Portland State University

PDXScholar

University Honors Theses

University Honors College

2015

Methods of Collecting and Separating Atmospheric Organic Aerosols for Analysis Using Two-Dimensional Gas and Liquid Chromatography with Mass Spectrometry

Craig Fairbaugh
Portland State University

Follow this and additional works at: <https://pdxscholar.library.pdx.edu/honorstheses>

Let us know how access to this document benefits you.

Recommended Citation

Fairbaugh, Craig, "Methods of Collecting and Separating Atmospheric Organic Aerosols for Analysis Using Two-Dimensional Gas and Liquid Chromatography with Mass Spectrometry" (2015). *University Honors Theses*. Paper 149.

<https://doi.org/10.15760/honors.155>

This Thesis is brought to you for free and open access. It has been accepted for inclusion in University Honors Theses by an authorized administrator of PDXScholar. Please contact us if we can make this document more accessible: pdxscholar@pdx.edu.

**Methods of Collecting and Separating Atmospheric
Organic Aerosols for Analysis Using Two-Dimensional Gas
and Liquid Chromatography with Mass Spectrometry**

by

Craig Fairbaugh

An undergraduate honors thesis submitted
in partial fulfillment of the requirements for the degree of

Bachelor of Science

In

University Honors

and

Environmental Engineering

Thesis Advisor

Dr. Kelley Barsanti

Portland State University

June 2015

Acknowledgements

Many thanks to the URMP program, the University Honors program, the EMSL laboratory, my invaluable advisor Dr. Kelley Barsanti, and research partner Daniel Wright. I would also like to thank Danielle Draper, Natalie Keehan, Lindsay Hatch, Dr. James Pankow and Dr. Wentai Luo for their gracious assistance.

Additionally, a very special thanks goes out to my family. To my parents, James and Sheryl Fairbaugh, thank you for the endless support. To my children, Jackson, Mina, and Delilah, thank you for bearing with Dad on all those endless nights of studying and coming home late. I hope my hard work will inspire you to explore the world around you. To Kimberly Michelle: truly, none of this could be possible without you. Thank you for being my partner in this adventure. I adore you.

Table of Contents

Acknowledgements	1
1 Abstract	3
2 Introduction	5
Aerosols and Volatility	5
Aerosols and Climate	6
Aerosols and Air Quality	8
3 Background	9
Analytical Techniques	9
Collection Media	10
Derivatization	12
4 Objectives	13
5 Reed Chamber Experiment (Objective 1)	14
6 Design and Sampling Approach (Objective 2)	18
7 SPE Filter Testing (Objective 3)	20
PSU Aerosol Samples – SPE Filters	21
EMSL Analysis – SPE Filters	22
8 Next Steps and Outlook	25
9 Citations	26
10 Appendix	28

1 Abstract

In the atmosphere, biogenic and anthropogenic emissions are oxidized to form secondary organic aerosols (SOA); however, the identities and concentrations of the compounds formed are inadequately known. In this work an aerosol (gas+particle) collection system was designed and tested in order to more fully characterize atmospheric volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) that contribute to SOA. Target compounds to be collected were C₆ to C₂₀ compounds with oxygenated functional groups such as aldehydes and alcohols. The collection system was designed to allow characterization of atmospheric aerosols using multiple analytical methods: two-dimensional gas chromatography with time of flight-mass spectrometry (GCxGC-TOFMS), with and without derivatization, and two-dimensional liquid chromatography with mass spectrometry (LCxLC-MS). The first stage of collection in the system uses a polytetrafluoroethylene (PTFE) filter to capture the low volatility compounds in the particle phase. The flow is then split for two different collection mechanisms: adsorption thermal desorption (ATD) cartridges for gas phase VOCs, and solid phase extraction (SPE) filters for SVOCs. In order to test the viability of aerosol collection on PTFE filters and subsequent analysis using derivatization, four aerosol samples were collected on PTFE filters at Reed College. The average mass collected over 4 trials was 10.15 µg. The U.S. Department of Energy Environmental and Molecular Science Lab (EMSL) performed extraction and derivatization on the Reed College samples, followed by GC-MS. Results show identifiable peaks that are significantly different than the filter blanks, suggesting that derivatization methods can be used to facilitate identification of relatively polar organic compounds sampled onto PTFE filters. Additional aerosol collection trials were conducted at Portland State University (PSU) using two SPE filters in series to collect gases and particles from tobacco smoke. A literature review was conducted to determine the type of SPE filter, time, and necessary flow rates to collect an optimum amount of sample for analysis. The tobacco smoke PM mass collected was 6mg/2mg and 2mg/0.9mg for trials one and two, respectively (front/back filter). PSU tobacco smoke samples

