Analysis of ambient VOCs using thermal desorption gas chromatography to identify smoke influence in urban areas

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Abstract

Smoke influence in urban areas is relatively easy to detect at high concentrations, but more challenging to detect at low concentrations. For this reason, we have evaluated an approach using thermal desorption gas chromatography mass spectrometry (TD-GC-MS) to detect volatile organic compounds (VOCs) in particular oxygenated VOCs in urban areas. The goal of this work is to develop a method that can reliably quantify smoke tracers in an urban environment at relatively low cost and complexity. We present here the development and validation of a double-bedded thermal desorption tube with an auto sampler to collect continuous samples of VOCs. To evaluate the method performance, we have tested stability during storage, interferences (e.g., water and O3), and reproducibility for six VOCs, namely, acetonitrile, acetone, pentane, iso-pentane, benzene, and toluene. The results demonstrate that these can be quantified reproducibly with an error [?] 20% between the collection and analysis with a storage time of up to 21 days. For acetone, similar results were obtained until day 14. Calibration experiments performed over a dynamic range of 10–150 ng loaded over thermal desorption tubes at different relative humidity showed excellent linearity (r2 [?] 0.91). At this time, we are utilizing this method during the summer 2019 FIREX-AQ intensive experiment at the Boise ground site in Idaho. These results will be presented along with the quality control data.

Development of a Simplified Method for six VOCs speciation to Trace Biomass Burning Plumes in Urban Areas

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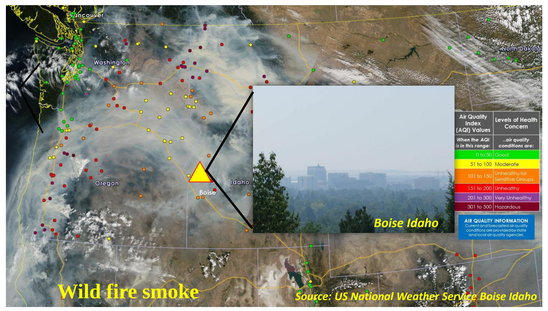
1. MOTIVATION



- Develop a simpler and lower cost method to measure VOCs and especially oxygenated VOCs.
- Provide a tool for cities and states to measure biomass burning tracers to assist with policy relevant analyses (e.g. exceptional event determinations)

2.1 VOC SAMPLING & ANALYSIS METHODOLOGY

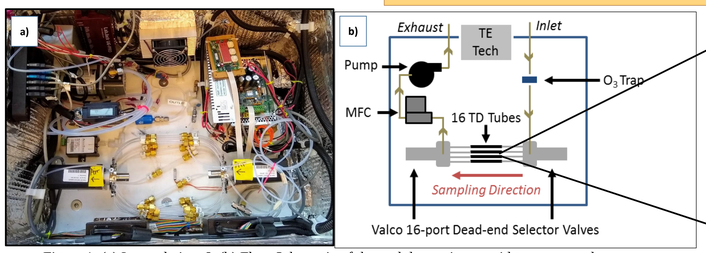


Figure 1: (a) Internal view & (b) Flow Schematic of thermal desorption cartridge auto-sampler

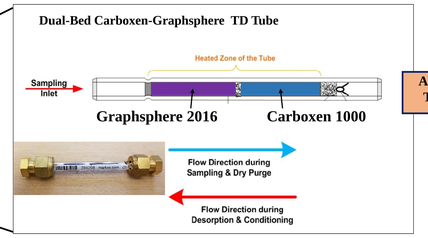


Figure 2: Schematic of double-bed thermal desorption tubes

Analysis with TD-GC-MS

Figure 3: Picture of Thermal Desorption Gas Chromotograpy- Mass Spectrometry (TD-GC-MS)

- Filter ozone using sodium thiosulfate filter
- Flow can be adjusted between 50-200 sccm
- 6 hour VOC Sample were collected on
- VOC sampler is heated to above ambient temperature to avoid condensation of water

- Graphsphere 2016 collects C_5-C_{12} VOCs
- Carboxen 1000 collects C_2-C_5 VOCs.

