

Comparison of GC–MS Calibration Properties of Volatile Organic Compounds and Relative Quantification Without Calibration Standards

Ji-Won Ahn, Sudhir Kumar Pandey, and Ki-Hyun Kim*

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

Abstract

In this study, the calibration properties of volatile organic compounds (VOCs) were evaluated using two different types of sample transfer approaches for gas chromatography with mass spectrometry (GC–MS), [i.e., direct injection (DI) and solid-phase microextraction (SPME)]. The calibration of liquid-phase VOCs conducted by both approaches showed that the sensitivity of the SPME method is two to three times lower than that of DI. If such a comparison was extended further to gas phase standards, the relative dominance of DI was more prominent by approximately a single order of magnitude than SPME. The basic response characteristics of GC–MS, when assessed for a given compound (X) against a reference compound of toluene (T), showed an increase in the response factor ratio $[R(X/T)]$ as a function of the carbon number $[C(X/T)]$, regardless of injection method. This relationship was useful to roughly predict the concentrations of certain compounds in the absence of a standard for their calibration.

Introduction

Volatile organic compounds (VOCs) have been treated as sensitive indicator of environmental pollution. VOCs are known to include a large variety of carbon-based molecules such as aldehydes, ketones, and light hydrocarbons. As the number of reported VOC exceeds 500, they can also be classified into three groups in terms of volatility: (i) very volatile organic compounds with a boiling point (BP) ranging from $< 0^{\circ}\text{C}$ to 100°C , (ii) volatile organic compounds with a BP value of $100\text{--}240^{\circ}\text{C}$, and (iii) semi-volatile organic compounds with a BP value of $240\text{--}400^{\circ}\text{C}$ (1–2).

The main anthropogenic sources of VOCs include industry, car, and building materials, while microorganisms and other biological activities are identified as their natural sources (3–5). As evidenced by sick-building syndrome, the impact of VOC pollution on human health can be detrimental (6). Some individual VOCs such as benzene and 1,3-butadiene have been reported to cause birth defects and cancer (7–8). Hence, VOCs

are often treated as an important component in the assessment of air quality in residential and office buildings and many other indoor settings (6). In addition, biogenic VOCs, including isoprene (C_5H_8), monoterpenes ($\text{C}_{10}\text{H}_{16}$), and several oxygenated species, can be emitted in large quantities from vegetation (9). Globally, emissions from biogenic VOCs account for approximately 86% of the total of VOC emissions (10). These VOCs present in outdoor ambient air are known to participate in photochemical reactions with nitrogen compounds through which ozone is formed (11–12). The harmfulness of many VOCs has not yet been evaluated thoroughly despite their potent role as major airborne pollutants.

The precise quantitation of VOCs in the atmosphere generally relies on gas chromatography (GC) with flame ionization detection (FID) or with mass spectrometry (MS). The GC–FID method has been applied extensively for quantitative analysis of VOCs in both gaseous and liquid matrices. The more-developed GC–MS technique is a potent tool, as it allows both qualitative and quantitative analysis at the same time (13–15). The quantification of VOC by GC or GC–MS can proceed with the aid of the following five major approaches (16,17): direct injection (DI), immobilized sorbent, cryogenic trapping, solvent extraction, and membrane. The determination of VOCs can be facilitated further by headspace (HS), and purge and trap methods (18–20). If high concentrations of VOCs are present in the liquid phase, one can analyze them by directly injecting a small quantity of a sample into GC injector. Furthermore, DI based methods allow the quantitation of compounds in water samples without discriminating more polar analytes (17). The usefulness of the HS technique, aided by the immobilized sorbent, is also well known, as it can effectively capture compounds extracted from both gas and liquid phases. Such a technique is highly advantageous because it simplifies the pretreatment procedure. Because of its merits, the HS method can be applied in diverse ways: HS-solid phase microextraction (HS-SPME), HS-solvent microextraction (HS-SME), and HS-stir bar sorptive extraction (HS-SBSE). The important parameters to consider for the development of SPME method are type of fiber employed, the extraction time, the extraction temperature, the sample amount, and the desorption time and temperature (21–22).

*Author to whom correspondence should be addressed: email khkim@sejong.ac.kr

Table I. The 54 VOCs Investigated in this Study*

Order	Compound	Formula	CAS No.	MW
1	1,1-Dichloroethylene	C ₂ H ₂ Cl ₂	75-35-4	96
2	Methylene chloride	CH ₂ Cl ₂	75-09-2	84
3	<i>trans</i> -1,2-Dichloroethylene	C ₂ H ₂ Cl ₂	156-60-5	96
4	1,1-Dichloroethane	C ₂ H ₄ Cl ₂	75-34-3	98
5	2,2-Dichloropropane	C ₃ H ₆ Cl ₂	594-20-7	112
6	<i>cis</i> -1,2-Dichloroethylene	C ₂ H ₂ Cl ₂	156-59-2	86
7	Chloroform	CHCl ₃	67-66-3	118
8	Bromochloromethane	CH ₂ BrCl	74-97-5	128
9	1,1,1-Trichloroethane	C ₂ H ₃ Cl ₃	71-55-6	132
10	1,1-Dichloropropene	C ₃ H ₄ Cl ₂	563-58-6	110
11	Carbon tetrachloride	CCl ₄	56-23-5	152
12†	1,2-Dichloroethane	C ₂ H ₄ Cl ₂	107-06-2	98
13	Benzene	C ₆ H ₆	71-43-2	78
14	Trichloroethylene	C ₂ HCl ₃	79-01-6	130
15	1,2-Dichloropropane	C ₃ H ₆ Cl ₂	78-87-5	112
16	Bromodichloromethane	CHBrCl ₂	75-27-4	162
17	Dibromomethane	CH ₂ Br ₂	74-95-3	172
18	<i>cis</i> -1,3-Dichloropropene	C ₃ H ₄ Cl ₂	10061-01-5	110
19	Toluene	C ₇ H ₈	108-88-3	92
20	<i>trans</i> -1,3-Dichloropropene	C ₃ H ₄ Cl ₂	10061-02-6	110
21	1,1,2-Trichloroethane	C ₂ H ₃ Cl ₃	79-00-5	132
22	1,3-Dichloropropane	C ₃ H ₆ Cl ₂	142-28-9	112
23	Tetrachloroethylene	C ₂ Cl ₄	127-18-4	164
24	Dibromochloromethane	CHBr ₂ Cl	124-48-1	206
25	1,2-Dibromoethane	C ₂ H ₄ Br ₂	106-93-4	186
26	Chlorobenzene	C ₆ H ₅ Cl	108-90-7	112
27	Ethylbenzene	C ₈ H ₁₀	100-41-4	106
28†	1,1,1,2-Tetrachloroethane	C ₂ H ₂ Cl ₄	630-20-6	168
29	<i>m</i> -Xylene	C ₈ H ₁₀	108-38-3	106
30†	<i>p</i> -Xylene	C ₈ H ₁₀	106-42-3	106
31	<i>o</i> -Xylene	C ₈ H ₁₀	95-47-6	106
32	Styrene	C ₈ H ₈	100-42-5	104
33	Isopropylbenzene	C ₉ H ₁₂	98-82-8	120
34	Bromoform	CHCBr ₃	75-25-2	250
35	1,1,2,2-Tetrachloroethane	C ₂ H ₂ Cl ₄	79-34-5	166
36	1,2,3-Trichloropropane	C ₃ H ₅ Cl ₃	96-18-4	146
37	<i>n</i> -Propylbenzene	C ₉ H ₁₂	103-65-1	120
38	Bromobenzene	C ₆ H ₅ Br	108-86-1	156
39	1,3,5-Trimethylbenzene	C ₉ H ₁₂	108-67-8	120
40	2-Chlorotoluene	C ₇ H ₇ Cl	95-49-8	126
41	4-Chlorotoluene	C ₇ H ₇ Cl	106-43-4	126
42	<i>tert</i> -Butylbenzene	C ₁₀ H ₁₄	98-06-6	134
43	1,2,4-Trimethylbenzene	C ₉ H ₁₂	95-63-6	120
44	<i>sec</i> -Butylbenzene	C ₁₀ H ₁₄	135-98-8	134
45	<i>p</i> -Isopropyltoluene	C ₁₀ H ₁₄	99-87-6	134
46	1,3-Dichlorobenzene	C ₆ H ₄ Cl ₂	541-73-1	146
47	1,4-Dichlorobenzene	C ₆ H ₄ Cl ₂	106-46-7	146
48	<i>n</i> -Butylbenzene	C ₁₀ H ₁₄	104-51-8	134
49	1,2-Dichlorobenzene	C ₆ H ₄ Cl ₂	95-50-1	146
50	1,2-Dibromo-3-chloropropane	C ₃ H ₅ Br ₂ Cl	96-12-8	234
51	1,2,4-Trichlorobenzene	C ₆ H ₃ Cl ₃	120-82-1	180
52	Hexachlorobutadiene	C ₄ Cl ₆	87-68-3	258
53	Naphtalene	C ₁₀ H ₈	91-20-3	128
54	1,2,3-Trichlorobenzene	C ₆ H ₃ Cl ₃	87-61-6	180

* EPA method 502–524, volatile organics calibration mix.