were analyzed at EMSL using GC-MS with derivatization. Results showed successful collection of polar compounds in the semi-volatile range of interest, including alcohols, aldehydes, and phenols. Next steps of this research include collecting aerosol samples with the whole system (PTFE + ATD + SPE) and subsequent analysis of samples using GCxGC-TOFMS, with and without derivatization, and LCxLC-MS. Results to date suggest a more complete characterization of atmospheric organic aerosols can be attained using multiple offline analyses. Further characterization of atmospheric organic aerosols is necessary to improve air quality and climate modeling and develop efficient air quality and climate change mitigation technologies.

2 Introduction

Aerosols and Volatility

Aerosols are defined as particles suspended in a gas (air in this work). Primary organic aerosols (POA) are particles that are directly emitted into the atmosphere from both anthropogenic sources (i.e. fossil fuels) and biogenic sources (vegetation). Secondary organic aerosols (SOA) are formed in the atmosphere and are of singular interest in this work; semi-volatile organic compounds (SVOCs) and volatile organic compounds (VOCs) from anthropogenic and biogenic sources are the precursors of SOA.

VOCs and SVOCs are distinguished from each other by boiling point, with boiling point temperatures ranging from approximately 50-250°C and 250-400°C respectively (Figure 1) (EPA, 2015). VOCs generally have low boiling points and evaporate at temperatures lower than 250°C; propane, benzene, and other components of gasoline are all VOCs (Art, 1993). SVOCs include phenols and polycyclic aromatic hydrocarbons (PAH).

Description	Abbreviation	Boiling Point Range (°C)	Example Compounds
Very volatile (gaseous) organic compounds	VVOC	<0 to 50–100	Propane, butane, methyl chloride
Volatile organic compounds	VOC	50–100 to 240–260	Formaldehyde, d-Limonene, toluene, acetone, ethanol (ethyl alcohol) 2-propanol (isopropyl alcohol), hexanal
Semi volatile organic compounds	SVOC	240–260 to 380–400	Pesticides (DDT, chlordane, plasticizers (phthalates), fire retardants (PCBs, PBB))

Figure 1: Classification of volatile organic compounds (EPA, 2015)

Gas-phase compounds are of interest because when emitted into the atmosphere they react with ozone (O₃), hydroxyl radicals (OH·), and other oxidants; are transformed to lower volatility compounds; and can then condense to form SOA (Figure 2).

Secondary Organic Aerosol (SOA) Formation

Figure 2: Gas-particle partitioning process (Pankow, 2014)

The mixtures of oxidized compounds formed in the atmosphere are inadequately characterized due to the complexity, as well as interdependent changes in composition and volatility. For example, compounds can switch between gas and condensed phase due to temperature and relative humidity changes, be broken down through photolysis, and undergo redox reactions. This constant flux between gas and particle phase makes collection, and therefore characterization, of atmospheric aerosols difficult.

Aerosols and Climate

Atmospheric aerosols play an important role in Earth's radiative heat budget and climate change, the hydrologic cycle, and air pollution. Radiative forcing (RF) is a measurement of the ability of forcing agents (i.e. gases, water molecules, particles) to affect the Earth's energy balance (SEI, 2011). Ramaswamy et al. (2001) further defines RF as "the change in net (down minus up) irradiance (solar plus longwave; in W/m^2) at the tropopause after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values." Aerosol particles indirectly affect RF by acting as cloud condensation nuclei (CCN)(NASA, 2015); once particles are large enough they provide "seeds" for water molecules to condense upon, which subsequently affects the hydrologic cycle (can alter precipitation). Figure 3 shows the formation of CCN from POA and SOA. The role of POA and SOA in cloud formation is one of the least understood aspects in climate change modeling.

Figure 3: Atmospheric aerosol cycle (Poschl, 2014)

Aerosol particles and cloud droplets can increase albedo and reduce incoming short wave radiation from the sun (NASA, 1999). Conversely, black carbon aerosols can trap outgoing radiation, which produces heat and contributes to direct warming. Developing a method of characterizing the gas- and particle-phase compounds of atmospheric aerosols is an important aspect in understanding and predicting global climate change: the Intergovernmental Panel on Climate Change (IPCC) states aerosols are “contributing the largest uncertainty to the total RF estimate” (Pachauri, 2015). Understanding the role of aerosols in RF will be required for developing important climate change mitigation strategies (Figure 4).