- Requires minimal oversight
- Portable
- Low in-field resource costs
- Simple analysis method
- Few physical/chemical interferences with adsorption

❖ **Trap settings** :
TD tubes heating = 270°C @ 6 min Temp. low = 15 °C: Temp. High = 280 °C (4 min hold) heating rate = max : Split :on

❖ **GC details:**
Column- Restex-Rxi(R)-624Sil MS (30m, 0.25 mmID, 1.4 Um df):constant input pressure 11 Psi; carrier gas = He; Oven temp ramp settings ====> initial temp 35°C (1 min hold); Ramp1: 15°C min^{-1} upto 100°C : Ramp2: 40°C min^{-1} upto 200°C

❖ **Mass Spec details:**
MS trans temp ====> 250°C (&)Ion source temp ====> 300°C

2.2 Chromatogram For Non Smoke & Smoke Samples

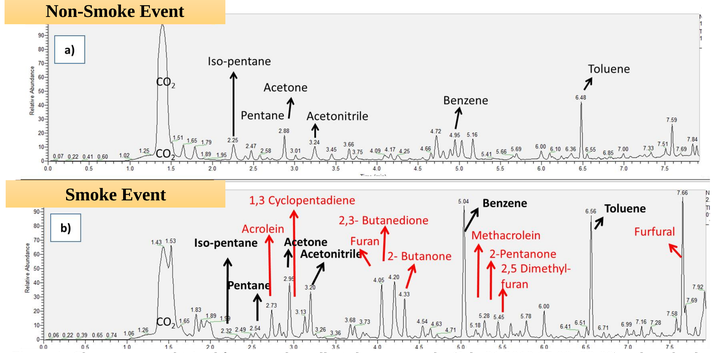


Figure 4 . Chromatogram obtained from samples collected on non-smoke (July 31,2019 17:00- 23:00) and smoky day (August 01, 2019 17:00-23:00) at Boise

2.3 Linearity Tests At Different RH For VOCs

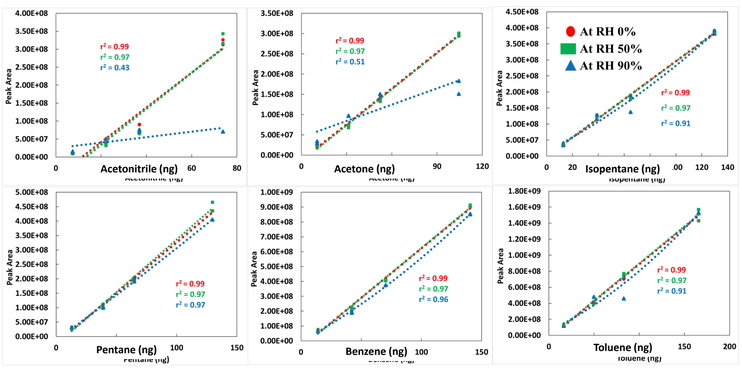


Figure 5: Linearity test for six volatile organic compounds sampled using dual-bed Carboxen-Graphsphere thermal desorption tubes at different relative humidity

2.4 Detection Limit And Precision Error

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

Compound name	DL (ng)	DL (ppb)	Precision error of duplicate pairs	Precision for the distributed volume pairs
Pentane	1.06	0.02	9.15	15.34
Iso-pentane	1.05	0.02	6.34	13.23
Acetone	1.69	0.03	5.48	12.78
Acetonitrile	1.08	0.03	4.0	12.34
Benzene	2.08	0.03	7.96	11.45
Toluene	2.03	0.03	4.57	10.23

