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Optimization and evaluation of multi-bed adsorbent tube method in collection of volatile organic compounds



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ABSTRACT

The feasibility of using adsorbent tubes to collect volatile organic compounds (VOCs) has been demonstrated since the 1990's and standardized as Compendium Method TO-17 by the U.S. Environmental Protection Agency (U.S. EPA). This paper investigates sampling and analytical variables on concentrations of 57 ozone (O₃) precursors (C₂-C₁₂ aliphatic and aromatic VOCs) specified for the Photochemical Assessment Monitoring Station (PAMS). Laboratory and field tests examined multi-bed adsorbent tubes containing a sorbate combination of Tenax TA, Carboxograph 1 TD, and Carboxen 1003. Analyte stabilities were influenced by both collection tube temperature and ambient O₃ concentrations. Analytes degraded during storage, while blank levels were elevated by passive adsorption. Adsorbent tube storage under cold temperatures (−10 °C) in a preservation container filled with solid silica gel and anhydrous calcium sulfate (CaSO₄) ensured sample integrity. A high efficiency (> 99%) O₃ scrubber (i.e., copper coil tube filled with saturated potassium iodide [KI]) removed O₃ (i.e., < 200 ppbv) from the air stream with a sampling capacity of 30 h. Water vapor scrubbers interfered with VOC measurements. The optimal thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) desorption time of 8 min was found at 330 °C. Good linearity ($R^2 > 0.995$) was achieved for individual analyte calibrations (with the exception of acetylene) for mixing ratios of 0.08–1.96 ppbv. The method detection limits (MDLs) were below 0.055 ppbv for a 3 L sample volume. Replicate analyses showed relative standard deviations (RSDs) of < 10%, with the majority of the analytes within < 5%.

1. Introduction

Volatile organic compounds (VOCs) contribute to the formation of tropospheric ozone (O₃) and secondary organic aerosols (SOA) (Cai et al., 2010; Wang et al., 2010; Ling and Guo, 2014; Gentner et al., 2017; Wu and Xie, 2017). They also pose human health threats and other environmental damage (Lau et al., 2010; Seco et al., 2013). Off-line analysis includes collection into a container (e.g., stainless steel canister or Tedlar sampling bag) (U.S.EPA, 1999a, 1999b; Mariné et al., 2012) or selectively trapping VOCs on a substrate (U.S.EPA, 1999c; Woolfenden, 2010a, 2010b; Wu and Chang, 2012). Evacuated canisters (e.g., 2–15 L) are easy to operate, but they are bulky to transport and have potential losses of polar and active compounds on the inner wall

(Woolfenden, 2010a).

Adsorbent tubes, including single-, dual- or multi-bed sorbents, offer portability with low operation cost. Adsorbent tubes can be reused approximately 100 times (after cleaning) before replacement (Woolfenden, 1997; Harper, 2000). Target compounds are collected by different adsorbents by either active sampling or passive diffusion (Woolfenden, 2010b; Seco et al., 2013; Magnusson et al., 2015). Each sorbent has specific retentions associated with individual VOCs, and a sorbate combination allows collection of a wide variety of target analytes (Ribes et al., 2007). The adsorbed components can be extracted in solvents or thermally desorbed, re-condensed, separated by chromatography, and detected by a mass spectrometer detector (MSD), a flame ionization detector (FID), or an electron capture detector (ECD).

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Thermal desorption (TD) methods yield detection limits at sub-ppbv to ppbv levels (Ribes et al., 2007; Ras et al., 2009; Wu and Chang, 2013).

Potential interferences include: 1) oxidation of VOCs by O₃ and other oxidants during sampling (Kumar and Viden, 2007); and 2) water vapor which reduces retention and breakthrough volumes and damages the analytical instruments (Woolfenden, 2010b; Agilent Technologies, 2011; Ho et al., 2017). Purging the adsorbent tube with inert gases (i.e., helium [He] gas) prior to thermal-desorption analysis removes some of the water condensed onto the adsorbent (Gawłowski et al., 2000). However, such pre-treatments may also remove highly volatilized compounds (i.e., C₂–C₃), resulting in lower concentrations of the target analytes. (Agilent Technologies, 2013; Ho et al., 2017).

Performance of the multi-bed adsorbent tubes is examined using Tenax TA, Carbograph 1 TD and Carboxen 1003 materials for 57 O₃ precursors (i.e., VOCs_{PAMS}, including C₂–C₁₂ saturated and unsaturated aliphatic and aromatic compounds) specified by the U.S. Photochemical Assessment Monitoring Station (PAMS) and other networks (U.S.EPA, 1998a, 1998b, 2016; Shao et al., 2016; Li et al., 2017). Effects of sampling, storage, and analysis are examined. Precisions and accuracies are estimated by replicate analyses of standards, ambient samples, and certified reference materials.

2. Experimental

2.1. Sorbent tube conditioning and storage

A multi-bed stainless steel adsorbent tube (mass capacity of 380 mg with bed length of 60 mm, 5 mm i.d., and 6 mm o.d.), combining Tenax TA (35–60 mesh), Carbograph 1 TD (40–60 mesh) and Carboxen 1003 (40–60 mesh) (C3-DXXX-5266, Markes, Llantrisant, UK), was used to collect the target VOCs_{PAMS}. Prior to sampling, the adsorbent tubes were cleaned for 20 min at 330 °C in a thermal conditioner (TC20, Markes, UK) with a purge of high-purity nitrogen gas (99.9999% purity, Teda cryogenic equipment Co. Ltd., Xi'an, China) at a rate of 50 ml min⁻¹. Both ends of these pre-conditioned tubes were sealed with Difflok caps (Markes, UK) and stored in a preservation container at –10 °C for a maximum of 14 days. The preservation container, functioning as a desiccator, includes an air-tight glass case (231 mm W × 182 mm l × 167 mm D) filled with 100 g of solid silica gel to adsorb moisture (AR grade, Sinopharm Chemical Reagent Co. Ltd., Ningbo, China) and 100 g of charcoal to remove organic vapor (AR grade, Sinopharm Chemical Reagent Co. Ltd., China).

