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The selection of the standard phase (gas vs. liquid) and the related matrix effect on the direct injection gas chromatographic analysis of VOCs at sub–ppm levels

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ABSTRACT

In this study, the matrix effect on the quantitation of volatile organic compounds (VOCs) at sub–ppm levels has been investigated in relation to the selected standard phase by direct injection gas chromatographic (GC) analysis. To this end, a series of calibration experiments were conducted using both liquid and gas phase standards containing identically a total of 13 target VOCs. Calibration datasets between liquid and gas standards were obtained at the four selected injection volumes, i.e., covering a 1 to 5 and 50 to 500 μL range, respectively. The results indicate that injection volume is a sensitive parameter, as sensitivity tends to decrease with increasing injection volume, especially with liquid standards. Loss of analytes in liquid standard occurred noticeably from ones eluting earlier than solvent used for standard (i.e., methanol). If the extent of such loss is expressed by the percent differences in the response factor (RF) values between two standard types, the results were low or insignificant for valeraldehyde (0.48%), benzene (7.6%), toluene (3.3%), and styrene (4.8%) but generally high for the others (i.e., between 10–80%). The relative sensitivities of VOCs in gaseous standards, if computed by normalization against benzene, generally complied well with those derivable from the literature on flame ionization detectors. In contrast, in case of liquid standards, the use of a small injection volume (≤1 μL) is recommended to maintain the optimal GC performance in light of the matrix effect.

Keywords: *Volatile organic compound (VOC), injection volume, sensitivity, fixed standard volume (FSV), calibration/ response factor*

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1. Introduction

Volatile organic compounds (VOCs) in atmosphere comprise of numerous diverse chemical compounds, while many are well known for their toxicity, irritating malodor, and health hazards (e.g., eye and respiratory tract irritation, olfactory damage, and carcinogenicity) (Sweet and Vermette, 1992; Ware et al., 1993; Mukund et al., 1996; Pappas et al., 2000; Schmitz et al., 2000; Tam and Neumann, 2004). VOCs are generally emitted from natural sources (i.e., predominantly biogenic), but anthropogenic emissions due to fuel combustion, industrial processes, solvents evaporation, food production, etc. are also very important in a quantitative sense (Seco et al., 2007). During 1983–1995, the total emissions of biogenic VOC were estimated to be in a range of 692–1 150 Tg C $year^{-1}$, whilst those of anthropogenic sources accounted for 103 Tg C $year^{-1}$ (Lathiere et al., 2006; Kansal, 2009).

The concentration of VOCs in ambient air is very low due to their conversion into secondary pollutants (e.g., ozone and secondary organic aerosols) through photochemical reactions (Na et al., 2003; Nguyen et al., 2009; Shao et al., 2009; Kim and Kim, 2013; Iqbal et al., 2014a). Hence, to quantify VOCs in ambient air (e.g., in sub–ppb range), gas chromatograph (GC) equipped with mass spectrometric (MS) or flame ionization detector (FID) is generally interfaced with a preconcentration system through the combination of sorbent tube (ST) and thermal desorber (TD) (Kim and Kim, 2012a; Iqbal et al., 2014b). As such, the selection of TD–GC–FID or TD–GC–MS is a common choice for the analysis of ambient VOCs. However, direct injection (DI) method may still be a preferable option when dealing with samples in a sub–ppm concentration range, e.g., polluted or processed air samples (Kim and Nguyen, 2007). Consequently, the instrumental setups for the VOC analysis can be made with a plain GC system (DI) or with preconcentration system (TD).

Regardless of the instrumental configurations chosen for the VOCs analysis, the selection of standard phase is often considered one important factor for their accurate quantification. In the analysis of VOCs in ambient air or polluted air, the use of gaseous standard is often preferred over liquid standard; this is because the former generally facilitates the elimination or suppression of the matrix effect which commonly acts as a key experimental variable (Kim and Kim, 2012a; Kim and Kim, 2012b; Kim and Kim, 2013). However, in practice, the use of liquid standards is made more frequently because of several advantages, e.g., low cost, easy handling, wide selectivity of target compounds, etc.

In this study, we evaluated the effect of two experimental parameters in the DI–based analysis of VOCs using GC–FID: (1) effect of standard phase (gas vs. liquid) and (2) standard injection volume. A total of 13 VOCs [acetaldehyde (AA), propionaldehyde (PA), butyraldehyde (BA), isovaleraldehyde (IA), valeraldehyde (VA), methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), butyl acetate (BuAc), isobutyl alcohol (i–BuAl), benzene (B), toluene (T), *p*–xylene (p–X), and styrene (S)] were selected as target compounds. To determine the effect of injection volume and standard phase, comparative calibrations were then made by injecting gas and liquid phase standards (of 13 VOCs) at two

different volume ranges: (1) 50–500 µL (gas) and (2) 1–5 µL (liquid). The former is a common range for the analysis of VOCs in polluted air (Kim and Nguyen, 2007). On the other hand, the latter may be selected, as the detection of VOC can be made without overloading on GC–column. To allow comparison of relative performance between two standard phases, the FID response factor (RF) values for all VOCs were derived based on the principle of fixed standard volume (FSV) approach (Kim and Nguyen, 2007). The results of this study are thus expected to account for the effect of key experimental parameters in DI–based analysis of VOCs such as standard phase and injection volume. Moreover, we also discuss the fundamental aspects of the experimental biases in the DI–based analysis of VOCs, mainly with respect to the matrix and solvent effect.

