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Optimization of a Method for the Detection of Biomass-Burning Relevant VOCs in Urban Areas Using Thermal Desorption Gas Chromatography Mass Spectrometry

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Received: 31 January 2020; Accepted: 10 March 2020; Published: 11 March 2020

Abstract: Forest fire smoke influence in urban areas is relatively easy to detect at high concentrations but more challenging to detect at low concentrations. In this study, we present a simplified method that can reliably quantify smoke tracers in an urban environment at relatively low cost and complexity. For this purpose, we used dual-bed thermal desorption tubes with an auto-sampler to collect continuous samples of volatile organic compounds (VOCs). We present the validation and evaluation of this approach using thermal desorption gas chromatography mass spectrometry (TD-GC-MS) to detect VOCs at ppt to ppb concentrations. To evaluate the method, we tested stability during storage, interferences (e.g., water and O_3), and reproducibility for reactive and short-lived VOCs such as acetonitrile (a specific chemical tracer for biomass burning), acetone, n-pentane, isopentane, benzene, toluene, furan, acrolein, 2-butanone, 2,3-butanedione, methacrolein, 2,5- dimethylfuran, and furfural. The results demonstrate that these VOCs can be quantified reproducibly with a total uncertainty of ≤30% between the collection and analysis, and with storage times of up to 15 days. Calibration experiments performed over a dynamic range of 10–150 ng loaded on to each thermal desorption tube at different relative humidity showed excellent linearity ($r^2 \geq 0.90$). We utilized this method during the summer 2019 National Oceanic and Atmospheric Administration (NOAA) Fire Influence on Regional to Global Environments Experiment–Air Quality (FIREX-AQ) intensive experiment at the Boise ground site. The results of this field study demonstrate the method's applicability for ambient VOC speciation to identify forest fire smoke in urban areas.

Keywords: VOC auto-sampler; acetonitrile; acetone; thermal desorption tubes; GC-MS

1. Introduction

Every year, forest fires inject several hundred million metric tons of reactive organic compounds into the atmosphere globally [1–3]. Forest fires pose a persistent adverse threat to urban air quality, particularly in relation to fine particulate matter ($PM_{2.5}$) and ozone (O_3) [4,5]. Production of O_3 from forest fires is highly variable [6], and each fire is unique in terms of emissions, transport pathway, plume injection heights, and photochemistry. Eulerian grid models often have difficulty accurately modeling downwind O_3 concentrations [4,7–9]. Because of these complexities and the impacts at relatively low particulate matter concentrations, it is critical to develop additional tracers for forest fire influence.

Several studies [10–13] have found acetonitrile to be an excellent tracer for biomass emission plumes in both laboratory and field studies and over a variety of ecosystems. Biomass burning is

the dominant source of acetonitrile, with contribution from automobiles and other sources less than 6% of the global budget [10]. Being a relatively inert molecule with an atmospheric lifetime of about 7 months [14], it is better suited than levoglucosan as a chemical tracer of emission from biomass burning. Along with acetonitrile, other oxygenated volatile organic compounds (VOCs) such as acetone, furan, acrolein, methacrolein, 2-butanone, 2,3-butanedione, 2,5-dimethylfuran, and furfural and aromatic VOCs, namely benzene and toluene, are also emitted in relatively large amounts from forest fires [1,15–17]. Measurements of these biomass burning tracers would help us identify the influence of forest fire plumes in urban areas.

Soft chemical ionization mass spectrometric, gas chromatographic, and spectroscopic techniques have been widely used for the quantification of VOC smoke tracers in ambient air [17–20]. However, on-site field deployment of such instruments is not always feasible because of cost and logistical issues. For reactive VOCs, the U.S. Environmental Protection Agency (EPA) recommends collecting whole air samples in stainless steel canisters for the determination of VOCs but the high cost per canister (>1000 USD per canister) and low time resolution are deterrents to large-scale usage. Offline samplers based on solid adsorbents and whole air Tedlar bags experience interferences due to reported changes in sample integrity that can occur at the collection, transfer, and analysis stages [21,22]. Several recent studies have further investigated the storage stability and have demonstrated improved application of diffusive VOC samplers and Tedlar bags for selected VOCs [23,24]. As an alternative to the canister-based sampling and to the previous sorbent-based methods (TO-1, TO-2, TO-14, and TO-15), the EPA has improved and presented the determination of VOCs in the ambient air using active sampling onto sorbent tubes in compendium method TO-17 [25].

However, to date, there has been no systematic study investigating the potential use of dual-bed thermal desorption (TD) tubes using an automated VOC sampler for sampling and offline gas-chromatography mass spectrometry (GC-MS) measurements of a suite of VOCs, in particular acetonitrile (a biomass burning tracer), reactive oxygenated VOC (acetone, furan, acrolein, methacrolein, 2-butanone, 2,3-butanedione, 2,5-dimethylfuran, and furfural), n-pentane, isopentane, benzene, and toluene.

Here, we evaluate a protocol for offline collection of a suite of VOCs using dual-bed TD tubes with an auto-sampler. This sampler does not require gas cylinders or high-maintenance vacuum pumps to collect a suite of VOC compounds. This sorbent approach to monitor VOCs is tested as per the criteria recommended by EPA TO-17 method. We assessed the stability of thirteen VOCs, namely acetonitrile, acetone, n-pentane, isopentane, benzene, toluene, furan, acrolein, methacrolein, 2-butanone, 2,3-butanedione, 2,5-dimethylfuran, and furfural over a 15-day storage period using a premixed gas standard and a complex wood smoke air sample. After the validation experiments, we deployed these TD tubes with an auto-sampler at two grounds sites: Spokane, Washington, and Boise, Idaho, as the part of the National Oceanic and Atmospheric Administration (NOAA) Fire Influence on Regional to Global Environments Experiment–Air Quality (FIREX-AQ) 2019 field experiment.

