

Quantitative Approaches for the Determination of Volatile Organic Compounds (VOC) and Its Performance Assessment in Terms of Solvent Types and the Related Matrix Effects

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ABSTRACT

For the quantitative analysis of volatile organic compounds (VOC), the use of a proper solvent is crucial to reduce the chance of biased results or effect of interference either in direct analysis by a gas chromatograph (GC) or with thermal desorption analysis due to matrix effects, e.g., the existence of a broad solvent peak tailing that overlaps early eluters. In this work, the relative performance of different solvents has been evaluated using standards containing 19 VOCs in three different solvents (methanol, pentane, and hexane). Comparison of the response factor of the detected VOCs confirms their means for methanol and hexane higher than that of pentane by 84% and 27%, respectively. In light of the solvent vapor pressure at the initial GC column temperature (35°C), the enhanced sensitivity in methanol suggests the potential role of solvent vapor expansion in the hot injector (split ON) which leads to solvent trapping on the column. In contrast, if the recurrent relationships between homologues were evaluated using an effective carbon number (ECN) additivity approach, the comparability assessed in terms of percent difference improved on the order of methanol (26.5%), hexane (6.73%), and pentane (5.24%). As such, the relative performance of GC can be affected considerably in the direct injection-based analysis of VOC due to the selection of solvent.

Key words: Volatile organic compound (VOC), Solvent effect, Sandwich injection (SI) technique, Response factor, Effective carbon number (ECN)

1. INTRODUCTION

In light of the effect on both human health and global

environment, volatile organic compounds (VOC) have become a major issue and concern for many environmentalists. VOCs are well known for their contribution toward global-scale environmental changes such as global warming, stratospheric ozone depletion, and photochemical ozone formation (Kavouras *et al.*, 2013; Sahu, 2012; Evtyugina *et al.*, 2009). It is also perceived that VOCs and their degradation products can be responsible for the high prevalence of various respiratory disorders and cancers (Sahu and Saxena, 2015; Yassaa *et al.*, 2011; Wang and Zhao, 2008; Boeglin *et al.*, 2006). Moreover, many members of VOCs can act as the source of odor nuisance on a regional scale (Lal *et al.*, 2012; Sahu and Lal, 2006).

To gain a better knowledge on the occurrence, behavior, and fate of environmental VOCs, acquisition of accurate concentration data is of primary importance in their research. In view of the physicochemical properties of these target compounds, analytical methods were developed for separation by gas chromatography (GC) and subsequent detection, e.g., via mass spectrometry (MS), flame ionization detection (FID), electron capture detection (ECD), and others (Kim *et al.*, 2011). For all methods, calibration is the key to quantify VOCs contained in an unknown sample. If the calibration is made incorrectly, it can lead to over- or under-estimation of a VOC in a sample. The general procedure of quantitation includes: 1) preparation of accurate standard mixtures; 2) the calibration, i.e., conducting a given analytical process for standard mixtures and; 3) establishing the relationship between final instrument response and analyte content (either in concentration or absolute amount) in a sample (Namięśnik *et al.*, 2000).

To conduct gas chromatographic analysis of VOC in a traditional way, each sample is introduced via direct injection and loaded onto the chromatographic column for the separation of compounds by manual (or automatic) injection (Harper, 2000). In contrast, if airborne

VOCs have been collected by trapping on a solid sorbent, it is necessary to volatilize analytes contained in samples or standards with the aid of a thermal desorption system (Ras *et al.*, 2009). To minimize the quantitation bias due to phase differences between real samples and laboratory standards, the use of gaseous samples and gaseous standards is the most preferable option. However, the use of liquid-phase standards are often inevitable for the analysis of gas samples due to the complexities (and high cost) in the preparation of gas standards and/or to the reactivity of the standard compounds. Hence, if the analyte is in either a liquid or gaseous matrix, their mixing ratio is also an important criterion for GC-based quantitation. The solvent to analyte ratio is commonly set at 1000 : 1 or greater in environmental analysis. Hence, it is important to choose a solvent that exhibits the least interference in the detection of the analytes. As is the case of direct injection, the solvent used for the liquid standards in the thermal desorption (TD) analysis should also be capable of effectively stripping the analytes off the sorbent. Moreover, it is imperative that such stripping should be made with high degree of efficiency and reproducibility (Harper, 2000).

Most commonly used solvents available in laboratory are acetone, acetonitrile, benzene, cyclohexane, dichloromethane, dimethyl ether, ethylacetate, tetrahydrofuran, toluene, methanol, hexane, and pentane (Ahn *et al.*, 2011; Pang *et al.*, 2011). Among those, the latter three (shortnames: MeOH, Hx, and Pn) have been the most common choice for VOC analysis. Although carbon disulfide (CS₂) is commonly used in solvent extraction of VOCs off sorbents (highest Hansen solubility parameters among the common solvents), CS₂ was not included in our study in light of its toxicity (Beauchamp *et al.*, 1983). In general, their properties seem neutral in that their presence minimally alters or interferes with chromatographic responses. Nonetheless, the results of an in-depth literature search demonstrated that information is insufficient to describe the details of solvent effects or to recommend an optimum solvent for the GC-based analysis of VOCs.

In this work, we attempted to describe relative response characteristics of VOCs in association with three different solvents (methanol, pentane and hexane). For this comparative analysis, a total of 19 VOCs (Table 1) were selected and investigated for the analysis of solvent effect which included acetaldehyde (AA), propionaldehyde (PA), butyraldehyde (BA), isovaleraldehyde (IA), valeraldehyde (VA), benzene (B), toluene (T), p-xylene (p-X), m-xylene (m-X), o-xylene (o-X), styrene (S), methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), butyl acetate (BuAc), isobutyl alcohol (i-BuAl), propionic acid (PPA), n-butyric acid (BTA),

isovaleric acid (IVA), and n-valeric acid (VLA). All of these compounds (except benzene) are classified as offensive odorants in S Korea (KMOE, 2010). In order to explore the feasibility of each solvent as the medium for VOC analysis, a comparative analysis was carried out based on direct injection of liquid standards of VOCs into a gas chromatograph (GC) equipped with a splitter and a flame ionization detector (FID). To evaluate relative response characteristics of different VOCs between different solvents, the calibration for each compound was done in triplicate. The reliability of each solvent in VOC analysis was then examined by evaluating the relative performance (e.g., sensitivity) and the basic quality assurance (QA) parameters (e.g., method detection limit (MDL) and relative standard error (RSE)).

2. MATERIALS AND METHODS

2.1 Preparation of Working Standards

In this study, the relative performance properties of the solvents were investigated for the quantitation of 19 selected target VOCs with four functional groups: i) five aldehydes (AA, PA, BA, IA, and VA), ii) five aromatic hydrocarbons (B, T, p-X, m-X, o-X, and S), iii) five fatty acid (PPA, BTA, IVA, and VLA), and iv) three ketones and an alcohol (MEK, MIBK, BuAc, and i-BuAl). For this study, relative performance of the three most widely used solvents in GC, e.g., methanol, pentane, and hexane were investigated. Basic information on the 19 target VOCs and three solvents selected in this study is summarized briefly in Table 1.