2.2. Standards and performance tests

A certified PAMS standard mixture (100 ppbv for each of the 57 VOCs) (Restek Corporation, Bellefonte, PA, USA) was used for calibration and performance tests. A 3-L Tedlar bag (Restek Corporation, USA) was filled with high-purity nitrogen gas and evacuated with a pump three times before each experiment. The standard gas was diluted with high-purity nitrogen gas to the desired concentrations (i.e., 0.08–1.67 ppbv for calibration and 2 ppbv for performance tests). These mixtures were drawn through the adsorbents with a low-flow pump (1–350 ml min⁻¹ ACTI-VOC, Markes, UK), calibrated with a mass flow calibrator (Defender 510, Bios, Torrance, CA, USA) with a stability of ± 2.7% at 50 ml min⁻¹. The sampling system used for the performance tests is illustrated in Fig. 1. Each experiment was repeated three times to obtain the average and standard deviation.

A certified reference standard (CRS) (C-TO17XX-10, Markes) containing 100 ng each of benzene, toluene, o-xylene, 1,2,4-trimethylbenzene, dichloromethane, 1,1,1-trichloroethane, methyl tert-butyl ether, methyl ethyl ketone, and ethyl acetate was used to evaluate the desorption accuracy.

2.3. Ozone and moisture removal tests

A laboratory-made O₃ scrubber was prepared using a coiled copper tube (length of 1 m with o.d. of 9.5 mm and i.d. of 6.4 mm) filled with saturated potassium iodide (KI) (Spaulding et al., 1999; Ho and Yu, 2002). To ensure that no water remained inside the tube, the scrubber was purged and dried under a gentle flow of high-purity nitrogen gas for 24 h. O₃ from an ozone generator (Model 1001, SABIO, Round Rock, TX, USA) and exhaust gases were discharged in a safety fume hood. The removal efficiency of the scrubber was examined under various O₃ concentrations and flow rates measured by an ozone analyzer (Model 205, 2B Technologies, Inc., Boulder, CO, USA). The removal efficiency was calculated as:

$$\text{Removal efficiency} = \left(\frac{O_{3 \text{ in}} - O_{3 \text{ out}}}{O_{3 \text{ in}}} \right) \times 100\% \quad (1)$$

where O_{3 in} and O_{3 out} are the concentrations of O₃ measured before and after the scrubber.

Two types of dryers (i.e., water trap and desiccant tube) were evaluated for their ability to remove moisture from the sampling stream. The water trap consisted of a cryogenic cooling unit (Bead Ruptor 24, OMNI, NW Kennesaw, GA, USA), which maintained a –50 °C temperature with a liquid nitrogen (N₂) supply. The desiccant tube consisted of a glass tube (length of 0.3 m with o.d. of 25.4 mm and i.d. of 19.1 mm) filled with 5.0 g of anhydrous calcium sulfate (CaSO₄) (AR grade, Sinopharm Chemical Reagent Co. Ltd., China). Both types of dryers were installed upstream of the sampling system, as shown in Fig. 1.

2.4. Sample analysis

The samples were analyzed using a TD unit (Series 2 UNITY-xr system with ULTRA-xr, Markes, UK) coupled with a gas chromatograph/mass spectrometric detector (TD-GC/MS, Models 7890A/5977B, Agilent Technology, Santa Clara, CA, USA). The adsorbent tube was connected to the TD unit at room temperature (~20 °C) and purged with ultra-high purity He gas at a flow rate of 40 ml min⁻¹ for 10 s to eliminate air and oxygen intrusion. For the first desorption stage, the analytes were desorbed at 330 °C for 8 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 10 s 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 refocused again onto a cold GC capillary column head (Rtx®-1, 105 m × 0.25 mm × 1 mm film thickness, Restek Corporation, USA) at –45 °C with liquid N₂ in the GC oven. After the second desorption, the oven temperature remained at –45 °C for 4 min, ramped to 230 °C at a rate of 6 °C min⁻¹, and stabilized at 230 °C for 5 min. Supplemental Fig. S1 illustrates the time events of the TD-GC/MS steps. The He carrier gas flow rate was 1.0 ml min⁻¹ for the duration of GC analysis. The selective ion monitoring (SIM) mode was applied to scan and identify the target analytes with the MSD in electron impact (EI) ionization (70 eV) mode.

2.5. Breakthrough

Collection efficiencies were determined by passing test atmospheres through two identical tubes connected in series for different temperatures and flow rates:

$$\text{Collection efficiency} = \left(1 - \frac{C_b}{C_f} \right) \times 100\% \quad (2)$$

where C_f and C_b are the amounts of a VOCs_{PAMS} collected on the front and back-up adsorbent tubes, respectively.

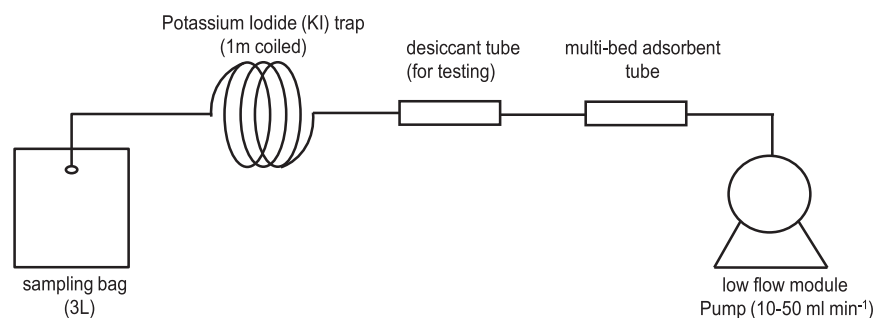


Fig. 1. Schematic of the sampling system for laboratory performance test.

Table 1

Breakthrough of the multi-bed tube in detection of 57 VOCs collected at different tube temperatures and flow rates.

Tube temperature (°C)	0		10		20		30		40	
Collection flow rate (ml min ⁻¹)	10	50	10	50	10	50	10	50	10	50
VOCs										
C ₂ -C ₃	n ^a	n	n	n	n	n	8 ± 6%	10 ± 4%	11 ± 6%	23 ± 7%
C ₄ -C ₅	n	n	n	n	n	n	n	n	12 ± 7%	13 ± 5%
C ₆ -C ₉	n	n	n	n	n	n	n	n	n	n
C ₁₀ -C ₁₂	n	n	n	n	n	n	n	n	n	n

^a The values presented are in percentage of the analytes in the second tube, and n represents the values < 5%.

