

Short communication

Influences of relative humidities and temperatures on the collection of C₂–C₅ aliphatic hydrocarbons with multi-bed (Tenax TA, Carbograph 1TD, Carboxen 1003) sorbent tube method



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HIGHLIGHTS

- Water vapor in the atmosphere affects VOCs sampling breakthrough with sorbent tube method.
- High relative humidities lead low collection efficiency for volatile C₂–C₅ aliphatic hydrocarbons.
- Dry-purge removes excessive water content but also causes loss of target analytes.
- Optimizes the tube temperature (~5–10 °C above ambient temperature) in order to reduce water condensation during sampling.

ARTICLE INFO

Article history:

Received 2 November 2016

Received in revised form

1 December 2016

Accepted 2 December 2016

Available online 5 December 2016

Keywords:

VOCs

Sorbent tube

Thermal desorption

Breakthrough

Relative humidity

ABSTRACT

Volatile organic compounds (VOCs) are measured with sorbent tubes followed by thermal desorption (TD) analysis. Water vapor in the atmosphere affects sampling breakthrough and results in low collection efficiency. This paper reports the effect of relative humidity (RH) and temperature on the collection of 57 ozone precursors with a multi-bed tube composed of three different strengths of adsorbents (Tenax TA, Carbograph 1 TD, and Carboxen 1003). Unacceptable breakthrough values for volatile C₂–C₅ aliphatic compounds were observed under high (>60%) RHs. The breakthrough volumes (BV) for C₂ aliphatic compounds were reduced 13–22 fold under 90% RH. Dry-purge with inert helium gas removes excessive water content before the TD analysis but also causes a maximum of 40% loss of target analytes. Condensation is another pathway for water retention. The tube temperature should be regulated at 5–10 °C above the air temperature to minimize condensation under RHs >30%.

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1. Introduction

Sorbent tube is a standard time-integrated sampling media (e.g., Compendium Method TO-17, U.S. EPA, 1999) to collect atmospheric volatile organic compounds (VOCs) both indoors and outdoors (U.S. EPA, 1999; Harper, 2000; Kumar and Viden, 2007; Ras et al., 2009; Brown et al., 2014). Dual- or multi-bed adsorbent tubes are often used to collect a wide variety of analytes (Gallego et al., 2011). The sorbent tube is highly selective to retain target analytes depending on the strength and composition of adsorbents (Woolfenden, 1997,

2010a and 2010b). Relative humidity (RH), air temperature (T), and sampling flow rate are factors that affect retention volume (RV) and breakthrough volume (BV) for a sorbent or sorbate combination (Woolfenden, 2010b). High RHs have been the most critical concern affecting the validity of VOC measurements (LeBouf and Coffey, 2015). Hydrophobic weak adsorbents including porous polymers (e.g., Tenax TA) and graphited carbons (e.g., Carboxen) efficiently collect low volatility VOCs (i.e., less volatile than benzene with a boiling point [b.p.] of 80 °C) and their performances were generally unaffected by atmospheric RHs (Woolfenden, 1997). Performance evaluations on both collection and desorption efficiencies have been conducted on common (e.g., Tenax TA) or single-bed sorbents (e.g., Kim et al., 2014). Strong adsorbents, typically less hydrophobic, such as Carboxen and Carbosieve (carbon molecular sieves

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[CMS]) can capture the analytes with high volatility or polarity. For example, the Carboxen 1003 facilitates the retention of highly volatiles (i.e., C₂–C₅ aliphatic). Excessive water retained on the adsorbents causes breakthrough, leading to artifacts in thermal desorption (TD) analysis (Woolfenden, 1997). The multi-bed tube with a combination of Tenax TA (porous), Carboxen 1003 (graphitized carbon) and Carboxen 1003 (CMS) (equal bed length of each sorbent, total amount of 380 mg, Markes, Llantrisant, UK) is an effective media to collect 57 ozone precursors (i.e., C₂–C₁₂ saturated and unsaturated aliphatic and aromatic) measured in U.S. Photochemical Assessment Monitoring Stations (PAMS) and other air monitoring networks (Helmig and Vierling, 1995; Gawłowski et al., 2000; Karbiwnyk et al., 2002). The effects of RHs and temperatures on multi-bed sorbent tube collection efficiencies are examined in this paper.