Primary grade chemicals were purchased from Sigma-Aldrich, USA at purities of, 97% (PA, IA, VA, and o-X), 99.5% (B, T, MIBK, and BuAc), and 99% for the rest of VOCs. For the three solvents, methanol (purity 100%), pentane (purity 100%) and hexane (purity 99.5% (95% n-hexane, 4.5% other C₆H₁₄ isomers, and with trace benzene and cyclopentane)) were purchased from J.T. Baker, USA. As shown in Table 2, four primary standards (PS) representing each of the four chemical groups were prepared. Their liquid phase working standards (L-WS) were then prepared by two step volumetric dilution of the four PS mixtures in each solvent (MeOH, Pn, and Hx). For the preparation of the PS of each chemical group, approximately 70 μL of each raw VOC (except AA (200 μL)) were mixed with each solvent to make a final volume of 1.5 mL. Hence, a mean concentration of each VOC was maintained at 40 $\mu\text{g } \mu\text{L}^{-1}$ (Table 2). The concentration of each VOC in the L-WS was adjusted to a similar level, except for AA (Table 2). The concentration of AA was set 2.5 times higher than the others due to its reduced FID sensitivity.

Table 1. Basic information on 19 target volatile organic compounds (VOCs) and three solvent used in this study.

Order	Group	Full name	Short name	Formula	CAS ^a number	RT ^b			RTI ^d (Wax column)	RTI Reference
						MeOH	Ph	Hx		
i	Solvents	pentane	Ph	C ₅ H ₁₂	109-66-0	9.24-14.10			500	
ii		methanol	MeOH	CH ₄ O	67-56-1	4.52-6.27			888	Chida <i>et al.</i> (2004)
iii		hexane	Hx	C ₆ H ₁₄	110-54-3		4.53-6.25		600	
1	Aldehydes	acetaldehyde	AA	C ₂ H ₄ O	75-07-0	4.71	- ^e	-	<500	
2		propionaldehyde	PA	C ₃ H ₆ O	123-38-6	5.58	6.37	6.34	571	
3		butyraldehyde	BA	C ₄ H ₈ O	123-72-8	6.77	8.29	8.28	832	Qian and Reineccius (2003)
4		isovaleraldehyde	IA	C ₅ H ₁₀ O	590-86-3	-	9.7	9.76	912	
5		valeraldehyde	VA	C ₅ H ₁₀ O	110-62-3	-	12.43	12.48	935	
6	benzene	benzene	B	C ₆ H ₆	71-43-2	-	10.68	10.78	938	Rahman and Kim (2013)
7		toluene	T	C ₇ H ₈	108-88-3	14.90	14.55	14.54	1038	Goodner (2008)
8	Aromatics	p-xylene	p-X	C ₈ H ₁₀	106-42-3	17.82	17.39	17.33	1149	Yanagimoto <i>et al.</i> (2004)
9		m-xylene	m-X	C ₈ H ₁₀	108-38-3	17.95	17.54	17.48	1150	Le Guen <i>et al.</i> (2000)
10		o-xylene	o-X	C ₈ H ₁₀	95-47-6	18.91	18.63	18.56	1182	Binder <i>et al.</i> (1990)
11		styrene	S	C ₈ H ₈	100-42-5	20.32	20.19	20.12	1273	Sanz <i>et al.</i> (2001)
12	Ketones & an alcohol	methyl ethyl ketone	MEK	C ₄ H ₈ O	78-93-3	-	9.22	9.19	923	Héberger and Görgényi (1999)
13		methyl isobutyl ketone	MIBK	C ₆ H ₁₂ O	108-10-1	14.42	13.43	13.46	974	Héberger and Görgényi (1999)
14		butyl acetate	BuAc	C ₆ H ₁₂ O ₂	123-86-4	16.36	15.65	15.61	1105	Culleré <i>et al.</i> (2004)
15	isobutyl alcohol	isobutyl alcohol	i-BuAl	C ₄ H ₁₀ O	78-83-1	16.86	16.29	16.20	1103	Goodner (2008)
16		propionic acid	PPA	C ₃ H ₆ O ₂	79-09-4	24.43	24.44	24.38	1525	Goodner (2008)
17	Fatty acids	n-butyric acid	BTA	C ₄ H ₈ O ₂	107-92-6	25.53	25.52	25.48	1628	Goodner (2008)
18		isovaleric acid	IVA	C ₅ H ₁₀ O ₂	503-74-2	26.00	25.98	25.95	1691	Culleré <i>et al.</i> (2004)
19		n-valeric acid	VLA	C ₅ H ₁₀ O ₂	109-52-4	26.81	26.79	26.75	1698	Goodner (2008)

^aChemical Abstracts Service (CAS) number, ^bRetention time (RT) determined in this study, ^cRaw chemical concentration, ^dKovats retention time index (RTI), ^eNot detected

Table 2. Preparation of liquid-phase VOC standard for the analysis with GC-FID by direct injection (Same for all three solvent types).

Group compounds		Aldehyde ^a				Aromatic ^a				Ketonic & alcohol ^a				Fatty acid ^a						
		AA	PA	BA	IA	VA	B	T	p-X	m-X	o-X	S	MEK	MIBK	BuAc	i-BuAl	PPA	BTA	IVA	VLA
Concentration (%)	99	97	99	97	97	99.5	99.5	99	99	97	99	99	99.5	99.5	99	99	99	99	99	
Reagent volume (µL)	200	76	76	78	77	69	69	71	71	72	67	75	75	69	76	61	63	65	65	
Solvent (µL) ^b			993				1081						1205						1246	
Concentration (ng µL ⁻¹)	103488	39809	40128	40201	40308	40117	39820	40346	40300	40088	40196	39848	39900	40278	40228	39857	39896	39683	39897	
B. Step-2: First stage working standard (1st L-WS)																				
PS volume (µL)	50 × 4 = 200																			
Solvent (µL)	3800																			
Compounds ^c	AA	PA	BA	IA	VA	B	T	p-X	m-X	o-X	S	MEK	MIBK	BuAc	i-BuAl	PPA	BTA	IVA	VLA	
Concentration (ng µL ⁻¹)	1294	498	502	503	504	501	498	504	504	501	502	498	499	503	503	498	499	496	499	
C. Step-3: Final working standard (final L-WS)																				
Order	WS-1	Solvent																		
	(µL)	(µL)																		
		Concentration (ng µL ⁻¹)																		
1	30	1470	25.9	10.0	10.0	10.1	10.1	10.1	10.1	10.1	10.0	10.0	10.0	10.1	10.1	10.0	10.0	10.0	9.9	10.0
2	60	1440	51.7	19.9	20.1	20.1	20.2	20.1	20.2	20.1	20.0	20.1	19.9	20.1	20.1	19.9	19.9	19.9	19.8	19.9
3	120	1380	103	39.8	40.1	40.2	40.3	40.1	40.3	40.1	40.2	39.8	39.9	40.3	40.2	39.9	39.9	39.9	39.7	39.9
4	210	1290	181	69.7	70.2	70.4	70.5	70.2	70.6	70.2	70.3	69.7	69.8	70.5	70.4	69.8	69.8	69.8	69.4	69.8
5	420	1080	362	139	140	141	141	140	141	140	141	139	140	141	141	140	140	140	139	140