2. Experimental Methods

2.1. Description of VOC Auto-sampler and Dual-be d Thermal Desorption Tube

Figure 1a shows the internal view of the VOC auto-sampler, which consists of two 16-port Valco dead-end selector valves (VICI Valco Microelectric actuated 16 port; Model-EMTSD16MWE), O_3 filter, mass flow controller (MFC) (Omega; Model-FMA5510A), pressure sensor (Auto Tran; Model-860-0.00/5.00-P-12-0-P), pump (Bison, Model-051-206-4005 Dc motor), labjack U6, peltier heating/cooling system (TE Technology; Model-PS-24-6.5), power supply (TE Technology; Model-TC-36-25-RS232), relays and USB hub. This sampling system uses TD tubes to collect and concentrate VOCs of interest. This system can accommodate up to 16 TD tubes using the 16-port valves to concentrate ambient air samples 1 tube at a time, while keeping the other tubes sealed. The instrument is built into a hard-backed suitcase for portability and ruggedness. This sampler can

be operated at any site with a 110–120 VAC power source and (optionally) an internet connection for off-site monitoring. Maximum current required is 2 A @110 VAC. Flow and sample volume are controlled with an MFC and pump, along with the sampling interval set in the accompanying LabVIEW program, which is operated from a laptop PC. Sampling intervals can be set to as short as a few minutes or as long as a few days. Delays between samples can also be added to fully maximize the time between maintenance intervals (e.g. filter paper change) and sampling efficiency. Configuration and sampling schedule options are easily managed through the LabVIEW interface for the collection of VOCs in any pollution event and environment.

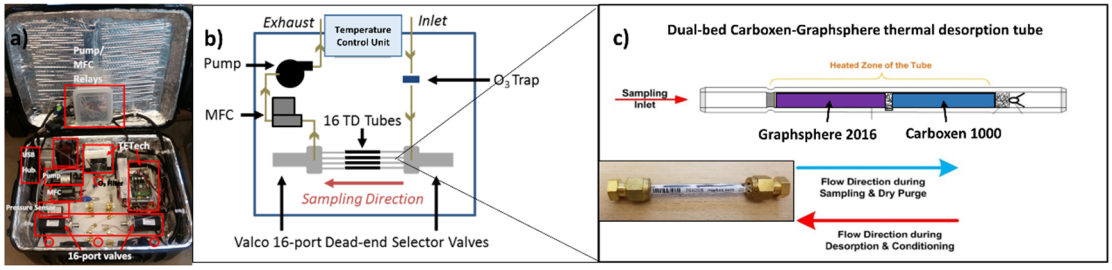

Figure 1. (**a**) Internal view of the volatile organic compound (VOC) suitcase sampler; (**b**) Flow diagram of VOC suitcase sampler; (**c**) Schematic diagram of the dual-bed Carboxen-Graphsphere TD tubes.

Figure 1b depicts the sample flow through the auto-sampler. Interference due to O_3 is removed by the in-line O_3 trap. The O_3 trap consists of a Gelman particle filter (1 µm) that has been coated in sodium thiosulfate pentahydrate (Sigma-Aldrich, USA). This filter will also remove $PM_{2.5}$. Previous studies by Helmig (1997) and Polmann et al. (2005) [26,27] have extensively discussed and demonstrated the preparation and validity of these O_3 traps for the measurements of various reactive VOCs reported in this study at various ambient ozone concentrations. The internal temperature is kept constant at room temperature (circa 25 °C) using a Peltier heating/cooling system. Keeping the instrument internally warmer than the outside temperature allows us to sample ambient air without the condensation of water in the TD tubes and subsequently out of the GC-MS. TD tubes are installed between the two 16-port Valco valves as shown in Figure 1b. Below the pump is the MFC, which regulates the sample flow through the TD tubes. Typically, samples are collected at a flow rate of 50 mL/min for 6 hours, each sample based on the break-through volume test as described in EPA TO-17 method. This particular MFC is manually controlled via a potentiometer. Upstream of the MFC, a nylon particulate inline filter is installed. A pressure sensor installed below the MFC (see Figure 1a) monitors the pressure during sampling and is helpful in the event of a valve misalignment or blockage in flow.

In this study, we used glass TD tubes with a 15mm restriction. These are 89 mm long and have a 6.4 mm outer diameter. The tubes arrived empty and are packed with two sorbents: Graphsphere 2016 (Sigma-Aldrich, St. Louis, MO, USA) and Carboxen 1000 (Sigma-Aldrich, St. Louis, MO, USA). Graphsphere 2016 collects C5–C12 hydrocarbons and is first in line in the sampling flow (see Figure 1c). Carboxen 1000 collects C2–C5 hydrocarbons and is second in the sampling flow. We used slightly more Graphsphere than Carboxen (C/G ratio = 0.85) to ensure that the Carboxen collects less "unwanted" compounds. Before packing any new tubes, it is essential to clean the glass tubes, torsion springs, and quartz wool. Glass tubes and torsion spring are sonicated in methanol for about 30 minutes and heated up to 150 °C. For the quartz wool, it is heated up to 550 °C for 24 hours with inert, clean N_2 gas flowing through the wool during heating. After conditioning, tubes are packed with ~122 mg of Graphsphere 2016 and ~103 mg of Carboxen 1000. After packing, each tube is conditioned at a temperature of 330 °C for 2 hours for the first conditioning. After tubes have been used for sampling, a 30-minute recondition at 330 °C is enough to clean.