2. Experimental

Certified PAMS standard mixtures (Restek Corporation, Bellefonte, PA, USA) were used in the laboratory experiments. Test atmospheres at different RHs (i.e., 0, 30, 60, and 90%) were prepared using Tedlar bag method (Ho and Yu, 2002). A 25-L Tedlar bag (SKC Inc., Eighty Four, PA, USA) was cleaned by filling it with high-purity nitrogen gas and evacuating it with a pump at least three times before use. The cleaned bag was then filled with known volumes of standard mixture and nitrogen. Appropriate amount of water was then injected into the bag with a gastight syringe through a septum to achieve the target RH. Liquid vaporization was assisted by gently heated the bag with a hair-dryer. The bag was also gently shaken to facilitate the uniform distribution of analytes. Details of analytical approaches to determine breakthrough have been described elsewhere (Woolfenden, 1997; U.S. EPA, 1999). Prior to sampling, the sorbent tubes were cleaned in a thermal conditioner (TC20, Markes, Llantrisant, UK) at 330 °C for 20 min before use. The breakthrough tests were conducted by passing the test atmospheres of standard gas mixtures through two identical sorbent tubes connected in series with a Swagelok Teflon connection union. The air samples were collected from the bag using a low-flow module sampling pump (ACTI-VOC, operation range at 1–350 mL min⁻¹, Markes). The pump was calibrated with a mass flow calibrator (Defender 510, Bios, Torrance, CA, USA). The stabilities of the flow rates at 10 and 50 mL min⁻¹ were ±4.5 and ± 2.7%, respectively. Each experiment was repeated at least four times to obtain the mean and standard derivation. All standard sampling tubes used for characterization were also prepared by the sampling bag method. All pre-conditioned and sampled tubes were sealed with Difflok caps (Markes) and stored in desiccators at 0 °C for a maximum of two weeks to minimize passive adsorption of organic vapor or moisture.

The samples were analyzed within one week using a TD unit (Series 2 UNITY-xr system with ULTRA-xr, Markes) coupled with a gas chromatograph/mass spectrometric detector (GC/MSD, Models 7890A/5977B, Agilent, Santa Clara, CA, USA). A tube was connected into the TD unit at room temperature (~25 °C) and purged with ultra-high purity (UHP) helium (He) gas at a flow rate of 40 mL min⁻¹ for a regular of 10s to 5 min to eliminate air and oxygen intrusion. For the primary desorption stage, the analytes were desorbed at 330 °C for 5 min and refocused onto a cryogenic-trap (U-T1703P-2S, Markes) to capture high volatility target compounds at -15 °C. For the secondary desorption stage, the trap was dry-purged for a regular of 10s to 5 min and rapidly heated from -15 °C to 320 °C and maintained for 5 min. The analytes were passed via a heated transfer line at 160 °C, and re-refocused onto a cold GC capillary column head (Rtx[®]-1, 105 m × 0.25 mm × 1 μm film thickness, Restek Corporation) at -45 °C with an aid of liquid nitrogen (N₂) in GC oven. Once the second desorption is completed,

the oven temperature program started at an initial temperature of -45 °C for 4 min, ramped to 230 °C at a rate of 6 °C min⁻¹, and maintained at 230 °C for 5 min. The constant flow rate of He carrier gas was 1.0 mL min⁻¹ throughout the GC analysis. The selective ion monitoring (SIM) mode was applied to scan and identify the target analytes with the MSD operated at electron impact (EI) ionization (70 eV). The desorption efficiency of the target analytes from the TD step was >98%. The method detection limit (MDL) for the 57 compounds ranged from 0.006 to 0.197 ppbv with a sampling volume of 3 L. The measurement precisions for the analysis of eight replicates of standard samples at 2 ppbv were ≤5%.

