



Generation of sub-ppb level vapor phase mixtures of biogenic volatile organic compounds from liquid phase standards and stepwise characterization of their volatilization properties by thermal desorption–gas chromatography–mass spectrometry



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ARTICLE INFO

Article history:

Received 29 April 2014

Received in revised form 24 October 2014

Accepted 25 October 2014

Available online 1 November 2014

Keywords:

Biogenic volatile organic compounds

Gaseous standard

Headspace

Sorbent tube

Spiked standard

Sweep cycle

ABSTRACT

In the analysis of biogenic volatile organic compounds (BVOCs) in ambient air, preparation of a sub-ppb level standard is an important factor. This task is very challenging as most BVOCs (e.g., monoterpenes) are highly volatile and reactive in nature. As a means to produce sub-ppb gaseous standards for BVOCs, we investigated the dynamic headspace (HS) extraction technique through which their vapors are generated from a liquid standard (mixture of 10 BVOCs: (1) α -pinene, (2) β -pinene, (3) 3-carene, (4) myrcene, (5) α -phellandrene, (6) α -terpinene, (7) R-limonene, (8) γ -terpinene, (9) *p*-cymene, and (10) Camphene) spiked into a chamber-style impinger. The quantification of BVOCs was made by collection on multiple-bed sorbent tubes (STs) and subsequent analysis by thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS). Using this approach, sub-ppb level mixtures of gaseous BVOCs were generated at different sweep cycles. The mean concentrations of 10 BVOCs generated from the most stable conditions (i.e., in the third sweep cycle) varied in the range of 0.37 ± 0.05 to 7.27 ± 0.86 ppb depending on the initial concentration of liquid standard spiked into the system. The reproducibility of the gaseous BVOCs generated as mixture standards, if expressed in terms of relative standard error using the concentration datasets acquired under stable conditions, ranged from 1.64 (α -phellandrene) to 9.67% (R-limonene).

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1. Introduction

Biogenic volatile organic compounds (BVOCs) are diverse enough to include terpenoids, alkanes, alkenes, carbonyls, alcohols, esters, ethers, and acids [1,2]. According to the BVOC emission inventory, terpenoids with one (five carbons) and two isoprene units (10 carbons) are emitted predominately from flora and subsequently contribute to the formation of aerosols [1,2]. For instance, monoterpenes (MTs: $C_{10}H_{16}$) are prone to oxidative conversion into secondary organic aerosols through reactions with ozone, hydroxyl radical, and oxides of nitrogen [1,3]. These chemically produced aerosols can affect the radiative and cloud nucleation properties of atmospheric particles [4–6].

For laboratory-based analysis of BVOCs, a gas chromatograph equipped with a flame ionization detector or mass spectrometer has been the common choice [2,5,7]. A number of recent and emerging analytical techniques (such as proton-transfer-reaction

mass spectrometry (PTR-MS), selected-ion-flow-tube mass spectrometry (SIFT-MS), and time-of-flight mass spectrometry (TOF-MS)) have greatly enhanced detection sensitivities of VOCs (and BVOCs) [7–9].

For the quantitative analysis of highly volatile compounds, preparation of standards is an important part of performing accurate quantification. For this purpose, the use of a gaseous standard is a common option, as it allows the elimination or suppression of major experimental drawbacks (e.g., the matrix effect) encountered due to the phase difference between the sample (gas) and the standard phases (liquid) [10,11]. However, the storage of diverse volatiles in gas phase may be complicated as sample integrity can degrade with time [12]. The stability of common storage media has been evaluated using diverse target volatiles, e.g., MTs in cylinders [13]; aldehydes and terpenes in canisters [14]; and alkanes, alkenes, aromatics, and BVOCs in both canisters and Tedlar bags [15]. The major drawbacks of these storage methods have been addressed by these authors. For instance, long-term standard integrity cannot be assured for certain MTs (e.g., α -pinene and β -pinene) due to isomerization to other MTs (e.g., D-limonene, camphene, and *p*-cymene) upon storage in metal cylinders [13]. Likewise, gaseous

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Table 1
Basic information of the target biogenic volatile organic compounds (BVOCs: $n = 10$) and reference anthropogenic volatile organic compounds (AVOCs: $n = 5$) investigated in this study.