Figure 4: Diagram illustrating how RF is linked to other aspects of climate change assessed by the IPCC (IPCC, 2007)

Aerosols and Air Quality

The National Ambient Air Quality Standards (NAAQS) were established by the U.S. Environmental Protection Agency (EPA) in order to protect public health and welfare. NAAQS currently exist for six criteria pollutants: carbon monoxide (CO), lead (Pb), nitrogen dioxide (NO₂), ground-level ozone (O₃), sulfur dioxide (SO₂), and two categories of particulate matter (Masters and Ela, 2008). PM₁₀ and PM_{2.5} are particles with diameters of < 10µm and < 2.5µm, respectively. POA and SOA contribute a substantial mass fraction to PM₁₀ and PM_{2.5} and thus more complete characterization of these organic aerosols can lead to better quantification and mitigation of particulate air pollutants (Figure 5).

Figure 5: Composition of PM_{2.5} at representative urban and rural locations, based on annual averages except Mexico City. Organic carbon (POA+SOA) represents a significant portion of PM_{2.5} (EPA, 2015)

3 Background

Analytical Techniques

Characterization of aerosols has traditionally been performed using either gas or liquid chromatography, both of which have the capacity to be run with two-dimensional (2D) separation (GC x GC and LC x LC, respectively). 2D analysis allows for characterization of more complex samples by separation of chemical compounds according to two different properties. The most common properties are size, polarity, and solubility. Effective 2D chromatography uses two orthogonal properties to achieve the most efficient separation for subsequent analysis. For atmospheric work, both GC and LC are most often used in conjunction with mass spectrometry (MS), which helps identify compounds by measuring mass (as a mass-charge ratio). Figure 6 shows the process of aerosol characterization, from collection through detection, including by MS (Poschl, 2005).

Figure 6: Major analytical procedures for chemical characterization of aerosol particles and components. Separation and detection techniques of interest are shown here (GC, LC, and MS) (Poschl, 2005)

Duarte et al. (2012) performed two-dimensional liquid chromatography (LCxLC) to better characterize the composition of natural organic matter (NOM). NOM compounds possess a similar complexity when compared to atmospheric organic particulate matter; size and polarity characteristics are difficult to characterize and current testing methods do not produce any distinguishing peaks in resulting data. In Duarte et al., two fluval acids were collected and separated in order to better understand the composition and range of acids present in aquatic systems. The authors employed LCxLC using a reverse-phase silica column for the first dimension and a size-exclusion column in the second dimension. Findings suggest that using two independent separation mechanisms can improve separation and characterization of NOM composition. Because of the similarities in analytical complexity between NOM and atmospheric aerosols, Duarte's work shows that there is potential for aerosol collection and characterization using independent separation mechanisms. In addition, LCxLC is shown to be viable for characterizing complex environmental samples.

Collection Media

Adsorption-thermal desorption (ATD) cartridges are widely used to collect samples for analysis by gas chromatography. ATD cartridges are filled with one or more adsorbents (e.g., Tenax) and can be successful in sorbing VOCs and SVOCs. Advantages include exhibiting a low analyte breakthrough, but consequentially, high flow-resistance can occur (Ligocki and Pankow, 1984). In Ligocki and Pankow (1984), low breakthrough was observed for volatile polar organics such as TCE (0-8%); *o*, *m*, and *p*-xylene (<1%); and 1,4-dichlorobenzene (<1%). Successful sampling volumes ranged from 280L to 570L and temperatures from 5°C to 9°C, yielding recovery for aerosols at the ng/m³ level (Ligocki and Pankow, 1984). Ligocki and Pankow used two different flow rates through the ATD cartridges and also collected lower-volatility compounds on Polyurethane foam plugs set up in parallel to the ATD cartridges (Figure 7). The parallel collection system in Figure 7 is similar to the

proposed design in this work: both systems operate with separate flow rates and are intended to collect compounds with different volatility ranges.

Figure 7: Air sampler designed for the collection of ambient particulate and vapor phase organic compounds (Ligocki and Pankow, 1984).

Limbeck et al. (2000) performed ambient sampling of atmospheric organic aerosols in the South African Savannah. Quartz fiber filters were used in series in order to catch breakthrough analytes. Oxalic acids were found to be the most dominant species followed by other polar organics such as carboxylic acids, phthalates, and aldehydes (Limbeck et al. 2000). A low volume sampler (15 L/min) was used with the quartz fiber filters and ambient sampling time was approximately one week. C₂-C₉ dicarboxylic acids and C₈-C₁₈ mono carboxylic acids were extracted using methanol/acetone/organic free water solutions and then separated using a C₁₈ solid phase extraction (SPE) cartridge. After extraction from the SPE, compounds were analyzed using GC-MS. The authors acknowledged analysis was incomplete due to lack of semi-volatile compound collection efficiency.

