

# An Evaluation of Two Calibration Procedures Using Thermal Desorption–Gas Chromatography in the Analysis of Odorous Volatile Compounds

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## Abstract

In this study, the relative performance of gas chromatography (GC) was investigated with respect to the differences in two types of calibration approaches with a thermal desorption (TD) method: the fixed standard concentration approach (FSC: the comparison of different sample volumes for a given standard) was compared with the fixed standard volume approach (FSV: the comparison of different concentration standards at a fixed loading volume). Gaseous working standards of seven odorants, including methyl ethyl ketone (MEK), butyl acetate, methyl isobutyl ketone, isobutyl alcohol, toluene, xylene, and a reference component, benzene, were prepared at four concentration levels (10–100 ppb). They were then analyzed by controlling the TD-loading volumes at six levels (40–1200 mL). The results derived by these contrasting calibration approaches showed moderate changes in the GC sensitivity, either with an increasing concentration (i.e., FSC), or with an increasing sample loading volume (i.e., FSV). Despite an eccentric trend of MEK, the TD-based analysis was fairly predictable and can be recommended for the analysis of the selected odorants.

## Introduction

Volatile organic compounds (VOCs) are a topic of interest in many scientific disciplines including (i) food, flavor, and fragrances; (ii) medical, pharmaceutical, and forensic sciences; and (iii) the environmental sciences. Both VOC and their degradation products may be important in the epidemiology of respiratory disorders and cancer (1–2). Apart from that, VOC contributes to major environmental problems, such as global warming, stratospheric ozone depletion, photochemical ozone formation, and odor nuisances (3). In recognition of their impact on human health and the global environment, tremendous efforts have been directed to the development and improvement of their measurement techniques under a variety of environmental conditions.

Gas chromatography (GC) is undoubtedly the method of choice for the separation of a wide range of VOCs in both aqueous and gas samples (4–6). For the quantification of VOCs,

flame ionization detection (FID) and mass spectrometry (MS) are the most sensitive techniques, either individually or in combination (7). FID is advantageous because of the price and operating costs, robustness, high sensitivity, extended linearity, and the relatively simple operation (8–10). Considering that the quantification of trace analytes can be restricted by the limited sensitivity of GC, application of the thermal desorber (TD) often becomes a mandatory option to resolve such limitations in many types of environmental samples (11).

In this study, GC employing the TD technique was investigated for a number of odorous VOCs [i.e., methyl ethyl ketone (MEK), butyl acetate (BuAc), methyl isobutyl ketone (MIBK), isobutyl alcohol (i-BuAl), toluene (T), and xylene (X)]. Note that these target compounds have been designated as offensive odorants by the Korean Ministry of Environment since 2008. As a reference compound, benzene (B) was also tested simultaneously along with these odorants. In an earlier study, the feasibility of the GC–FID system for these target compounds was studied to assess the relative performance of the GC–TD method in relation to direct injection (DI) into a GC injection port (12). In the present work, the GC-based analytical technique for the selected odorants was examined further in concert with two different sample transfer approaches for TD in terms of two different calibration approaches defined as fixed standard concentration (FSC) and fixed standard volume (FSV) method.

## Materials and Methods

The basic physicochemical properties (e.g., chemical formula, molecular weight, functional group, and CAS number) of the target compounds are briefly summarized in Table I. The seven target compounds selected in this study can be divided into the following four functional groups: aromatic (T and X), ketone (MEK and MIBK), alcohol (i-BuAl), and ester (BuAc). In order to prepare the working standards of all seven VOCs and the reference compound (B), the primary standard (PS) gases were purchased separately in two cylinders referred to as Type I and II. Cylinder I contained four VOCs (i.e., MEK, MIBK, BuAc, and i-BuAl) at an equimolar concentration of 10 ppm (or  $\mu\text{mol/mol}$ ),

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while Cylinder II had 3 VOCs (B, T, and X) at 20 ppm (or  $\mu\text{mol/mol}$ ) (Ri Gas Corp., Dae Jeon, Korea). The working standards (WS) of all the VOCs were thus prepared at equimolar concentrations representing four different values (10, 20, 50, and 100 ppb) in four 10 L Tedlar bags (in Tedlar film, SKC corp., Eighty Four, PA). In the case of the 10 ppb (or  $\text{nmol/mol}$ ) WS, 10 and 5 mL of PS were taken from Cylinder I and II, respectively, and mixed together with ultrapure nitrogen gas ( $\text{N}_2$ ) to make the final volume of 10 L. To eliminate possible sources of bias in the standard preparation stage, all Tedlar bags in this experiment

were thoroughly flushed with ultrapure  $\text{N}_2$  prior to use. For this mixing procedure, gas tight syringes of various capacities were employed. The WS samples were then kept at room temperature to reach equilibrium, and then injected into the GC system.