❖**With in the compliance of EPA TO-17 Method**

3 RESULTS

3.1 Validation Tests For VOC Stability With Gas Standard Mixture

3.2 Validation Tests For VOC Stability With Wood Smoke

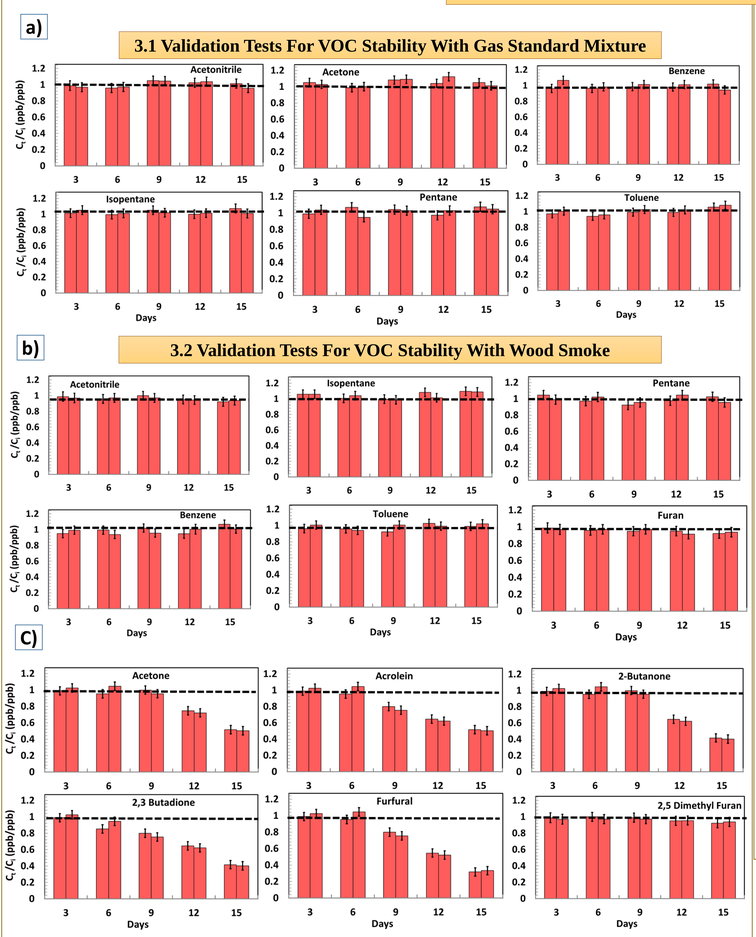
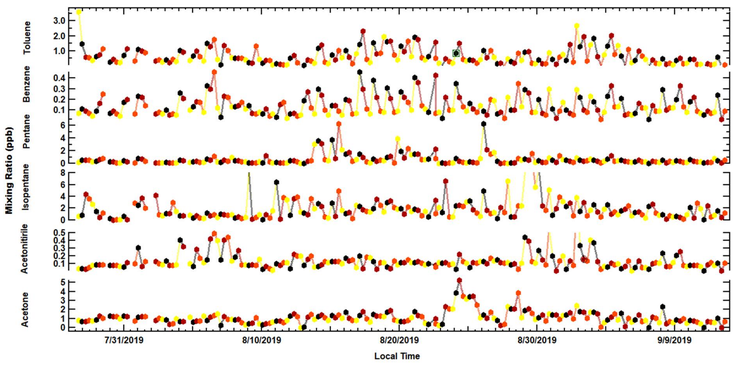


Figure 6: Ascertaining the stability of VOCs over the storage of 15 days inside the dual-bed Carboxen-Graphsphere thermal desorption tubes sampled using (a) Calibration gas matrix , (b) & (c) wood burning plume. Histograms in each VOC plot correspond to the ratio of VOC concentration measured after "t" days of storage (C_t (ppb)) to the initially measured concentration of VOC from the flask on day 0 (C_i (ppb)). Error bars on each histogram corresponds to the total uncertainty of the measurement with TD-GC-FID