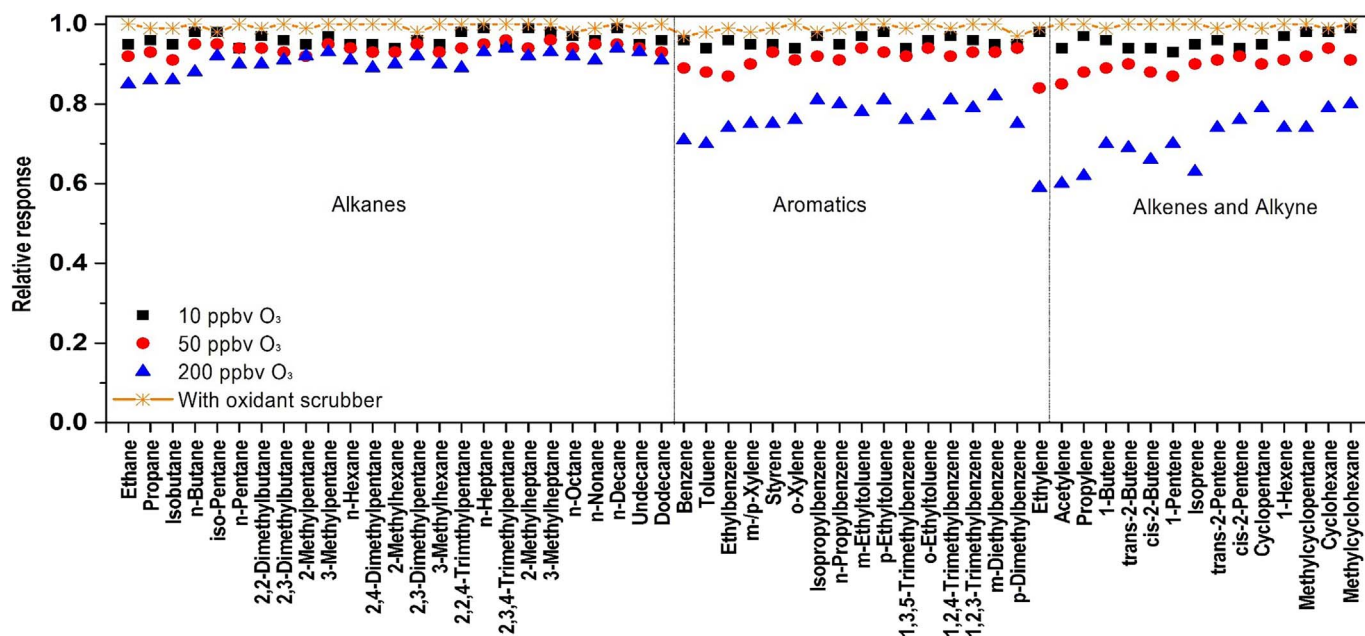


Fig. 2. Relative responses of the 57 VOCs collected at ozone concentrations of 10, 50, and 200 ppbv. Relative response with O₃ scrubber is also shown for comparison.

2.6. Ambient sample collection

Five sets of collocated samples from roadside locations (i.e., Shapo Overpass of the South Secondary Ring Road in Beilin District, Xi'an) were used to determine the reproducibility for 57 VOCs_{PAMS} in ambient air. Detailed sampling conditions are reported by Li et al. (2017). Each set of samples was collected at a flow rate of 50 ml min⁻¹ for 60 min. During the sampling period, ambient temperatures ranged from 27.8–32.1 °C with 46.7–62.2% RHs.

3. Results and discussion

3.1. Breakthrough tests

Table 1 summarizes the breakthrough of the target VOCs_{PAMS} at

various tube temperatures (i.e., 0, 10, 20, 30, and 40 °C) and flow rates (10 and 50 ml min⁻¹) as recommended in the manufacturer's technical notes (Agilent Technologies, 2013). The tests were conducted at high concentrations (i.e., 2 ppbv for each of the 57 VOCs_{PAMS}) under a dry atmosphere (~0% RH), as RH may influence measurements (Ho et al., 2017).

Breakthrough is considered to be negligible when analytes are < 5% for the backup adsorbent tube (U.S.EPA, 1999c). No breakthrough was found for tube temperatures ≤ 20 °C; low breakthrough (8–10%) was observed for C₂-C₃ at 30 °C. At a tube temperature of 40 °C, breakthrough was found for C₂-C₃ (11–23%) and C₄-C₅ (12–13%). Table 1 shows lower abundances of highly volatile compounds (i.e., C₂-C₃) for samples collected at higher tube temperatures. High temperatures minimize the extent of water condensation, but they also reduce the retention of adsorbed VOCs_{PAMS}, which may lead to desorption of

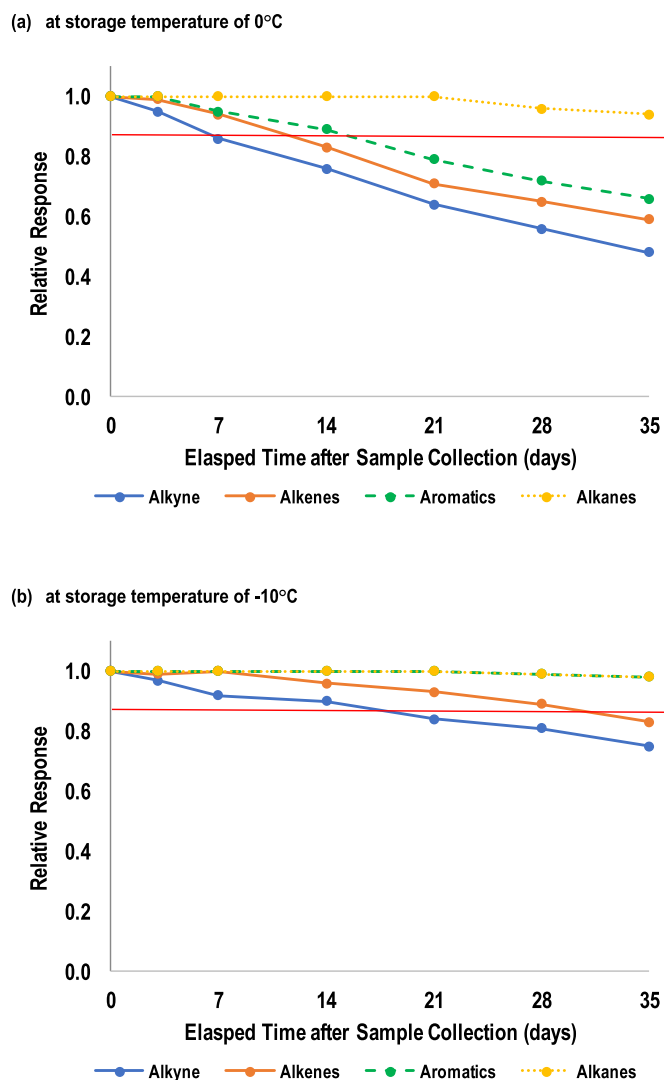


Fig. 3. Relative responses of VOC_{SPAMS} collected on the adsorbent tubes stored at 0 and 10 °C for the duration of 35 days (the red line represents the relative responses at 90%). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

