Journal of Chromatography A, 1216 (2009) 5436–5444

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Comparative analysis of odorous volatile organic compounds between direct injection and solid-phase microextraction: Development and validation of a gas chromatography–mass spectrometry-based methodology

Sudhir Kumar Pandey, Ki-Hyun Kim*

Atmospheric Environment Laboratory, Department of Earth and Environmental Sciences, Sejong University, 98 Goon Ja Dong, Gwang Jin Goo, Seoul 143-747, South Korea

ARTICLE INFO

Article history:
Received 12 March 2009
Received in revised form 5 May 2009
Accepted 12 May 2009
Available online 18 May 2009

Keywords:
Gas chromatography with mass spectrometry
Odorants
Solid-phase microextraction
Volatile organic compounds
Environmental *air* samples

ABSTRACT

In this study, the feasibility of GC–MS was evaluated for the quantification of odorous volatile organic compounds (VOCs) in environmental samples. These included methyl ethyl ketone, isobutyl alcohol, methyl isobutyl ketone, and butyl acetate plus benzene, toluene, and xylene (BTX). For this purpose, the gaseous standard for these VOCs were analyzed by GC–MS with the aid of both direct injection (DI) into the GC injector and solid-phase microextraction (SPME). The liquid phase standard prepared independently was tested additionally by the DI method as a reference to gaseous calibration. The detection limit (DL) values, when tested for basic quality assurance in this study, showed large differences between DI (0.002–0.007 ng) and SPME method (1.03–1.81 ng) in terms of absolute mass. The DL values, when expressed in terms of concentration (v/v), showed considerable improvement in SPME (below 0.40 nmol mol^{-1}) relative to the DI method (~6–15 nmol mol^{-1}). The reliability of the GC–MS method was further validated through an analysis of real environmental samples collected from an industrial area.

1. Introduction

The monitoring of volatile organic compounds (VOCs) is often considered a crucial element in the assessment of indoor and outdoor air quality [1]. This is because many VOCs exert adverse impacts on human health and comfort, while some can also act as the precursors to photochemical smog. Considering their socio-economic impact, a number of VOCs have recently been designated as criteria offensive odorants in South Korea such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), butyl acetate (BuAc), toluene (T), xylene (X), and isobutyl alcohol (i-BuAl) [2].

MEK is released into the environment from such sources as building materials, consumer products, and tobacco smoke [3], whereas MIBK is released from the use of numerous commercial chemical products such as paints, adhesives, and pesticides [4]. BuAc is commonly used as a solvent in the production of lacquers or as a synthetic fruit flavor in foods such as candy, ice cream, cheese, and baked goods. Likewise, i-BuAl is used as starting material in the manufacture of isobutyl acetate in analogue to BuAc [5]. The two aromatic VOCs, i.e., T and X are well known for their characteristic odors in vehicular exhaust, paints, paint thinners, fingernail polish, lacquers, and adhesives [6,7].

Occasionally, certain agencies and authors have prescribed the odor threshold values of these odorants in a wide range. The values were given by the US Environmental Protection Agency (i.e., 5400 nmol mol^{-1} (MEK), 830 nmol mol^{-1} (BuAc), and 2900 nmol mol^{-1} (T)) [8], OSHA (1600 nmol mol^{-1} (i-BuaAl)) [9], Verschueren (100–680 nmol mol^{-1} (MIBK)) [10], ASTDR (1500 nmol mol^{-1} (B)) [11], and AIHA (81–5400 nmol mol^{-1} (xylenes)) [12]. These values are much higher than reported by Nagata et al., i.e., 16 nmol mol^{-1} (BuAc), 170 nmol mol^{-1} (MIBK), 58 nmol mol^{-1} (X), 330 nmol mol^{-1} (T), and 440 nmol mol^{-1} (MEK) through an application of a triangular bag method [13]. In terms of human health, these odorants can be harmful even below their normal human perception level.

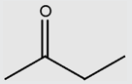
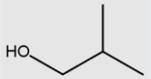
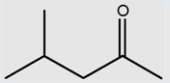
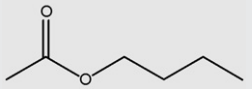
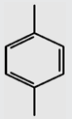
The quantification of odorous and/or polar VOCs in air has always been a challenge because of their highly reactive nature and presence in complex matrices at a wide concentration range [14]. The analysis of airborne VOCs is most commonly accomplished by techniques relying on gas chromatography (GC). The combination of GC with mass spectrometry (MS) is considered to be the most incisive tool to determine VOCs in both qualitative and quantitative terms with high sensitivity [15].

Depending upon the phase and/or the concentration range of environmental samples, there are a number of options for chromatographic detection. For instance, direct injection (DI) with a gas-tight syringe or through a loop system can be adopted for highly concentrated gaseous samples [16,17]. However, in the case of low concentration gaseous samples (e.g., sub-nmol mol^{-1} level),

* Corresponding author. Tel.: +82 2 499 9151; fax: +82 2 499 2354.
E-mail address: khkim@sejong.ac.kr (K.-H. Kim).

0021-9673/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2009.05.022

Table 1
Basic information regarding the seven odorous volatile organic compounds (VOCs) used to investigate the feasibility of different calibration approaches with GC–MS methodology.

Order	Gaseous standard group	Concentration of primary standard ($nmol\,mol^{-1}$)	Compounds	CAS number	Functional group	Acronym[a]	Chemical formula	Structure	MW ($g\,mol^{-1}$)	Primary quantification ion (m/z)	Secondary quantification ion (m/z)	Retention time (min)
1[b]	I	10 000	Methyl ethyl ketone	78-93-3	Ketone	MEK	$CH_3COC_2H_5$		72.1	43	72	6.74
2			Isobutyl alcohol	78-83-1	Alcohol	i-BuAl	$CH_3(CH_2)_3OH$		74.1	43	74	6.96
3[b]			Methyl isobutyl ketone	108-10-1	Ketone	MIBK	$CH_3COCH_2CH(CH_3)_2$		100	43	58 and 100	9.49
4[b]			Butyl acetate	123-86-4	Ester	BuAc	$CH_3COO(CH_2)_3CH_3$		116	43	56 and 73	10.88
5	II	20 000	Benzene	71-43-2	Aromatic	B	C_6H_6		78.1	78	51	8.13
6[b]			Toluene	108-88-3		T	$(CH_3)C_6H_5$		92.1	91	92	10.39
7[b]			*p*-Xylene	106-42-3		X	p-$(CH_3)_2C_6H_4$		106	91	106	12.59

[a] Acronyms for seven compounds used in this study.
[b] All compounds except order numbers 2 and 5 were recently added as criteria offensive odorants for malodor regulation purposes by the Korean Ministry of Environment (KMOE) from the year 2008.