Order	Group	Compounds	Short name	Formula	Molecular weight (g mol ⁻¹)	Density (g cm ⁻³)	Water solubility (mg L ⁻¹)	Henry's law constants (K_H : M atm ⁻¹) ^a	CAS number
1	BVOCs	α -Pinene	α -PN	C ₁₀ H ₁₆	136.23	0.858	4.967 (Est) ^b	0.0093 (Est)	7785-70-8
2		β -Pinene	β -PN	C ₁₀ H ₁₆	136.23	0.872	4.886 (Est)	0.0147 (Exp)	127-91-3
3		3-Carene	3-CN	C ₁₀ H ₁₆	136.23	0.857	2.91 (Est) ^c	0.0093 (Est)	13466-78-9
4		Myrcene	MRC	C ₁₀ H ₁₆	136.23	0.791	5.6 (Exp)	0.0155 (Exp)	123-35-3
5		α -Phellandrene	α -PD	C ₁₀ H ₁₆	136.23	0.85	2.862 (Est)	0.0182 (Exp)	99-83-2
6		α -Terpinene	α -TP	C ₁₀ H ₁₆	136.23	0.837	7.56 (Est)	0.0290 (Exp)	99-86-5
7		R-limonene	R-LN	C ₁₀ H ₁₆	136.23	0.842	13.8 (Exp)	0.0356 (Exp)	5989-27-5
8		γ -Terpinene	γ -TP	C ₁₀ H ₁₆	136.23	0.85	8.68 (Est)	0.0388 (Exp)	99-85-4
9		<i>p</i> -Cymene	<i>p</i> -CM	C ₁₀ H ₁₄	134.21	0.86	23.4 (Exp)	0.0909 (Est)	99-87-6
10		Camphene	CMP	C ₁₀ H ₁₆	136.23	0.866	4.6 (Exp)	0.0062 (Exp)	79-92-5
11	AVOCs (Reference)	Benzene	B	C ₆ H ₆	78.11	0.878	1790 (Exp)	0.18 (Exp)	71-43-2
12		Toluene	T	C ₇ H ₈	92.14	0.866	526 (Exp)	0.16 (Exp)	108-88-3
13		<i>p</i> -Xylene	<i>p</i> -X	C ₈ H ₁₀	106.2	0.865	162 (Exp)	0.14 (Exp)	106-42-3
14		Methyl ethyl ketone	MEK	C ₄ H ₈ O	72.11	0.805	223,000 (Exp)	17.9 (Exp)	78-93-3
15		Methyl isobutyl ketone	MIBK	C ₆ H ₁₂ O	100.2	0.802	19,000 (Exp)	7.69 (Exp)	108-10-1

^a At 25 °C. Source: SRC Database [27].

^b Est – Estimated.

^c Exp – Experimental.

standards prepared and stored in canisters were subject to significant losses over time due to physical adsorption or chemical reactions on the canister walls [14]. To overcome these limitations of storing gas-phase standards of volatile compounds, some researchers investigated their generation using liquid-phase standards [12,16–19]. To this end, many authors introduced diverse methods (e.g., capillary diffusion) to convert the liquid phase chemicals into the gaseous standards [16,17,19].