^aPrimary standard for each group (1500 µL) of compound has been made^bMethanol, pentane, and hexane have been used as solvent^cMixture of all 19 VOC's made at a total volume of 4000 µL

ty (e.g., Pal and Kim (2008)). In the second step, this PS was diluted further with each solvent to make the final L-WS for the five point calibrations with the concentration of each VOC at approximately 10, 20, 40, 70, and 140 ng μL^{-1} (except AA). In case of pentane (as solvent), some special precautions were necessary because of its high volatility (and low boiling point); i) maintaining laboratory temperature as low as possible and ii) using a small micropipette (10-100 μL capacity) to take a large volume ($> 100 \mu\text{L}$) solute. After making the final L-WS with each solvent, five point calibration experiments were carried out by introducing (injecting) 1 μL volumes of each (final) L-WS into the GC-FID system.

2.2 Instrumental System and Analytical Technique

All calibration experiments for 19 VOCs in each of the three solvents were carried out in this study using a GC-FID system (IGC 7200, DS Science, Korea) by direct injection of L-WS in a 1 : 5 split injection mode. The injector was set at 250°C. A 10 μL SGE syringe was used to introduce liquid standard of VOC into GC. The injected VOCs were separated on CP-Wax 52 CB Varian capillary column (60 m (length) \times 0.25 mm (internal diameter) \times 0.25 μm (film thickness) at a carrier gas (N_2) flow rate of 1 mL min^{-1} . In addition, the FID flow rates of N_2 (makeup gas), H_2 , and air were set at 30, 30, and 300 mL min^{-1} , respectively. To allow parallel comparison of solvent effects, the same operational settings were maintained for all L-WS calibrations for each of the three solvents. For instance, GC oven temperature was initially set at 35°C for 10 minutes and then programmed to ramp at 10°C min^{-1} to 200°C with the final hold for 5 minutes. The detector temperature was set at 250°C.

The liquid samples were injected using the “sandwich injection (SI) technique” as defined by Grob (2001). In this method, syringe was initially cleaned several times with the solvent used to prepare the L-WS under investigation. Into the syringe were sequentially drawn a plug of air (1 μL), then the sample (1 μL), and finally another air plug (1 μL). The needle of the syringe (SGE, Australia, 10 μL glass fixed needle, needle length 50 mm) used in this study can hold 0.6 μL sample. Hence, by the using SI technique, a more precise sample volume can be injected into the GC to yield optimal calibration results.

3. RESULTS

In this study, the liquid standards containing all target VOCs were analyzed based on SI technique through

GC-FID system. To examine the chromatographic separation patterns between liquid standards with three solvent types, individual VOC standard was initially analyzed using methanol as solvent. The experimental retention time (RT) in conjunction with literature Kovats retention time index (RTI) for all compounds was used for the identification of individual from the mixture (Table 1).

Although retention time of different compounds varied slightly with different solvents, their overall trend of elution order remained constant. In all cases elution of all 19 VOCs were seen on the order of AA, PA, BA, MEK, IA, B, VA, MIBK, T, BuAc, i-BuAl, p-X, m-X, o-X, S, PPA, BTA, IVA, and VLA. This elution order also matches well with their RTI values with a few exceptions. In all analyses, three exceptions to the expected (RTI) elution order were noted for the following pairs of analytes (having similar RTIs): 1) MEK (923) and IA (912), 2) B (938) and VA (935), and 3) BuAc (1105) and i-BuAl (1103). In general, all VOCs eluted according to their RTI values. However, in mixture standard, such order was moderately disrupted in certain occasions. For compounds with similar RTI values, elution order is influenced by solvent/analyte thermochemical factors (Gonzalez and Nardillo, 1999).

Typical chromatograms obtained in this study for 140 ng injection mass are presented in Fig. 1. Out of the 19 VOCs, only AA was missing, when either pentane or hexane was used as solvent. As the instrumental setting for all L-WS with different solvents were identical for parallel comparison, instrumental settings are unlikely to be the key factor in the non-detection of AA if using Pn and Hx solvents. In the case of methanol solvent, four out of 19 VOCs was not detected which include MEK, IA, B, and VA. Probably, the peaks for these missing compounds could have merged with solvent peak. Consequently, their elution from methanol (used as solvent) may not be easy to confirm by FID alone, unless aided by MS. An extra peak was observed on the base of toluene peak which may reflect an esterification process of a fatty acid with methanol or formation of an acetal from aldehyde with methanol (Fujiwara and Fujiwara, 1963). Under appropriate conditions, aldehydes and ketones will react with alcohols to produce hemiacetals and acetals in high yields (Guthrie, 1975). The extent of the propanoic acid/methanol esterification reaction was found to be dependent on reaction time and concentration of acid (Lilja *et al.*, 2002). In the case of toluene, the presence of this extra peak can induce errors in its quantitation. However, the least biased quantitation could be achieved if analysis was done within 5 minutes after the L-WS preparation with the least elapsed time.