† Three compounds not quantified in this study.

In this study, the performance characteristics of GC–MS system were investigated for a list of VOCs by comparative calibration between direct injection and HS-SPME analysis. For this comparative analysis, the liquid phase VOC standard containing 54 individual compounds were used as the major target compounds. The relative response properties of these VOCs were then compared using two distinctive injection approaches on a parallel basis. The results derived as calibration data sets were examined to describe the relative response properties of VOCs in relation to two different sample loading approaches and to assess the concentrations of certain compounds in the absence of calibration standards.

Materials and Methods

Preparation of working standard

Because of multiplicity, many VOCs have been investigated as the target components of air or water quality. As one of the common standards of VOC, the 502/524 volatile organics calibration mix (Supelco, St. Louis, MO) including 54 individual VOCs [such as benzene, toluene, xylene, styrene, etc. (Table I)] was selected as target compounds for the present study. These VOCs are often designated as the major pollutants of drinking water (23), and many of them are also found ubiquitously in soil and atmosphere. Primary standard (PS) of VOC was purchased to contain each VOC at a concentration of 2000 ng/μL in methanol (Supelco). Working standards (WS) for successive calibration experiments were prepared at 4 concentration levels through a two-step dilution. In the first-step, WS-I was prepared by mixing the primary standard (250 μL) and methanol (750 μL) in a 1-mL vial. Then, the certain proportions of WS-I (10, 20, 40, and 80 μL) were withdrawn and put together with methanol (990, 980, 960, and 920 μL) in 1-mL vial; this mixing step yielded WS-V concentrations of 5, 10, 20, and 40 ng/μL. All working standards of VOC contained in amber vials were closed by a cap with PTFE/Silicone septum and placed in a refrigerator at ~5°C.

Method of sample injection

In this study, the calibration characteristics of VOCs were investigated based on two injection approaches: (*i*) direct

Table II. Experimental Conditions of the GC–MS System for the Analysis of VOC

GC-MS system (Model: GCMS-QP2010, Shimadzu, Japan)		
a. Temperature (°C)	GC Injector	250°C
	Oven initial	35°C (4 min holding)
	Oven ramping rate	4°C per min for a total 41.25 min
	Oven maximum	200°C 10 min holding
b. Flow rate (mL/min)	Column (He)	1.2
	Split	12
c. MS system	Ionization mode	El (70 eV)
	Ion source temp.	200°C
	Interface temp.	200°C
	TIC scan range	35–250 <i>m/z</i>
	Threshold	100

injection (DI): WS of VOC prepared in the liquid phase are injected directly into a GC injector and (ii) HS-SPME method: SPME fiber is injected into GC after inducing adsorption of VOCs from headspace samples (or standard). As a result, the relative recovery rate of VOC was examined by evaluating the performance of SPME against DI method.

For the DI-based calibration, WS was prepared at 4 concentration levels and injected into the GC injector at a fixed volume (1 μL) to yield a 4 point calibration at 5, 10, 20, and 40

ng. The relative performance of HS-SPME method was also tested as a 4 points calibration. Extraction analysis based on the HS-SPME method was conducted in the following order. A 22-mL vial was filled up with 10 mL distilled water and closed by cap with Silicone/PTFE septum. Identical quantities of VOC used for DI-based calibration, (i.e., 1 μL of each VOC standard with concentrations of 5, 10, 20, and 40 ng/ μL) were introduced into the vial by submerging the syringe needle inside the water contained in vial (to secure the direct delivery of liquid-phase standard). Hence, the absolute mass of VOCs taken from vial samples was maintained at 5, 10, 20, and 40 ng.

In this study, carboxen-polydimethylsiloxane (CAR-PDMS, 75 μm , Supelco) was selected for SPME analysis. Before each calibration analysis, SPME fiber was conditioned for 30 min in GC injector at 300°C. The GC system in this study was interfaced with MS (Model: GCMS-QP2010, Shimadzu, Japan). Vocol column (length: 60 m, i.d.: 0.32 mm, film thickness: 1.8 μm , Supelco) was used for the separation of VOCs. Other operation conditions for GC-MS are described briefly in Table II.

The adsorption conditions for SPME in headspace were set as follows: temperature = 50°C, stirring velocity = 1200 rpm, and adsorption time = 30 min. These volatilization conditions (temperature, stirring velocity, and adsorption time) of HS-SPME method are based on its optimization scheme for the liquid phase VOC (24). After the adsorption, SPME fiber was withdrawn from vial and injected into the GC for 5 min duration at 250°C to induce desorption of target compounds from SPME fiber.

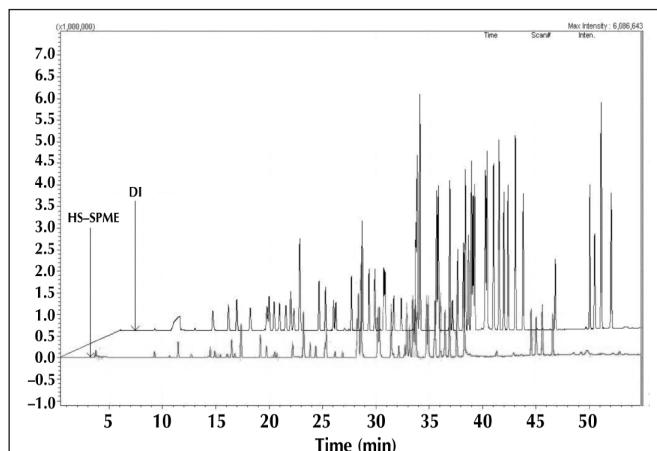


Figure 1. Comparison of chromatograms derived by both the DI and HS-SPME approaches (after extraction from liquid-phase mixture): 40 ng of VOCs in liquid-phase standard.

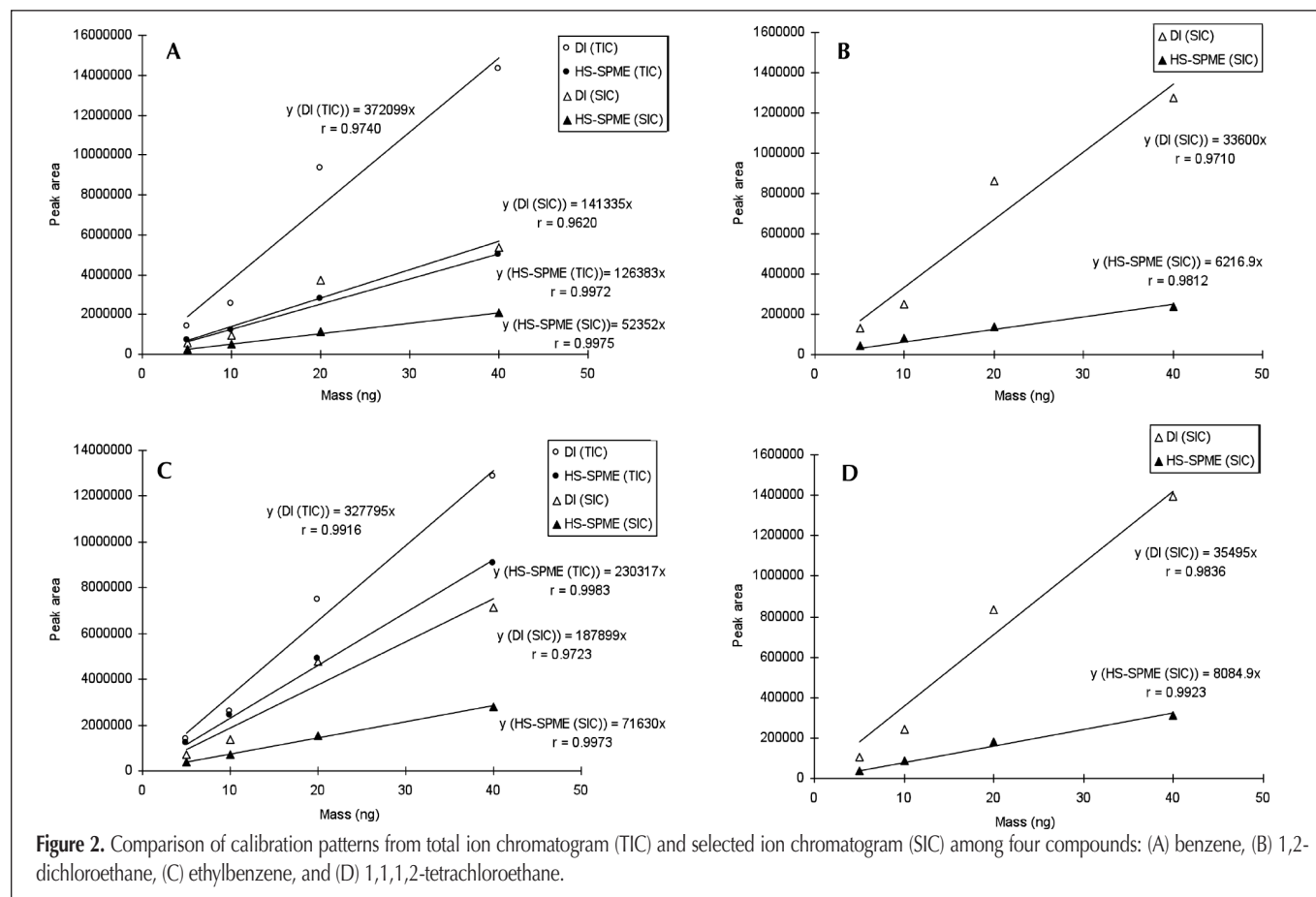


Table III. Calibration Results of a Liquid-phase Standard Containing 54 VOCs Obtained by Two Types of Calibration Approaches Between DI and HS-SPME