All GC–TD experiments were designed to derive and compare the two different types of calibration approaches of FSV and FSC. As this TD system allows the direct analysis of samples collected in either the tube or bag sampler, this study was intended to evaluate the basic aspects of a combined application between TD performance and a bag sampling approach. The details of these

**Table I. Basic Information of Seven Odorous Volatile Organic Compounds (VOCs) Analyzed in This Study\***

Order <sup>†</sup>	Standard Group	Primary Standard (ppm)	Compound Name	CAS No.	Functional Group	Acronym	Chemical Formula	Molecular Weight (g/mol)	Boiling Point (°C)	Solubility (g/L)	Vapor Pressure (mm Hg at 25°C)
1	I	10	Methyl ethyl ketone	78-93-3	Ketone	MEK	$\text{CH}_3\text{COC}_2\text{H}_5$	72.1	79.6	290	95.1
2			Isobutyl alcohol	78-83-1	Alcohol	i-BuAl	$\text{CH}_3(\text{CH}_2)_2\text{OH}$	74.1	108	95	10.5
3			Methyl isobutyl Ketone	108-10-1	Ketone	MIBK	$\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$	100	117	19	20
4	II	20	Butyl acetate	123-86-4	Ester	BuAc	$\text{CH}_3\text{COO}(\text{CH}_2)_3\text{CH}_3$	116	126	7	15
5			Benzene	71-43-2		B	$\text{C}_6\text{H}_6$	78.1	80.1	0.8	95
6			Toluene	108-88-3	Aromatic	T	$(\text{CH}_3)\text{C}_6\text{H}_5$	92.1	111	0.5	28.4
7			Xylene	106-42-3		X	$(\text{CH}_3)_2\text{C}_6\text{H}_4$	106	139	0.2	9

\* Source: Annual Environmental Report. Malodor regulation in Korea. Korean Ministry of Environment (KMOE), 2008.  
<sup>†</sup> Orders 1, 3–4, and 6–7 were added as criteria offensive odorants in Korea by Korean Ministry of Environment (KMOE) from 2008. Compounds with the Orders 2 and 5 were analyzed as reference odorants.

**Table II. Experimental Scheme for the TD-Based Calibration of VOCs Prepared at Four Different Concentrations (10, 20, 50, and 100 ppb)\***

Working STD concentration (ppb)	TD loading time (min)	Sample volume (mL)	Absolute quantity (ng)							
			(pmol)	Benzene	Toluene	Xylene	MEK	MIBK	BuAc	i-BuAl
10	1	40	16.5	1.30	1.54	1.75	1.20	1.66	1.92	1.22
	2	80	33.0	2.59	3.07	3.49	2.41	3.31	3.84	2.45
	5	200	83.0	6.48	7.69	8.73	6.02	8.28	9.60	6.12
	10	400	166.0	13.00	15.4	17.5	12.0	16.6	19.2	12.2
	20	800	330.0	25.90	30.7	34.9	24.1	33.1	38.4	24.5
	30	1200	498.0	38.90	46.1	52.4	36.1	49.7	57.6	36.7
20	1	40	33.0	2.59	3.07	3.49	2.41	3.31	3.84	2.45
	2	80	66.0	5.19	6.15	6.98	4.81	6.62	7.68	4.90
	5	200	166.0	13.0	15.4	17.5	12.0	16.6	9.6	12.2
	10	400	332.0	25.9	30.7	34.9	24.1	33.1	19.2	24.5
	20	800	664.0	51.9	61.5	69.8	48.1	66.2	38.4	49.0
	30	1200	996.0	77.8	92.2	105.0	72.2	99.3	115.0	73.5
50	1	40	83.0	5.19	6.15	6.98	6.02	8.28	9.60	6.12
	2	80	166.0	10.4	12.3	14.0	12.0	16.6	19.2	12.2
	5	200	415.0	25.9	30.7	34.9	30.1	41.4	48.0	30.6
	10	400	830.0	51.9	61.5	69.8	60.2	82.8	96.0	61.2
	20	800	1660.0	104.0	123.0	140.0	120.0	166.0	192.0	122.0
	30	1200	2490.0	156.0	184.0	209.0	180.0	248.0	288.0	184.0
100	1	40	166.0	10.4	12.3	14.0	12.0	16.6	19.2	12.2
	2	80	332.0	20.8	24.6	27.9	24.1	33.1	38.4	24.5
	5	200	830.0	51.9	61.5	69.8	60.2	82.8	96.0	61.2
	10	400	1660.0	104.0	123.0	140.0	120.0	166.0	192.0	122.0
	20	800	3320.0	208.0	246.0	279.0	241.0	331.0	384.0	245.0
	30	1200	5000.0	311.0	369.0	419.0	361.0	497.0	576.0	367.0