volatiles during sampling. The effect of sampling rates on breakthrough was not apparent with an increasing trend for the C₂–C₃ group at high tube temperatures (30–40 °C) when flow rates increased from 10 to 50 ml min⁻¹.

3.2. Sample stability

Fig. 2 demonstrates the relative responses for the target analytes collected in the absence (i.e., using O₃ scrubber) and presence of varying O₃ levels (i.e., 10, 50, and 200 ppbv). The tests were conducted at a temperature of 20 °C with a concentration of 2 ppbv for each of the 57 VOC_{SPAMS}. Without the O₃ scrubber, the effect of O₃ is most apparent for alkenes and aromatics with decreasing response (~14–41%) at 200 ppbv of O₃; < 15% variation was found for alkanes. The reduction in response was 37–41% for ethene, acetylene, propylene, and isoprene. Oxidation or degradation of the analytes occurred as ambient O₃ concentrations exceeded 200 ppbv, supporting the need for an O₃ scrubber during VOC sampling.

In contrast to canisters, adsorbent tubes are not completely sealed and isolated from surrounding environments by hand-tightened caps. Therefore, adequate sample storage is essential to ensure the integrity of samples. Fig. 3 shows the relative responses of four classes of target

analytes (i.e., alkanes, alkenes, alkyne [only acetylene] and aromatics) for adsorbent tubes stored at 0 and –10 °C. While alkanes remained stable at 0 °C, lower concentrations for alkynes (36%), alkenes (29%), and aromatics (21%) were found after 21 days in storage.

As shown in Fig. 3b, VOCs are stable at –10 °C for 14 days. Degradation of alkynes and alkenes (~15–20%) is less than those of aromatics (~10%). In addition to high reactivity, alkenes might also evaporate due to a low boiling point (b.p. = –83.4 °C). Similar to aromatics, alkanes remain stable over 35 days, except for ethane (b.p. = –88.6 °C) and propane (b.p. = –42.1 °C). These tests indicate that the sampled adsorbent tubes should be stored in air-tight containers under cold temperatures (–10 °C) and analyzed within 14 days after sampling.

3.3. Adsorbent tube blanks

The variable blank levels of the adsorbent tubes can increase the method detection limits (MDLs). To examine the passive adsorption of VOCs, Table 2 compares the detected VOC_{SPAMS} among fresh and aged thermally-cleaned adsorbent tubes along with field and transport blanks. Only trace amounts (< 0.13 ng per tube) of propylene, benzene, and toluene were detected in the fresh thermal-cleaned blanks. A sharp increase in cyclopentane, followed by 2,3-dimethylbutane and 1-hexene, was found after 14 days of storage at –10 °C. Cyclopentane, a cyclic aliphatic C₅, has been used to produce polyurethane insulating foam (used in freezers and refrigerators); replacing the chlorofluorocarbons (Choczynski et al., 2011) which have been found to destroy O₃ layers.

Without use of a cold-temperature storage container, Table 2 shows that VOC levels from passive adsorption are similar to those of field and transport blanks. Therefore, the use of the air-tight preservation container at –10 °C could efficiently reduce undesired passive adsorption.

3.4. Ozone removal

Fig. 4 illustrates the removal efficiency for 200 and 1000 ppbv O₃ using KI-coated coil tubes at a flow rate of 50 ml min⁻¹. The saturated KI maintained excellent efficiency (99%) to remove 200 ppbv O₃ for ~30 h; but saturated with 1000 ppb O₃ after 6 h of exposure. The lifetime of the O₃ scrubber may vary due to non-equivalent amounts of KI coated in each tube. Although application of the KI coating presents a technical challenge, field testing shows that the O₃ scrubber is adequate for integrated 24-h sampling at ambient O₃ levels < 200 ppbv. Other media are also used to remove O₃, such as combining impregnated granular activated carbon powder with copper chloride (CuCl₂) or potassium nitrate (KNO₃) (Takeichi and Itoh, 1993). However, the activated carbon treatment may lead to the adsorption of organics and increase the uncertainties of VOC measurements.

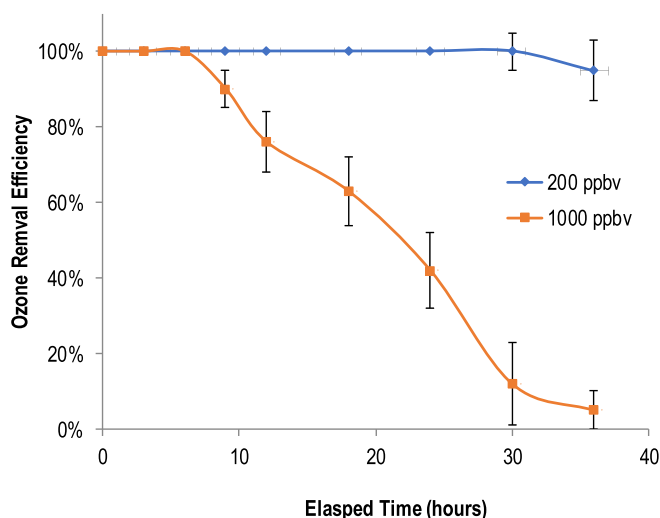
3.5. Water removal

Previous studies have illustrated the influence of atmospheric water vapor on adsorbent tubes (Helmig and Vierling, 1995; Gawłowski et al., 2000; Karbiwnyk et al., 2002; Ho et al., 2017). The U.S. EPA Compendium Method TO-14A recommends using a Nafion® permeable membrane dryer to remove water vapor upstream of the sampling train. As volatile and polar organics also permeate this membrane similar to water vapor pathways, it may bias the VOC measurements due to the acid nature of the dryer (Compendium Method TO-15; U.S.EPA, 1999a, 1999b). Models have been developed to estimate compound losses due to physical adsorption of VOCs on canister walls and to dissolution of the water condensed VOCs in the canisters (Coutant, 1993). A systematic approach to correct the biases caused by water vapor in the adsorbent tubes requires further investigation.