Order	Name	a. Direct injection				b. HS-SPME method			
		RF	r	RSE (%)	MDL (ng)	RF	r	RSE (%)	MDL (ng)
1	1,1-Dichloroethylene	98643	0.9850	3.75	0.40 [†]	22595	0.9915	2.40	15.2
2	Methylene chloride	119388	0.9800	1.67	0.09	*	*	*	*
3	<i>trans</i> -1,2-Dichloroethylene	137005	0.9783	1.31	0.26	44783	0.9987	1.15	7.68
4	1,1-Dichloroethane	105231	0.9826	2.64	0.38	14482	0.9772	0.81	23.8
5	2,2-Dichloropropane	76970	0.9744	2.17	0.13	8409	0.9135	0.71	40.9
6	<i>cis</i> -1,2-Dichloroethylene	104683	0.9790	1.59	0.20	34524	0.9970	0.95	10.0
7	Chloroform	125753	0.9816	0.40	0.31	23671	0.9860	0.36	0.64
8	Bromochloromethane	103298	0.9630	6.75	0.38	9442	0.9948	0.49	36.4
9	1,1,1-Trichloroethane	115916	0.9818	2.07	0.16	17592	0.8721	0.79	19.6
10	1,1-Dichloropropene	150469	0.9744	1.41	0.17	63435	0.9984	1.21	0.21
11	Carbon tetrachloride	97155	0.9742	1.22	0.41	17798	0.9697	0.90	19.3
12	1,2-Dichloroethane	ND [‡]	ND	–	ND	ND	ND	ND	ND
13	Benzene	372099	0.9740	3.51	0.15	126383	0.9972	1.51	0.19
14	Trichloroethylene	180219	0.9761	2.89	0.13	75036	0.9983	2.05	4.58
15	1,2-Dichloropropane	159566	0.9818	1.77	0.08	39323	0.9941	0.83	8.75
16	Bromodichloromethane	98572	0.9897	6.41	0.40	22456	0.9977	0.26	15.3
17	Dibromomethane	89562	0.9906	9.16	0.12	14524	0.9994	0.23	23.7
18	<i>cis</i> -1,3-Dichloropropene	173021	0.9832	2.21	0.06	47909	0.9983	0.58	7.18
19	Toluene	384687	0.9795	3.25	0.10	173839	0.9924	5.33	1.98
20	<i>trans</i> -1,3-Dichloropropene	180830	0.9864	1.40	0.12	41349	0.9992	0.53	8.32
21	1,1,2-Trichloroethane	200720	0.9878	1.84	0.13	38314	0.9957	0.55	8.98
22	1,3-Dichloropropane	85888	0.9819	2.76	0.15	46308	0.9993	0.86	7.43
23	Tetrachloroethylene	60328	0.8938	1.30	0.21	89111	0.9980	1.77	0.61
24	Dibromochloromethane	112445	0.9817	7.29	0.11	20428	0.9975	0.85	16.8
25	1,2-Dibromoethane	101985	0.9804	8.82	0.09	19350	0.9987	0.79	17.8
26	Chlorobenzene	114275	0.9774	3.56	0.13	124752	0.9988	2.91	2.76
27	Ethylbenzene	327795	0.9916	2.77	0.12	230317	0.9983	1.60	0.13
28	1,1,1,2-Tetrachloroethane	ND	ND	–	ND	ND	ND	ND	ND
29	<i>m</i> -Xylene	840023	0.9757	6.54	0.11	364545	0.9989	1.92	0.09
30	<i>p</i> -Xylene	*	*	*	*	*	*	*	*
31	<i>o</i> -Xylene	364964	0.9813	4.32	0.11	169456	0.9990	1.20	0.15
32	Styrene	310801	0.9854	1.03	0.11	168866	0.9995	1.05	0.23
33	Isopropylbenzene	514803	0.9814	7.29	0.10	191197	0.9993	1.50	0.13
34	Bromoform	91925	0.9837	7.02	0.09	14163	0.9978	2.15	24.3
35	1,1,2,2-Tetrachloroethane	263647	0.9942	2.08	0.15	39725	0.9898	1.29	8.66
36	1,2,3-Trichloropropane	237992	0.9930	1.12	0.12	40046	0.9966	0.56	8.59
37	<i>n</i> -Propylbenzene	473256	0.9876	0.45	0.10	191571	0.9988	1.37	0.14
38	Bromobenzene	296751	0.9923	2.31	0.11	108912	0.9996	1.60	0.14
39	1,3,5-Trimethylbenzene	440474	0.9894	0.95	0.11	207969	0.9994	0.89	0.15
40	2-Chlorotoluene	272410	0.9852	3.41	0.10	167819	0.9996	2.34	0.17
41	4-Chlorotoluene	363124	0.9923	0.73	0.11	171443	0.9994	1.41	0.19
42	<i>tert</i> -Butylbenzene	414009	0.9879	1.89	0.10	213061	0.9997	1.39	0.26
43	1,2,4-Trimethylbenzene	426524	0.9851	1.27	0.11	203363	0.9991	2.26	0.13
44	<i>sec</i> -Butylbenzene	559816	0.9902	1.79	0.09	190895	0.9994	1.99	0.14
45	<i>p</i> -Isopropyltoluene	615956	0.9912	1.25	0.04	207693	0.9995	1.56	0.17
46	1,3-Dichlorobenzene	431589	0.9910	1.20	0.10	142393	0.9999	1.46	2.42
47	1,4-Dichlorobenzene	441353	0.9911	0.79	0.11	150407	0.9995	1.91	0.18
48	<i>n</i> -Butylbenzene	605130	0.9919	1.42	0.11	197134	0.9989	2.74	0.21
49	1,2-Dichlorobenzene	433475	0.9913	1.27	0.10	135053	0.9984	2.00	0.22
50	1,2-Dibromo-3-chloropropane	217563	0.9932	4.01	0.18	15390	0.9995	2.25	22.4
51	1,2,4-Trichlorobenzene	457152	0.9926	1.66	0.09	138511	0.9994	3.13	2.48
52	Hexachlorobutadiene	323909	0.9935	1.20	0.12	115930	0.9993	2.45	2.97
53	Naphtalene	751025	0.9912	1.49	0.13	150269	0.9964	6.09	2.29
54	1,2,3-Trichlorobenzene	467779	0.9926	2.14	0.11	132429	0.9992	3.68	2.60

* Results are excluded because of eccentricity

† DL value based toluene peak are underlined

‡ ND = not detected

Results and Discussion

Calibration of VOCs working standards by DI and SPME

The calibration of VOCs was initially conducted for both DI and SPME methods using liquid phase working standards prepared at 4 concentration levels (5, 10, 20, and 40 ng/μL). Each of all the individually detected compounds was verified based on two types of libraries: the National Institute of Standards and Technology (NIST) and the Wiley. Basically, almost all compounds were detected with the similarity exceeding 95% (Figure 1). However, 3 out of 54 compounds were not identified initially in total ion chromatogram (TIC) mode due to common overlapping problems for the 3 paired sets: benzene (with 1,2-dichloroethane), ethylbenzene (with 1,1,1,2-tetrachloroethane), and two xylenes (*m*- and *p*-xylene). Thus, chromatograms for these overlapping pairs were treated separately by allocating the selected ion number for (1) 1,2-dichloroethane (62 *m/z*) and benzene (78 *m/z*) and (2) 1,1,1,2-tetrachloroethane (131 *m/z*) and ethylbenzene (91 *m/z*). However, *m*-xylene and *p*-xylene were not separated because they share the identical ion number (91 *m/z*). The calibration results of four separated compounds showed high linearity [r (correlation) ≥ 0.96] (Figure 2). However, RF values of these selected ion number were significantly lower by approximately 2 times than those derived from the unseparated TIC mode.