Derivatization

Isaacman et al. (2015) used SV-TAG (semi-volatile thermal desorption aerosol gas chromatography) with derivatization to characterize highly -polar semi-volatile and low-volatility compounds (Isaacman, 2015). The SV-TAG is an online sampler that quantifies gas and particle phase compounds hourly, resulting in mass concentration and gas-particle partitioning data. Derivatization is performed in situ using helium saturated with a derivatizing agent, providing a way to characterize compounds that otherwise are not captured by the SV-TAG system. Highly-polar semi-volatile and low-volatility compounds were reacted with silylating agents to convert OH groups into larger esters and ethers. In order to quantify the “parent” compounds, derivatization was reproduced in the laboratory using auto injection of 43 oxygenated compounds. The authors reported highly reproducible derivatization with 3% variability in the laboratory setting, and 20-25% variability when collected in the field. Derivatization was shown to have great potential in characterizing highly-polar organic compounds, yet the method still contains a large range of error and requires an internal standard to correct for variability in detector response, consumption of the derivatization agent, desorption efficiency, and transfer losses (Isaacman et al., 2015). In comparison to SV-TAG, the design proposed in this work aims to provide a less expensive, offline aerosol collection system.

4 Objectives

The goal of this work was to design a sampling system that uses multiple media types to collect compounds with a wide range of volatility that can then be characterized using multiple analytical approaches. Three objectives were defined to achieve this goal.

Objective 1:

Test GC with derivatization. GC with derivatization has been shown to be successful in promoting elution of volatile and semi-volatile organic compounds from a GC column. It is necessary to test if this analytical method is feasible for the samples of interest in this work because that will influence the design of the collection apparatus.

Objective 2:

Design collection apparatus. Sequencing of media and flexibility of analytical approaches will be important for full characterization.

Objective 3:

Test the collection capabilities of SPE filters, particularly their ability to trap SVOCs. Trapping SVOCs is important because ATD cartridges can trap VOCs and PTFE filters can trap low-volatility compounds, leaving a range of SVOCs that are inadequately collected and characterized.

5 Reed Chamber Experiment (Objective 1)

A proof of concept experiment was performed during August and September of 2014. The first purpose of this experiment was to collect aerosol mass on PTFE filters and determine if this method was effective in trapping the low-volatility organic compounds of interest. The second purpose was to determine if GC-MS with derivatization was effective in removing compounds of interest from the GC column.

Six PTFE filters were prepped at PSU to ensure background contamination would be minimized. Foil packets were created for each filter and heated at 150°C for 4 hours. Tongs for filter handling were also heated at 150°C. PTFE filters were conditioned using a 5x5 methanol and acetone rinse (5ml rinse, 5 times for each solution). Each PTFE filter was then pre-weighed and masses were recorded on the foil packets. Two filters were marked blank for use as control samples. The prepped filters were taken to the Reed College Chemistry Department (Portland, OR) and used to collect SOA from a PFA Teflon chamber. The SOA was generated by reaction of alpha-pinene, a biogenic VOC, with ozone in the chamber (Figure 7).

Figure 7: Aerosol sampling chamber at Reed College, Portland, OR. Alpha-pinene was the VOC source reacted with ozone. Schematic provided by Danielle Draper, Reed College, 2014.

For each trial a PTFE filter was inserted into a Teflon filter holder in the chamber outflow path. Flow rate was recorded throughout the trial to ensure a constant rate was achieved and to monitor filter performance. A change in flow rate could indicate too much sample was collected and the filter had become occluded. Following each trial, the filter was placed in the foil packet, then in a glass jar, and stored in a freezer in order to prevent further reactions from occurring. Mass collected on the filters is shown in Table 1. Average mass loadings in the chamber were approximately $400\mu\text{g}/\text{m}^3$, depending on initial concentrations of reactants and experimental conditions. Following the collection experiment, filters were packaged in dry ice and sent to EMSL for analysis.

Table 1: Reed chamber experiment data. Mass flow rate $\sim 400\mu\text{g}/\text{m}^3$.