Two types of dryers (i.e., water trap and desiccant tube) were installed upstream of the collocated adsorbent tubes (two tubes in series)

Table 2Variations of average blanks levels (in ng per multi-bed adsorbent tube) for VOCs_{PAMS} at different storage environments.

Preservation box	Cleaned tubes stored at $-10^{\circ}\text{C}^{\text{a}}$				Dynamic blanks ^b				Fresh cleaned thermal desorption tubes
	Yes		No		Yes		No		
	14	28	14	28	Field	Transport	Field	Transport	
No. of storage day	14	28	14	28	Field	Transport	Field	Transport	
VOCs ^c									
Ethylene	0.159	0.223	0.504	0.689	0.215	0.198	0.469	0.415	nd
Ethane	0.046	0.056	0.077	0.145	0.065	0.051	0.079	0.083	nd
Propylene	0.138	0.236	0.281	0.362	0.156	0.155	0.265	0.258	0.124
Propane	0.069	0.086	0.119	0.190	0.077	0.056	0.122	0.105	nd
Isobutane	nd ^d	nd	0.062	0.174	nd	nd	0.017	0.015	nd
n-Butane	nd	nd	0.053	0.101	nd	nd	0.044	0.041	nd
cis-2-Butene	nd	nd	0.020	0.050	nd	nd	0.035	0.028	nd
iso-Pentane	nd	nd	0.026	0.053	nd	nd	0.007	0.006	nd
1-Pentene	nd	nd	0.048	0.073	0.045	0.023	0.066	0.054	nd
n-Pentane	nd	nd	0.101	0.230	nd	nd	nd	nd	nd
2,3-Dimethylbutane	nd	nd	0.392	1.120	nd	nd	nd	nd	nd
Cyclopentane	nd	nd	5.020	18.381	nd	nd	nd	nd	nd
2-Methylpentane	nd	nd	0.015	0.046	nd	nd	0.029	0.025	nd
1-Hexene	nd	nd	0.236	0.867	nd	nd	0.066	0.051	nd
n-Hexane	nd	nd	0.020	0.037	nd	nd	0.023	0.017	nd
Benzene	0.148	0.169	0.359	0.501	0.225	0.155	0.412	0.391	0.129
Toluene	0.026	0.036	0.026	0.061	0.024	0.021	0.017	0.022	0.019
Styrene	0.017	0.019	0.059	0.081	0.021	0.018	0.056	0.053	nd
p-Diethylbenzene	nd	nd	0.014	0.027	nd	nd	0.022	0.017	nd

^a Cleaned tubes were stored in the laboratory's freezer at -10°C .^b Blanks were cleaned tubes which shipped to fields at -10°C . Field blank represents passive deposition; it refers to a blank adsorbent tube connected to the sampler without turning on the pump (no air passes through the tube). Transport blank refers to a blank tube shipped to and from the field along with ambient samples.^c Only lists the 19 species that were detected in the blanks.^d Only denotes values below the method detection limit.**Fig. 4.** Efficiencies of ozone removal for a laboratory-made potassium iodide coated copper tube for O_3 concentrations of 200 and 1000 ppb.

for field testing. Fig. 5 shows the negative relative response for VOCs_{PAMS} measurements. Using the water trap (Fig. 5a), there was clearly a loss (35–87%) of C_2 – C_5 aliphatic compounds, presumably due to the condensation or dissolution from water vapor at lower temperatures; large reductions (27–46%) were also found for aromatics. The negative responses were less uniform using the CaSO_4 -filled desiccant tube (Fig. 5b). It is possible that the desiccants become progressively loaded with water, which leads to unanticipated gas adsorption. These non-selective water removal approaches are therefore not appropriate for VOC sampling.

3.6. Thermal desorption duration

The optimal desorption duration is the minimum time required for complete desorption of target analytes from the adsorbent tube before transfer to the cryogenic trap (Karbiwnyk et al., 2002; Fernandez-Villarrenaga et al., 2004; Ribes et al., 2007; Ras et al., 2009; Gallego et al., 2011; Wu and Chang, 2012; Agilent Technologies, 2013; Brown et al., 2014). Fig. 6 compares the responses for VOCs_{PAMS} measured at five durations (i.e., 1, 3, 5, 8, and 10 min) during the first stage of thermal desorption (Fig. S1) at 330°C (Agilent Technologies, 2013). Lower responses were found for desorption durations ≤ 5 min. Heavier VOCs_{PAMS} (C_6 – C_{12}) had the slowest desorption rates among the five VOC groups (i.e., C_2 , C_3 , C_4 , C_5 , and C_6 – C_{12}), attributed to their relatively high boiling points and high retention of the sorbate combination. Declines in responses were found for C_2 , C_3 and C_4 at 10 min intervals. It is possible that the cryogenic trap might not efficiently retain all of the desorbed analytes for the extended desorption duration. Negligible (1%) amounts of the target analytes were found in the subsequent re-analysis of the same desorbed tube at 330°C , suggesting that no carryover occurred. An optimal desorption duration of 8 min is recommended as it demonstrates complete desorption of target analytes.