The calibration results of all VOCs, when estimated by linear regression analysis, showed fairly high linearity ($r \geq 0.97$) for both methods (Table III). To check the compatibility of two different injection methods, the strengths of correlation between DI and SPME method was examined using response factor (RF) values of all compounds derived by both methods. The results shown in Figure 3 indicate that the RF values of the HS-SPME method are approximately 36% of those derivable by DI. Despite relatively low recovery rate of HS-SPME, coefficient of r between two injection methods shows a strong resemblance ($r = 0.862$ and $P = 9.39E - 16$).

As a means of testing the basic quality assurance (QA) of the methodology, the

precision of DI methods was evaluated in terms of the relative standard error (RSE) by three replicate injections of 20 ng WS (injection volume of 1 μL) into GC injector. Likewise, RSE of HS-SPME method was also evaluated by 1 μL of WS (20 ng) mixed with 10 mL distilled water. In the case of DI, chloroform showed the best reproducibility (0.4%), and dibromomethane had the least (9.16%). In the case of the HS-SPME method, dibromomethane was the most reproducible (0.23%), and naphthalene was the least (6.09%). In terms of the mean RSE values of all target compounds, the HS-SPME method (1.61%) was superior to DI (2.79%).

The method detection limit (MDL) of both methods was estimated by seven repetitive injections of the least detectable quantity of WS (e.g., ~ 0.2 ng) into the GC injector. The MDL value for each compound was derived by multiplying the standard deviation (SD) by 3.14 [t-value for 7 samples at 99% confidence interval (CI)]. The DI-based MDL values for all VOCs generally ranged between 0.04 (*p*-isopropyltoluene) \sim 0.41 ng (carbon tetrachloride). Considering that the HS-SPME method is based on the partial extraction of vaporized compounds, its MDL was tested by mixing 1 μL of WS (prepared at 0.4 ng/ μL) with 10 mL distilled water. The MDL for HS-SPME method was estimated in the range of 0.09 (*m*-xylene) \sim 40.9 ng (2,2-dichloropropane) the largest value of which was higher by two orders of magnitude than the DI counterpart.

Relative recovery rate between different injection methods

The sum of well-known aromatic compounds like benzene (B), toluene (T), ethylbenzene (E), xylene (X), and styrene (S), commonly referred to as BTEXS, are often treated as the major target compounds in the pollution research. If the human intake of these compounds exceeds the guidance level, they have the potential to cause health problems such as damage to the central nervous system (25). For instance, benzene is a well-known toxic compound categorized as a carcinogen by the US National Toxicology Program (26). Because of a relatively small threshold value as an odorant, styrene (S) has been designated as one of the major offensive odorants in Korea or Japan (Korean Ministry of Environment (KMOE) (27). As such, the environmental significance of many aromatic VOCs has attracted a great deal of attention in air quality management and odor control (28).

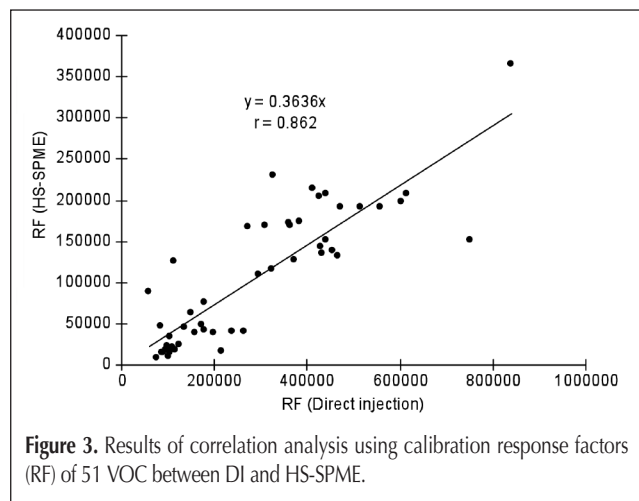


Figure 3. Results of correlation analysis using calibration response factors (RF) of 51 VOC between DI and HS-SPME.

Hence, the GC-MS calibration pattern of BTEXS was examined with the major emphasis in this study.

As a simple means to test the relative sensitivity of different VOCs, RF values of the major aromatic compounds were evaluated between the two methodologies. The RF value of DI, when assessed among BTEXS, was the highest for *m*-X (840,023), and the lowest was for S (310,801). However, in case of HS-SPME, *m*-X (364,545) recorded the highest RF, and that of B (126,383) was the lowest. If the relative recovery rate is computed between the two methods, the results of these aromatic compounds were 33–70%.

Comparison of calibration properties between gas and liquid phase standards

It is well known that the VOC calibration properties are strongly influenced by the matrix types and/or by the injection methods (29). Moreover, it is also influenced by the diffusion pattern and adsorption affinity of target gas to the stationary phase of the SPME fiber (30). Hence, to examine the effect of the matrix used as a standard (i.e., gas vs. liquid), a comparative analysis was conducted in an ancillary experiment. This comparative analysis was however confined to a few VOC species (i.e., BTX), as they are

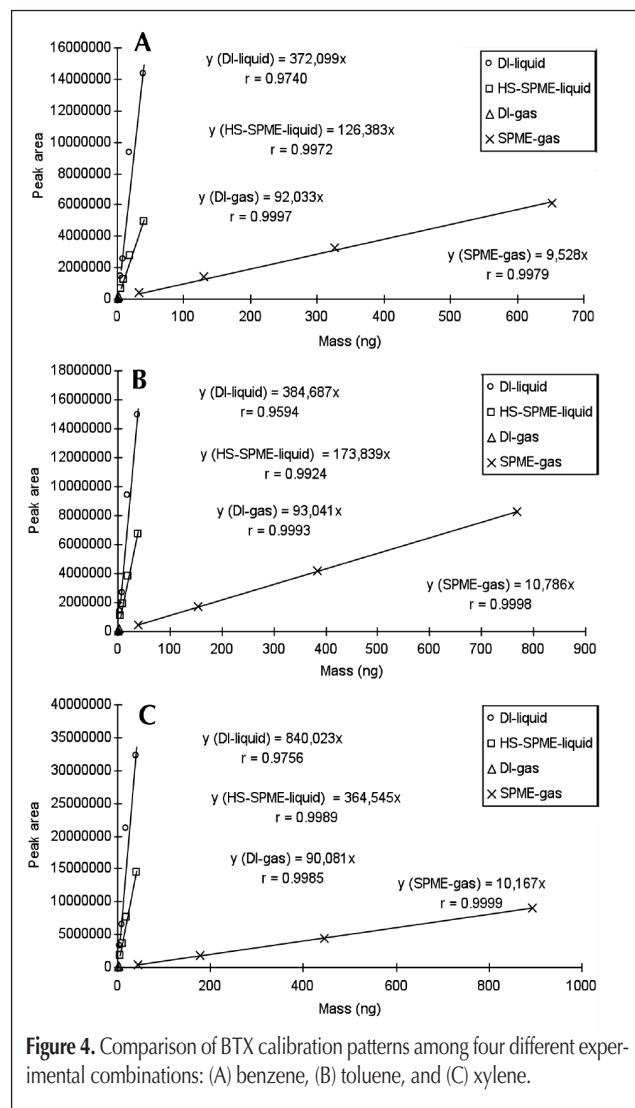


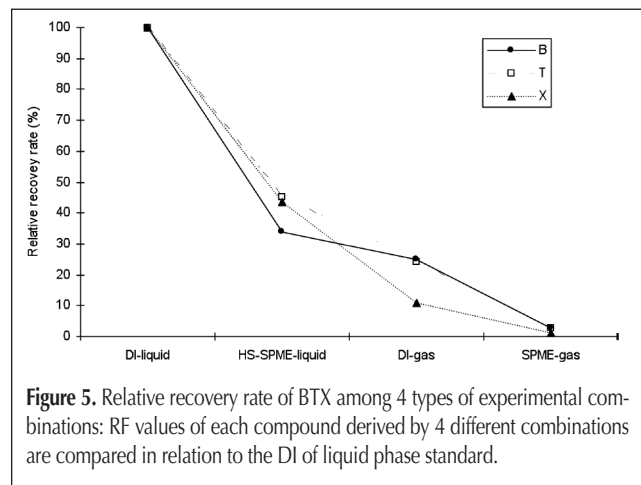
Figure 4. Comparison of BTX calibration patterns among four different experimental combinations: (A) benzene, (B) toluene, and (C) xylene.

commonly available and analyzed in the laboratory. For the purpose of this ancillary experiment, gaseous WS containing B, T, and p-X were also prepared at 4 concentration levels of 0.5, 1, 2, and 5 $\mu\text{mol/mol}$ (Rigas, Dae Jeon, Korea). To begin with, 100 μL of each working standard was directly injected into GC injector (absolute mass of 0.19–1.92 ng in case of toluene). In addition, HS-SPME was also applied to gaseous WS prepared at much diluted concentration levels (10, 40, 100, and 200 nmol/mol) and contained in a 1-L Tedlar bag (38.4 ~ 768 ng of toluene). For the extraction of gaseous BTX WS in a Tedlar bag, SPME fiber (CAR–PDMS, 75 μm) was injected inside Tedlar bag for 10 min.