In this study, we investigated an experimental approach to generate sub-ppb level BVOC diffusing from a liquid standard by dynamic headspace (HS) analysis. In the course of this research, we adopted an experimental procedure introduced in our previous study in which an impinger-based system was employed to constantly generate the vapor-phase standards of 14 anthropogenic VOCs (AVOC) including aromatics, aldehydes, ketones, an ester, and an alcohol [11]. To further explore the steady-state dynamic HS conditions to generate gaseous standards of diverse chemical properties, we expanded our efforts to include some important BVOC species in this work. To this end, we have also characterized the volatilization properties of BVOCs at different liquid-phase concentrations. To provide more insights into this standard generation approach, the volatilization trends of target BVOCs were also compared with some reference AVOCs.

2. Materials and methods

In this study, nine MTs and one alkylbenzene (*p*-cymene) were selected as target BVOCs: (1) α -pinene, (2) β -pinene, (3) 3-carene, (4) myrcene, (5) α -phellandrene, (6) α -terpinene, (7) R-limonene, (8) γ -terpinene, (9) *p*-cymene, and (10) camphene (Table 1). A total of five AVOCs (some may also have biogenic origin) were also added as reference compounds: (1) benzene, (2) toluene, (3) *p*-xylene, (4) methyl ethyl ketone, and (5) methyl isobutyl ketone. Experiments were conducted in two different stages, (1) calibration and basic quality assurance (QA) of BVOCs through direct loading of liquid standard on to sorbent tubes (ST) and (2) dynamic HS sampling of BVOCs from spiked standards (SSs) (Table 2).

2.1. Preparation of sorbent tubes (STs) and liquid phase standards for experimental purposes

In this study, multiple-bed STs were employed for the collection of all target and reference volatiles. To prepare the STs, quartz

tubes were packed with three types of sorbent materials (50 mg of each) in the following order (from weakest to strongest in direction of sample flow): Tenax TA (60/80 mesh, Restek, USA), Carboxen B (60/80 mesh, Supelco, USA), and Carboxen X (40/60 mesh, Supelco, USA) (Fig. 1A). Before use, the STs were conditioned for 12 h at 320 °C by passing 99.999% N₂ (flow rate = 100 mL min⁻¹) through the STs using a tube conditioner (ATC-1200, ACEN Co. Ltd., Korea). The detailed procedure for preparing these STs is reported and presented in our recent study [18]. Note that the reliability of multiple-bed STs for the collection of volatiles has also been validated in a number of recent studies [5,9,20–23].

For an ST-based calibration, liquid standards containing all the target BVOCs and reference AVOCs were prepared (in methanol) at five different concentration levels (C1–C5: approximately 5, 10, 20, 50, and 100 ng μ L⁻¹ for each of the 10 BVOCs and reference AVOCs) by a three-step dilution in methanol of the raw chemicals purchased from Sigma–Aldrich, USA (Table 1S in the supplementary information).

2.2. Calibration, instrumentation, and basic quality assurance (QA) parameters of the BVOCs analysis

To perform calibration, liquid standards were directly loaded on the sorbent tubes (STs). In this process, the inlet of the ST was connected (via 2 cm long Teflon tubing) to a 10 L polyester aluminum (PEA) bag filled with back-up gas (ultra-pure N₂); the outlet was connected to a mini vacuum pump (Sibata Σ MP-30, Japan) (Fig. 1A). One microliter of the liquid standard was directly injected (using a 10 μ L syringe) onto the internal wall of the ST through puncturing the Teflon tubing connection. At the same time, the back-up gas was introduced into the ST at a constant flow rate of 100 mL min⁻¹ for 5 min to facilitate adsorption of analytes onto the sorbent materials. The result obtained through this calibration (experiment stage 1) was used to calibrate BVOCs collected in dynamic HS samples in experiment stage 2.

The STs were analyzed by thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) using a gas chromatograph (QP2010, Shimadzu, Japan) equipped with a TD unit (UNITY, Markes International Ltd., UK). The detailed operational conditions of the TD–GC system are described in Table 2S. In brief, after being placed in the TD system, STs were heated at 300 °C for 5 min using He (99.999%) as the carrier gas (split ratio

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