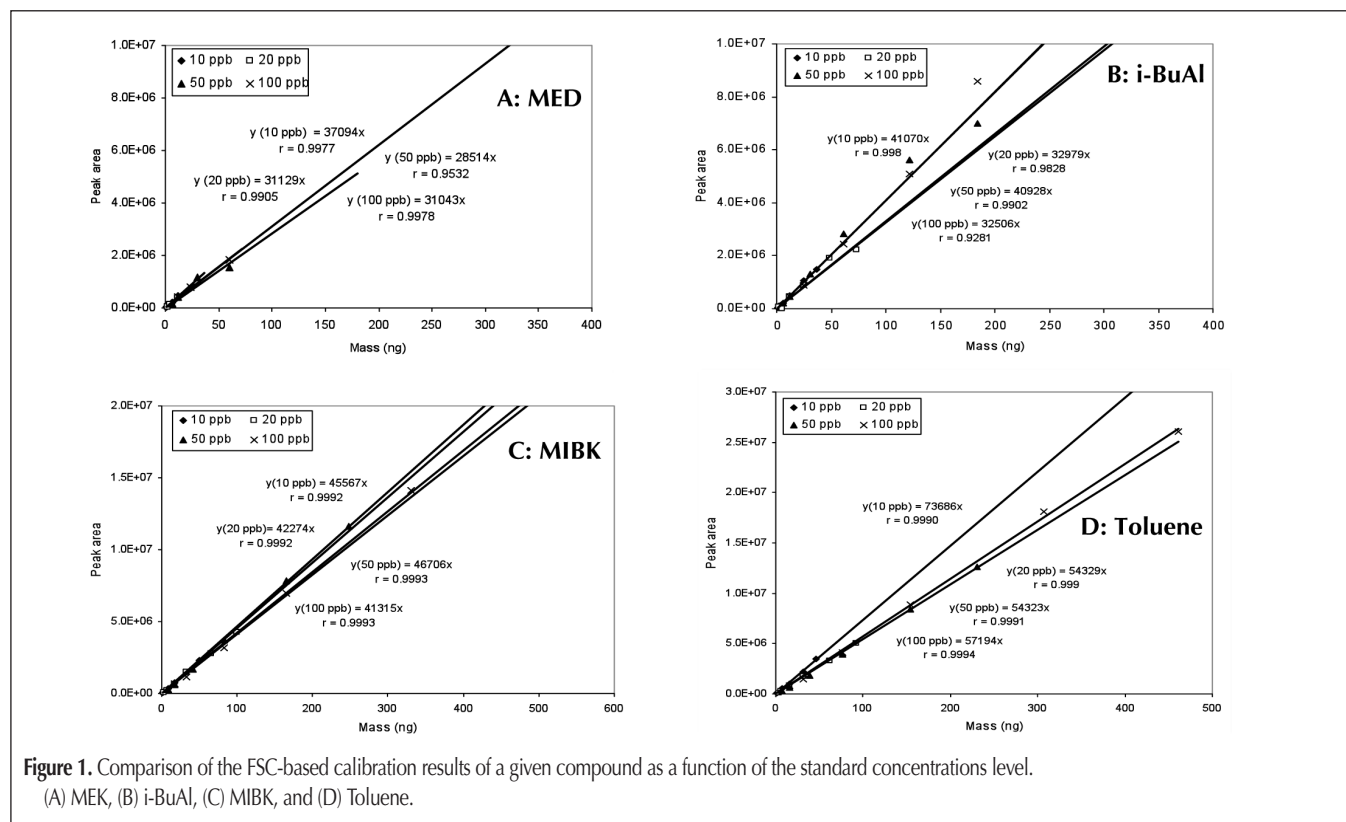
\*All flow rates for the standard loading was unified at 40 mL/min.

experimental schemes are provided in Table II. Each WS prepared at four concentrations (i.e., 10, 20, 50, and 100 ppb) were initially analyzed by transferring a given standard consecutively at six loading volumes (i.e., 40, 80, 200, 400, 800, and 1200 mL) into the TD system. Hence, the calibration points are determined by increases in the loading volumes for a standard of a given concentration (FSC approach: Table II). As such, the experimental task of this study was basically conducted as an FSC-based calibration. However, these results can be examined simultaneously in terms of varying standard concentration levels at a fixed standard (loading) volume (FSV approach). For instance, if the results are re-arranged for each loading volume, standards analyzed across all different concentration levels can also yield a new set of calibration data for a given volume (e.g., each of all six loading volumes). As a result, the calibration results obtained in this study can be compared both in terms of the FSC and FSV approaches (13). It should be noted that as field samples collected using Tedlar bags were analyzed directly through the TD unit at a single or multiple volume(s), the experimental reliability of the calibration approach is an important parameter to evaluate.

If one considers the basic experimental scheme of this study, all data collected are based on six ( $n = 6$ ) repetitive analyses on each of all four standards prepared to cover concentration levels of 10 to 100 ppb (refer to Table II). Note that each working standard was analyzed six times, all at a single, identical supply flow rate into TD. However, as it was intended to examine the results with respect to the effect of the sample loading volumes (FSV) and the standard concentration changes (FSC), the sample supply duration was modulated at six different intervals of 1 to 30 min. Hence, in case of the FSC-based analysis, all the calibration

data for a given concentration standard could be plotted as a function of the standard concentration level (or corresponding mass) of each analyte. As such, a six point calibration of each analyte can be compared on a parallel basis (Figures 1 and 2). On the other hand, those of the FSV-based results can also be plotted for a given sample loading volume between four different concentrations to yield a four point calibration curve (Figure 3).