The results, shown in Figure 4, indicate that response properties of each compound are highly consistent for all 4 combinations. If the sensitivity of BTX is compared, the pattern is systematically distinguished between the matrix phases [gas (G) vs. liquid (L)] and the injection methods (DI vs. SPME). The relative ordering of each combination is thus found on the order of DI (L) > SPME (L) > DI (G) > SPME (G). The results of this analysis were examined further in terms of the relative recovery rate for each combination in relation to the results of DI (L) for all three compounds (Figure 5). This shows that relative ordering in inter-compound sensitivity can also change among these experimental choices, as such compound as benzene tends to exhibit enhanced sensitivity in gas phase relative to liquid phase. If the relative sensitivity of different approaches is computed by the mean values of all three compounds against DI (L) values, the results fell on the order: 100% [DI (L)] > 40.9 \pm 6.03% [HS–SPME (L)] > 19.9 \pm 7.93% [DI (G)] > 2.19 \pm 0.85% [SPME (G)] (Figure 5). The observed differences in relative sensitivity between the 4 combination types imply that the performance of GC–MS analysis can be affected very sensitively by the phase type and injection method. This is because the recovery pattern of BTX between different injection methods/phase types is governed by such factors as partitioning properties of analytes between water and gas phase (HS) or between gas phase and solid stationary phase on SPME fiber (31). In addition, the equilibrium conditions for the diffusion can also be important.

Consideration of Henry's law for HS-SPME analysis

According to the experimental design of this study, the SPME-based analysis of VOCs relies on the extent of partitioning



between gas and liquid phases. Although the HS-SPME experiment was not designed to measure the equilibrium partitioning of VOCs, the effect of such processes on calibration properties can be roughly compared by considering Henry's law. In fact, as the SPME based calibration was made consistently with 12-mL headspace in a 22-mL vial, the calibration can also be evaluated in terms of the maximum quantity of VOC partitioning into gas phase instead of all VOCs initially added into the standard solution. After the WS of VOCs was introduced into distilled water, the vial was sealed and stirred at 50°C for 30 min to vaporize liquid-phase VOCs towards the headspace.

To facilitate a simple estimation of this partitioning equilibrium, SPME-based calibration of BTEXS was re-evaluated by applying the dimensionless Henry's law constant (HLC, $K_H = C_{\text{gas}}/C_{\text{liquid}}$). These K_H values for BTEXS were estimated to be 0.72, 0.99, 1.43, 1.28, and 0.45 at 50°C, respectively (32). By assuming the full equilibrium concentration of BTEXS in the gas phase, the relative sensitivity of VOC tends to improve significantly (Figure 6). As the relative proportion of BTEXS partitioning into the gas phase is different from each other, the relative effect of such factor differs greatly across different compounds. After all, the consideration of HLC tends to improve their sensitivity notably so that differences in sensitivity between DI and HS-SPME can be dramatically reduced.

Relationship between carbon number and calibration result

In numerous studies previously conducted, the GC–FID and GC–MS methods were widely used in the analysis of VOCs. In the case of the GC–FID system, samples passing through the end of

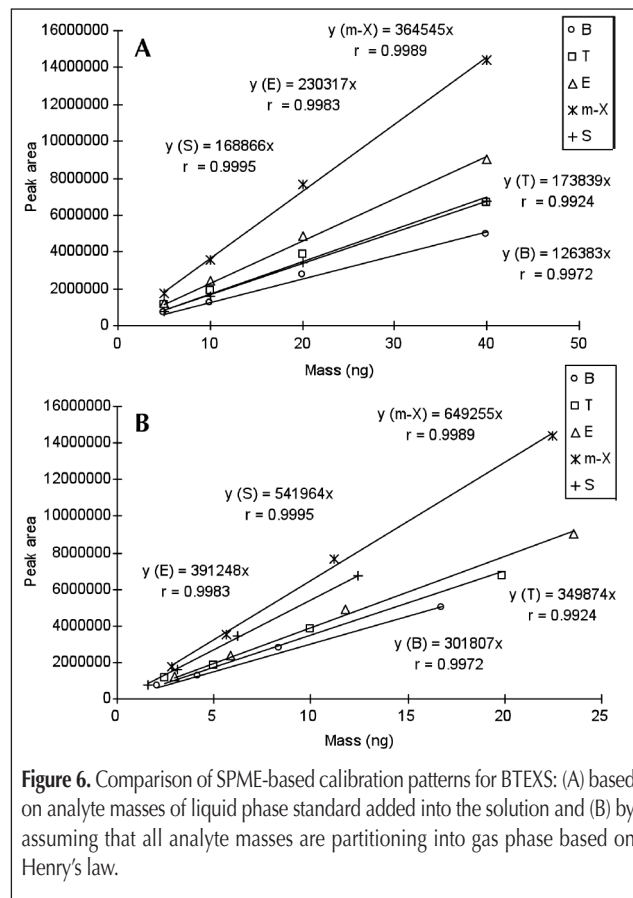


Table IV. Comparison of Calibration Response Factor Ratios Between Unknown (X) and Toluene (T), R(X/T) Derived by DI and SPME as a Function of Carbon Number

Order	Name	Formula	Number of C	C(X/T) [†]	R(X/T) [‡]	
					DI	HS-SPME
1	Methylene chloride	CH ₂ Cl ₂	1	0.14	0.31	*
2	Chloroform	CHCl ₃	1	0.14	0.33	0.14
3	Bromochloromethane	CH ₂ BrCl	1	0.14	0.27	0.05
4	Carbon tetrachloride	CCl ₄	1	0.14	0.25	0.10
5	Bromodichloromethane	CHBrCl ₂	1	0.14	0.26	0.13
6	Dibromomethane	CH ₂ Br ₂	1	0.14	0.23	0.08
7	Dibromochloromethane	CHBr ₂ Cl	1	0.14	0.29	0.12
8	Bromoform	CHClBr ₃	1	0.14	0.24	0.08
9	1,1-Dichloroethylene	C ₂ H ₂ Cl ₂	2	0.29	0.26	0.13
10	trans-1,2-Dichloroethylene	C ₂ H ₂ Cl ₂	2	0.29	0.36	0.26
11	1,1-Dichloroethane	C ₂ H ₄ Cl ₂	2	0.29	0.27	0.08
12	cis-1,2-Dichloroethylene	C ₂ H ₂ Cl ₂	2	0.29	0.27	0.20
13	1,1,1-Trichloroethane	C ₂ H ₃ Cl ₃	2	0.29	0.30	0.10
14	1,2-Dichloroethane	C ₂ H ₄ Cl ₂	2	0.29	*	*
15	Trichloroethylene	C ₂ HClCl ₃	2	0.29	0.47	0.43
16	1,1,2-Trichloroethane	C ₂ H ₃ Cl ₃	2	0.29	0.52	0.22
17	Tetrachloroethylene	C ₂ Cl ₄	2	0.29	0.16	0.51
18	1,2-Dibromoethane	C ₂ H ₄ Br ₂	2	0.29	0.27	0.11
19	1,1,1,2-Tetrachloroethane	C ₂ H ₂ Cl ₄	2	0.29	*	*
20	1,1,2,2-Tetrachloroethane	C ₂ H ₂ Cl ₄	2	0.29	0.69	0.23
21	2,2-Dichloropropane	C ₃ H ₆ Cl ₂	3	0.43	0.20	0.05
22	1,1-Dichloropropene	C ₃ H ₄ Cl ₂	3	0.43	0.39	0.36
23	1,2-Dichloropropane	C ₃ H ₆ Cl ₂	3	0.43	0.41	0.23
24	cis-1,3-Dichloropropene	C ₃ H ₄ Cl ₂	3	0.43	0.45	0.28
25	trans-1,3-Dichloropropene	C ₃ H ₄ Cl ₂	3	0.43	0.47	0.24
26	1,3-Dichloropropane	C ₃ H ₆ Cl ₂	3	0.43	0.22	0.27
27	1,2,3-Trichloropropane	C ₃ H ₅ Cl ₃	3	0.43	0.62	0.23
28	1,2-Dibromo-3-chloropropane	C ₃ H ₅ Br ₂ Cl	3	0.43	0.57	0.09
29	Hexachlorobutadiene	C ₄ Cl ₆	4	0.57	0.84	0.67
30	Benzene	C ₆ H ₆	6	0.86	0.97	0.73
31	Chlorobenzene	C ₆ H ₅ Cl	6	0.86	0.30	0.72
32	Bromobenzene	C ₆ H ₅ Br	6	0.86	0.77	0.63
33	1,3-Dichlorobenzene	C ₆ H ₄ Cl ₂	6	0.86	1.12	0.82
34	1,4-Dichlorobenzene	C ₆ H ₄ Cl ₂	6	0.86	1.15	0.87
35	1,2-Dichlorobenzene	C ₆ H ₄ Cl ₂	6	0.86	1.13	0.78
36	1,2,4-Trichlorobenzene	C ₆ H ₃ Cl ₃	6	0.86	1.19	0.80
37	1,2,3-Trichlorobenzene	C ₆ H ₃ Cl ₃	6	0.86	1.22	0.76
38	Toluene	C₇H₈	7	1.00	1.00	1.00
39	2-Chlorotoluene	C ₇ H ₇ Cl	7	1.00	0.71	0.97
40	4-Chlorotoluene	C ₇ H ₇ Cl	7	1.00	0.94	0.99
41	Ethylbenzene	C ₈ H ₁₀	8	1.14	0.85	1.32
42	m-Xylene	C ₈ H ₁₀	8	1.14	2.18	2.10
43	p-Xylene	C ₈ H ₁₀	8	1.14	*	*
44	o-Xylene	C ₈ H ₁₀	8	1.14	0.95	0.97
45	Styrene	C ₈ H ₈	8	1.14	0.81	0.97
46	Isopropylbenzene	C ₉ H ₁₂	9	1.29	1.34	1.10
47	n-Propylbenzene	C ₉ H ₁₂	9	1.29	1.23	1.10
48	1,3,5-Trimethylbenzene	C ₉ H ₁₂	9	1.29	1.15	1.20
49	1,2,4-Trimethylbenzene	C ₉ H ₁₂	9	1.29	1.11	1.17
50	tert-Butylbenzene	C ₁₀ H ₁₄	10	1.43	1.08	1.23
51	sec-Butylbenzene	C ₁₀ H ₁₄	10	1.43	1.46	1.10
52	p-Isopropyltoluene	C ₁₀ H ₁₄	10	1.43	1.60	1.19
53	n-Butylbenzene	C ₁₀ H ₁₄	10	1.43	1.57	1.13
54	Naphtalene	C ₁₀ H ₈	10	1.43	1.95	0.86