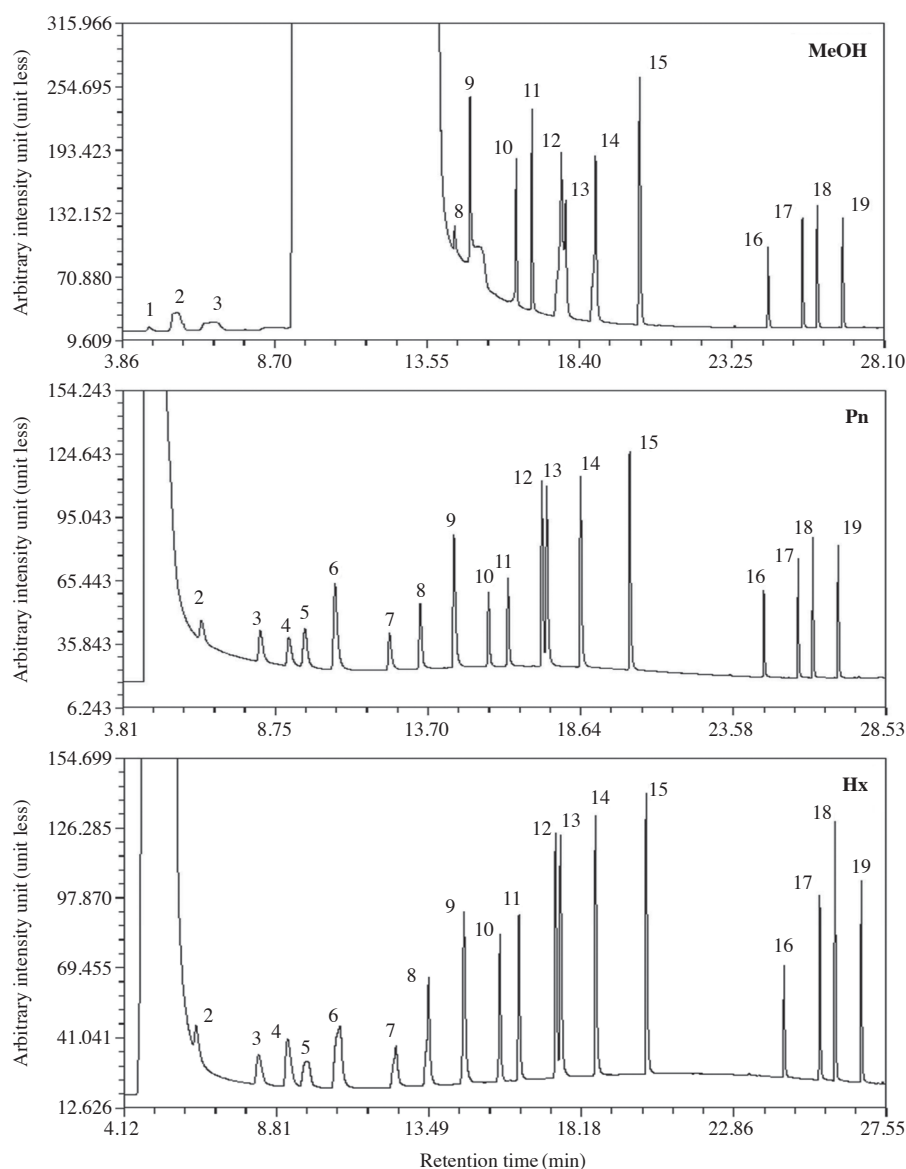


Fig. 1. Chromatogram of 19 VOCs analyzed by GC-FID: 1) AA, 2) PA, 3) BA, 4) MEK, 5) IA, 6) B, 7) VA, 8) MIBK, 9) T, 10) BuAc, 11) *i*-BuAl, 12) *p*-X, 13) *m*-X, 14) *o*-X, 15) S, 16) PPA, 17) BTA, 18) IVA, and 19) VLA (All compound injection mass was 140 ng, except AA).

4. DISCUSSION

4.1 Comparison of Calibration Result between Different Solvent

To obtain the calibration data of 19 VOCs, 1 μL of each L-WS at five different concentration levels (≈ 10 , 20, 40, 70, and 140 $\text{ng } \mu\text{L}^{-1}$) was analyzed by GC-FID. To check the reproducibility of each calibration, triplicate analysis was carried out with two consecutive blank run between each cycle of calibration. The calibration data for each target VOCs are compiled in terms of the response factor (RF) and linearity (by correla-

tion coefficient (R^2) of regression analysis) in Table 3. The results of our VOC calibrations indicate a potent role of solvent selection, while the relative calibration patterns may be influenced by solvent vapor pressure. As shown in Table 3, the RF values of different VOCs varied widely with the solvent used.

All aromatic compounds gave much enhanced RF values for all target solvents, while the largest observed RF value was for *p*-X in methanol (135,773). According to our analysis, methanol was found to be a good solvent, especially for aromatic compounds in terms of higher sensitivity relative to other compounds. In the

Table 3. Results of five point calibration of 19 volatile organic compounds prepared in three different solvent types.

Order		Methanol (n = 3) ^a		Pentane (n = 3)		Hexane (n = 3)	
		RF	R ²	RF	R ²	RF	R ²
1	AA	4356 ± 2534 ^b	0.83 ± 0.20 ^b	– ^c	–	–	–
2	PA	44295 ± 5380	0.99 ± 0.00	10653 ± 994	0.99 ± 0.00	10485 ± 285	0.94 ± 0.01
3	BA	33612 ± 1860	0.99 ± 0.00	18963 ± 1344	0.99 ± 0.01	20375 ± 779	0.99 ± 0.01
4	IA	–	–	24306 ± 1494	0.98 ± 0.01	24792 ± 1152	0.99 ± 0.01
5	VA	–	–	17496 ± 967	0.97 ± 0.01	22812 ± 908	0.99 ± 0.00
6	B	–	–	50501 ± 3021	0.98 ± 0.01	55038 ± 2290	0.99 ± 0.01
7	T	55423 ± 5933	0.99 ± 0.01	50347 ± 3041	0.97 ± 0.01	56537 ± 2822	0.99 ± 0.01
8	p-X	135773 ± 32870	0.99 ± 0.01	49113 ± 3071	0.97 ± 0.01	55573 ± 3061	0.99 ± 0.01
9	m-X	74090 ± 1106	0.99 ± 0.00	53721 ± 3235	0.96 ± 0.01	60777 ± 3253	0.99 ± 0.01
10	o-X	109230 ± 17212	0.99 ± 0.00	53127 ± 3522	0.97 ± 0.01	61552 ± 3220	0.99 ± 0.01
11	S	103030 ± 16420	0.99 ± 0.00	53315 ± 3228	0.96 ± 0.01	59245 ± 3222	0.99 ± 0.01
12	MEK	–	–	18146 ± 1242	0.99 ± 0.01	32860 ± 1094	0.99 ± 0.01
13	MIBK	9639 ± 788	0.98 ± 0.01	24526 ± 1502	0.98 ± 0.01	42124 ± 2331	0.99 ± 0.01
14	BuAc	51327 ± 7862	0.99 ± 0.01	20661 ± 1209	0.98 ± 0.01	34431 ± 1825	0.99 ± 0.01
15	i-BuAl	60874 ± 9047	0.99 ± 0.00	23130 ± 1481	0.98 ± 0.01	40431 ± 1628	0.99 ± 0.01
16	PPA	26148 ± 3679	0.99 ± 0.01	14938 ± 1665	0.98 ± 0.01	18001 ± 1644	0.99 ± 0.01
17	BTA	33173 ± 4476	0.99 ± 0.01	20212 ± 2097	0.98 ± 0.01	28891 ± 2121	0.99 ± 0.00
18	IVA	37715 ± 4830	0.99 ± 0.01	24364 ± 2449	0.98 ± 0.01	40638 ± 2629	0.99 ± 0.01
19	VLA	33853 ± 3989	0.99 ± 0.01	22697 ± 2467	0.98 ± 0.01	31507 ± 2330	0.99 ± 0.01
	Mean	54169	0.98	30568	0.98	38670	0.99
	SD	37248	0.04	15779	0.01	16317	0.01
	RSE	17.8	1.12	12.2	0.23	9.95	0.28
	N	15	15	18	18	18	18