A TD system (APK 2100 model, KNR Co., Korea) was operated to analyze the WS of all seven VOCs. The TD system allows the electronic cooling of a cold trap unit by using water as a coolant in a separate cooling unit at a constant temperature of  $-15^{\circ}\text{C}$ . This cooling unit consists of a 2 L plastic bottle (two thirds fraction filled with deionized water), a small pump to circulate water, and a chiller to maximize cryofocusing up to  $-30^{\circ}\text{C}$ . The cryofocusing of the target compounds was, however, reconciled to  $-15^{\circ}\text{C}$  to avoid clogging the cold trap unit by  $\text{H}_2\text{O}$  vapor in the sample gas streams. The cold trap was built by packing 25 mg of Tenax TA (60/80 mesh, porous organic polymers with specific surface area of  $35\text{ m}^2/\text{g}$ ) in a quartz tube with the following dimension: length 90 mm, outer diameter 6 mm, and inner diameter 3 mm. It is generally acknowledged that Tenax A is suitable for the collection of VOCs with  $\text{C}_7\text{--C}_{26}$  (14). Note that Tenax TA has been recommended by the European Collaborative Action-Indoor Air Quality (ECA-IAQ) working group for the determination of the total VOC concentration (15). The analysis of VOCs was made by transferring WS gases to a Tedlar bag, and then to the cold trap unit. Desorption of the target VOCs was conducted at a temperature of  $300^{\circ}\text{C}$ . Because of the concern over the alteration in transmission properties of polar VOCs, the gas-drying system (e.g., a Nafion dryer) was not used in the TD line. To initiate the TD operation, each Tedlar bag containing WS

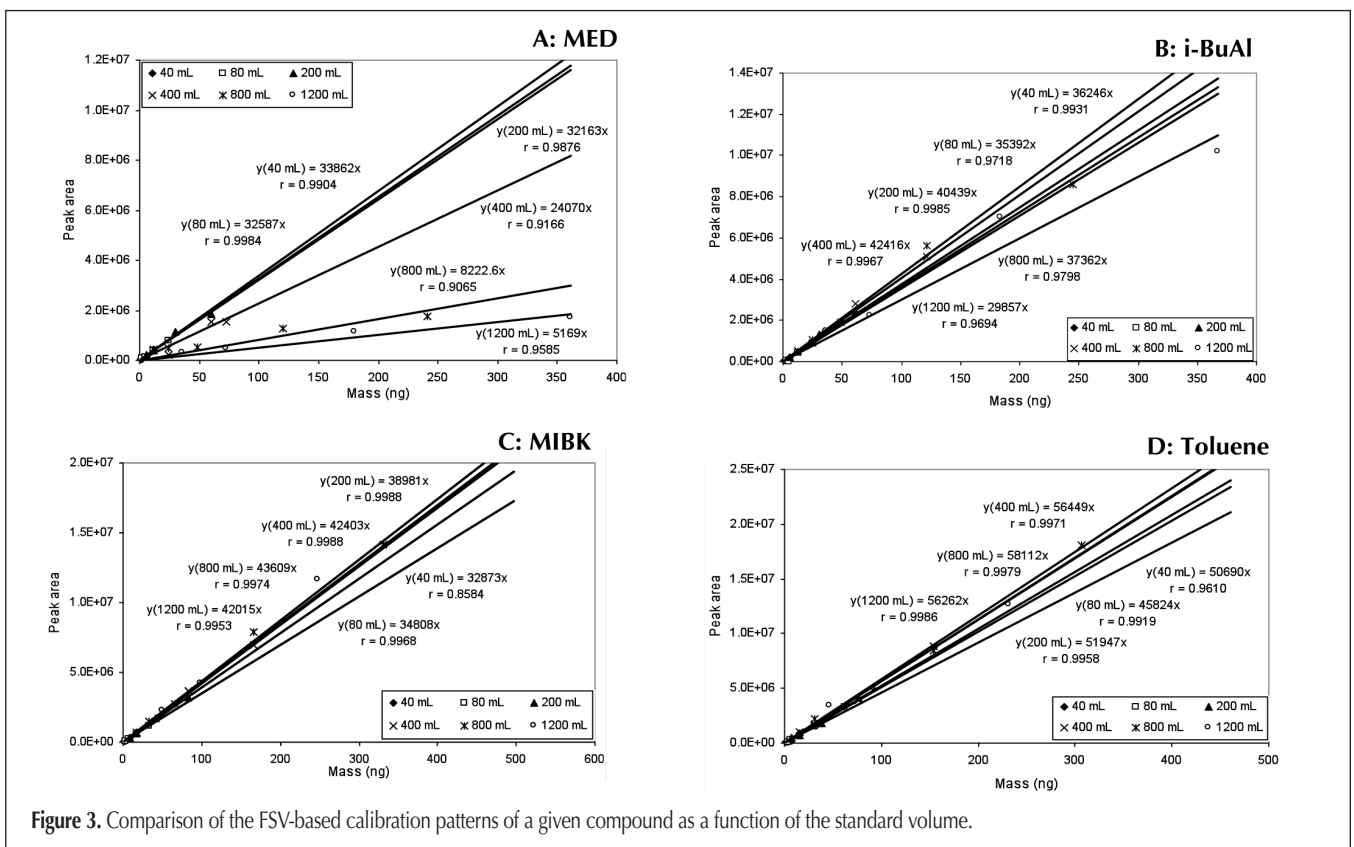
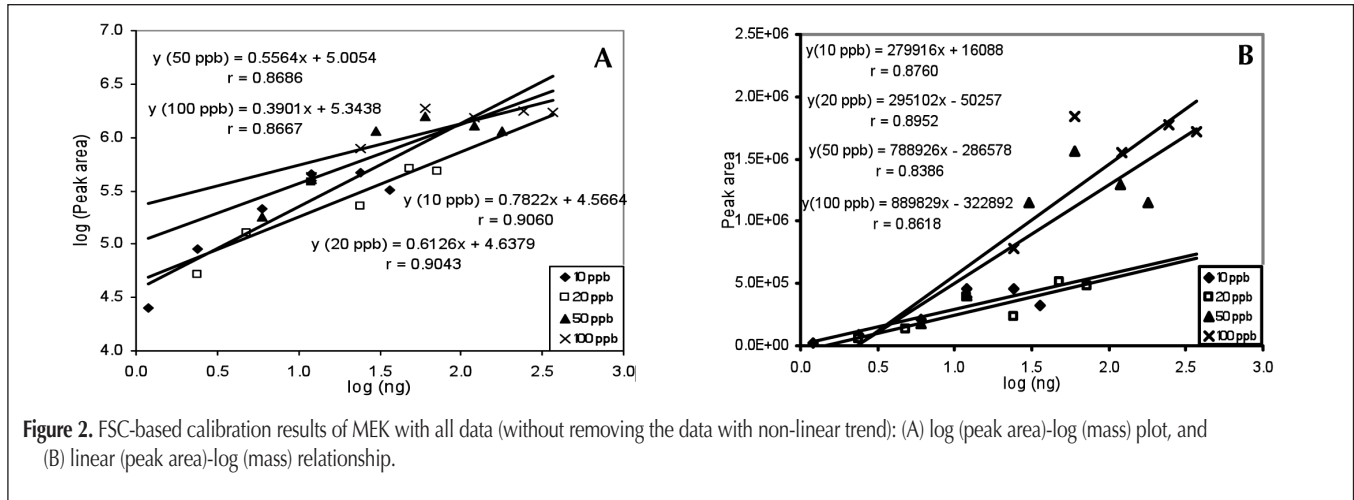