3.7. Method detection limits (MDLs), precision, and accuracy

Table 3 summarizes the calibration parameters and MDLs of the 57 VOCs_{PAMS} using the optimized analytical protocol. The calibration curve for each target analyte was established by collecting a series of adsorbent tubes from the certified standard gas in the range of 0.08 to 1.67 ppbv, based on a collection volume of 3 l (i.e., 50 ml min^{-1} for 60 min). These levels were in-line with VOCs_{PAMS} concentrations found in China (Cai et al., 2010; Zhang et al., 2012). Excellent linearity of each target analyte was demonstrated with correlation coefficients (R^2) of > 0.995 , with the exception of acetylene ($R^2 = 0.9334$) which had the lowest response factor (i.e., calibration slope). For relative standard derivation (RSDs) $< 30\%$, the MDL was calculated as three times the

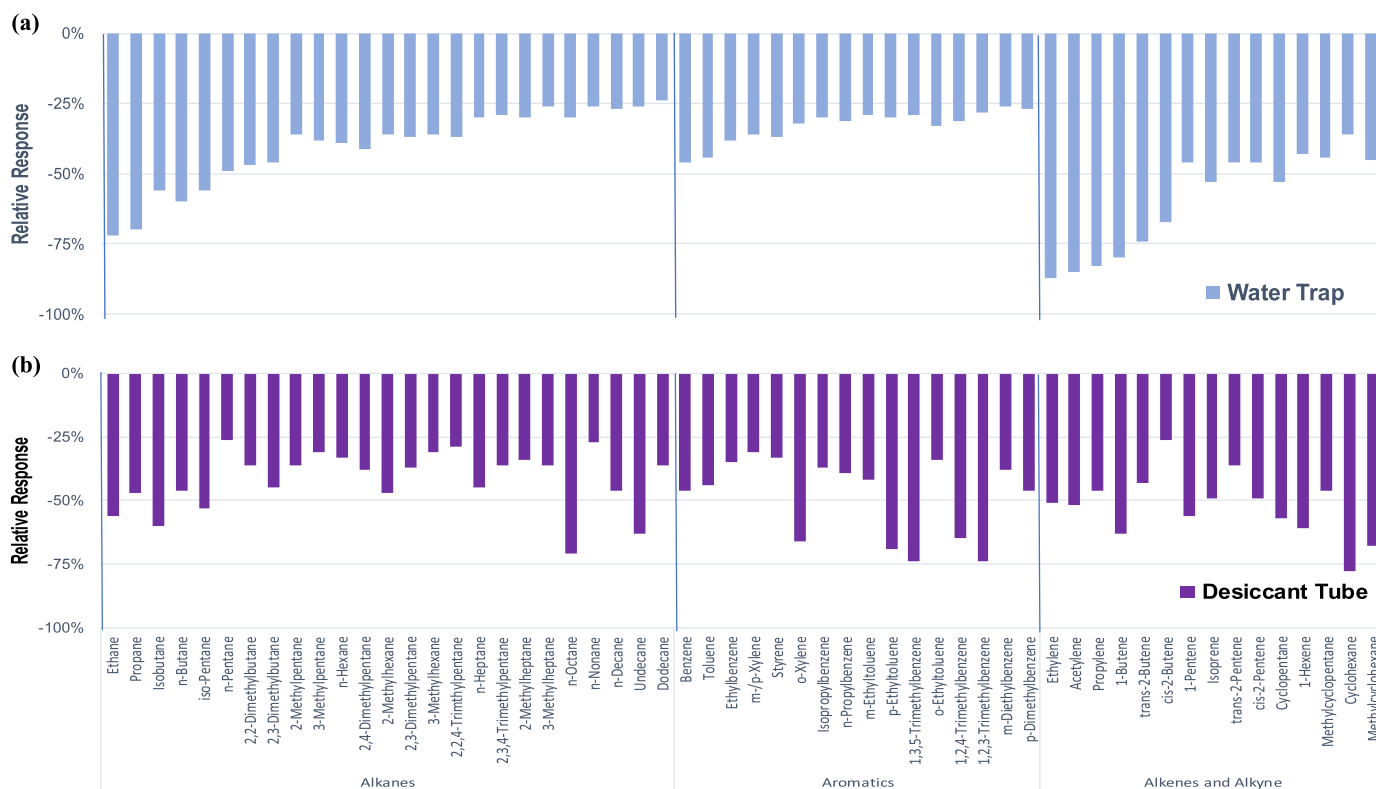


Fig. 5. Relative responses for the target VOCs using two types of dryers: a) water tap and b) desiccant tube dryers with calcium sulfate (CaSO_4). Samples are normalized to measurements without preceding dryers.

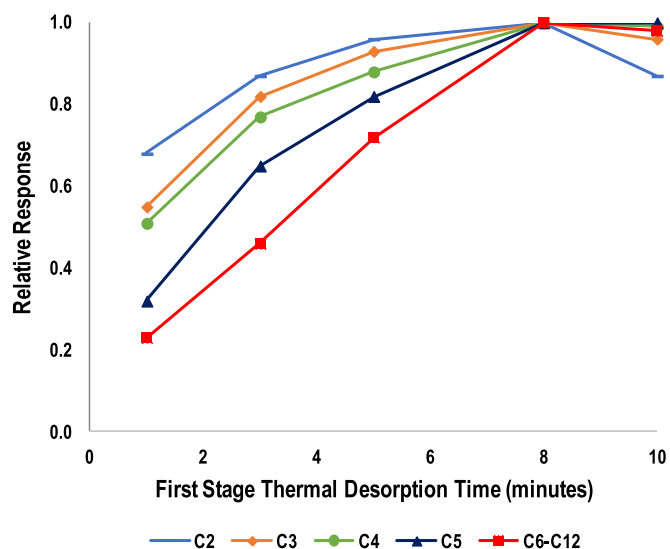


Fig. 6. Relative responses of $\text{VOC}_{\text{SPAMS}}$ desorbed from the adsorbent tubes loaded with standard at 330°C in the first stage of thermal desorption for 1–10 min.

RSD of the average peak areas from seven replicates at the lowest mixing ratio (i.e., 0.08 ppbv) (U.S.EPA, 1999c). The MDLs of all target analytes ranged from 0.001 to 0.055 ppbv, which are lower than, or close to, those reported in other studies (Ribes et al., 2007).

Reproducibility has been examined with regard to both laboratory standards and field samples. Replicate analyses with laboratory standards verify the reproducibility of the analytical methods, whereas replicate analyses of field samples incorporate variabilities of the laboratory process, transport to and from the field, and ambient sampling under different environmental conditions to better represent real-world reproducibility.