^aTriplicate analysis for all solvent, ^bMean ± SD and ^cNot detected

case of methanol solvent, aromatics exhibited a 2.85 times higher RF values compared to the two other solvents. Unlike the case of either pentane or hexane, methanol is suspected to form a liquid film at the beginning of the wax stationary phase GC column at 35°C due to a combination of two main factors, the largest heat of vaporization (ΔH_{vap}) and second highest boiling point (BP). Under such circumstances, methanol is likely to experience solvent trapping effect more effectively as noted by the increased retention times of analytes eluting after the methanol solvent peak (Grob Jr, 1982) and larger RF values. These phenomena may contribute to generally enhanced response factors for aromatics and alcohols. For pentane and hexane, the lowest RF value was attained from PA. In contrast, the smallest RF value of methanol was found from AA (4356) which is also 9.4 times (89.4%) lower than the mean RF of all other VOCs for all three solvents. In general, the calibration linearity was highly significant and excellent for most analytes e.g., average $r^2 > 0.98$ (except AA (0.83) for methanol solvent). The mean correlation coefficients of all targeted VOCs, if evaluated for each individual solvent, methanol, pentane, and hexane were 0.991(excluding AA), 0.979 and 0.989, respectively. In Fig. 2, the RF patterns of target VOCs in pentane and hexane solvents were more or

less similar. However, the results of methanol are different from others, especially for the heavier aromatics.

If we compare the relative sensitivity of each solvent type by the average RF values of the detected VOCs common to all three different solvents, it was found on the order of methanol, hexane and pentane. The RF values of methanol and hexane were larger by 84% and 27%, respectively than that of pentane. Although methanol yielded enhanced RF values, it was more selective to cover a limited number (N = 10 of 19 VOCs) of targets relative to other solvents in this study. In addition, its standard deviation of RF (for triplicate analyses) is worse than other solvents. There is a wide variation of RF for methanol among the same group of compounds, while those of pentane and hexane were found nearly constant. However, except aldehydes and PPA, hexane generally yielded higher RF than pentane. Hence, for most selected target compounds, there was little solvent effect between the two on their GC-FID based quantitation, although it was not for methanol.

4.2 The Importance of the Time Factor (Injection Intervals) on the Relative Response of GC-FID with Three Types of Solvent

To further evaluate relative response properties of

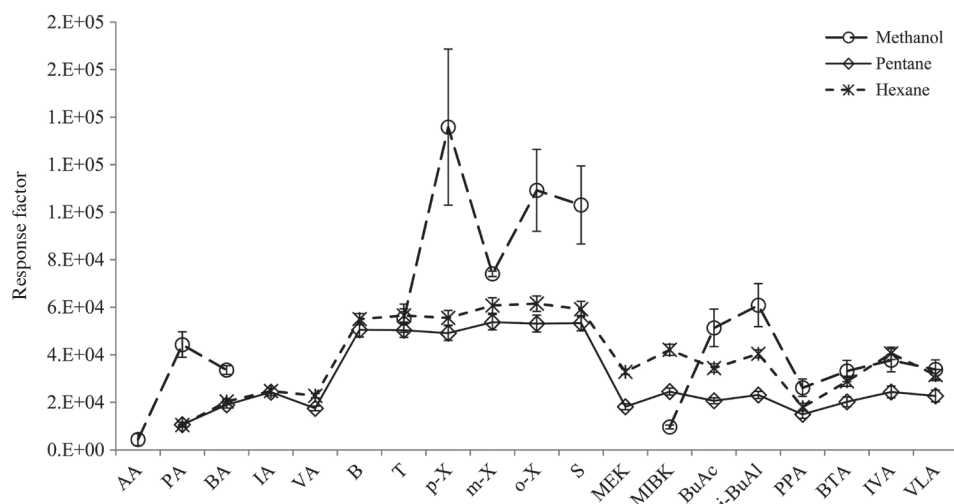


Fig. 2. Comparison of response factor between 19 volatile organic compounds using three different solvent by GC-FID.

GC-FID for the three different solvent, an ancillary experiment has been performed using L-WS of a single concentration level. Out of five concentration level L-WS, only the medium level (e.g., $40 \text{ ng } \mu\text{L}^{-1}$) was selected for this purpose. Samples were injected a few minutes after preparation to reduce potential analyte losses over time which can possibly occur depending on solvent types, e.g. the fatty acids in methanol yielding methyl esters (Lilja *et al.*, 2002). The identical amounts of standard sample ($1 \mu\text{L}$) prepared in three solvents were injected at varying intervals (single injection for each interval in this order: pentane, methanol, and hexane). As depicted in Fig. 3, all 19 VOCs exhibited moderate changes in relative sensitivity trend with different solvents. However, for the same group of compounds, similar sensitivities were maintained except aromatic compounds with methanol. These findings suggest that the response properties are also affected by time interval of injection (or time elapsed after standard preparation) such as sequentially (Fig. 3A) or extended interval (Fig. 3B). In Fig. 3B, sensitivity variations were monitored at 4-hourly intervals for each solvent. If reproducibility of VOCs quantitation is compared between solvents types, the maximum variation occurred with methanol solvent. From Fig. 3B, it is found that methanol represented larger standard deviation of peak area (for all VOCs) than other solvents, with the highest values for p-X. Pentane and hexane showed similar reproducibility for all group of compounds except fatty acid, while methanol and pentane had a similar reproducibility for fatty acid compound.

4.3 Basic Quality Assurance of Instrumental Setup

As a simple means to assess the relative effect of

different solvents, the basic quality assurance (QA) parameters (such as method detection limit (MDL) and precision (e.g., reproducibility expressed in terms of a relative standard error (% RSE) of measurements)) were determined by heptaplicate and triplicate analyses of the smallest detectable quantity of L-WS, respectively. The L-WS concentration for MDL calculations was 5 ng (except MIBK for methanol and PA for pentane, $40 \text{ ng } \mu\text{L}^{-1}$). The results of the QA analysis for three different solvent types are summarized in Table 4. In all cases, RSE tended to be $< 5\%$, while MDL was below the few nanogram level with a few exceptions.

