



Characterization of quality assurance properties of biogenic volatile organic compounds with an emphasis on the breakthrough behavior, recovery, and temporal stability



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ABSTRACT

In this research, we investigated the breakthrough volume (BTV) and temporal performance of two types of sorbent tube (ST) sorbent beds toward 10 (target) biogenic volatile organic compounds (BVOCs) ((1) isoprene, (2) (+)- α -pinene, (3) camphene, (4) (+)- β -pinene, (5) (+)-3-carene, (6) α -phellandrene, (7) α -terpinene, (8) (R)-(+)-limonene, (9) γ -terpinene, and (10) *p*-cymene) and two (reference) anthropogenic volatile organic compounds (AVOCs) ((11) benzene and (12) toluene). The analysis of their vaporized liquid-phase working standards was carried out using thermal desorption–gas chromatography–mass spectrometry (TD-GC/MS). To this end, the performance of two ST types (CC (Carbopack C) and CBX (Carbopack C, Carbopack B, and Carbopack X)) was tested as a function of a few key variables, e.g., sorbent type, N₂ gas purge volume, and sampling temperature. The CBX ST gave recoveries of 100 ± 10% at 60 °C for two BVOCs (camphene and α -terpinene). However, three compounds (isoprene, (+)- α -pinene, and (+)- β -pinene) showed poor recoveries (0.7, 59.3, and 11.3%, respectively), whilst *p*-cymene recorded an excess recovery (~190%). In contrast, for the CC ST, BT for (+)- α -pinene and camphene increased with purge volume, while isoprene was not detected. Accordingly, the range of BTV_{5%} and BTV_{50%} values (L/g) for each compound with CC ST were 1.7 (toluene)–17 (camphene) and 15 (toluene)–570 ((+)- α -pinene), respectively. In summary, a three-bed CBX with the higher BTV is the preferred choice for environmental sampling for a wide range of BVOCs compared to a one-bed CC ST. The recovery of CBX ST for 10 out of 12 analytes (after > 150 reconditioning/loading/TD cycles) remained constant in terms of response factor, while the response factors of isoprene and β -pinene were highly variable. Both the present work and the reported literature recoveries showed similar and divergent results which are discussed in terms of high temperature on-sorbent reactions.

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1. Introduction

Volatile organic compounds (VOCs) are commonly defined as having vapor pressures greater than 1 Pa at 298 K [1]. A vast range of VOCs are known to be produced by either biogenic (BVOCs) or anthropogenic (AVOCs) sources. The total BVOC emissions are estimated as 1150 TgC/year, whereas AVOCs as 142 TgC/year [1]. According to an inventory study [2], isoprene (33.0%) and monoterpenes (25.5%) are known to make up the bulk of the BVOC emissions. Once released into the atmosphere, BVOCs are oxidized further by ozone to form secondary pollutants [3].

The concentrations of some AVOCs in the environment (air, soil, and water) are regulated and monitored by national and international exceedance guideline criteria. However, because of the diverse nature of

source processes, it is yet difficult to implement appropriate bio-engineering measures to control the emissions of BVOCs nor it is necessary as they are biogenic [4]. As isoprene (2-methyl-1,3-butadiene, C₅H₈) is the basic BVOC synthon unit, compounds that contain two or more isoprene units (C₅) are described as isoprenoid or terpenoid. If the BVOCs contain two or three isoprene units, they are referred to as monoterpenes and sesquiterpenes, respectively. Monoterpenes have distinct pleasant pine-like odors, whereas sesquiterpenes are less odorous [5,6].