2.2. Analysis of VOCs Sampled TD Tubes using TD-GC-MS

A Markes TD 100 is used for desorption of the TD tubes. This instrument can hold up to 100 TD tubes. Tubes are heated to ~280 °C for a 6-minute desorption cycle and re-concentrated on the downstream cold trap (Markes U-T15ATA-2S), which is kept at 15 °C. Next, the cold trap is flash heated (100 °C/second) to ~280 °C for quick injection into the GC-MS via a heated (120 °C) sample line.

For VOC analysis, a Restek Rxi-624Sil MS column (30 m, 0.25 mm interior diameter, 1.4 μm df) is used. Initially, the column temperature is maintained at 35 °C for 1 minute, and then the temperature is increased at 15 °C/minute up to 100 °C (with no maximum temperature hold) and finally temperature is increased by 40 °C/minute up to 200 °C (with no maximum temperature hold). A single quadrupole mass spectrometer operated in scan mode (35–200 a.m.u) is used for the detection of VOCs. The temperature of the mass transfer line and ion source are maintained at 250 °C and 300 °C, respectively. Carrier and purge gases used in this analysis are helium and nitrogen, respectively. This desorption procedure is adopted and optimized from earlier studies [25–27].

A gas standard mixture (Apel Riemer Environmental, Inc., Miami, Florida, USA) contained VOCs at a mixing ratio of circa 500 nmol mol^{-1} and is used to perform calibrations. Calibrations are performed at different levels of humidity (~0% RH, 50% and 90% RH) by dynamic dilution with zero air at four different VOC loadings (in the range of 9–150 ng) for each VOC as shown in Figure S1. The standard gas flow (~10 sccm) was diluted with ~200 sccm synthetic air (99.999% purity; Sigma gases). The diluted gas standard mixture is sampled onto the TD tubes at room temperature using the VOC suitcase sampler for various durations (2–10 minutes) to get the desired loading. The flows of both the standard gas and zero air are controlled using MFCs. Flows from MFCs were also measured independently before and after the calibration experiments using a Gilibrator flow meter. Calibration results, shown in Figure S1, showed excellent linearity over the entire dynamic range ($r^2 > 0.90$) of VOC loadings and at different relative humidities; the exceptions are acetonitrile and oxygenated VOCs (acetone, furan, acrolein, 2-butanone, 2,3-butanedione, methacrolein, 2,5-dimethylfuran, and furfural) at 90% RH, which showed linearity up to 40 ng and 60 ng of loading, respectively. Breakthrough volumes while sampling circa 4 ppb concentrations at 90% RH for n-pentane, isopentane, benzene, toluene, furan and 2,5-dimethylfuran is about 8 liters and for acetone, acrolein, methacrolein, 2,3-butanedione, 2-butanone, and furfural is about 4 liters. Each of the individually detected compounds was verified based on their retention time compared to calibration gas standard and compare with the National Institute of Standards and Technology (NIST) library. Acetonitrile, acetone, isopentane, n-pentane, benzene, toluene, furan, acrolein, 2-butanone, 2,3-butanedione, methacrolein, 2,5-dimethylfuran and furfural were detected at selected organic ions: m/z 41, m/z 58, m/z 43, m/z 43, m/z 78, m/z 91, m/z 68, m/z 56, m/z 72, m/z 83, m/z 70, m/z 96 and m/z 96, respectively. Figure 2a–c illustrates the retention time of the species in gas standard and in ambient air samples, which are consistent.

The TD tubes can be re-used and/or reconditioned for additional sampling. Tubes are conditioned using Markes T-20 cleaner as described in the EPA-TO-17 method. The expected lifetime of each sorbent is approximately 100–200 cycles before the sorbent needs to be replaced.

Detection limits and precision errors of the duplicate pairs and for the distributed volume pairs for the reported VOCs are shown in Table 1 as determined per the EPA TO-17 method. Detection limits are determined by sampling the VOC free zero air for 30 minutes at a flow rate of 50 sccm. Detection limit for n-pentane, isopentane, acetone, acetonitrile, benzene, toluene, furan, acrolein, methacrolein, 2-butnaone, 2,3-butanedione, 2,5-dimethylfuran, and furfural are in the range of 0.02–0.05 ppb. Precision error of duplicate pairs and for distributed volumes are within the compliance of the EPA TO-17 requirement of 15% and 25%, respectively. For acetonitrile, global background concentrations are circa 0.07 ppb [10–14]. Hence, this procedure should be sufficient for determining acetonitrile in nearly all environments.