3. Results and discussion

3.1. Breakthrough

Table 1 summarizes the breakthrough of the target analytes with collection flow rates of 10 and 50 mL min⁻¹ as suggested by the technical guidelines (Agilent, 2013). The tests were conducted with various RHs (e.g., 90% RH corresponding to a humid environment or rainy day) and high VOCs concentration of 2 ppbv for each of the 57 analytes. Breakthrough is defined as negligible (marked as “N” in Table 1) if analytes present at levels <5% in backup tube (U.S. EPA, 1999). Under dry atmospheres (~0% RH), no breakthrough was found. At 30% RH, breakthrough of 7–9% for C₂ aliphatic (i.e., ethylene, acetylene, and ethane) and propylene were detected in the backup tubes with a sampling volume of 3.0 L. At 60% RH, breakthrough of 6–13% occurred for six aliphatic compounds (C₂ to C₄) at sampling volume of 1.0 L. At sampling volume of 3.0 L, breakthrough increased to 7–19% for alkanes and alkenes (C₂ to C₅). Irrespective of sampling flow rate or RH level, breakthrough of 6–29% for C₂ to C₅ aliphatic was found. At 90% RH, the extent of breakthrough of the C₂ to C₅ aliphatic increased by 7–13% as sample volume increased from 1.0 to 3.0 L. These results are consistent with those found by Helmig and Vierling (1995) in that RH plays an important role in desorbing VOCs with the multi-bed tube. Water vapor retained by the adsorbent (e.g., less hydrophobic Carboxen 1003) can either mask the adsorption (active) sites or displace the adsorbed compounds (Brown, 2013). Without Carboxen 1003, the combined tubes with Tenax TA and Carboxen 1003 collect less volatile compounds such as polyfluorinated alkyl substances (PFASs) efficiently (Wu and Chang, 2012), but had poor collection efficiencies for highly volatile compounds. In addition, single-bed Tenax-TA tube had a BV (in term of mass per unit volume of adsorbent) of 19.7 mg L⁻¹ for ethane (C₂) (i.e., lower than 55 mg L⁻¹ for water), orders of magnitude lower than the 44,000 mg L⁻¹ for benzene at 20 °C. It is thus necessary to include a strong but less hydrophobic adsorbent for collection of the volatile compounds.

Fig. 1 shows the apparent reduction in BVs with increasing RHs from C₂ to C₅ aliphatic. As shown in Fig. 1a, for C₂ aliphatic, the BVs were 4.1–4.4 L at 0% RH and reduced by 13–23 fold to 0.2–0.3 L at 90% RH, greater than the factor of 10 for the less volatile compounds (i.e., ≥C₆) specified in the TO-17 Method (U.S. EPA, 1999). As documented in United Kingdom Health and Safety Executive (U.K. HSE), the safe sampling volume (SSV) defined by U.S. EPA (U.S. EPA, 1999), typically two-thirds (~66%) of the BV, in collection of aliphatic hydrocarbon (C₃–C₆) and benzene should be reduced by a factor of two for porous polymers and a factor of ten for carbonaceous sorbents at a high RH of >95% (U.K. HSE, 1993). However, at 60% RH, the BVs of ≥1.0 L were found for all target analytes in this study, higher than the recommended sampling volume of 0.5 L with 65% RH using other standard multi-bed tubes (Woolfenden, 1997). C₆ have not been demonstrated as their BVs were much greater than the maximum sampling volume (i.e., 3.0 L) at 90% RH.

Table 1

Breakthrough for the multi-bed tube in detection of 57 ozone precursors at different relative humidities (RHs).