 # Results from calibration gas standard mixture: Ratio of C_t / C_i for acetonitrile, acetone, pentane, iso-pentane, benzene and toluene varied between 0.9-1.1 and comparable with in the 10% of total uncertainty of measurement over the storage period of 15 days

 # Results from wood smoke plume: Ratio of C_t / C_i for acetonitrile, pentane, iso-pentane, furan, 2,5 dimethyl furan, benzene and toluene varied between 0.9-1.1 and comparable with in the 10% of total uncertainty of measurement over the storage period of 15 days and for acetone and 2-butanone over the storage period of 9 days and for acrolein, 2,3 butadiene and furfural over the storage period of 6 days

3.3 Time series of 6 hour Averaged mixing ratios of VOCs measured at Boise, Idaho



Black Markers: Night samples (11:00 PM to 5:00 AM)

Red Markers: Early morning samples (5:00 AM to 11:00 AM)

Orange Markers: Afternoon samples (11:00 AM to 17:00 PM)

Evening Markers: Evening rush hours (17:00 PM to 11:00 PM)

Table 2. Comparison of average mixing ratio (ppb) of VOCs measured at Boise and Spokane with other similar sites in the Unites States . Numbers in the parenthesis indicated the ambient variability

Compounds (ppb)	Boise (n=183)	Spokane (n=16)	Baltimore (Baker et al., 2008)	Boston (Baker et al., 2008)	Houston (Baker et al., 2008)	Pitts burg (Baker et al., 2008)	Richmond (Baker et al., 2008)	Sandiago (Baker et al., 2008)	Washington DC (Baker et al., 2008)	Wetren Springs, IL (panckow et al., 2003)
Pentane	0.64 (0.61)	0.43 (0.40)	0.15 (0.04)	0.11 (0.03)	0.23 (0.12)	0.31 (0.15)	0.11 (0.07)	0.4 (0.4)	0.27 (0.2)	-
Isopentane	1.89 (1.82)	0.30 (0.30)	0.4 (0.1)	0.31 (0.09)	0.6 (0.3)	0.4 (0.2)	0.24 (0.18)	1.21 (0.69)	0.64 (0.48)	-
Benzene	0.14 (0.09)	0.06 (0.05)	0.19 (0.15)	0.09 (0.02)	0.16 (0.07)	0.09 (0.03)	0.11 (0.06)	0.12 (0.07)	0.19 (0.1)	0.17 (0.11)
Toluene	0.64 (0.56)	0.15 (0.15)	1.5 (0.8)	0.2 (0.06)	0.6 (0.34)	0.26 (0.14)	0.19 (0.16)	0.2 (0.13)	0.4 (0.4)	0.23 (0.10)
Acetone	1.14 (0.74)	0.69 (0.39)	-	-	-	-	-	-	-	0.66 (0.41)
Acetonitrile	0.14 (0.11)	0.04 (0.02)	-	-	-	-	-	-	-	-

❖**Ambient concentrations of pentane, isopentane, benzene, toluene, acetone measured at Boise and Spokane are comparable with other cites in the US reported earlier**

4. CONCLUSIONS

- We have tested and evaluated a simplified method for the collection of ambient VOC and Oxygenated VOCs using a double bedded Thermal-Desorption Cartridge with GCMS analysis
- We have assessed the stability of a variety of VOCs and OVOCs including acetonitrile, isopentane, pentane, benzene & toluene. These can be quantified reproducibly with an error ≤ 10% between the collection and analysis with in the storage time of up to 9 days. For acetone and 2-butanone until 9 days and for acrolein, 2,3 butadiene and furfural until 6 days.
- This study demonstrate that TD GCMS can be used to quantify the spatial and temporal distributions of biomass burning tracers, including a number of N-and O-VOCs in urban areas and that this method is useful for urban areas as tracers of biomass burning smoke.

5. References

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6. Acknowledgment

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