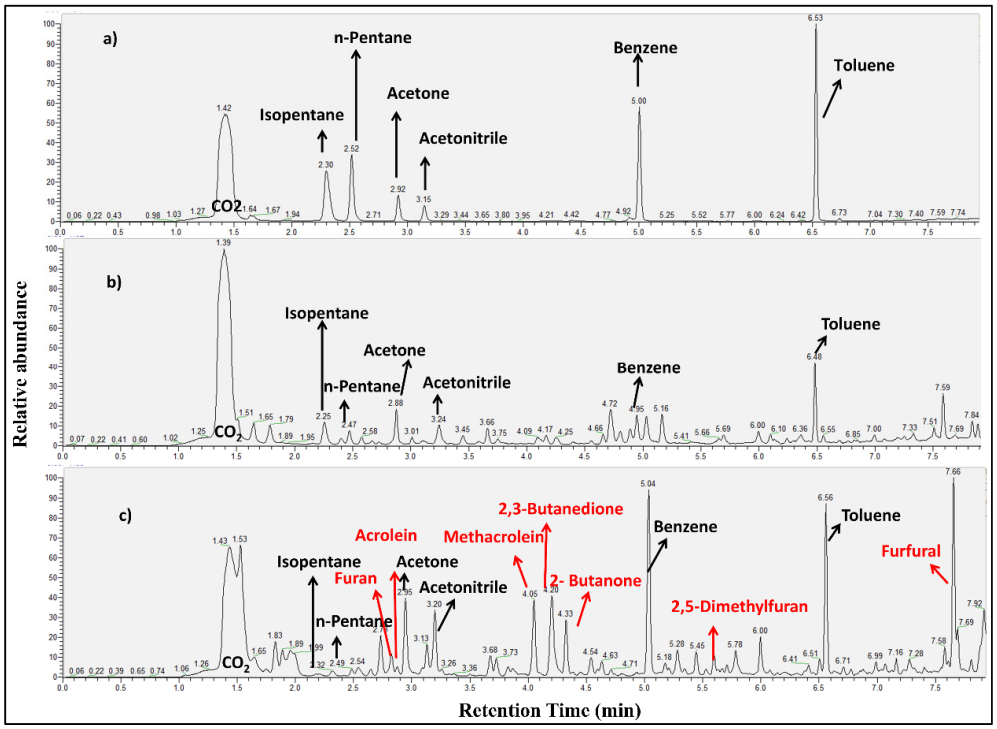

Figure 2. Chromatogram obtained using TD-GC-MS from the dual-bed samples collected from (**a**) Premixed gas standard (Apel Riemer); (**b**) Boise, Idaho, on a non-smoky day at (07.30.2019 11:00 PM to 07.31.2019 05:00 AM); and (**c**) Boise, Idaho, on a smoky day (07.31.2019 11:00 PM to 08.01.2019 05:00 AM). Peaks labelled in red are rarely reported VOCs in the ambient air.

Table 1. Detection limits and precision errors for the sampled VOCs measured using dual-bed Carboxen-Graphsphere thermal desorption (TD) tubes.

Compound Name	DL (ng)	DL (ppb)	Precision Error of Duplicate Pairs (%)	Precision for the Distributed Volume Pairs (%)
Acetonitrile	1.08	0.03	4.35	12.34
Acetone	1.69	0.03	5.48	12.78
n-Pentane	1.06	0.02	9.15	15.34
iso-pentane	1.05	0.02	6.34	13.23
Benzene	2.08	0.03	7.96	11.45
Toluene	2.03	0.03	4.57	10.23
Furan	1.10	0.03	7.21	15.94
Acrolein	1.59	0.04	8.47	18.74
2-Butanone	1.76	0.04	10.16	19.89
2,3-Butanedione	1.92	0.04	11.37	18.14
Methacrolein	2.10	0.03	13.66	19.95
2,5-Dimethylfuran	2.12	0.04	12.55	15.13
Furfural	2.05	0.05	14.50	20.59

The total uncertainty associated with measurements of each VOC reported in this study was less than 30%. This was calculated using the root mean square propagation of individual uncertainties including the 6% accuracy error inherent in the VOC gas standard concentration, the 2 σ instrumental precision error while sampling duplicate pairs of the VOC and error in the flow reproducibility of the two MFCs.

3. Results and Discussion

3.1. Validation Experiments Assessing Stability of VOCs inside TD Tubes over a 15-day Period

In order to assess the stability of acetonitrile, acetone, isopentane, n-pentane, benzene, toluene furan, acrolein, methacrolein, 2-butanone, 2,3-butanedione, 2,5-dimethylfuran, and furfural in the TD tubes, we conducted experiments with (1) gas mixtures containing these six VOCs at circa 5 ppb (total: 12 TD tubes) and (2) with wood smoke samples containing these six VOCs (total: 12 TD tubes).

3.1.1. Experiments with Gas Mixtures Containing the Thirteen VOCs

Using the VOC auto-sampler, 12 dual-bed TD tubes (Graphsphere 2016 and Carboxen 1000) were sampled for 5 minutes at a flow rate of 50 sccm with the gas stream containing thirteen VOCs at circa 5 ppb at room temperature. The gas stream mixtures of ~5 ppb concentration was generated by dynamic dilution of the VOC gas standard containing acetonitrile, acetone, isopentane, n-pentane, benzene, toluene, furan, acrolein, methacrolein, 2-butnaone, 2,3-butanedione, 2,5-dimethylfuran, and furfural each at ~ 500 ppb. Dilution using VOC-free zero air was accomplished using a synthetic air (99.999% purity; Sigma). The tubes were then stored in a dark container at room temperature (~ 25 °C).

Out of 12 sampled TD tubes, 2 tubes were analyzed on the same day (termed day 0) and then 2 were analyzed every 3 days on days 3, 6, 9, 12, and 15. The choice for a 15-day study period was based on the rationale that 15 days would be adequate for transportation of air samples from remote locations to an instrumental facility with a TD-GC-MS instrument.

Figure 3 summarizes the stability results of VOCs over the storage of 15 days. The vertical axes show the ratio C_t/C_i (ppb/ppb), where C_t is the VOC's concentration in the flask after "t" days ($t \leq 15$) of storage and C_i is the averaged VOC concentration measured from the two TD tubes on the day it was sampled. Vertical error bars in each histogram in Figure 4 represent the 1σ precision error when measuring the VOCs from the two TD tubes analyzed after every 3 days, and so on. The ratio of C_t/C_i for all thirteen VOCs was always within the 1σ instrumental precision error varying between 0.9 and 1.1. Therefore, as shown in Figure 3, the synthetic gas mixture containing six VOCs was stable over the 15-day study period.