* Results are excluded because of eccentricity

[†] R(X/T) denotes toluene-normalized slope value of each compound[‡] C(X/T) denotes toluene-normalized carbon number of each compound

the column eventually eject from the jet system inside the FID. As the carbon compound in the sample are ionized by the flame above the jet nozzle, the number of ions in the sample responds proportionately to the number of reduced carbons in the flame (33). For the GC-MS system, the detection proceeds in a similar manner such that target compounds enter the mass spectrometer under high vacuum conditions after passing through the column. These ionized species are separated and detected based on its atomic weight (in ion source) (33).

In an effort to describe the analytical performance of the GC-MS system, the response properties of each compound investigated in this study were first examined in relation to carbon number. For this purpose, all target compounds were classified first by carbon number in reference to toluene (T, C₇H₈) to allow relative comparison across all different VOCs. (The use of toluene as a reference compound has been commonly applied to the quantification of TVOC (34), as such, the relative calibration property of a given compound (X) can be established against toluene (T); their RF ratio [R(X/T)] can be compared with their carbon number ratio of C(X/T). For example, in the case of benzene (B, C₆H₆), its carbon number ratio [C(B/T) = 6/7] is assigned as 0.86. The relative sensitivity (RF) values of benzene R(B/T) derived for the DI and HS-SPME methods were 0.97 and 0.73, respectively (Table IV). If the R(X/T) values of all target VOCs are plotted against their respective carbon number ratios C(X/T), the correlation coefficient (r) values for DI and HS-SPME were 0.889 (P = 1.27E - 15) and 0.943 (P = 4.1E - 19), respectively (Figure 7). According to this

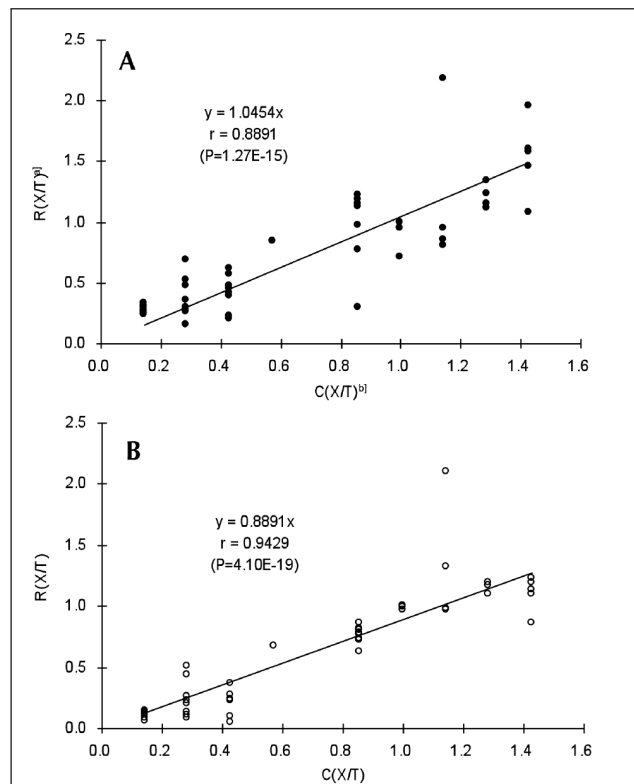


Figure 7. Comparison of R(X/T) ratio vs. carbon number ratio [C(X/T)] between the two experimental methods: (A) DI and (B) HS-SPME method. Here, R(X/T) implied that RF value of each compound divided by that of toluene, and C(X/T) is carbon number of each compound divided by that of toluene.

analysis, the HS-SPME results exhibit slightly enhanced correlation patterns between the two parameters relative to those of the direct injection method.

The relationship between the two parameters was also examined between the compounds of high vs. low carbon numbers. If low carbon numbered compounds are arbitrarily defined as $C \leq 6$ (molecular weight of 12 ~ 72 g/mol), their $R(X/T)$

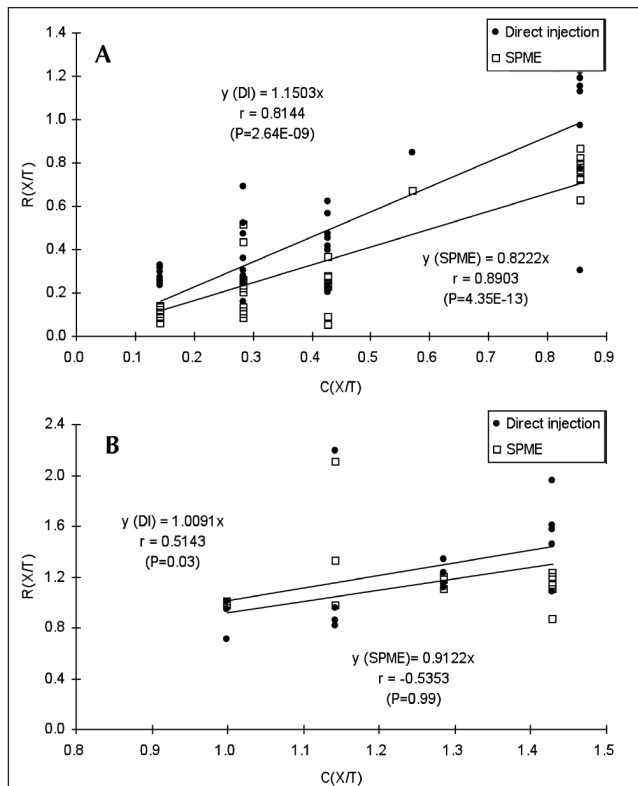


Figure 8. Comparison of $R(X/T)$ ratio vs. $C(X/T)$ ratio after grouping in two categories based on their carbon number: (A) carbon number 1 ~ 6 and (B) carbon number 7 ~ 10.

values generally fell below 1. In contrast, $R(X/T)$ values for high carbon numbered compounds [$C \geq 7$ (molecular weight of 84~120 g/mol)] generally exceeded one (Table IV). The results of the linear regression analysis (Figure 8) based on this grouping scheme showed $r \leq 0.8$ for the former group (DI: $P = 2.64E - 09$ and SPME method: $P = 4.35E - 13$). In contrast, slightly reduced correlations were seen for the latter group [DI: 0.5143 ($P = 0.03$) and SPME method: -0.5353 ($P = 0.99$)]. As such, the relative sensitivity of most VOC tended to increase with the increasing carbon number $C(X/T)$ ratio values. The observed patterns between these normalized terms suggest that the basic response properties of GC-MS can be highly sensitive to the changes in variables such as carbon number.