Seven replicate analyses of standard gas samples reported RSDs of 0.31–7.10% with a median RSD of 2.56% for 57 $\text{VOC}_{\text{SPAMS}}$ (Table 3). These levels are similar to the three replicate analyses of five roadside samples (i.e., RSDs ranged 1.23–9.47%, with a median of 3.88%). RSDs for different classes of organic compounds did not exceed 10% with the exception of acetylene (C3) for two sets of roadside samples (Li et al., 2017). Most (> 80%) of the RSDs were < 5%. Among the quantified compound classes (excluding alkyne), alkenes had higher RSDs (1.70–6.52%) than the other two compound classes with a median RSD of 3.24%. Roadside samples are affected by the sampling environment in addition to the uncertainties of the analytical process. Consistent precisions between the laboratory standards and the vehicle-dominant samples confirm that the combination of sampling and analytical protocol developed in this study is highly reproducible for $\text{VOC}_{\text{SPAMS}}$ quantification. The RSDs also attained the performance criteria for VOCs measured by the adsorbent method followed by thermal desorption analysis established by Compendium Method TO-17 (U.S.EPA, 1999c).

For analyses of five CRS tubes, Table 4 shows that the differences from the certified values ranged from –2.55% to 0.85% for benzene, toluene, o-xylene, and 1,2,4-trimethylbenzene. Five additional reference standard tests were included (i.e., dichloromethane, 1,1,1-trichloroethane, methyl tert-butyl ether, methyl ethyl ketone, and ethyl acetate) for independent quality assurance; not part of the list of $\text{VOC}_{\text{SPAMS}}$. The desorption accuracy for other $\text{VOC}_{\text{SPAMS}}$ cannot be verified due to the availability of certificate standards.

4. Conclusion

The collection, sample preservation, and analytical protocols for thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) have been optimized for $\text{VOC}_{\text{SPAMS}}$ measurement by the multi-bed adsorbent tube method. Oxidants present in the sample stream, such as O_3 (< 200 ppb), interfere with the stability of target analytes and can

Table 3
Physical properties, linear regression parameters for calibration curves, method detection limits, and method precisions.