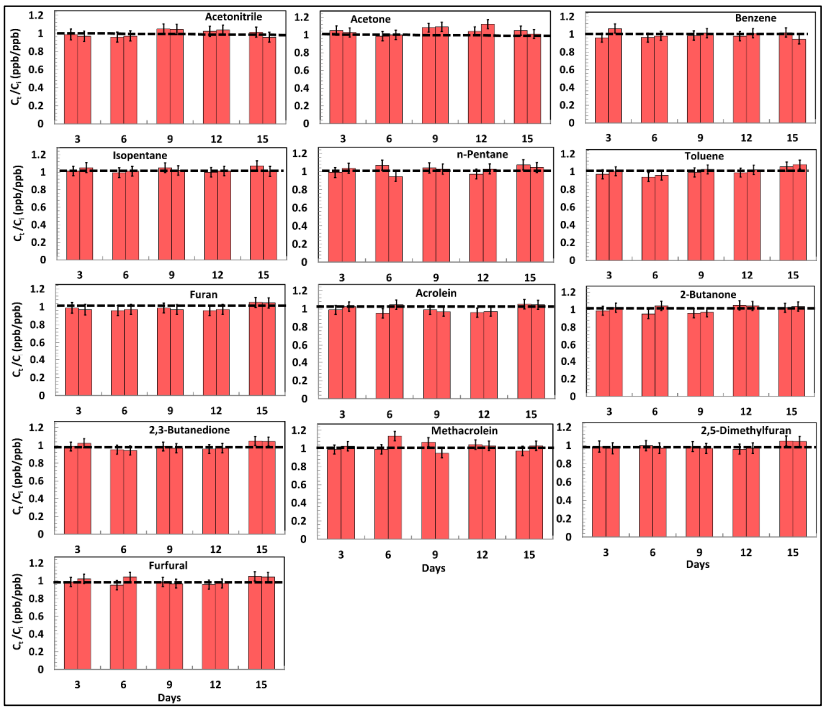

Figure 3. Stability of VOCs over the storage of 15 days inside the dual-bed Carboxen-Graphsphere TD tubes sampled using calibration gas. Histograms in each VOC plot correspond to the ratio of VOC concentration measured after "t" days of storage (C_t (ppb)) relative to the initial concentration on day 0 (C_i (ppb)). Error bars on each histogram correspond to 1 σ precision from the two TD tubes analyzed every 3 days.

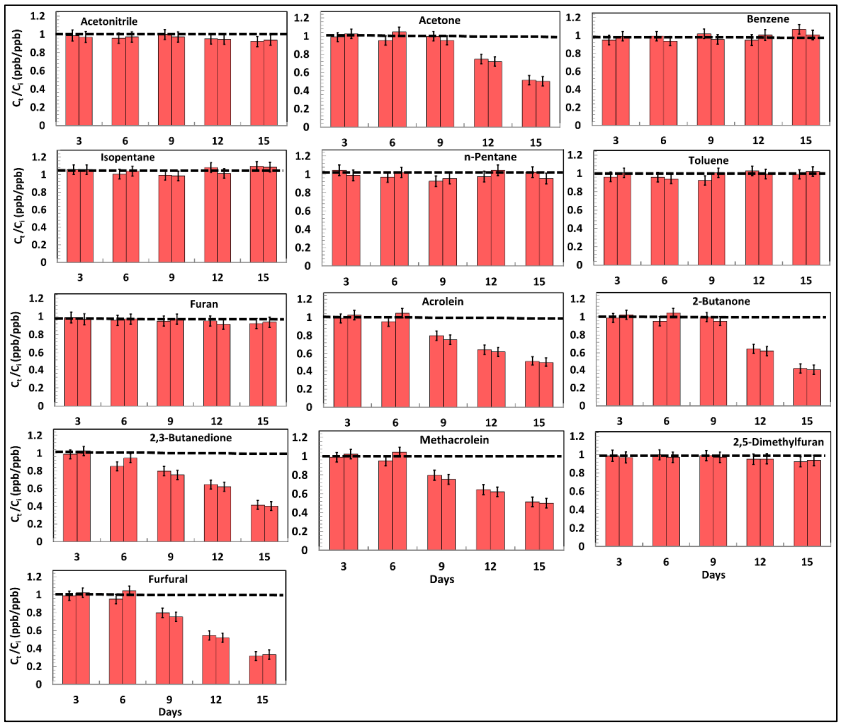

Figure 4. Stability of VOCs over the storage of 15 days inside the dual-bed Carboxen-Graphsphere TD tubes sampled using wood smoke. Histograms in each VOC plot correspond to the ratio of VOC concentration measured after "t" days of storage (C_t (ppb)) to the initially measured averaged concentration of VOC on day 0 (C_i (ppb)). Error bars on each histogram correspond to 1 σ precision error when measuring the VOCs from the two TD tubes analyzed every 3 days.

3.1.2. Experiments with Wood Smoke Containing the Thirteen VOCs

In a second series of experiments, we assessed the stability of the thirteen VOCs in wood smoke samples that were collected and stored in the TD tubes over a 15-day period. For this experiment, small wood logs were burnt at a fire pit on the University of Washington Bothell campus. To obtain a uniform sample, we collected wood smoke into a preconditioned Tedlar bag (volume 25 liters) similar to active sampling procedure followed by Chandra et al. (2017) [20]. The Tedlar bag was preconditioned by filling it with VOC free zero air and evacuated thrice to remove any potential residual effects before collecting the wood smoke. This Tedlar bag was immediately transported to the analysis lab within 10 minutes of sample collection and sub-sampled into 12 TD tubes. These samples were then analyzed over 15 days as described previously.