Compound				RH=0%				RH = 30%				RH = 60%				RH = 90%			
	Sum of analytes (mg) ^a			0.225	0.225	0.451	1.351	0.225	0.225	0.451	1.351	0.225	0.225	0.451	1.351	0.225	0.225	0.451	1.351
Water content in air (mg) ^b			-0	-0	-0	-0	3.5	3.5	7.0	21.0	7.0	7.0	14.0	42.0	10.5	10.5	21.0	63.0	
Flow rate (mL/min)			10	50	50	50	10	50	50	50	10	50	50	50	10	50	50	50	
Sample Volume (L)			0.5	0.5	1.0	3.0	0.5	0.5	1.0	3.0	0.5	0.5	1.0	3.0	0.5	0.5	1.0	3.0	
MW ^c Qual Ion ^d b.p. ^e																			
Ethylene	28	27	-103.7	N ^f	N	N	N	N	N	N	9 ± 5%	N	N	13 ± 6%	18 ± 6%	9 ± 5%	9 ± 6%	16 ± 5%	29 ± 8%
Acetylene	26	26	-83.4	N	N	N	N	N	N	N	7 ± 7%	N	N	8 ± 5%	19 ± 5%	7 ± 3%	8 ± 5%	13 ± 3%	25 ± 5%
Ethane	30	27	-88.6	N	N	N	N	N	N	N	7 ± 5%	N	N	7 ± 3%	17 ± 3%	7 ± 4%	8 ± 3%	14 ± 4%	21 ± 9%
Propylene	42	41	-47.4	N	N	N	N	N	N	N	8 ± 6%	N	N	N	11 ± 3%	7 ± 5%	6 ± 6%	6 ± 5%	14 ± 6%
Propane	44	29	-42.1	N	N	N	N	N	N	N	N	N	N	10 ± 4%	8 ± 3%	7 ± 5%	8 ± 5%	13 ± 5%	
Isobutane	58	43	-11.8	N	N	N	N	N	N	N	N	N	N	7 ± 3%	7 ± 3%	6 ± 4%	N	7 ± 4%	9 ± 3%
1-Butene	56	41	-6.3	N	N	N	N	N	N	N	N	N	N	8 ± 3%	6 ± 3%	N	6 ± 6%	7 ± 5%	11 ± 6%
n-Butane	58	43	-0.5	N	N	N	N	N	N	N	N	N	N	N	9 ± 3%	8 ± 3%	N	6 ± 3%	13 ± 5%
trans-2-Butene	56	41	0.9	N	N	N	N	N	N	N	N	N	N	6 ± 3%	N	7 ± 4%	7 ± 3%	N	8 ± 3%
cis-2-Butene	56	41	3.7	N	N	N	N	N	N	N	N	N	N	N	7 ± 4%	N	6 ± 6%	6 ± 5%	9 ± 6%
iso-Pentane	72	43	27.8	N	N	N	N	N	N	N	N	N	N	N	N	N	7 ± 3%	6 ± 5%	6 ± 5%
1-Pentene	70	42	30.1	N	N	N	N	N	N	N	N	N	N	N	N	N	7 ± 4%	7 ± 3%	7 ± 3%
n-Pentane	72	57	36.1	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	8 ± 6%
Piperylene	68	67	27.8	N	N	N	N	N	N	N	N	N	N	N	N	N	N	8 ± 5%	7 ± 5%
trans-2-Pentene	70	55	37.0	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
cis-2-Pentene	70	55	37.0	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
2,2-Dimethylbutane	86	71	49.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Cyclopentane	70	42	50.0	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
2,3-Dimethylbutane	86	43	58.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
2-Methylpentane	86	43	60.3	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
3-Methylpentane	86	57	64.0	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
1-Hexene	84	56	63.3	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
n-Hexane	86	57	68.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Methylcyclopentane	84	56	71.8	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
2,4-Dimethylpentane	100	57	80.5	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Benzene	78	78	80.1	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Cyclohexane	84	84	80.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
2-Methylhexane	100	43	90.0	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
2,3-Dimethylpentane	100	56	89.8	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
3-Methylhexane	100	43	90.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N