Detection limits (DL) are key criteria to assess the sensitivity performance of any analytical system. For the DL calculation, the concept of MDL was taken in this study. The MDL value for each compound was derived by multiplying the SD of seven replicate analyses with 3.14 (Student's t-value at the 99.9% confidence interval) and then divided by the relevant RF value (US-EPA, 1986). The average MDLs (ng) of pentane, methanol, and hexane were computed 0.50 ± 0.22 , 0.59 ± 0.42 , and 0.73 ± 0.40 , respectively. As PA (in pentane solvent) and MIBK (in methanol solvent) co-eluted with solvent, they generally had higher MDL values (PA (11.90 ng) and MIBK (5.25 ng)). Hence, these MDL values were not included in the computation of the mean MDL for each solvent. These results suggest that pentane is a better solvent choice for lower MDL values. If we consider reproducibility of analysis, pentane gave the lowest RSE values for all our target VOCs. The average VOC RSE values for Hx, MeOH, and Pn solvents were 2.92 ± 1.32 , 2.73 ± 1.41 , and $2.61 \pm 0.91\%$, respectively. The MDL values found in this study were significantly larger (10-30 times higher) than Agilent's GC-FID claimed DL values for propane

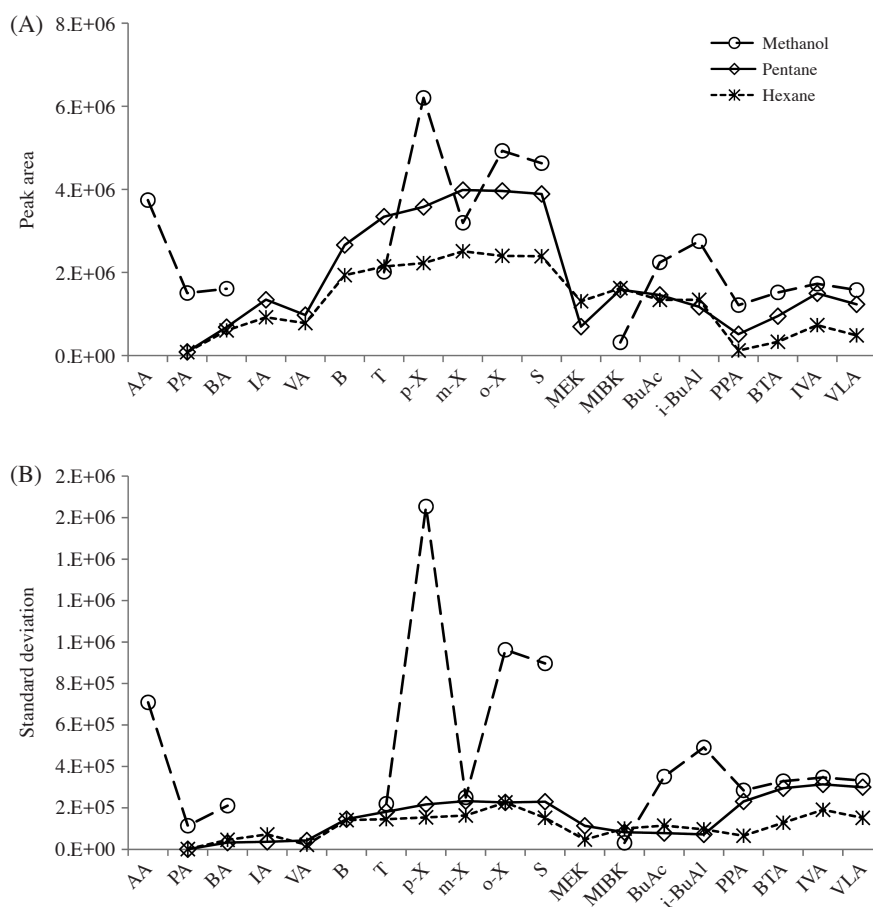


Fig. 3. GC-FID sensitivity variation for 19 VOC's with different solvent; A (peak areas) = standards in 3 different solvents (Pn, MeOH, Hx) were analyzed sequentially 1 hour apart (GC run time = 31 minute, cool down time = 29 minute) respectively vs. B (standard deviation) = same as for (A) but repeated 3 times, 4 hours apart.

on a C mass basis. Average MDL values found in this study are highly comparable with the GC-MS/olfactometry results of Zhang *et al.* (2010). They determined PPA, BTA, IVA, VLA, and 11 other VOCs using the thermal desorption method. Jia *et al.* (2006) used TD-GC-MS method for airborne VOCs, while Cavalcante *et al.* (2010) used HS-GC-PID-FID method for the VOCs in environmental aqueous matrices. Their MDL values for aromatics were about 5 to 10 times lower than our study. If we compare average precision level (2.61%-2.91%) of all solvent types determined in this analysis, our values are highly comparable with those reported previously by Jia *et al.* (2006) in a range of 1.9-4.9%.

4.4 Comparability of Calibration Results between Experiment and Prediction

In practice, gaseous samples of VOCs are collected using adsorptive cartridges (or bag sampler) and subjected to laboratory GC analysis. To quantify pollutants

in a real sample, it is often desirable to carry out calibration using an internal standard. Realistically, because of the presence of complex mixtures of organic compounds in environmental samples, it is nearly impossible or impractical to prepare and spike all authentic analytical standards into the matrix (either gas or liquid) of a sample. Many researchers have been trying to resolve this issue through the generation of predictive equations to compensate the unavailability of authentic standards such as the use of effective carbon number (ECN) concept (Faiola *et al.*, 2012; Kállai *et al.*, 2001; Jones, 1998). According to Morris and Chapman (1961), the basic concept of ECN was described and stated as, "The molar response of a compound in the hydrogen flame detector can be estimated by summing the atomic contributions and multiplying by a proportionality constant characteristic of burner configuration and operating conditions employed." Based on such theory, the response characteristics of VOCs (e.g., RF values of a given VOC) can be predicted as a function

Table 4. Basic quality assurance found for 19 VOCs using three different solvent in this study.

Order	Short name	Method detection limit (ng) ^a			Relative standard error (%)		
		MeOH	Pn	Hx	MeOH	Pn	Hx
1	AA	0.56	– ^b	–	0.11	–	–
2	PA	0.58	11.90	1.50	2.19	1.96	3.68
3	BA	1.80	0.56	1.27	4.96	3.13	2.61
4	IA	–	0.50	1.43	–	2.07	2.02
5	VA	–	0.74	0.85	–	1.85	1.35
6	B	–	0.19	0.40	–	2.17	2.34
7	T	1.16	0.32	0.80	3.84	2.10	2.65
8	p-X	0.55	0.31	0.50	4.14	1.93	2.05
9	m-X	0.57	0.33	0.64	2.77	2.15	2.25
10	o-X	0.43	0.37	0.57	2.62	2.22	1.99
11	S	0.37	0.29	0.49	2.50	2.09	1.97
12	MEK	–	1.08	1.35	–	2.87	2.73
13	MIBK	5.25	0.57	0.15	3.28	2.04	2.19
14	BuAc	0.42	0.85	0.57	3.12	2.43	2.40
15	i-BuAl	0.37	0.51	0.31	1.33	2.44	1.84
16	PPA	0.12	0.54	0.50	3.85	4.58	4.99
17	BTA	0.40	0.48	0.47	3.54	4.67	4.97
18	IVA	0.39	0.50	0.59	3.83	3.21	4.73
19	VLA	0.46	0.41	0.67	4.19	2.62	4.73
	Mean	0.59 ^c	0.50 ^d	0.73	2.73	2.61	2.92
	SD	0.42 ^c	0.22 ^d	0.40	1.41	0.91	1.32
	RSE	19.0 ^c	10.7 ^d	13.0	13.3	8.20	10.6
	N	14 ^c	17 ^d	18	15	18	18

^aInjected sample (7 replicate) concentration for all compounds (except MIBK for MeOH & PA for Pn, 40 ng μL^{-1}) was 5 ng μL^{-1}

^bNot detected, ^{c,d}excluding MIBK and PA, respectively to avoid biased calculation

of ECN (Szulejko *et al.*, 2013).