of all seven odorous VOCs was connected to the TD inlet. These VOCs were then pulled into the TD at a fixed flow rate of 40 mL/min with a vacuum pump.

The TD system used in this study was interfaced with GC-FID (DS 6200, Donam Instrument, Korea). The VOCs were separated on a DB-VRX column (60 m × 0.32 mm, i.d., 1.8 μm film thickness, J. & W., Folsom, CA) at a carrier gas flow rate of 1.5 mL/min. Although the composition of DB-VRX is proprietary, it was engineered for the separation of purgeable VOCs identified in US Environmental Protection Agency (EPA) methods 502.2 and 524.2 (16). It is also known to have separation characteristics similar to poly stationary phases containing a 5% diphenylsiloxane monomer (16). The GC system was operated at the following temperature (T) settings: 1) T (initial): 50°C (for 5 min);

2) T (ramping): 6°C/min (for 30 min); and 3) T (final): 230°C (for 5 min), at a 40 min duration. The detector temperature was set as 240°C, while gas flows were maintained at 30 (N<sub>2</sub> and H<sub>2</sub>) and 300 mL/min (air).

To examine the method detection limit (MDL) of the system, the detection limit (DL) values for each individual VOC were calculated in terms of both absolute mass (ng) and concentration (ppb). The MDL values of most odorous VOCs tend to fall in between 0.43 (MEK) to 0.17 ng (X). However, if the sample loading volume of 800 mL is considered, the practical DL values correspond to 0.18 (MEK) to 0.05 ppb (X). The precision of the TD-based analysis was computed in terms of the relative standard deviation (RSD in %) for a triplicate analysis (the use of 40 ppb WS) and fell in the range of 2.2% to 4.4%.



## Results and Discussion

### Calibration with the FSC approach

All calibrations in this study were designed to facilitate the comparison of two contrasting sample transfer approaches (i.e., FSC vs. FSV) for TD-based analysis. To this end, all calibration experiments were initiated based on the FSC method (refer to Table II). In Figure 1, the FSC-based calibration results are plotted for each compound as a function of the sample loading volume (after conversion into analyte mass). According to the FSC-based calibration, most target compounds show a good linearity in relation to changes in their loading volume for standards of all concentration levels, with only a few exceptions.

A comparison of the FSC-based data indicates two unique patterns between different chemical groups. The slope values of BTX were notably higher than those of the non-aromatic compounds. The relative sensitivity of three aromatic VOCs tend to increase in line with their molecular weight (e.g., B < T < X). These three aromatic VOCs showed a highly constant pattern, except for the occurrences of the maximum calibration slope values at the lowest standard concentrations. In contrast, in spite of a moderate difference in absolute sensitivities, most non-aromatic compounds showed an improvement in their sensitivities with an increasing molecular masses (i.e., MEK < i-BuAl < MIBK), with an exception of BuAc. Note that BuAc displayed gradually decreasing slope values with increasing sample concentrations. In addition, MEK, i-BuAl, and MIBK experienced a moderate reduction in sensitivity with increases in the standard concentration levels.

In the evaluation of the calibration trends of all the compounds, the patterns of MEK were strongly distinct from the others. In fact, the linearity of MEK was no longer apparent, especially after the fourth calibration points (or loading volumes) for standards of 20 and 100 ppb, and after the fifth points for those of 10 and 50 ppb. Hence, the FSC-based calibration results for MEK shown in Figure 1 were made by the data points

with the good linearity range (i.e., removing after the fourth or fifth points). Considering this unique behavior of MEK, its full calibration data sets were examined further in a number of ways. As shown in Figure 2, the best dose-response relationship for MEK is in fact attained in log-log scales due to the early deflection of its linearity. As such, this non-linear trend of MEK suggests that the response of MEK is less stable in the TD-based analysis than the others. (In-depth discussions on the unusual pattern of the MEK data are provided in "Results and Discussion: the eccentricity in TD-based calibration".)

