Simulation of the breakthrough behavior of volatile organic compounds against sorbent tube sampler as a function of concentration level and sampling volume

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HIGHLIGHTS

- Breakthrough (BT) is the key property to evaluate the performance of sorbent sampling.
- Reliability of the sorbent sampling is tested in terms of concentration levels and sample volume.
- The factors controlling BT behavior of VOCs are estimated through simulation of key variables.
- The basic sorptive properties of Tenax TA are quantitatively described for a suite of 13 VOCs.

GRAPHICAL ABSTRACT
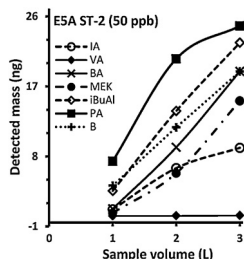
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ABSTRACT

The breakthrough (BT) properties of Tenax TA sorbent were challenged by gaseous standards containing a suite of 13 volatile organic compounds (VOC): (1) aromatic hydrocarbons: benzene (B), toluene (T), *p*-xylene (*p*-X), and styrene (S), (2) aldehydes: acetaldehyde (AA), propionaldehyde (PA), butyraldehyde (BA), isovaleraldehyde (IA), and valeraldehyde (VA), (3) ketones: methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK), and (4) two others: isobutyl alcohol (*i*-BuAl) and butyl acetate (BuAc). To this end, 1–3 L of standards (10–50 ppb) were loaded on the two sorbent tubes (ST) connected in series at $100 \, mL \, min^{-1}$. The front ST-1 was used for calibration purposes, while the ST-2 for breakthrough (recovery criterion of <1% with *p*-xylene as the key datum point). Although aromatic hydrocarbons generally met such criterion, benzene was readily distinguishable with the maximum BT. The BT for the aldehydes exhibited ~100% (AA) ≥ 85% (PA) ≥ 45% (BA) ≥ 30% (VA and IVA). There is good correlation between ST-2 recovery vs. carbon number for >C=O entity (aldehydes, ester, and ketones). As such, BT is essentially concentration independent and relatively predictable across different functional groups and between the homologues. However, the BT behavior of ppb level VOCs is no longer consistent for certain species (like benzene or MEK) relative their ppm counterparts. This variation is explained by the Langmuir equation in which the 1/BTV is proportional to analyte gas-phase concentration, if the gas-phase/sorbent partition coefficient is large.

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1. Introduction

The overall analytical bias in the measurements of trace atmospheric constituents is determined by the combined effects of both the sample collection and analytical quantitation stages. In

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general, the magnitude of bias in the latter stage can be ascertained with prudent quality assurance (QA) checks in the laboratory. Consequently, for the accurate quantitation of trace components in environmental samples, it is imperative to minimize the diverse sources of inherent experimental biases, especially at the sampling stage as a crucial first step in the overall analysis method.

The advancement of sensitive spectroscopic techniques permits real-time concentration measurements of many gas- or vapor-phase pollutants (e.g., important pollutants like ozone and Hg). Such evolving techniques are driving the underlying paradigms in environmental monitoring by increasing the instrumental sensitivity and/or by reducing the number of steps leading to the quantitation of various trace pollutants [1]. Despite such advancement in environmental analysis to date, the improvement of sampling techniques (e.g., sorbent tube) still remains as a critical Achilles heel component in need of urgent improvement for the accurate quantitation of many pollutant species in air or gaseous matrices.

The collection of VOCs in air is generally made either by whole air sampling method (e.g., EPA TO-14) or by sorbent tube (ST) method (e.g., EPA TO-17). There is a very extensive body of research devoted to each sampling technique where analysts are well aware of the advantages and disadvantages of each approach in practice. The use of each method is thus expected to yield reasonably accurate data sets, as long as their application is optimized for a given situation. To capture gaseous VOCs by the ST method, a wide variety of sorbents (either used singly or in combination) have been employed [2]. To evaluate the performance of different sorbents, breakthrough (BT) is considered the most fundamental property, i.e., what is the safe sampling volume (SSV) before the

analyte of interest is quantitatively eluted off the sorbent bed and hence lost and/or undetected. Consequently, to attain the optimum ST performance, one should have a keen appreciation and understanding of the physicochemical basis of sorbent sampling in addition to the subsequent analysis stages. As such, ST method has been developed to improve the performance of the thermal desorption (TD) technique for optimal GC/MS-based quantitation of VOC.