2. Materials and Methods

In this study, a total of 13 VOCs were selected to assess the relative performance between standard phases (gas vs. liquid) and in relation to varying injection volume. For this purpose, we designed a series of experiments to characterize the calibration properties of different VOCs in a systematic manner. The calibration results for gaseous standards with varying concentrations were obtained for each of all four different injection volumes (50, 100, 200, and 500 µL) (see the Supporting Material, SM, Table S1). These calibrations were conducted using gaseous standards of four different concentrations (0.5, 1, 2, and 5 ppm for each VOC, except AA). On the other hand, liquid standards were prepared at five different concentration levels (0.22, 0.67, 2.22, 5.55, and 8.88 ng μL^{-1} for each VOCs, except AA) for their calibration at four different injection volumes (1, 2, 3, and 5 µL) (see the SM, Table S2). Finally, peak areas (A) were plotted against injected mass (m) to obtain response factor (RF) values at each injection volume (V_{FS}) (see the SM, Figure S1).

2.1. Preparation of gas– and liquid–phase standards

The basic physicochemical properties of the 13 target compounds analyzed in this study are summarized in Table 1. In order to prepare the gaseous working standards (G–WS) of 13 target VOCs, the primary standard (PS) gases were purchased separately in three cylinders (Rigas Corp., Korea). The first cylinder contained four carbonyls (PA, BA, IA, and VA) at 20 parts per million (ppm) and AA at 100 ppm concentration. Four aromatic hydrocarbons (B, T, p–X, and S) and four other VOCs (MEK, MIBK, BuAc, and i–BuAl) were contained in the second (each at 20 ppm) and third cylinders (each at 10 ppm), respectively. The G–WS for calibration was prepared at 0.5, 1, 2 and 5 ppm by one step dilution of the PS with ultra–pure nitrogen (99.999%) with the aid of a gas–tight syringe into 1 L polyester aluminum (PEA) bags (Top Trading Co., Korea).

The liquid–phase working standard (L–WS) of the same target VOCs was also prepared by a three step dilution of pure chemicals for direct comparison with gas–phase standards described above. The primary grade chemicals (≥97% purity, unless otherwise stated, (1) PA, IA, and VA; (2) AA, BA, S, p–X, MEK, i–BuAl, and BuAc (99.0%); and (3) B, T, and MIBK (99.5%)) were purchased from Sigma–Aldrich, USA. To prepare the PS, we treated carbonyls, aromatic hydrocarbons, and other VOCs independently. For the carbonyls, we added 70, 30, 30, 40, and 30 µL of liquid AA, PA, BA, IA, and VA, respectively to 1.80 mL of methanol. In case of aromatics, mixture of liquid B, T, p–X, and S (30, 40, 40, and 40 µL, respectively) was added to 1.85 mL of methanol. Finally, we mixed 30, 40, 40, and 40 µL of liquid MEK, MIBK, BuAc, and i–BuAl, respectively to make a 2.0 mL solution in methanol.

To prepare the 1st WS, these PSs were diluted separately in three different vials. From each of all three groups, 60 µL of each PS was diluted in 1.94 mL of methanol in separate vials. The final WSs at five different concentration levels (average 0.2, 0.7, 2.2, 5.5, and 8.8 ng μL^{-1} of each target compound, except AA) were prepared in five different vials by mixing different amounts of the 1st WS and diluted with methanol. Finally, liquid phase working standards (L–WS) of all 13 target VOCs were stored at five different 1.5 mL vials (Agilent Technologies, USA).

2.2. Instrumental system

In this research, liquid and gas phase standards of VOCs were analyzed by the direct injection method. As presented in Table 2, experiments were conducted using a GC system equipped with an FID (Model iGC 7200, DS Science, Korea). The analysis of gas phase standard was done through direct injection in a splitless mode, while that of liquid standard was made on 1:5 split mode. Direct injection analysis was made using both gas (50 to 500 µL) and liquid working standards (1 to 5 µL) into the GC injector using gas–tight and liquid–injection syringes (SGE, Australia), respectively. The injected standards were then separated on a DB–WAX column (length=60 m, internal diameter=0.25 mm, and film thickness= 0.50 µm: Agilent Technologies, USA).

The details on temperature programming of the GC–injector, oven, and detector for both liquid and gas–phase standard analysis are given in Table 2. The GC carrier gas (N_2: 99.999% purity) was supplied at a flow rate of 1.5 mL min^{-1}. The flow rates for the FID system were 30 (H_2 and N_2) and 300 (air) mL min^{-1}.

Table 1. *Basic information of the 13 target compounds (VOCs) investigated in this study*

Order	Group	Compound	Abbreviation	MW (g mol^{-1})	Density (g cm^{-3})	Formula	CAS Number
1	Aldehydes	Acetaldehyde	AA	44.05	0.79	C_2H_4O	75–07–0
2		Propionaldehyde	PA	58.08	0.81	C_3H_6O	123–38–6
3		Butyraldehyde	BA	72.11	0.81	C_4H_8O	123–72–8
4		Isovaleraldehyde	IA	86.13	0.79	$C_5H_{10}O$	590–86–3
5		Valeraldehyde	VA	86.13	0.81	$C_5H_{10}O$	110–62–3
6	Ketones	Methyl ethyl ketone	MEK	72.11	0.81	C_4H_8O	78–93–3
7		Methyl isobutyl ketone	MIBK	100.2	0.80	$C_6H_{12}O$	108–10–1
8	Ester	Butyl acetate	BuAc	116.2	0.88	$C_6H_{12}O_2$	123–86–4
9	Alcohol	Isobutyl alcohol	i–BuAl	74.12	0.80	$C_4H_{10}O$	78–83–1
10	Aromatics	Benzene	B	78.11	0.87	C_6H_6	71–43–2
11		Toluene	T	92.14	0.87	C_7H_8	108–88–3
12		p–Xylene	p–X	106.2	0.86	C_8H_{10}	106–42–3
13		Styrene	S	104.2	0.91	C_8H_8	100–42–5