Under favorable conditions, the concentration of compounds in air can be determined by collecting very small sample volumes of air. However, it generally requires several liters of air or more in practice [7]. In this respect, the use of sorbent tubes (ST) is one of the preferred methods for collecting and analyzing VOCs in air as it ultimately eliminates the inconvenience of handling, transporting, or storing large air sample volumes. For the application to VOC analysis, the sorbents have to be chosen carefully by considering certain critical properties,

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e.g., sorbent strength, inertness, hydrophobicity, temperature stability, and breakthrough [8]. Generally, the use of the ST packed with three types of sorbents (e.g., Carboxack C, Carboxack B, and Carboxack X: namely, CBX ST) is the preferred option to obtain a wide range of sorbent strengths (e.g., weak, medium, to medium/strong, respectively in the direction of sample flow). This type of ST has thus commonly been used to capture VOCs with a wide range of volatility, e.g., carbon number of three or greater as seen from a number of previous studies [9,10].

The breakthrough volume (BTV) of an analyte on each sorbent is an important metric; the BTV is a function of several variables (e.g., sample analyte concentration, sampling temperature, humidity, sampling flow rate, sorbent amount, porosity, sorptive capacity, and specific sorbent surface area) [11–21]. Hence, for accurate quantitation of BVOC, it is crucial to set the safe sampling volume (SSV) of target compounds (e.g., the actual SSV below e.g., 2/3 of the BTV) [8,22,23].

In an effort to improve BVOC quantitation approaches by thermal desorption–gas chromatography (TD–GC), we conducted a series of laboratory experiments in which the breakthrough properties were assessed for 10 BVOCs in relation to a number of key variables (such as type of sorbent material, purge volume, purge time, and sampling temperature). In the course of this study, a comparison was made to allow sample recovery of all target BVOCs between two types of STs (a three-bed CBX vs. a single bed CC) and to assess the differences in sorption efficiency (between two STs bed materials and a CC single bed ST). Based on our experiments, the BT characteristics were evaluated for all of our target BVOCs and applied to suggest specific protocols needed for their safe sampling.

2. Materials and method

2.1. Preparation of the working standard

The preparation of accurate liquid working standards is very important to assess the basic properties of quality assurance/quality control (QA/QC) and to apply external calibration of target compounds. To this end, a primary standard (PS) was prepared to contain 10 BVOCs in methanol ((1) isoprene, (2) (+)- α -pinene, (3) camphene, (4) (+)- β -pinene, (5) (+)-3-carene, (6) α -phellandrene, (7) α -terpinene, (8) (R)-(+)-limonene, (9) γ -terpinene, and (10) *p*-cymene) and two reference compounds ((11) benzene and (12) toluene) (Table 1). The PS of all compounds (except camphene) was prepared by mixing the reagent grade chemicals (RGC: purities of >98.5% except camphene (>95%), Sigma-Aldrich, USA) in methanol (Daejung, South Korea). In the case of camphene, PS was prepared by stepwise dilution of solid RGC (purity: >95%) in methanol (Sigma-Aldrich, USA). The analyte concentrations in the 2nd working standard (2nd WS) were made to ~35.4 ng/ μ l (in the case of (+)- α -pinene) by diluting the PS in methanol (refer to Table 1S). The concentrations of two reference compounds were ~36.4 ng/ μ l (benzene) and ~35.9 ng/ μ l (toluene), respectively. Once prepared, the calibration L-WS was then used over a 2-month period (Table 1S).

Table 1
Information of 10 target BVOCs and 2 reference AVOCs.