In our study, as a means to test compatibility of each solvent in GC-FID analysis, we examined our calibration data for three different solvents (methanol, pentane, and hexane) in relation to ECN theory. We converted all experimental RF values of each solvent to molar RF values referenced to benzene with the following equation.

$$\text{RF (mole)} = \frac{\text{RF (mass)} \times \text{MW of each VOC}}{\text{MW of Benzene}}$$

Then, based on the ECN concept, we constructed an additive scheme (Eqn. 1) using selected molecular descriptors.

$$\text{ECN} = \text{CN} + a*(\text{CNE H}) + b*(\text{CNE O}) + c*(\text{CNE-CH}_3) + d*(\text{CNE-CH}_2-) + e*(\text{CNE-O-}) + f*(\text{CNE} > \text{C=O}) + g*(\text{CNE-CHO}) + h*(\text{CNE-CO}_2\text{H}) + i*(\text{CNE B ring}) + j*(\text{CNE} > \text{C=C} <)$$

(Eqn. 1)

In Eqn. 1, the concept of carbon number equivalent (CNE) is used for each atom or functional group descriptor (D=C, H, O, (-CH₃), (-CH₂-), (-O- or -OH), (>C=O), (-CHO), (-CO₂H), (Bnz ring) and aliphatic >C=C<). In addition, a, b, c, d, e, f, g, h, i, and j are the number of occurrences of each descriptor in a given

VOC's molecular structure. Hence, the best R² values (Fig. 4) are obtained by plotting the relationship between RF vs. ECN. The output of ECN calculation is presented in Table 5. The molar responses of 19 VOCs for each solvent are compared against carbon number (CN) and effective carbon number (ECN) in Fig. 4A and 4B, respectively. In both cases, the slope values for three solvents were found in the order of methanol > hexane > pentane. However, in terms of correlation coefficient (R²), a reversed order (pentane > hexane > methanol) has been seen.

These findings suggest the possibility that the higher responses associated with a selected solvent should be limited to the analysis of complex mixture of analyte. Although pentane and hexane show acceptable correlation coefficients, methanol represent the least acceptable correlation coefficient (R²: 0.692 (experimental) and 0.775 (calculated)). As methanol has yielded different RF values for similar CN/ECN, its reliability (or predictability) in the analysis of complex VOC mixture seemed to decrease. If we compute the mean of ΔRF error (%) (Table 5), then error percentage is found on the descending order of methanol (26.5), hexane (6.73), and pentane (5.24). Although ΔRF error (%) mean for 19 VOCs was the highest for methanol, it yielded zero error percentage for S (styrene). Another

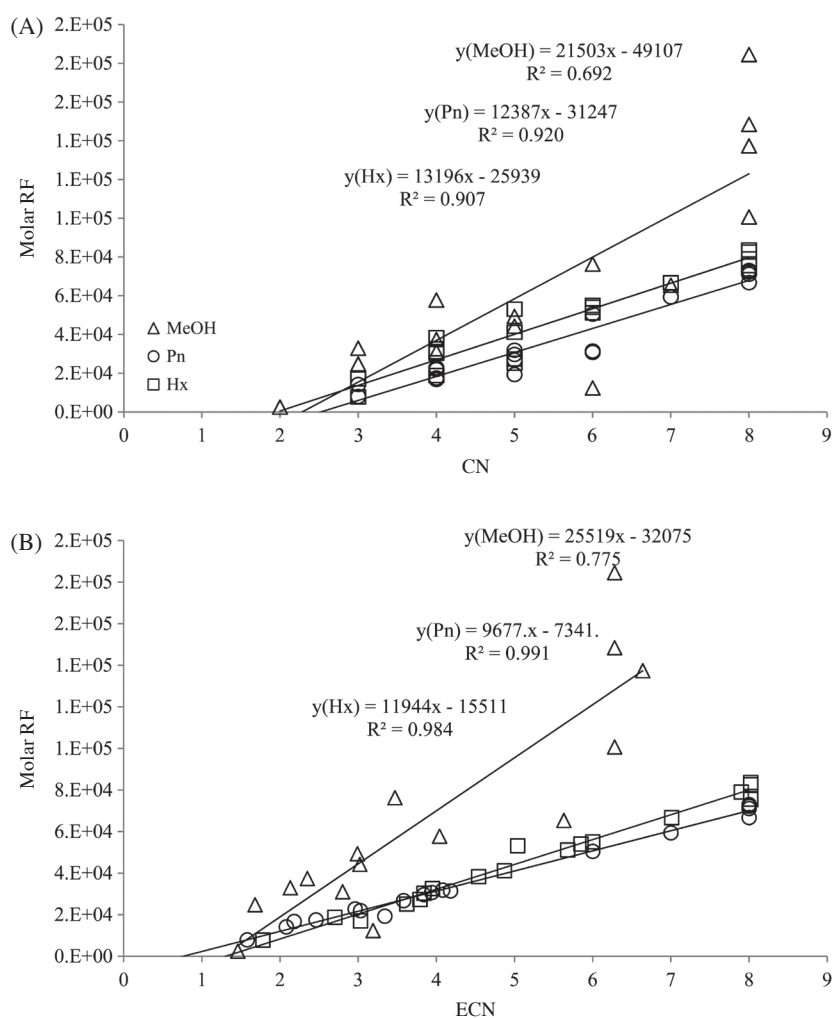


Fig. 4. Comparative analysis of calibration results of 19 VOCs for three solvent with carbon number (A) and with effective carbon number (B).

er solvent hexane also exhibited zero error for S and MEK. Like other calculations (VOC elution pattern, MDL, and RSE), pentane and hexane also exhibited similar types of ΔRF error (%) in ECN calculation approaches. However, hexane yielded 27% higher response than pentane. Thus, overall finding of our study suggests that hexane is good enough for the analysis of complex mixture of VOCs (e.g., 19 VOCs) by GC-FID. In addition, it is noteworthy that the relative ordering in mean response factor values between solvents (methanol > hexane > pentane) in fact inversely correlates with their vapor pressure (calculated using the Antoine equation) (pentane (99.6 kPa at 35°C) > hexane (31.2 kPa at 35°C) > methanol (28.5 kPa at 35°C) (Linstrom and Mallard, 2013)). As such, it is expected that the physical parameter such as solvent vapor pressure should make certain contributions on the GC performance characteristics of VOCs analysis.