Figure 4 summarizes the results observed for the wood smoke samples in 12 TD tubes in a manner analogous to Figure 3. The results showed that even for the air samples with the complex chemical composition of wood smoke, the stability of the thirteen VOCs in ambient air samples was comparable to simpler mixtures containing only these compounds (Section 3.1.1). The ratios of "C_t/C_i (ppb/ppb)" for acetonitrile, isopentane, n-pentane, benzene, toluene, furan, and 2,5-dimethylfuran varied between 0.9 and 1.1 over a period of 15 days and were always within the respective 1σ precision error. For acetone, acrolein, methacrolein, 2-butanone, 2,3-butanedione, and furfural, similar results were observed up to 6 days of storage but after this time showed decay by 40%. This could be due to the surface reactions with the inner walls of the TD tube and/or unwanted chemical reaction at the adsorbent sites with moisture and other oxidants present in the wood smoke. It is known that several oxidants such as organic acids (acetic acid, formic acid) and oxides of nitrogen emit from wood smoke [15–17]. Haper (2000) [28] stated that co-sampling of carbonyls along with other oxidants and water on the adsorbents could have cause negative artifacts on storage of carbonyl compounds due to several unwanted chemical reactions (e.g. aldol condensation and hydration) on the surface of adsorbent/inner walls of TD tube. Hence, our results indicate the decay of carbonyl oxygenated VOCs can occur after the 6 days of storage, likely due to the factors discussed previously [28].

Note that the seven oxygenated VOCs reported in this study namely furan, acrolein, methacrolein, 2-butanone, 2,3-butanedione, 2,5-dimethylfuran, and furfural have been rarely measured in the ambient air due to several analytical constrains. Nevertheless, using this sampling protocol these seven VOCs were observed in a few samples collected in Boise, Idaho, as a part of the NOAA FIREX AQ-2019 experiment discussed in later sections. Several previous studies [1,15–17,29] have shown significant emissions of these oxygenated VOCs from biomass burning. In principle, measurements and the emission ratios of these additional seven oxygenated VOC smoke tracers could help estimate the age of a smoke plume [29,30].

In order to ascertain the statistical difference if any pertaining to stability of the thirteen VOCs (acetonitrile, acetone, isopentane, n-pentane, benzene, toluene, furan, acrolein, methacrolein, 2-butanone, 2,3-butanedione, 2,5-dimethylfuran, and furfural) during storage, a paired t-test was employed for each VOC using the concentration values measured after "t" days (C_t) of storage in the TD tube and the initial concentration on day 0 (C_i). This test was performed by combining the data from all 24 TD tubes. Based on the t-tests, it could be concluded with more than 95% confidence that there was no difference in the VOC concentrations measured from the TD tube on day 0 and on each of the subsequent days for a period of up to 15 days for acetonitrile, isopentane, n-pentane, benzene, toluene, furan, and 2,5-dimethylfuran. There was no difference with a confidence level of 95% through day 6 for acetone, acrolein, methacrolein, 2-butanone, 2,3-butanedione, and furfural. Therefore, the experiments and the statistical tests demonstrate that the methodology presented in this work is suitable for characterizing acetonitrile, isopentane, n-pentane, benzene, toluene, furan, and 2,5-dimethylfuran in ambient air reproducibly within the respective precision errors, if analyzed within 15 days of sample collection in the TD tubes, and within 6 days for acetone, acrolein, methacrolein, 2-butanone, 2,3-butanedione, and furfural.

3.2. Application of the Dual-bed TD Tubes with VOC Auto-samplers in Ambient Air at A Ground Site in Boise, Idaho

After the validation experiments described above, we employed the dual-bed TD tubes with the VOC auto-sampler at Gonzaga University, Spokane, Washington (47.6670° N, 117.4014° W, 20 m a.g.l), and at St. Luke's Meridian, Boise, Idaho (43.6123° N, 116.3937° W, 10 m a.g.l.), as a part of the NOAA FIREX AQ-2019 field experiment. We chose these sites because they are frequently affected by biomass burning each year [7]. The ambient samples were collected using dual-bed TD tubes at Spokane and Boise from 06/14/2019 08:00 PM to 07/19/2019 09:30 AM and 07/27/2019 11:00 AM to 09/12/2019 03:00 PM, respectively. Each sample was collected over 6 hours at a sample flow rate of 50 ml/min. The collected samples were transported in a dark container stored at ambient temperature and analyzed within 7 days of collection at University of Washington Bothell lab for the 13 VOCs, namely, acetonitrile, acetone, isopentane, n-pentane, benzene, furan, acrolein, methacrolein, 2-butanone, 2,3-butanedione, 2,5-dimethylfuran, and furfural using TD-GC-MS as described in Section 2.2. Figures 2b and 2c show the chromatogram obtained using TD-GC-MS from the samples collected at Boise, Idaho, on a non-smoky day (07/30/2019 11:00 PM to 07/31/2019 05:00 AM) and a smoky day (07/31/2019 11:00 PM to 08/01/2019 05:00 AM), respectively.