For the selection of the best sorbent for a given application, the basic sorptive properties of each material, e.g., breakthrough volume (BTV), detection limits (DL), recovery (R), and recovery after storage (RS) need to be evaluated critically. In addition, the kinetics and thermodynamics of adsorption (or desorption) should also be considered (i.e., the sampling BTV (the larger the better) vs. thermal desorption BTV (the smaller the better)). The ST can be viewed basically as a gas–solid chromatograph (GSC). The BTV temperature dependence is governed in part by the vant Hoff equation ($\ln(BTV) = a + b/T$)) where a is an entropic term and b is an enthalpic term. To maximize the ST performance, it is strongly recommended to gain a basic knowledge on the interaction between target compounds and sorbent materials.

To this end, a series of calibration experiments were carried out to precisely characterize the breakthrough properties of a suite of 13 VOCs (Table 1) for Tenax TA used most commonly in the collection of trace-level VOCs. Although Tenax TA is a relatively weak sorbent at 20 °C, it has the distinct advantage of low desorption BTV ($L g^{-1}$) at 130 °C: benzene (0.12) and MEK (0.065) [3]. In the course of this study, the gaseous standards of 13 VOCs prepared at five concentration levels were collected on two STs connected in series (ST-1 and ST-2). Each of them was then

Table 1
Basic information on target VOCs investigated in this study and some related quality assurance (QA) parameters.

Order	VOC Class	Target compound names		MW (g/mol)	Density (g mL^{-1})	Molecular Formula	CAS number	Tenax TA 20 °C BTV (L.g^{-1})[a]	MD[b]		RSE[c]
		Full chemical name	Short name						ng	ppb	%
A. Aldehydes											
1		Acetaldehyde	AA	44.1	0.785	C_2H_4O	75-07-0	0.65	NM	NM	NM
2		Propionaldehyde	PA	58.1	0.798	C_3H_6O	123-38-6	5	1.20	0.50	1.93
3		Butyraldehyde	BA	72.1	0.805	C_4H_8O	123-72-8	30	0.15	0.05	1.27
4		Isovaleraldehyde	IA	86.1	0.797	$C_5H_{10}O$	590-86-3	67	0.10	0.03	3.83
5		Valeraldehyde	VA	86.1	0.81	$C_5H_{10}O$	110-62-3	112	0.11	0.03	1.47
B. Aromatics											
10		Benzene	B	78.1	0.878	C_6H_6	71-43-2	70	0.06	0.02	0.61
11		Toluene	T	92.1	0.866	C_7H_8	108-88-3	400	0.06	0.02	3.18
12		*p*-xylene	*p*-X	106	0.87	C_8H_{10}	106-42-3	1550	0.06	0.01	4.36
13		Styrene	S	104	0.906	C_8H_8	100-42-5	1500	0.07	0.02	1.19
C. Ketones											
6		Methyl ethyl ketone	MEK	72.1	0.805	C_4H_8O	78-93-3	40	0.12	0.04	3.01
7		Methyl isobutyl ketone	MIBK	100	0.802	$C_6H_{12}O$	108-10-1	1000[d]	0.08	0.02	1.70
D. Ester											
8		Butyl acetate	BuAc	116	0.881	$C_6H_{12}O_2$	123-86-4	880	0.09	0.02	4.51
E. Alcohol											
9		Isobutyl alcohol	*i*-BuAl	74.1	0.801	$C_4H_{10}O$	78-83-1	20	0.14	0.05	2.64

[a] BTV data available at this URL: (http://www.sisweb.com/index/referenc/tenaxta.htm).
[b] Method detection limit (MDL): initially determined by liquid standard, and the sampling volume of 1 L (at 25 °C and 1 atm) is assumed to estimate concentrations in ppb.
[c] Relative standard error (RSE): triplicate analyses of 20 ppb standard (at flow rate = 100 mL min^{-1} and loading time = 10 min).
[d] 2-Hexanone used as a surrogate for MIBK.