Order	VOC type	Compounds	Formula	MW (g/mol)	Density (g/ml)	Purity (%)	Boiling point (°C)	CAS number
1		Isoprene	C ₅ H ₈	68.1	0.681	99.5	34.1	78-79-5
2		(+)- α -Pinene	C ₁₀ H ₁₆	136	0.858	99	155	7785-70-8
3		Camphene	C ₁₀ H ₁₆	136	0.850	95	159	79-92-5
4		(+)- β -Pinene	C ₁₀ H ₁₆	136	0.872	98.5	155	19902-08-0
5	Target BVOC	(+)-3-Carene	C ₁₀ H ₁₆	136	0.857	90	168-169	13466-78-9
6		α -Phellandrene	C ₁₀ H ₁₆	136	0.850	99.95	171-172	99-83-2
7		α -Terpinene	C ₁₀ H ₁₆	136	0.837	95	173.5-174.8	99-86-5
8		(R)-(+)-Limonene	C ₁₀ H ₁₆	136	0.842	99	176	5989-27-5
9		γ -Terpinene	C ₁₀ H ₁₆	136	0.850	98.5	183	99-85-4
10		<i>p</i> -Cymene	C ₁₀ H ₁₄	134	0.860	99	177	99-87-6
11	Reference AVOC	Benzene	C ₆ H ₆	78.1	0.878	99.5	80.1	71-43-2
12		Toluene	C ₇ H ₈	92.1	0.866	99.5	111	108-88-3

2.2. Preparation of sorbent tube and calibration

In this study, two types of quartz sampling ST ((1) a three-bed CBX ST (Carboxack C (40/60 mesh) = 70 mg, Carboxack B (40/60 mesh) = 50 mg, and Carboxack X (40/60 mesh) = 50 mg: namely, 'CBX') and (2) a 1-bed CC ST (Carboxack C (40/60 mesh) = 70 mg: namely, 'CC')) were prepared. The weight of Carboxack C in the CC ST was same as the weight of Carboxack C in the CBX ST for comparison purposes. Quartz wool plugs were used to either separate or hold the sorbents in place (Table 2). Only one sorbent tube of each type was prepared to eliminate variability among sorbent tubes and used repeatedly over the 2-month study period. Both STs were conditioned prior to all experiments at 350 °C for 1 h using N₂ purging gas in a ST conditioner (ATC 1200, ACEN Co., Ltd., South Korea). The quartz wool and the sorbents were all purchased from SUPELCO (Sigma-Aldrich, USA).

For the 4-point calibration, 1 μ l of a given L-WS was loaded on to a CBX ST (at ambient lab temperature, ~25 °C) using a 10 μ l syringe piercing a piece of silicone tubing (into flowing N₂) connecting the front of the ST to the 1 L polyester aluminum (PEA) bag (Top Trading ENG., South Korea) containing ultrapure 99.999% N₂. The 1 L PEA bags were blank-tested, and no contamination was detected. An MFC pump (MP- Σ 30, Sibata, Japan) was used to pull the N₂ through the ST at a rate of 100 ml/min for 2 min. In order to check the reproducibility of the results, triplicate analysis was made for each calibration point. The temporal stability of the calibration was monitored using CBX ST over a 2 month period (Fig. 1A).

2.3. BVOC breakthrough testing as a function of purge volume and temperature

To conduct a series of BT tests using both ST types (CBX and CC) as a function of purging volume and temperature, 1 μ l of L-WS (the 4th calibration point: 35.4 ng/ μ l in the case of (+)- α -pinene) was quickly injected into each ST (as described above in Section 2.2) into a N₂ gas (99.999%) stream. Then N₂ gas was pulled through the CBX ST at a flow rate of 100 ml/min to give a total of 6 purging volumes (0.15, 1, 5, 10, 20, and 50 L) in separate experiments. In the case of the CC ST, the maximum purging volume was thus limited to 20 L in light of its reduced sorptive capacity. After completing each ST purging step, the ST was analyzed by the same TD-GC/MS system. The two STs were loaded at 25 °C and analyzed in triplicate.

In the second stage of BT testing, the sorption capacity of the CBX ST was evaluated by determining the amount of BVOC standard adsorbed at four different sampling temperatures (i.e., 25, 35, 45, and 60 °C) with the supply of N₂ at a fixed flow rate of 100 ml/min for 100 min (total volume of 10 L). In the case of the CC ST, experiments were performed to assess more detailed BT features by extending the purging temperature range up to 100 °C at 10 different temperatures (30, 40, 50, 55, 60, 65, 70, 75, 80, and 100 °C) under the same purging conditions.

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