At last, it may be worth considering the effect of the GC initial temperature on the sensitivity between solvent types. Most importantly, it was technically impractical in our laboratory to lower the GC initialization temperature from 35 to say, 20°C so that hexane's vapor pressure (17.7 kPa) became low enough for on-column condensation to occur to permit solvent trapping. However, if such a situation was possible, then the RF values for hexane solvent would have increased similar to those of the methanol counterpart. Even at 35°C GC initialization temperature, hexane showed limited solvent trapping to yield a 27% enhanced RF values compared to pentane. Bear in mind that the BP of pentane (36°C at 1 atm) is too low (or its 20°C vapor pressure of 57.7 kPa is too high) to permit solvent trapping. The BP and vapor pressure data were from NIST (Linstrom and Mallard, 2013).

Table 5. Comparison of RF value for different solvent using effective carbon number (ECN) method.

Group	Short name	CN ^a	ECN ^c			RF from experiment ^d			RF from calculation			ΔRF error (%)		
			MeOH ^f	Pn ^f	Hx ^f	MeOH	Pn	Hx	MeOH	Pn	Hx	MeOH	Pn	Hx
Aldehyde	AA	2	1.46	0.70	0.86	2457	– ^b	–	5183	–567 ^e	–5239 ^e	111 ^e	–	–
	PA	3	2.13	1.58	1.78	32935	7921	7796	22280	7949	5750	32	0.4	26
	BA	4	2.80	2.46	2.70	31028	17505	18808	39378	16466	16739	27	5.9	11
	IA	5	3.44	3.58	3.79	–	26801	27338	55710	27304	29758	–	1.9	9
	VA	5	3.47	3.34	3.62	–	19293	25154	56476	24982	27728	–	29.5	10
Aromatic	B	6	5.98	6.00	6.00	–	50501	55038	95010	50724	56155	–	0.4	2
	T	7	6.63	7.00	7.01	65376	59388	66690	111597	60402	68219	71	1.7	2
	p-X	8	7.28	8.00	8.02	184535	66751	75531	128185	70079	80283	31	5.0	6
	m-X	8	7.28	8.00	8.02	100698	73014	82605	128185	70079	80283	27	4.0	3
	o-X	8	7.28	8.00	8.02	148459	72208	83657	128185	70079	80283	14	2.9	4
	S	8	7.64	8.00	7.90	137374	71087	78993	137372	70079	78850	0.0	1.4	0
Ketonic and alcohol	MEK	4	1.88	2.18	3.84	–	16750	30333	15901	13756	30355	–	17.9	0
	MIBK	6	3.19	4.18	5.85	12359	31448	54014	49331	33111	54364	299 ^e	5.3	1
	BuAc	6	3.47	3.94	5.68	76327	30725	51202	56476	30788	52333	26	0.2	2
	i-BuAl	4	4.04	3.03	4.54	57765	21948	38365	71022	21982	38716	23	0.2	1
Fatty acid	PPA	3	1.68	2.08	3.03	24798	14167	17072	10797	12788	20680	56	9.7	21
	BTA	4	2.35	2.96	3.95	37417	22798	32588	27895	21304	31669	25	6.6	3
	IVA	5	2.99	4.08	5.04	49313	31856	53134	44227	32143	44689	10	0.9	16
	VLA	5	3.02	3.84	4.87	44263	29676	41196	44992	29821	42658	2	0.5	4
Mean			4.11	4.37	4.97	67007	36880	46640	64642	36880	46640	26.5	5.24	6.73
SD			2.16	2.40	2.17	53322	22255	23873	43725	22155	23684	19.6	7.46	7.58
RSE			12.05	12.59	10.00	21	14	12	19	14	12	22.1	33.7	26.5
N			19	19	19	15	18	18	19	18	18	13	18	18

^aCarbon number, ^bNot detected^cECN = CN + a*(CNE H) + b*(CNE O) + c*(CNE-CH₃) + d*(CNE-CH₂-) + e*(CNE-O-) + f*(CNE > C=O) + g*(CNE-CHO) + h*(-CO₂H) + i*(CNE Bnz) + j*(CNE > C=C <)^dRF values converted to molar RF in referenced to benzene, RF (mole) = (RF (mass)*MW of each VOC)/MW of Benzene^eOutlier values were excluded for statistical calculation^fCalculated carbon number equivalent (CNE) of each descriptor obtained for three different solvent as follows:

Factor	a	b	c	d	e	f	g	h	i	j
MeOH	-0.17	0.25	-0.01	0.01	1.50	-1.00	-0.10	-0.80	1.00	0.00
Pn	0.00	0.00	0.00	-0.12	-0.85	-1.70	-1.30	-0.80	0.00	0.00
Hx	0.00	0.00	0.01	-0.08	0.60	-0.10	-1.15	0.10	0.00	-0.10

5. CONCLUSION

In this research, the relative response characteristics of 19 target VOCs were evaluated using three different solvents (methanol, pentane and hexane). Most of the selected VOCs for this comparative purpose are well known regulated offensive odorants by many government authorities. Among the commonly used GC detectors, the most widely used GC-FID system has been employed to assess the solvent effect on VOCs quantification. To compare relative response of target VOCs with different solvents, we evaluated the acquired calibration data for standards in each solvent in two different aspects. Firstly, the difference in observed sensitivities of target VOC between different solvent types was used as the main criterion. Accordingly, comparison of the mean RF values of detected VOCs (common to all

three different solvents) showed that methanol was the largest in this respect exhibiting an 84% enhancement relative to the lowest, pentane. Moreover, as a means to assess the reliability of each solvent type, the extent of sensitivity deviation across target homologues has also been estimated in terms of ΔRF for each corresponding solvent between experimental and calculated RF data based on ECN concept. The mean ΔRF values for methanol, hexane, and pentane were calculated as 26.5, 6.73, and 5.24%, respectively. The use of methanol hence appeared to be unreliable in the sense of the weakest predictability between homologues (e.g., ECN concept), despite the fact that it had the highest response of all three solvents.

The intricacy of solvent selection was also recognized, when the sensitivity trends for each solvent were compared across different target compounds. Although

methanol showed the best sensitivity for aromatic hydrocarbons, it was not so for the other VOCs in the 19 VOC mixture. It was also found that hexane yielded more or less similar results as pentane, while overall, hexane maintained a 27% greater response advantage than pentane. It may hence suggest that hexane can be a potentially good choice for the analysis of complex mixtures of VOCs (e.g., 19 VOCs) through GC-FID, if the GC initialization temperature was low enough to permit solvent trapping. The overall findings of the solvent effect in VOC analysis, as demonstrated in this study, suggest that the solvent selection should be one of the crucial factors in determining GC performance in the analysis of specific target compounds. Thus, a thorough consideration on such variable is recommended in the experimental design stage so as to optimize the GC performance in VOC analysis.

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