Compound				RH=0%				RH = 30%				RH = 60%				RH = 90%			
	Sum of analytes (mg) ^a			0.225	0.225	0.451	1.351	0.225	0.225	0.451	1.351	0.225	0.225	0.451	1.351	0.225	0.225	0.451	1.351
Water content in air (mg) ^b			-0	-0	-0	-0	3.5	3.5	7.0	21.0	7.0	7.0	14.0	42.0	10.5	10.5	21.0	63.0	
Flow rate (mL/min)			10	50	50	50	10	50	50	50	10	50	50	50	10	50	50	50	
Sample Volume (L)			0.5	0.5	1.0	3.0	0.5	0.5	1.0	3.0	0.5	0.5	1.0	3.0	0.5	0.5	1.0	3.0	
MW ^c Qual Ion ^c b.p. ^d																			
2,2,4-Trimethylpentane	114	57	99.2	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
n-Heptane	100	43	98.8	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Methylcyclohexane	98	83	100.9	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
2,3,4-Trimethylpentane	114	71	113.5	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Toluene	92	91	110.6	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
2-Methylheptane	114	57	117.8	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
3-Methylheptane	114	85	118.8	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
n-Octane	114	43	125.8	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N

(continued on next page)

Table 1 (continued)

Compound	RH=0%			RH = 30%				RH = 60%				RH = 90%						
	Sum of analytes (mg) ^a	0.225	0.225	0.451	1.351	0.225	0.225	0.451	1.351	0.225	0.225	0.451	1.351	0.225	0.225	0.451	1.351	
Water content in air (mg) ^b		~0	~0	~0	~0	3.5	3.5	7.0	21.0	7.0	7.0	14.0	42.0	10.5	10.5	21.0	63.0	
Flow rate (mL/min)		10	50	50	50	10	50	50	50	10	50	50	50	10	50	50	50	
Sample Volume (L)		0.5	0.5	1.0	3.0	0.5	0.5	1.0	3.0	0.5	0.5	1.0	3.0	0.5	0.5	1.0	3.0	
MW ^c	Qual Ion ^c	b.p. ^d																
Ethylbenzene	106	91	136.2	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
m-/p-Xylene ^g	106	91	139.1	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Styrene	104	104	146.0	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
o-Xylene	106	91	144.4	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
n-Nonane	128	57	151.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Isopropylbenzene	120	105	152.4	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
n-Propylbenzene	120	91	159.2	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
m-Ethyltoluene	120	105	159.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
p-Ethyltoluene	120	105	162.0	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
1,3,5-Trimethylbenzene	120	105	164.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
o-Ethyltoluene	120	105	165.2	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
n-Decane	142	57	169.4	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
1,2,4-Trimethylbenzene	120	105	174.2	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
1,2,3-Trimethylbenzene	120	105	176.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
m-Diethylbenzene	134	105	182.0	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
p-Diethylbenzene	134	119	183.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Undecane	156	57	195.6	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Dodecane	170	57	200.7	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N

^a Theoretical amount of analytes collected.

^b Theoretical amount of water passed through the tube.

^c Molecular weight.

^d Qualified ion.

^e Boiling point.

^f The values presented are in percentage of the analyte in the second tube, and N represents the values < 5%.

^g m-xylene and o-xylene are co-eluted in the chromatographic separation.