### Calibration with the FSV approach

In Figure 3, all FSV-based calibration results of each compound are plotted across different loading volumes in terms of analyte mass. Hence, one can evaluate the effect of the TD-loading volume on the GC-TD sensitivity. The calibration slope values derived by the FSV approach showed fairly strong correlation coefficients for all the target compounds, relative to the FSC counterpart. In the case of aromatic compounds, the slope values tend to increase with the increasing sample loading volume (up to 800 mL) (Table III). Likewise, MIBK and BuAc displayed generally similar calibration trends. However, MEK and BuAl showed an opposite trend, with increases in sample volume. It is interesting to note that the FSV results of MEK are highly correlated without a single exception, although its sensitivity tended to drop systematically and considerably in conjunction with the loading volume changes (Figure 3A).

An evident feature in the FSV approach is that the sensitivity tends to be reduced slightly after a loading volume of ~800 mL (Table III). This observation suggests that the performance of the GC-TD analysis can be affected by basic experimental variables like the loading volume, as described in a previous study of RSCs (11). In addition, it was also found that the sensitivity of the three aromatic VOCs decreased with increases in molecular mass (i.e., B > T > X). However, the FSV-based results of MEK, i-BuAl, and MIBK showed an improved sensitivity with an increasing mole

**Table III. Statistical Summary of the Calibration Slope Values of Odorous VOC Derived by Both a Fixed Standard Concentration (FSC) and a Fixed Standard Volume (FSV) Approach**

Order	Compound		FSC (ppb)				Mean (RSE)	FSV (mL)					Mean (RSE)	
			10	20	50	100		40	80	200	400	800		1200
1	MEK*	slope	37094	31129	28514	31043	31945 (5.70)	33862	32587	32163	24070	8222	5169	22679 (23.2)
		r	0.998	0.991	0.953	0.998	0.990	0.998	0.988	0.917	0.907	0.959		
2	i-BuAl	slope	41070	32979	40928	32506	36871 (6.47)	36246	35392	40439	42416	37362	29857	36952 (4.83)
		r	0.998	0.983	0.990	0.928	0.993	0.972	0.999	0.997	0.980	0.969		
3	MIBK	slope	45567	42274	46706	41315	43966 (2.93)	38954	34808	38981	42403	43609	42015	39114 (4.59)
		r	0.999	0.999	0.999	0.999	0.858	0.997	0.999	0.999	0.997	0.995		
4	BuAc	slope	37311	35447	33057	29604	33855 (4.91)	25276	21841	25910	29470	31359	30315	27362 (5.42)
		r	0.998	0.925	0.998	0.999	0.987	0.997	0.999	0.999	0.992	0.995		
5	B	slope	68285	50932	50752	50343	55078 (8.00)	60630	57985	60426	63277	57450	45653	57570 (4.40)
		r	0.999	0.992	0.984	0.975	0.973	0.975	0.996	0.996	0.999	0.997		
6	T	slope	73686	54329	54323	57194	59883 (7.77)	50690	45824	51947	56449	58112	56262	53214 (3.54)
		r	0.999	0.999	0.999	0.999	0.960	0.992	0.996	0.997	0.998	0.999		
7	X	slope	110386	66526	63777	62040	75682 (15.3)	45194	49077	55871	60420	63751	63409	54807 (7.89)
		r	0.997	0.996	0.997	0.999	0.852	0.964	0.982	0.991	0.984	0.990		

\* Only using the data with a linear trend: removing the data after the fourth (20 and 100 ppb standard gas) and fifth calibration points (10 and 50 ppb standard gas).

ular mass (i.e., MEK < i-BuAl < MIBK), which is quite comparable to the pattern in the FSC approach. In Figure 3, the unique patterns of the FSV-based calibration appear most noticeably from either MEK or X. Interestingly, unlike the FSC-based approach for MEK, the FSV data did not show any outlying data point in each loading volume, although its slope values varied noticeably between a low and high sample volume. As such, the absolute magnitude of MEK's sensitivity was affected fairly sensitively by the size of volume transferred into the TD unit. The mean slope value derived at low loading volumes (40 to 400 mL) was 30,670 and 6,695 at upper loading volumes (800 to 1200 mL). This simple comparison thus shows that the GC sensitivity for MEK dropped roughly five times at a high sampling volume, relative to the low-bound ones. Such a unique pattern of loadable volume dependency has in fact been observed by a previous TD-based calibration of highly reactive species like H<sub>2</sub>S (17). This relative pattern, however, suggests that the calibration of MEK can be conducted more reliably with FSV, as long as the control of the sample volume is carefully managed.

