas sample (solubility dependent pattern) and those following the initial ones, i.e., the 2nd-4th sweep gas samples (steady state equilibrium). Hence, it is possible to infer that the efficiency of vaporization should be distinguished between the initial dynamic and subsequent steady-state equilibrium stages. In this section, to further investigate the relationship between VOC concentrations generated in the gas phase and those in

the original liquid standard, the vaporization efficiencies of VOCs were evaluated by their concentrations in sweep gas samples (with T_{SI} > 10 min) with respect to the solubility of each target VOC with the aid of Henry's law for the liquid–gas equilibrium state.

Figure 2A shows the correlation between the concentrations of VOCs determined experimentally from the first sweep gas
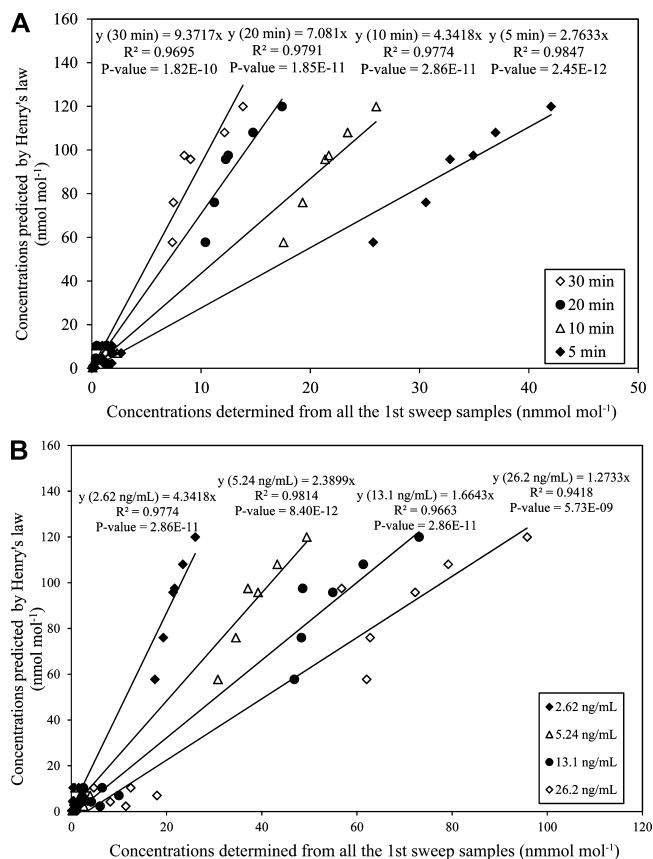
Figure 2. Comparison of VOC concentrations between the values predicted by Henry's law and those produced in the early dynamic sweep stage by the vapor generation system.

samples at different intervals (sample code: [1] 5-1st, [2] 10-1st, [3] 20-1st, and [4] 30-1st) and the gaseous concentrations of VOCs predicted theoretically by Henry's law with the input information of the SS (concentration of benzene in the SS = 2.62 ng mL^{-1}). The gaseous concentrations of VOCs predicted by Henry's law were calculated in light of the volume of spiking standard and sweep gas in the impinger (Table 5S in the Supporting Information). As shown in Figure 2A, the concentrations of four types of the first sweep gas samples exhibited strong correlations with those predicted by Henry's law, regardless of the differences in sampling duration (R^2 > 0.96 and P-value < 1.82 × 10^{-10}). Especially, the correlation increased with the decreasing sampling intervals of the first sweep gas samples.

The results of this comparative analysis thus imply that the VOC vaporized during the most dynamic vaporization stages should follow the equilibrium conditions defined by Henry's law. As such, the static-equilibrium principle of Henry's law (between liquid and gas phases) is closely reflected in the dynamic initial sweeping stage, while vaporization of VOCs proceeds most rapidly. In contrast, once the vapor-phase VOC

concentrations have reached a steady-state equilibrium their relationship with the VOC concentration in the original liquid standard did not correlate with Henry's law, as shown in Figure 4S in the Supporting Information ($R^2 < 0.4263$ and P-value > 1.13×10^{-2}). The strength of the correlation (P-value) with Henry's law diminished systematically with sampling time.

To examine the differences in VOC vaporization, this comparison was extended to the data sets obtained in the second experiment stage. The correlation between the sweep gas and spiking standard were also evaluated using liquid working standard with four different concentrations (concentration of benzene = [1] 2.62, [2] 5.24, [3] 13.1, and [4] 26.2 ng mL^{-1}) at a fixed sampling period for 10 min. If the same sampling condition of the "10-1st" is considered (Figure 1), the comparison of this second experiment stage data can also be made as shown in Figure 2B. Results showed that the concentrations of VOCs vaporized from the four different concentrations of standard also exhibited significant correlations with those predicted by Henry's law ($R^2 > 0.94$; P-value < 5.73×10^{-9}). As the initial concentration of SS increased, the extent of VOC vaporization in the initial dynamic stage also varied in a tight relationship with those predicted by Henry's law (slope values (benzene concentration in the spiked standard) = [1] 4.34 (2.62 ng mL^{-1}), [2] 2.39 (5.24 ng mL^{-1}), [3] 1.66 (13.1 ng mL^{-1}), and [4] 1.27 (26.2 ng mL^{-1})). As such, the concentrations of VOC vaporized in the initial sweeping stage complied well with general expectations based on solubility. These results imply that the solubility equilibrium between gas and liquid phases defined by Henry's law can be reached rapidly using the sweep gas generation platform described in this study. However, after the initial dynamic period, the steady-state equilibrium took over and the degree of correlation with Henry's law reduced.

CONCLUSIONS

In this study, in an effort to accurately produce a gaseous VOC standard at low concentrations, a simple approach to control vaporization of the liquid VOC standards was tested using an impinger that can provide sweep gas continuously. In the first experiment stage, the vaporization patterns of VOCs were assessed using a liquid standard containing VOCs at a single concentration level by collecting sweep gas samples continuously four times at each of the four different sampling intervals. In the second experiment stage, the effect of the concentration difference in SS on the VOCs generated from a sweep gas system was also evaluated.

In the first experiment stage, the vapor-phase VOC concentration released from the liquid standard, as collected during the steady-state equilibrium stage (i.e., after the initial sweeping of 10 min ($T_{SI} \geq 10$ min)), generally maintained a fairly stable concentration (mean RSE of the 14 VOC concentrations = 4.49 ± 2.26%). In the second experiment stage, the vapor-phase VOC mole fractions in the steady-state equilibrium stage were also analyzed under different concentration levels of spiking standards at a fixed sampling interval (10 min). In this case, their concentrations increased predictably with increasing the concentration of spiking. It implies that our system can be controlled to maintain vapor-phase concentration of VOC at a fairly constant level, once the steady-state equilibrium stage has been reached.

In this study, we evaluated the vaporization characteristics of VOCs by employing an impinger as a sweep device. We found the optimal time to generate the VOCs with respect to both dynamic (solubility dominant period) and equilibrium stages (steady-state dominant period). Moreover, the equations to predict the concentrations of VOCs in the latter stage were also developed by considering the concentration levels between SS and steady-state equilibrium. As the experimental approach used in this study was conjugated, diverse kinds of VOC standards with stable concentrations can be obtained by applying the sweep gas generation system. Furthermore, because of its simplicity, this experimental approach can be used as a very keen analytical technique for low-level VOC analysis.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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