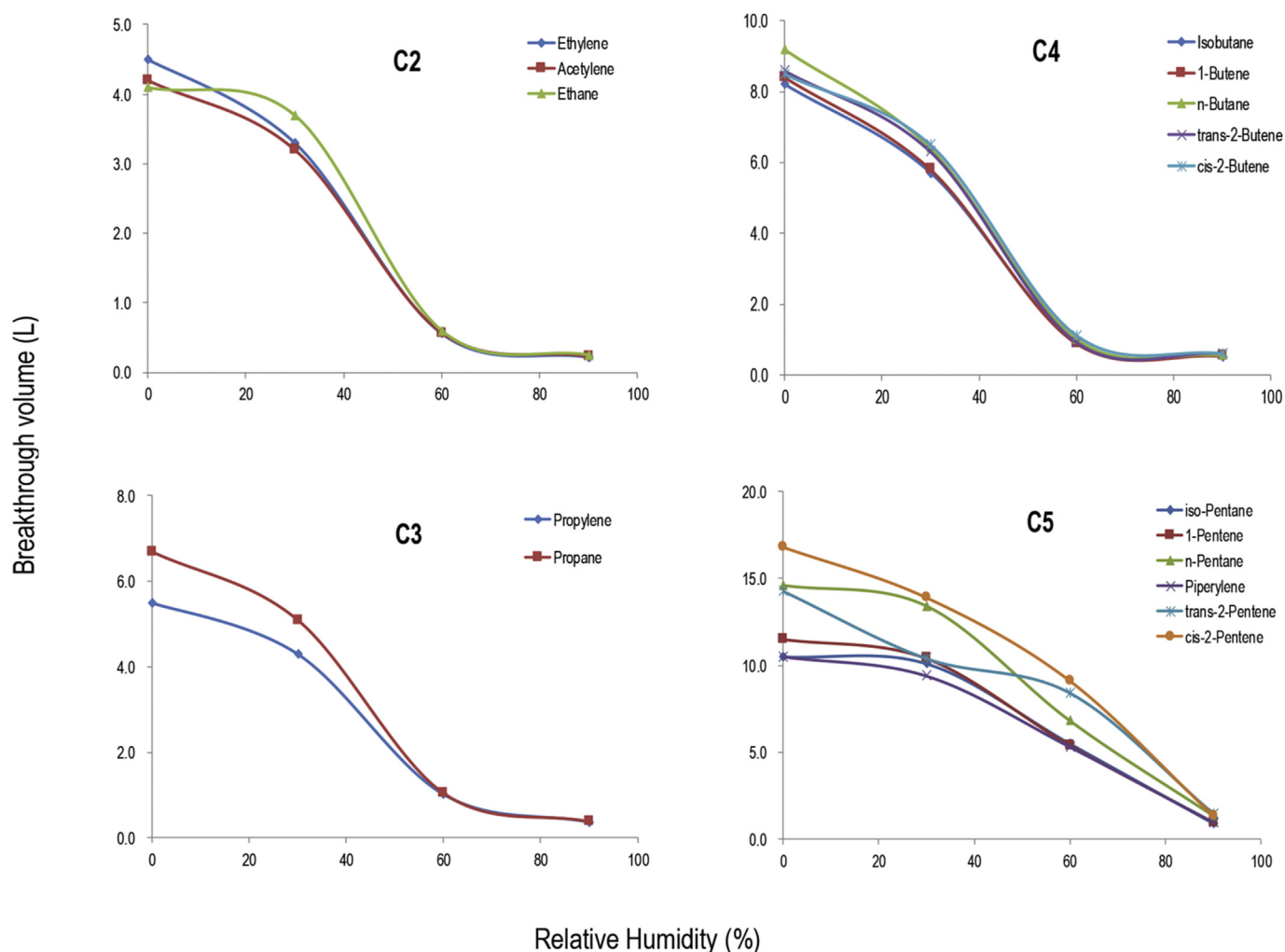


Fig. 1. Breakthrough volumes (BVs) for C₂-C₅ aliphatic hydrocarbons at different RHs using multi-bed tube at room temperature (~25 °C).

3.2. Dry-purge

The GC/MS technology is sensitive to water interference. Adverse effects include baseline anomalies and unpredictable quenching of the detector responses for target compounds with co-eluted water signal. Excessive water may shorten capillary column lifetime, cause burn out of ion source filaments, and destroy ion detection interface (Agilent, 2011).

Dry-purge is a practical way to eliminate water in the sorbent tube which could be conducted either: (a) purging the sorbent tube with He or N₂ gas (at 50 mL min⁻¹) prior to TD analysis (i.e., Prior Dry-Purge [PDP] step) (0–6 min), or (b) applying dry-purge on two-stage TD steps (each of 10 s –5 min) (Gawłowski et al., 2000). Brown (2013) suggests that the PDP step is necessary if more than 1 mg of matter has been collected (i.e., the net sample weight >1 mg), which identified as severe water accumulation. The two-stage TD dry-purge steps are practical ways to eliminate water and oxygen intrusion inferences from the tube to the cold trap and from the cold trap to the capillary column, respectively. Fig. 2 illustrates the percentage recoveries of the target analytes from different dry-purge steps. In order to reduce the net sample weight (from 1.92 to 2.36 mg to <1 mg) with 28 measures, the PDP step with inert He gas lasted 6 min. As shown in Fig. 2a, the PDP step resulted in loss of volatile analytes (Karbiwnyk et al., 2002) with <60% recovery for C₂ and C₃ aliphatics. Better recoveries (>80%) can