Figure 5 shows the time series of the ambient concentrations (as 6-hour means) for the six VOCs and $PM_{2.5}$ during 07/27/2019 11:00 AM to 09/12/2019 03:00 PM. In total, 183 samples were collected during this period. Hourly averaged $PM_{2.5}$ measurements were obtained from the St. Luke's Meridian EPA measurement site in Boise, Idaho. These were further averaged to 6 hours as per VOC sampling time periods to be consistent with our analysis. Figure S2 summarizes the Spokane VOC concentrations in a manner analogous to Figure 5. A data gap between 7/2/2019 and 7/11/2019 occurred was due to malfunctioning of VOC auto sampler due to pump failure. The average ambient concentrations observed at Boise during the study period for acetonitrile, acetone, n-pentane, isopentane, benzene, and toluene were 0.14 ± 0.11 ppb, 1.14 ± 0.74 ppb, 0.64 ± 0.61 ppb, 1.89 ± 1.82 ppb, 0.14 ± 0.09 ppb, and 0.64 ± 0.61 ppb, respectively. We note that in most of the samples collected at the Spokane and Boise measurement sites, the ratios of isopentane (IP) to n-pentane (P) were in range of 2.2 to 3.8 which are characteristic of traffic emission ratios [31,32] and very few samples had ratios less than 1, which is characteristic of biomass burning emissions [15]. Hence, during 2019 the two measurement sites in this study were significantly influenced by urban traffic emissions and only occasionally influenced by the mild forest fire smoke. All evidence points to an unusually low smoke season in 2019 in the western U.S.

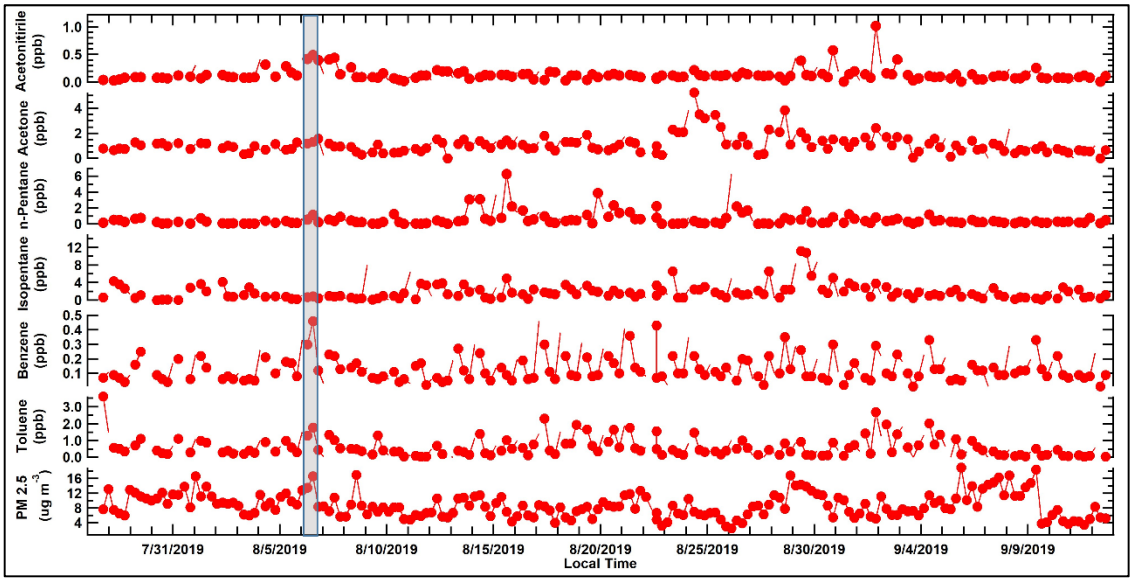

Figure 5. Time series of 6-hour averaged mixing ratios of VOCs and $PM_{2.5}$ measured at Boise, Idaho. Shaded period shows the influence of forest fire smoke.

On a few occasions, we found elevated concentrations of acetonitrile (>0.2 ppb), a marker for biomass burning (see Figure 5) [10–13]. For example, elevated acetonitrile was observed on 08/06/2019 7:00 AM to 01:00 PM, shaded in Figure 5. During this period, benzene (~0.5 ppb), toluene (~1.8 ppb), and $PM_{2.5}$ (~16 ug m^{-3}) showed co-synchronous enhancements with acetonitrile (~0.5 ppb), consistent with their co-emission from the fires [15–19]. Note that during this period, the ratio of IP/P was 0.8, consistent with the reported IP/P emissions ratios for different biomass burning plumes [15]. A 24-hour back trajectory calculation for air masses arriving at Boise at 100 m, 500m, and 1000m a.g.l (47.6670° N, 117.4014° W) on 08/06/2019 7:00 AM (local time) were performed using the NOAA HYSPLIT model using Global Data Acquisition System meteorology [33]. The trajectory was plotted on a Google Earth map along with the NOAA National Environmental Satellite, Data, and Information Service (NESDIS) Hazard Mapping System (HMS) smoke and fire product (Figure S3). It clearly shows that the air parcel arriving at Boise had an origin from a smoke-affected region. Therefore, the enhanced ambient concentration of acetonitrile and other tracers, IP/P emission ratio and trajectory analysis unequivocally shows that this period is influenced by forest fire emissions.

In addition to these six compounds, additional oxygenated VOCs, namely, furan, acrolein, methacrolein, 2,5-dimethylfuran, 2-butanone, 2,3-butanedione, and furfural were identified in eight samples collected at the Boise, Idaho, site (see Figure 3c). In all these samples, acetonitrile was above 0.2 ppb, indicating the influence of biomass burning smoke. Thus, these results from these first field applications of the dual-bed TD tubes with an auto-sampler demonstrate its applicability for ambient VOC speciation to identify forest fire smoke in urban areas using acetonitrile and other oxygenated VOCs.