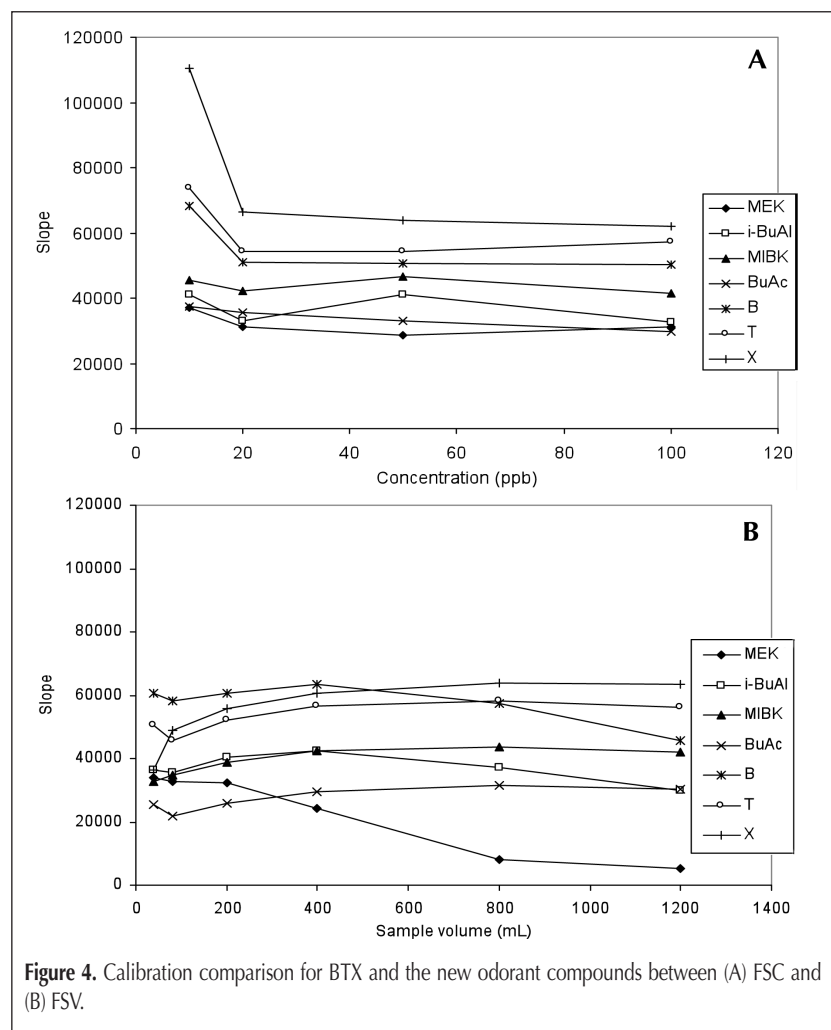
### Comparison between FSC vs. FSV approaches

The results of this comparative analysis indicates that there are no pronounced differences in GC sensitivity between the two distinct calibration approaches (i.e., FSV vs. FSC), although alterations from the general trend can be observed from the

most reactive compound, such as MEK. The sensitivity of the aromatic compounds, when examined in terms of FSC, exhibited recognizable variations at varying concentration levels. The FSC-calibration results of the 100 ppb standard showed moderate reductions in sensitivity (around 26% for B, 29% for T, and approximately 44% for X), relative to the values obtained using the 10 ppb standard. In contrast, the BTX results of the FSV approach experienced increases in slope values with an increasing loading volume. The sensitivity increase between the lowest (i.e., 40 mL) and the highest (i.e., 1200 mL) loading volume was around 25% for B, 10% for T, and 40% for X. Nonetheless, the relative sensitivities of aromatic VOCs examined in terms of the two contrasting calibration approaches do not alter greatly with the adoption of the GC-TD method. As seen from TD-based calibration experiments for RSCs, a comparison of the two calibration approaches for RSC also yielded the results that are practically indistinguishable in their relative magnitude (11). The results of these TD-based analyses, however, contrast with the previous study of the DI method in which sensitivity of GC-FID increased significantly with a decreasing injection volume, despite the lack of trend in the sample concentration change (18).

Through a computation of the relative standard error (RSE), the precision of the GC-TD method for these target compounds was evaluated. The RSE values of the FSV-based calibration slope values, when assessed for aromatic compounds, generally fell in the range of 3.5 to 8%. In contrast, those made by the FSC-based calibration are 8 to 15.3%. In both approaches, X showed the highest RSE value, while T displayed the least. As such, the RSE values derived by the FSC slopes of aromatic compounds were approximately two times higher than the FSV counterparts. In contrast, the non-aromatic compounds did not show much difference in terms of the RSE values in both approaches, which varied between 3 to 7% (except for MEK). The RSE value of MEK derived from the FSC approach was 17% with all data. However, after excluding all the non-linear data, the value was reduced to 5.7% (Table III). Note that Chauvenet's criterion was used to evaluate the outlier data (19). In contrast, the RSE values of MEK were more variable with FSV (23%).

The slope values derived by each transfer approach were put together to extract comparative patterns as a function of the concentration levels or the sample volumes used (Figure 4). This confirmed that the results derived from both approaches generally became stable with increases in the volume or the standard concentration. In the FSC approach, the slope values for the aromatic compounds and BuAc tended to decrease with increasing concentrations, while the patterns for MEK, i-BuAl, and MIBK were no longer uniform or consistent. The uniqueness of the MEK calibration observed from the FSC results was consistently recognized from the FSV approaches. However, unlike the patterns seen from the FSC



analysis, its linearity was maintained highly consistently at each of all the loading volumes in all the FSV results, at least in terms of correlation coefficients, despite a noticeable drop in its sensitivity with increasing loading volumes (Figure 3). Although they contrast between FSV and FSC, all these unique patterns of MEK appear to be bound tightly from each other in certain respects.