To further examine the detection properties of GC-MS, the results derived in this study were also analyzed in terms of functional group (Table V). To this end, all the quantifiable VOCs in the liquid phase working standard was classified as the alkane, alkene, alkadiene, alkyne, and aromatic compound groups. However, a compound of the alkadiene group was excluded for this comparison, because it is represented by a single compound (hexachlorobutadiene). Hence, the relationships between carbon number ratio and RF ratio were basically analyzed for all possible combinations between different VOC groups (Table V): alkane (I), alkene (II), alkyne (III), and aromatic compound (IV) (except alkadiene).

The results of the analyses based on individual functional groups from I through IV show highly contrasting patterns. The r values in group alkane (I) were very low for the DI (-0.414) and SPME methods (0.190). In the case of alkene (II) and alkyne (III), it was also difficult to find strong correlations between the two variables. In contrast, r values for aromatic (IV) group were moderately high between the two parameters such as 0.518 and 0.482. These results suggest the possibility that the relationship between RF and carbon number ratio can be estimated in the absence of a standard when analyzing aromatic compounds. A possible relationship between the two was investigated further in

permutations and combinations. Significantly correlated cases (e.g., r value > 0.7) were commonly seen from such combinations as I + IV, II + IV, III + IV, II + III + IV, I + II + IV, and I + II + III + IV.

As another means to examine the relationship between the two parameters, all individual compounds were divided into two groups based on molecular weights: low (78–126 g/mol) and high (128–256 g/mol) molecular weight groups. In case of the former, the results for DI and HS-SPME are highly comparable to each other to yield the r values of 0.8084 ($P = 2.02E - 06$) and 0.8783 ($P = 3.78E - 09$), respectively (Figure 9). As such, their relationships are fairly indistinguishable between the methods, especially in low weight compounds. On the other hand, the strengths of correlation improved moderately in the heavy group with r values of 0.9235 ($P = 1.53E - 12$) and 0.9441 ($P = 4.44E - 13$), respectively.

Table V. Results of Correlation Analysis Among Different Chemical Groups: Comparison Between the Two Methods

Order	Chemical group	Number	Direct injection			SPME		
			RF	r	P	RF	r	P
1	Alkane (I)	17	1.1695	-0.4141	0.11	0.4641	0.1902	0.07
2	Alkene (II)	3	*	*	*	*	*	*
3	Alkyne (III)	5	*	*	*	*	*	*
4	AC (IV)	24	1.0345	0.5177	0.01	0.9076	0.4816	0.01
5	I + II	20	1.1287	-0.3671	0.04	0.5238	0.5572	0.01
6	I + III	22	1.1561	-0.4275	0.09	0.5961	-0.1005	0.22
7	I + IV	41	1.0407	0.8376	$3.98E^{-12}$	0.8875	0.8988	$6.14E^{-16}$
8	II + III	8	1.0592	0.3200	$1.09E^{-01}$	0.8483	-0.5584	$8.98E^{-01}$
9	II + IV	27	1.0343	0.6845	$8.00E^{-05}$	0.9037	0.7342	$1.28E^{-05}$
10	III + IV	29	1.0356	0.7857	$9.56E^{-07}$	0.9097	0.7792	$4.24E^{-07}$
11	I + II + III	25	1.1254	-0.3630	$3.55E^{-02}$	0.6159	0.3012	$6.46E^{-02}$
12	I + II + IV	44	1.0403	0.8442	$2.91E^{-13}$	0.8841	0.9009	$2.44E^{-17}$
13	II + III + IV	32	1.0353	0.8101	$3.59E^{-08}$	0.9058	0.8218	$7.23E^{-09}$
14	I + II + III + IV	49	1.0454	0.8891	$1.82E^{-15}$	0.8891	0.9429	$6.47E^{-19}$

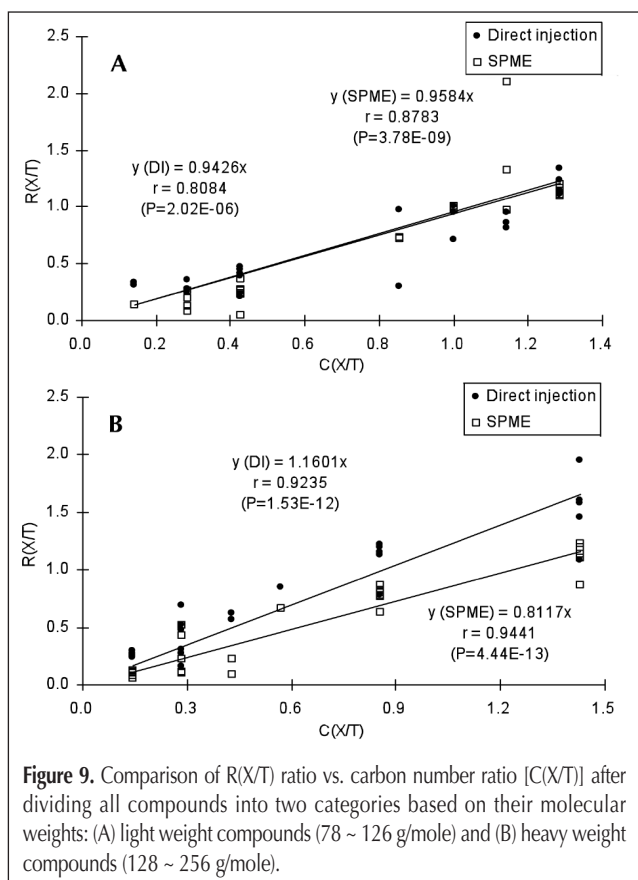
* Results are excluded because $C(X/T)$ value is a kind.

† AC = Aromatic compound

The relationship between the two ratio values was further examined based on the chemical composition of hydrocarbons (Figure 10). For this comparison, compounds were classified into two groups: pure hydrocarbons (PHC) and halogenated hydrocarbons [HHC: chlorine (Cl) and bromine (Br)]. The analysis showed moderately weak correlations ($r \leq 0.4$) for the PHC group, regardless of injection methods. In contrast, the results of the HHC group showed comparatively strong correlations for both the direct injection ($r = 0.7827$, $P = 8.70E-09$) and SPME ($r = 0.8966$, $P = 7.00E-15$) methods. As such, based on the comparative analysis, the calibration results of VOCs can be evaluated with the aid of diverse classification categories.

Conclusions

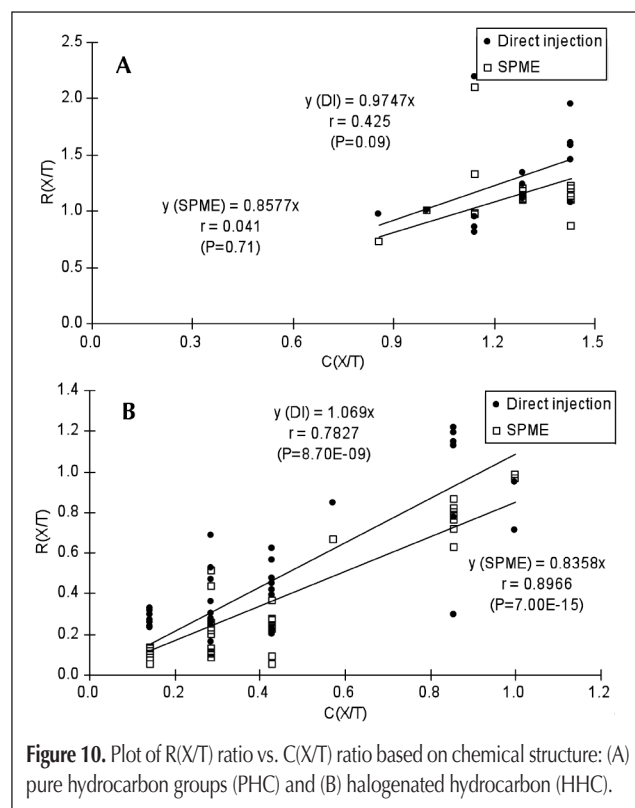
In this study, a list of VOCs was investigated to describe their calibration characteristics on GC–MS methodology. For this purpose, liquid phase standards of 54 VOCs were calibrated by the two injection methods (DI and SPME). Based on these comparative experiments, 51 compounds (over 95% similarity) were detected and quantified. The results of calibration experiments showed that all detected compounds exhibited strong linearity ($r \geq 0.99$) for both direct injection and HS-SPME. As the HS-SPME method relies on the partial extraction of vaporized fractions, the sensitivities of the HS-SPME method are lower by 33–70% than those of direct injection. Comparison of the RF between the two injection methods, however, showed



that they were significantly correlated with each other. The relatively reduced sensitivity of the former reflects that the immobilization of analyte occur proportionally during the extraction of VOC in liquid phase into headspace and onto SPME fiber. However, if one designs to induce the full equilibrium of analytes into gas phase, the analysis based on HS-SPME can attain much improved sensitivity.