Compound	CAS No	M.W. ^a	B.P.(°C) ^b	SIM ^c	Formula	Slope	Intercept	R ²	MDL (µg/m ³) ^d	MDL (ppbv) ^d	RSD _{STD} ^e	RSD _{Sample} ^f
Ethylene	74-85-1	28	-103.7	26	C2H4	1393.8	129.5	0.9995	0.045	0.039	4.11	6.52
Acetylene	74-86-2	26	-83.4	26	C2H2	160.7	764.4	0.9334	0.058	0.055	3.37	9.47
Ethane	74-84-0	30	-88.6	27	C2H6	506.5	-69.1	0.9950	0.040	0.033	1.96	5.23
Propylene	115-07-1	42	-47.4	41	C3H6	7779.2	13,151.0	0.9996	0.071	0.042	2.49	8.22
Propane	74-98-6	44	-42.1	43	C3H8	7218.8	564.6	0.9993	0.035	0.019	5.51	6.12
Isobutane	75-28-5	58	-11.8	43	C4H10	16,474.4	4798.7	0.9992	0.056	0.024	2.49	5.23
1-Butene	106-98-9	56	-6.3	56	C4H8	13,364.6	6182.9	0.9989	0.017	0.008	6.03	4.22
n-Butane	106-97-8	58	-0.5	43	C4H10	16,962.1	1959.4	0.9993	0.040	0.017	1.70	6.25
trans-2-Butene	107-01-7	56	0.88	56	C4H8	11,244.7	765.3	0.9999	0.024	0.010	1.83	3.22
cis-2-Butene	590-18-1	56	3.7	56	C4H8	9601.0	1669.2	0.9993	0.014	0.006	0.12	0.98
iso-Pentane	78-78-4	72	27.8	57	C5H12	8778.0	1642.5	0.9994	0.005	0.002	6.35	3.56
1-Pentene	109-67-1	70	30.1	70	C5H10	7528.3	2752.8	0.9998	0.038	0.013	2.83	5.22
n-Pentane	109-66-0	72	36.1	72	C5H12	13,049.8	4356.6	0.9997	0.057	0.019	0.46	1.98
Isoprene	2004-70-8	68	27.8	67	C5H8	8335.0	1444.0	0.9998	0.013	0.005	3.40	2.56
trans-2-Pentene	646-04-8	70	37.0	70	C5H10	13,758.2	-1252.6	0.9998	0.033	0.012	0.17	1.22
cis-2-Pentene	627-20-3	70	37.0	70	C5H10	13,644.7	-2324.7	1.0000	0.017	0.006	2.27	4.65
2,2-Dimethylbutane	75-83-2	86	49.7	71	C6H14	9815.1	-339.0	0.9993	0.015	0.004	0.78	4.23
Cyclopentane	287-92-3	70	50.0	70	C5H10	6092.3	-236.6	0.9993	0.037	0.013	0.28	3.27
2,3-Dimethylbutane	79-29-8	86	58.7	86	C6H14	5272.2	-692.2	1.0000	0.016	0.004	4.83	5.29
2-Methylpentane	43,133-95-5	86	60.3	71	C6H14	15,300.6	4467.0	0.9999	0.083	0.024	2.47	3.33
3-Methylpentane	96-14-0	86	64.0	57	C6H14	16,539.4	-1970.1	1.0000	0.020	0.006	0.28	2.86
1-Hexene	592-41-6	84	63.3	84	C6H12	7314.1	-256.2	0.9992	0.011	0.003	3.10	3.56
n-Hexane	110-54-3	86	68.7	86	C6H14	28,313.9	-4038.9	0.9999	0.064	0.018	3.38	4.11
Methylcyclopentane	96-37-7	84	71.8	84	C6H12	6239.1	549.5	0.9975	0.026	0.008	4.85	5.23
2,4-Dimethylpentane	108-08-7	100	80.5	85	C7H16	5285.3	-1159.5	0.9999	0.015	0.004	1.00	2.71
Benzene	71-43-2	78	80.1	78	C6H6	31,919.0	36,200	0.9957	0.049	0.015	7.10	6.55
Cyclohexane	110-82-7	84	80.7	84	C6H12	13,066.2	-557.5	1.0000	0.016	0.005	0.27	3.08
2-Methylhexane	591-76-4	100	90.0	85	C7H16	15,283.9	-3302.2	1.0000	0.027	0.007	0.31	2.20
2,3-Dimethylpentane	565-59-3	100	89.8	71	C7H16	14,588.6	-955.7	0.9996	0.029	0.007	0.73	3.65
3-Methylhexane	589-34-4	100	90.7	71	C7H16	11,495.7	-1034.9	0.9990	0.024	0.006	1.45	2.69
2,2,4-Trimethylpentane	540-84-1	114	99.2	99	C8H18	29,132.5	-4351.2	0.9995	0.047	0.010	0.56	1.77
n-Heptane	142-82-5	100	98.8	100	C7H16	10,845.4	-2048.3	0.9991	0.028	0.007	0.38	1.23
Methylcyclohexane	108-87-2	98	100.9	98	C7H14	14,972.1	-3500.1	0.9999	0.019	0.005	1.26	3.22
2,3,4-Trimethylpentane	565-75-3	114	113.5	71	C8H18	15,529.0	-4127.4	0.9997	0.033	0.007	0.69	1.89
Toluene	108-88-3	92	110.6	91	C7H8	31,669.0	-12,279	0.9992	0.083	0.026	4.34	5.13
2-Methylheptane	592-27-8	114	117.8	99	C8H18	17,137.1	-5425.8	0.9996	0.022	0.005	0.36	2.47
3-Methylheptane	589-81-1	114	118.8	85	C8H18	12,497.1	-2902.8	0.9991	0.030	0.006	0.08	1.69
n-Octane	111-65-9	114	125.8	114	C8H18	14,439.9	-3520.6	0.9994	0.025	0.005	0.70	1.56
Ethylbenzene	100-41-4	106	136.2	106	C8H10	36,066.8	8217.9	0.9995	0.018	0.004	1.77	3.29
m-Xylene ^g	108-38-3	106	139.1	106	C8H10	60,865.4	1499.5	0.9992	0.036	0.008	1.82	3.56
p-Xylene ^g	106-42-3	106	138.3	106	C8H10	60,865.4	1499.5	0.9992	0.036	0.008	1.82	3.56
Styrene	100-42-5	105	146	104	C8H8	13,775.3	-810.4	0.9992	0.028	0.006	3.64	4.21
o-Xylene	95-47-6	106	144.4	106	C8H10	27,197.4	-2886.3	0.9997	0.013	0.003	0.91	1.89
n-Nonane	111-84-2	128	151.7	128	C9H20	15,897.5	-2478.7	1.0000	0.021	0.004	0.91	1.74
Isopropylbenzene	98-82-8	120	152.4	120	C9H12	34,700.6	-8199.4	0.9997	0.018	0.004	1.08	2.06
n-Propylbenzene	103-65-1	120	159.2	120	C9H12	50,739.5	-1587.0	0.9991	0.015	0.003	3.64	4.13
m-Ethyltoluene	620-14-4	120	159.7	120	C9H12	38,892.1	-332.8	0.9958	0.011	0.002	1.87	3.08
p-Ethyltoluene	25,550-14-5	120	162.0	120	C9H12	39,026.5	-1995.6	0.9984	0.014	0.003	0.44	3.21
1,3,5-Trimethylbenzene	108-67-8	120	164.7	120	C9H12	29,195.7	-4027.4	0.9986	0.007	0.001	0.61	2.46
o-Ethyltoluene	611-14-3	120	165.2	120	C9H12	32,171.0	-5983.4	0.9996	0.014	0.003	1.14	2.26
1,2,4-Trimethylbenzene	95-63-6	120	169.4	105	C9H12	28,174.9	-3504.3	0.9960	0.014	0.003	0.73	1.71
n-Decane	124-18-5	142	174.2	85	C10H22	20,272.0	-2165.3	0.9997	0.015	0.002	0.87	2.69
1,2,3-Trimethylbenzene	526-73-8	120	176.7	105	C9H12	22,142.4	-3807.1	0.9995	0.012	0.002	0.61	3.23
m-Diethylbenzene	141-93-5	134	182.0	134	C10H14	15,486.0	-2208.4	0.9996	0.013	0.002	1.30	2.22
p-Dimethylbenzene	105-05-5	134	183.7	134	C10H14	15,132.9	-2766.0	0.9996	0.012	0.002	1.88	3.68
Undecane	1120-21-4	156	195.6	85	C11H24	14,248.3	-4151.5	0.9998	0.023	0.004	1.76	4.10
Dodecane	112-40-3	170	200.7	85	C12H26	8963.9	-809.6	0.9998	0.026	0.004	3.43	3.69

^a Molecular weight.

^b Boiling point.

^c Selective ion used for quantification by MS.

^d Minimum detection limit is expressed in assumption of a sampling volume of 3 l.

^e Relative standard derivation from seven replicates of standard.

^f Relative standard derivation for three collocated roadside samples.

^g m-Xylene and p-xylene are co-eluted.

be efficiently removed by a laboratory-made potassium iodide (KI) scrubber installed upstream of the sampling system. No proper media was found that can efficiently remove water content without biasing VOCs_{PAMS} measurements. Low storage temperature (-10 °C) of the adsorbent tubes allows the best preservation of both blanks and samples. The optimized multi-bed adsorbent tube sampling and analytical protocols result in low method detection limits (MDLs) of 0.055ppbv,

good precisions (< 10%), and high accuracy (< 3%) for the quantification of VOCs_{PAMS}.

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Table 4
Concentrations (ng/tube) of four VOCs in certified CRS standard tubes determined by the TD-GC/MS method.

	VOC concentrations (ng/tube) determined by the TD-GC/MS method					CRS certified value (ng)		Relative difference (%) ^a	
	Tube 1	Tube 2	Tube 3	Tube 4	Tube 5	Average	Standard deviation		
VOCs									
Benzene	100.5	103.4	104.2	101.1	104.4	102.7	1.80	100.1	− 2.55%
Toluene	101.8	100.2	101.7	104.4	100.1	101.6	1.74	100.5	− 1.12%
o-Xylene	99.9	99.2	97.1	98.9	99.2	98.9	1.05	99.7	0.85%
1,2,4-Trimethylbenzene	97.3	101.1	99.2	100.4	100.0	99.6	1.46	100.2	0.60%

^a The relative difference is expressed as $(b - a)/a$ %, where a is the CRS certified value and b is the TD-GC/MS value.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosres.2017.11.026>.

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