Table 2 provides the comparison of ambient VOC mixing ratios measured at Spokane (n = 88) and Boise (n = 183) during the NOAA FIREX AQ-2019 fire period with the available VOC mixing ratios reported at other urban environments in the U.S. The ranking in the average VOC mixing ratios at Spokane was isopentane (2.20 ± 2.20 ppb) > acetone (0.72 ± 0.46 ppb) > n-pentane (0.37 ± 0.37 ppb) > toluene (0.25 ± 0.25ppb) > acetonitrile (0.11 ± 0.09 ppb) > benzene (0.09 ± 0.07 ppb). At Boise, relative ranking among was [toluene] = [n-pentane] > [benzene] = [acetonitrile], suggesting a different source and sink strength than in the Spokane environment. Note that the Meridian Boise site is very close (circa 0.5 km) to a major freeway. The averaged mixing ratio of toluene and benzene observed at Boise were comparable to reported values of Baltimore and Houston and higher than reported values in Boston, Pittsburgh, Richmond, and San Diego by 1.2 to 3 times. The n-pentane and isopentane observed in Boise were 1.5 to 9 times higher than in Baltimore, Houston, Boston, Pittsburgh, Richmond, and San Diego.

Table 2. Comparison of average mixing ratio (ppb) of VOCs measured at Boise and Spokane with other similar sites in the U.S.

Compounds (ppb)	Spokane (n = 88)	Boise (n = 183)	Baltimore *	Boston *	Houston *	Pittsburgh *	Richmond *	San-Diego *
Acetonitrile	0.11 (0.09)	0.14 (0.11)	-	-	-	-	-	-
Acetone	0.72(0.46)	1.14 (0.74)	-	-	-	-	-	-
n-Pentane	0.37 (0.37)	0.64 (0.61)	0.15 (0.04)	0.11 (0.03)	0.23 (0.12)	0.31 (0.15)	0.11 (0.07)	0.4 (0.4)
Isopentane	2.2 (2.20)	1.89 (1.82)	0.4 (0.1)	0.31 (0.09)	0.6 (0.3)	0.4 (0.2)	0.24 (0.18)	1.21 (0.69)
Benzene	0.09 (0.07)	0.14 (0.09)	0.19 (0.15)	0.09 (0.02)	0.16 (0.07)	0.09 (0.03)	0.11 (0.06)	0.12 (0.07)
Toluene	0.25 (0.25)	0.64 (0.56)	1.5 (0.8)	0.2 (0.06)	0.6 (0.34)	0.26 (0.14)	0.19 (0.16)	0.2 (0.13)

Numbers in parentheses indicate the ambient variability. * Baker et al. (2008) [33].

4. Conclusions

This study has validated and demonstrated the suitability of custom-made dual-bed TD tubes with a VOC auto-sampler for use in ambient VOC speciation to carry out measurements of acetonitrile, acetone, n-pentane, isopentane, benzene, toluene, furan, acrolein, methacrolein, 2,5- dimethylfuran, 2-butanone, 2,3-butanedione, and furfural in laboratory and ambient field experiments. Experiments and statistical tests to assess the stability of VOCs during storage showed that acetonitrile, pentane, iso-pentane, benzene, toluene, furan, and dimethylfuran can be quantified reproducibly, for samples

analyzed within 15 days of collection. For acetone, acrolein, methacrolein, 2-butanone, 2,3-utanedione, and furfural, similar results were obtained through day 6. Results from two ambient field experiments identified a few days with multiple tracers of smoke, elevated $PM_{2.5}$ and trajectory from known locations. Hence, the use of the low-cost dual-bed TD tubes with a VOC auto-sampler affords the opportunity to significantly advance our understanding of the spatial and temporal distributions of these ambient VOCs as well as determination of the influence of forest fire smoke in urban areas.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/11/3/276/s1, Figure S1: Linearity test for thirteen VOCs sampled using dual-bed Carboxen-Graphsphere TD tubes at different relative humidities; Figure S2: Time series of 6-hour averaged mixing ratios of VOCs measured at Spokane, Washington; Figure S3: Google Earth image (obtained on 01/14/2020 09:00 AM PST) showing the 24-hour back trajectory ensemble of air masses that arrived at 07:00 LT in Boise, Idaho (47.6670° N, 117.4014° W; 20 m a.g.l) on 06/08/2019 along with fire and smoke detected on the same day by the Hazard Mapping System (HMS).

Author Contributions: Conceptualization, D.A.J.; Data curation, B.P.C.; Formal analysis, C.D.M. and B.P.C.; Funding acquisition, D.A.J.; Investigation, B.P.C.; Methodology, B.P.C.; Project administration, D.A.J.; Resources, J.M. and D.A.J.; Supervision, D.A.J.; Validation, B.P.C.; Visualization, B.P.C.; Writing – original draft, B.P.C.; Writing – review & editing, B.P.C. and D.A.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Oceanic and Atmospheric Administration (No.NA17OAR431001).

Acknowledgments: We acknowledge Detlev Helmig for providing valuable insights on adsorbents. We acknowledge the help and support of the members of Gonzaga University: Ethan Victor Durbano and Marc Baumgardner for technical assistance during field sampling in Spokane. We thank Andrew Nutting and Hannah Spero for help and support in the replacement and shipment of thermal desorption tubes during field sampling in Boise. We also thank Shahbaz Qureshi and Noah Bernays for technical assistance

Conflicts of Interest: The authors declare no conflict of interest

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