In recent years, the GC-based analytical technique has been enriched through diverse modifications (e.g., low-flow cold trap, short-path TD, on-line sorbent trapping and membrane extraction, etc.) (20). Improvement of accuracy (−4.8 to 4.9%) and precision (0.05–11.5%) was attained for 132 non-polar compounds through an in-injection port TD–GC–MS analysis. To conduct an in-injection analysis, samples were placed inside the GC injector port so that thermal desorption took place in the injector port. In principle, it offered the highest transfer efficiency with the elimination of transfer lines between the sample and the analytical instrument (21). Moreover, the use of TD was basically a solvent-free method to yield an excellent separation. It also prevented analyte losses by minimizing sample manipulation and risk of contamination due to the solvents (22).

#### The eccentricity in TD-based calibration

The unique properties of MEK calibration observed in both FSC and FSV approaches merit further discussion. In the previous study based on TD and DI approach, MEK showed the least stable calibration patterns of all the target compounds (12). A comparison of the relative sensitivity loss between TD and DI indicated that the relative loss rates of the others were around 35%, while it was more than 50% for MEK. The effect of the TD-based bias in the analysis of MEK was in some senses also comparable to that observed previously from the GC–TD analysis of carbonyl compounds (23). In that study, the calibration of the lighter carbonyls (e.g., acetaldehyde) was considerably defective, while such problems were not apparent with heavier ones (23). In the end, the calibration of acetaldehyde resumed a normal linear trend with the replacement of stronger multi-sorbents in cold trap unit.

In another study, a dynamic air sampling method was investigated by trapping gas and vapor on multi-sorbent tubes filled with Carbotrap (70 mg), Carboxen-569 (90 mg), and Carboxen X (100 mg) (22). Due to the combined effect of sorbent, column, and detector characteristics, the method performance was somewhat poorer for carbon disulfide, alcohols, aldehyde, and amides (22). Similarly, the blank chromatograms derived from multi-sorbent beds of Tenax/Carbograph 1TD and Carbograph 1/Carboxen 1000 were also examined with respect to a number of aromatic VOCs (e.g., B, T, X, styrene, and naphthalene) (24). Based on this comparative analysis, the use of the former combination was recommended for its low memory effect. Complicated behavior of sorbent material has in fact been recognized from its application to cryotrapping, as it showed systematic deviations of 40–80% between gaseous and liquid samples (25). Hence, to correct the analytical bias and to improve the limited precision resulting from the TD application, the use of an internal standard was suggested as one possible option (25).

If one considers all the variabilities involved in the MEK analysis, one may ascribe such a unique trend to an interaction between chemical properties (e.g., strong reactivity) and bias

involved in thermal desorption. The reason behind the unusual calibration pattern of MEK, the lightest compound in this study, can be first explained by its unique physicochemical properties, including its highest solubility values (around 290 g/L) and vapor pressure (95.1 mm Hg at 25°C) with a low boiling point (79.6°C) (refer to Table I). In previous studies, the competitive adsorption between different compounds, if occurring, was ascribed to differences in physicochemical properties of adsorbates (26,27). It was, in fact, found that the desorption of MEK took place at 80°C and continued up to 250°C (28). Hence, the physisorption of MEK with its boiling point of 79.6°C is unlikely to proceed more effectively than others. Although the boiling points of MEK and B are almost the same under similar adsorbate concentrations, MEK may exhibit a much greater pore diffusion coefficient than B (29). This may be due in part to its smaller molecular size with a polar molecular structure. Because of all these complicated properties of MEK, its analysis by TD should be handled with more caution (e.g., selection of a narrow linearity range for calibration), unless the TD setup or sorbent material was optimized at the cryofocusing stage. In addition, it is worth mentioning that the DI-based linearity of BTX can be limited considerably with FSC due to the matrix effect (18). In contrast, when the TD-based method was tested against gaseous RSC standards, fairly extended linearities were maintained consistently for all RSCs even with the FSC method (11). The existence of contrasting calibration patterns thus suggests that the linearity of the target compounds could be affected sensitively by the combined effects of various factors involved in the analysis.

#### Conclusions

Essential aspects of the TD-based calibration were examined in this study with respect to several odorous VOCs that were recently added as offensive odorants in Korea. By comparing the calibration results derived by two different sample transfer approaches (namely FSC and FSV), the calibration properties of odorous VOCs were evaluated in a number of respects. According to this comparative study, the sensitivity of three aromatic VOCs (B, T, and X) generally exhibited a highly comparable pattern with each other, in relation to the increasing sample concentration (in the FSC approach), or to the increasing sample volumes (in the FSV approach). In the case of other (polar) VOCs (i-BuAl, MIBK, and BuAc), similar patterns were maintained with moderate alterations. Especially in the case of MEK, the calibration patterns were greatly affected by changes in the sample loading volume, regardless of the sample transfer approach (i.e., FSV or FSC approaches). It may thus be imperative to put more effort into deriving a more stable calibration pattern of MEK with the GC–TD setup. However, observations from this study suggests that its calibration can still be made quite reliably, as long as certain variables are considered that tend to accompany changes in sample loading volumes. The overall results of this study thus confirm that there is no significant difference in calibration properties between the FSC and FSV approaches for most odorous VOCs investigated in this study, with the exception of the relatively reactive compound, MEK.

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