be achieved by applying dry-purge on two-stage TD steps without the PDP step (Fig. 2b and c) but this reduced chromatographic resolutions. It should be noted that the cryogenic-trap comprise of strong strength CMS with refocus of the volatile desorbed analytes (Fernandez-Villarrenaga et al., 2004). The recovery efficiency of secondary dry-purge taken place inside the TD unit needs to be further verified (Gawłowski et al., 2000). Water in the sorbent tube may also vary the split ratio while the analytes enter into capillary column introducing additional measurement uncertainties (8.7–24%).

3.3. Condensation

Besides adsorption, condensation is another pathway for water retained onto the sorbent tube. Table 2 lists the net weights of the multi-bed and single-bed Tenax TA tubes after collections of the standard analyte under different RHs and temperatures. The tube temperatures were regulated by situating the tubes inside of a custom-made thermal controller 5 min before sampling. With the exception of 0% RH, higher weight reductions were measured in uncontrolled tube temperatures as compared to heated samples. Note that the tube's temperature was generally below the air temperature as the tubes were refrigerated before sampling. The outer tube was made of stainless steel with high thermal conductivity, keeping the tube cool for an extensive period. A large

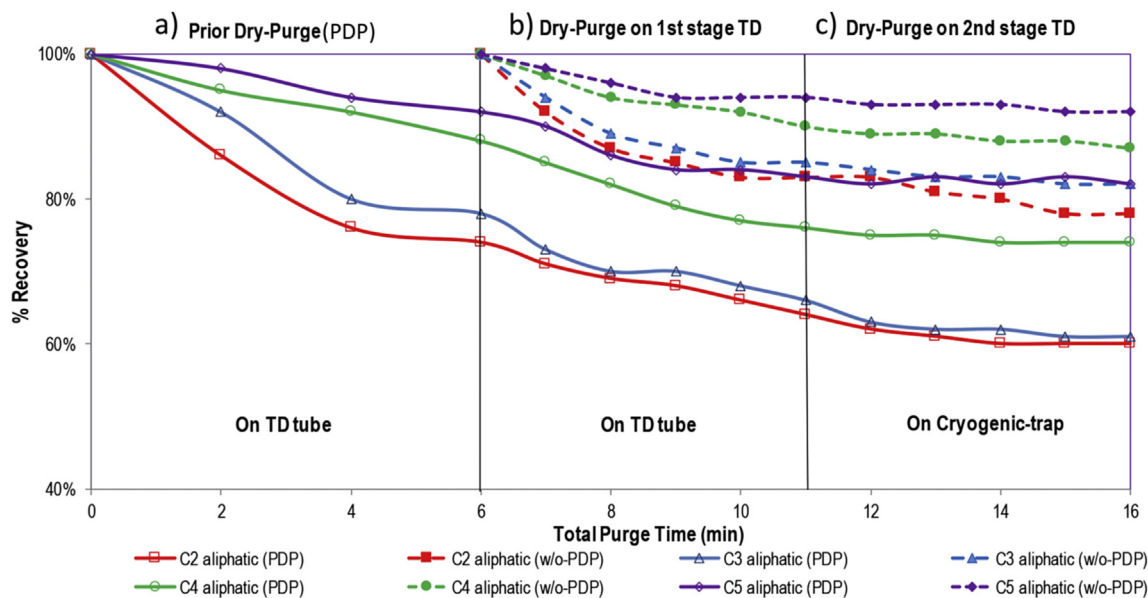


Fig. 2. Recoveries of C₂–C₅ aliphatic hydrocarbons (at 2 ppbv standard PAMS atmosphere) at 60% RH, sample volume 1 L for: a) prior dry-purge (PDP) with inert helium gas before TD analysis, b) dry purge on 1st stage TD, and c) dry purge on 2nd stage TD.