According to the analysis of GC–MS technique, the relative sensitivity of VOCs can be affected considerably by the combined effects of such variables as injection method of sample, sample matrix type, pretreatment types, and physicochemical properties of individual VOCs. To specifically characterize the calibration properties of VOCs, the relationship between carbon number ratio and RF ratio was evaluated through an application of diverse grouping schemes. The results suggest that carbon number (or molecular mass) of a compound has a considerable effect on the relative detection properties of GC–MS. If the results are compared between different functional groups, aromatic compounds tend to show fairly strong correlations between the ratios of carbon number and RF. Such distinctions were also evident, as the results were compared between high and low molecular weight compounds.

The results of GC–MS analysis conducted in this study demonstrates that the detection properties of VOC are fairly predictable in terms of the relationship between sensitivity and their physicochemical properties including molecular weight (carbon number) of target compounds. As such, it is possible to roughly predict the quantities of certain compounds even under the absence of known standards. Thus, more efforts are desirable to extend the reliability of GC–MS technique for the accurate quantification of various constituents in environmental matrices both with and without calibration standards.



Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (MEST) (No. 2009-0093848).

References

- World Health Organization (WHO), Indoor Air Quality: Organic Pollutants, Euro Reports and Studies No, World Health Organisation III, Copenhagen, Denmark (1989).
- C. Yu and D. Crump. A review of the emission of VOCs from polymeric materials used in buildings. *Build. Environ.* **33**: 357–374 (1998).
- Y.C. Su, C.C. Chang, and J.L. Wang. Construction of an automated gas chromatography/mass spectrometry system for the analysis of ambient volatile organic compounds with on-line internal standard calibration. *J. Chromatogr. A* **1201**: 134–140 (2008).
- J.W. Leff and N. Fierer. Volatile organic compound (VOC) emissions from soil and litter samples. *Soil. Biol. Biochem.* **40**: 1629–1636 (2008).
- U.B. Celebi and N. Vardar. Investigation of VOC emissions from indoor and outdoor painting processes in shipyards. *Atmos. Environ.* **42**: 5685–5695 (2008).
- N. Kagi, S. Fujii, H. Tamura, and N. Namiki. Secondary VOC emissions from flooring material surfaces exposed to ozone or UV irradiation. *Build. Environ.* **44**: 1199–1205 (2009).
- P.W.G. Liu, Y.C. Yao, J.H. Tasi, Y.C. Hsu, L.P. Chang, and K.H. Chang. Source impacts by volatile organic compounds in an industrial city of southern Taiwan. *Sci. Total Environ.* **398**: 154–163 (2008).
- J.Y. Hoshi, S. Amano, Y. Sasaki, and T. Korenaga. Investigation and estimation of emission sources of 54 volatile organic compounds in ambient air in Tokyo. *Atmos. Environ.* **42**: 2383–2393 (2008).
- M. Komenda, E. Parusel, A. Wedel, and R. Koppmann. Measurement of biogenic VOC emissions: sampling, analysis and calibration. *Atmos. Environ.* **35**: 2069–2080 (2001).
- R. Fedele, I.E. Galbally, N. Porter, and I.A. Weeks. Biogenic VOC emissions from fresh leaf mulch and wood chips of *Grevillea robusta* (Australian Silky Oak). *Atmos. Environ.* **41**: 8736–8746 (2007).
- Q. Wang, Z. Han, T. Wang, and R. Zhang. Impacts of biogenic emissions of VOC and NO_x on tropospheric ozone during summertime in eastern China. *Sci. Total Environ.* **395**: 41–49 (2008).
- J.M. Delgado-Saborit and V.J. Esteve-Cano. Assessment of tropospheric ozone effects on citrus crops using passive samplers in a western Mediterranean area. *Agr. Ecosyst. Environ.* **124**: 147–153 (2008).
- O. Ezquerro, G. Ortiz, B. Pons, and M.T. Tena. Determination of benzene, toluene, ethylbenzene and xylenes in soils by multiple headspace solid-phase microextraction. *J. Chromatogr. A* **1035**: 17–22 (2004).
- R. Samuelsson, C. Nilsson, and J. Burvall. Sampling and GC–MS as a method for analysis of volatile organic compounds (VOC) emitted during oven drying of biomass materials. *Biomass Bioenerg.* **30**: 923–928 (2006).
- K. Demeestere, J. Dewulf, and K.D. Roo. P.D. Wispelaere, and H.V. Langenhove. Quality control in quantification of volatile organic compounds analysed by thermal desorption-gas chromatography-mass spectrometry. *J. Chromatogr. A* **1186**: 348–357 (2008).
- K. Demeestere, J. Dewulf, B. Witte, and H.V. Langenhove. Sample preparation for the analysis of volatile organic compounds in air and water matrices. *J. Chromatogr. A* **1153**: 130–144 (2007).
- C. Aeppli, M. Berg, T.B. Hofstetter, R. Kipfer, and R.P. Schwarzenbach. Simultaneous quantification of polar and non-polar volatile organic compounds in water samples by direct aqueous injection-gas chromatography/mass spectrometry. *J. Chromatogr. A* **1181**: 116–124 (2008).
- A. Mouchili, J.J. Wichtel, J.O. Bosset, I.R. Dohoo, M. Imhof, D. Altieri, S. Mallia, and H. Stryhn. HS-SPME gas chromatographic characterization of volatile compounds in milk tainted with off-flavour. *Int. Dairy J.* **15**: 1203–1215 (2005).
- S. Ojala, U. Lassi, and R.L. Keiski. Testing VOC emission measurement techniques in wood-coating industrial processes and developing a cost-effective measurement methodology. *Chemosphere* **62**: 113–120 (2006).
- S.K. Golfinopoulos and T.D. Lekkas, A.D. Nikolaou, Comparison of methods for determination of volatile organic compounds in drinking water. *Chemosphere* **45**: 275–284 (2001).
- E.T. Sousa, F.M. Rodrigues, C.C. Martins, F.S. Oliveira, P.A.P. Pereira, and J.B. Andrade. Multivariate optimization and HS-SPME/GC–MS analysis of VOCs in red, yellow and purple varieties of *Capsicum chinense* sp. peppers. *Microchem. J.* **82**: 142–149 (2006).
- V.A. Isidorov, V.T. Vinogorova, and K. Rafalowski. HS-SPME analysis of volatile organic compounds of coniferous needle litter. *Atmos. Environ.* **37**: 4645–4650 (2003).
- United States Environmental Protection Agency: <http://www.epa.gov/microbes/methmans.html#Metals%20Supp%20I> (1991).
- S.Y. Park, K.-H. Kim, H.S. Yang, J.Y. Ha, K.H. Lee, and J.W. Ahn. Determination of VOC in aqueous samples by the combination of headspace (HS) and solid-phase microextraction (SPME). *Anal. Sci. Technol.* **21**: 93–101 (2008).
- A. Sarafraz-Yazdi, A.H. Amiri, and Z. Es'haghi. BTEX determination in water matrices using HF-LPME with gas chromatography-flame ionization detector. *Chemosphere* **71**: 671–676 (2008).
- C. Liang, Y.-J. Chen, and K.-J. Chang. Evaluation of persulfate oxidative wet scrubber for removing BTEX gases. *J. Hazard. Mater.* **164**: 571–579 (2009).
- Korean Ministry of Environment (KMOE), Offensive Odor Control Law (2005).
- K.-H. Kim, S.K. Pandey, and R. Pal. Analytical bias among different gas chromatographic approaches using standard BTX gases and exhaust samples. *J. Sep. Sci.* **32**: 549–558 (2009).
- K.-H. Kim and H.T. Nguyen. Effects of injection volume change on gas chromatographic sensitivity determined with two contrasting calibration approaches for volatile organic compounds. *J. Sep. Sci.* **30**: 367–374 (2007).
- L. Tuduri, V. Desauziers, and J.L. Fanlo. Potential of solid-phase microextraction fibers for the analysis of volatile organic compounds in air. *J. Chromatogr. Sci.* **39**: 521–529 (2001).
- L. Tuduri, V. Desauziers, and J.L. Fanlo. Dynamic versus static sampling for the quantitative analysis of volatile organic compounds in air with polydimethylsiloxane-carboxen solid-phase microextraction fibers. *J. Chromatogr. A* **963**: 49–56 (2002).
- E.M. Bisonette, J.J. Westrick, and J.M. Morand. Determination of Henry's coefficient for volatile organic compounds in dilute aqueous systems, In Proceedings of the Annual Conference of the American Water Works Association, Cincinnati, OH, June 17–21, 1990. 1913–1922 (1990).
- D.A. Skoog, F.J. Holler, and T.A. Nieman. Principles of instrumental analysis, 5th Ed., Brooks/Cole 498–534 and 706–707 (1998).
- S. Kim. Incombustibility, physico-mechanical properties and TVOC emission behavior of the gypsum-rice husk boards for wall and ceiling materials for construction. *Ind. Crop. Prod.* **29**: 381–387 (2009).

Manuscript received November 26, 2009;
revision received February 2, 2010.