Table 2

Net weight of the multi-bed and single-bed Tenax TA tubes (in unit of mg) after collection of 2 ppbv standard PAMS gases with a sampling volume of 1L.

Air temp (°C)	Tube Temp (°C)	Multi-bed tube				Single-bed Tenax TA tube			
		RH				RH			
		0%	30%	60%	90%	0%	30%	60%	90%
10	Uncontrolled ^a	0.467	0.944	2.13	2.86	0.413	0.867	1.70	2.32
	25	0.469	0.743	1.12	1.35	0.393	0.611	0.918	1.05
	30	0.482	0.722	1.09	1.30	0.403	0.630	0.905	1.04
	35	0.473	0.716	1.05	1.29	0.386	0.576	0.777	1.01
	40	0.462	0.711	1.07	1.27	0.380	0.586	0.779	1.00
15	uncontrolled	0.457	1.01	1.98	3.03	0.375	0.884	1.64	2.50
	25	0.472	0.762	1.11	1.43	0.391	0.629	0.918	1.18
	30	0.477	0.743	1.02	1.32	0.395	0.615	0.854	1.09
	35	0.469	0.722	1.02	1.29	0.387	0.599	0.827	1.07
	40	0.466	0.721	0.962	1.27	0.385	0.595	0.785	1.03
20	uncontrolled	0.456	1.13	2.22	3.21	0.395	0.955	1.79	2.62
	25	0.474	0.892	1.72	1.46	0.391	0.718	1.37	1.17
	30	0.463	0.758	1.58	1.36	0.392	0.632	1.28	1.11
	35	0.471	0.734	1.38	1.27	0.37	0.569	1.05	1.02
	40	0.473	0.704	1.07	1.28	0.375	0.551	0.839	1.03
25	uncontrolled	0.462	1.23	2.26	3.63	0.406	1.07	1.83	2.95
	25	0.472	1.02	1.87	2.17	0.392	0.842	1.54	1.68
	30	0.472	0.824	1.62	1.37	0.393	0.704	1.34	1.10
	35	0.456	0.734	1.24	1.30	0.375	0.594	1.06	1.02
	40	0.472	0.723	0.968	1.30	0.387	0.586	0.767	1.00

^a No temperature regulating on the tube. The tube should be below room temperature from the cooling.

difference between the air and tube temperatures induced more water condensation. Reductions of 1.3–1.8 mg of net weight were found on the tubes regulated at 5–10 °C above the air temperature. Further increase in tube temperature (to 30 and 40 °C) shows little effect on net weight by RHs. Larger (>0.5 mg) weight reductions were found between uncontrolled and heated tube temperatures under high RHs (≥60%), suggesting less water condensation occurred with heated sorbent tubes. Similar phenomenon was also found on hydrophobic Tenax TA tube, demonstrating the importance of condensation over adsorption. These results are consistent with the findings of Karbiwnyk et al. (2002), where the collection efficiencies (≥90%) for non-methane VOCs, biogenic VOCs, and

chlorofluorocarbons were improved with 10 °C increase in tube temperature. Warm-up and proper temperature control on the sorbent tube are recommended for sampling. However, there is a 5% reduction in BV for each temperature increase of 10 °C (U.S. EPA, 1999). An optimal regulated tube temperature should be established.

4. Conclusion

The RH influences the collections of volatile C₂–C₅ aliphatic hydrocarbons. Water can be either adsorbed or condensed onto the tube under high RHs. Although dry-purge with helium or nitrogen

gas removes water from the sampled tube, it leads to 13–42% analyte loss. Proper precautions should be taken to optimize the tube temperature (~5–10 °C above ambient temperature) in order to reduce water condensation during sampling.

Acknowledgement

This research was financially supported by the National Key Research and Development Program of China (2016YFA0203000), the National Science Foundation of China (41401567, 41503117, 41573138), and the “Strategic Priority Research Program” of the Chinese Academy of Sciences (Grant No. XDB05000000). Yu Huang is also supported by the “Hundred Talent Program” of the Chinese Academy of Sciences.

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