<i>Alpha Pinene Ozonolysis Aerosols Collected on PTFE Filters</i>						
Date	Time	Elapsed Time	Collected Vol (L)	Collected Vol (m^3)	Q (L/min)	Mass Collected (μg)
8/20/14	1:30:20	0	-	-	0.92	-
	3:01:30	1:31:10	83.51	0.084	0.916	4.25
	4:27:20	1:25:50	78.11	0.078	0.91	9.03
9/3/14	12:57:20	0	-	-	0.75	-
	2:31:10	1:33:50	66.62	0.067	0.71	11.60
	4:04:45	1:33:35	68.32	0.068	0.71	15.70

Sample analysis was performed by Young-Mo Kim at EMSL in Richland, WA. Aerosol mass was extracted from the PTFE filters and derivatized using methoxyamination and trimethyl silylation [communication with Young-Mo Kim]. With the exception of different derivatizing agents, the extraction procedure in Pietrogrande et al. (2013) was followed. The chromatograms for the Reed PTFE filters are shown in Figure 8.

Overall chromatogram – Reed PTFE Filter Samples

Figure 8: GC-MS chromatogram for the Reed filter samples. PTFE filter samples were extracted with a derivatizing agent. Analysis performed by Young Mo Kim, DOE EMSL, 2014.

The chromatograms show the relative abundance vs. elution time. The blank filters are shown in red and blue, with the sample filters shown in grey, teal, green, and purple. Figure 8 shows visible differences in mass between the 2 blank filters and sampled filters, particularly after approximately 10 minutes. The more volatile compounds eluted first (under 10 minutes), with a few lower-volatility compounds eluting after 20 minutes (Figure 8). Figures 9, 10, and 11 show chromatogram results between 10 to 13 minutes, 13 to 15 minutes, and 15 to 19 minutes respectively; observable differences in peaks between the blank filters and sampled filters are shown by red arrows. It is important to note that observable differences in peaks only occurred for samples 3 and 4, suggesting that not enough aerosol mass was collected on filters 1 and 2. However, the peak separation in filters 3 and 4 do suggest that SVOCs may be detected in samples of interest using filter collection and GC-MS with derivatization.

Chromatograms (10 to 13 min) – Reed PTFE Filter Samples

Figure 9 (above) and Figure 10 (below): GC-MS chromatograms for the Reed filter samples. PTFE filter samples were extracted with a derivatizing agent. Red arrows show successfully derivatized compounds in samples (grey and green traces); red and blue traces are blank filters. Analysis performed by Young Mo Kim, DOE EMSL, 2014.

Chromatograms (13 to 15 min) – Reed PTFE Filter Samples

Chromatograms (15 to 19 min) – Reed PTFE Filter Samples

Figure 11: GC-MS chromatogram for the Reed filter samples, between 15 to 13 minutes. PTFE filter samples were extracted with a derivatizing agent. Red arrows show successfully derivatized compounds in samples (grey and green traces); red and blue traces are blank filters. Analysis performed by Young Mo Kim, DOE EMSL, 2014.

6 Design and Sampling Approach (Objective 2)

A PTFE filter was placed at the beginning of the collection system to trap low-volatility, particulate-phase compounds. Trapping larger particulate-phase compounds in the beginning of collection creates more opportunity for the subsequent media to capture VOCs and SVOCs (Figure 12). Following the PTFE filter the flow is split; one flow-path towards the ATD cartridge and the other towards the SPE filter. Prior to collection on the ATD cartridge, volatile compounds will pass through an O₃ scrubber. The O₃ scrubber traps ozone and prevents further oxidation of volatile compounds on the ATD cartridge. The ATD cartridge media proposed is pre-packed with Tenax GC, although multiple options for media packing exist, dependent on the compounds of interest. Tenax GC ATD cartridges have been shown to be effective in collecting higher volatility compounds (Ligocki and Pankow

1985). The SPE path is intended for intermediate-volatility compound collection, however there is limited literature available on collection of SVOCs in air using SPE.

Figure 12: Aerosol collection apparatus.

A unitless flow meter was calibrated to measure flow in both sides of the sampler. Flow was initiated using compressed N₂ gas and an SKC PCXR8 Universal Sample Pump. Flow meter calibration data and results are located in the Appendix (Tables A1 and A2, Figures A1 and A2). Advantages of the SKC pumps include their small size and battery operation. The use of small portable pumps makes the sampling apparatus ideal for either laboratory sampling or field sampling.

7 SPE Filter Testing (Objective 3)

With promising derivatization results from the Reed chamber experiment, solid phase extraction (SPE) was considered for gas-phase SVOC collection. To determine the best adsorbent, a literature review was conducted to gather data such as flow rates used, concentrations of aerosol, and types of compounds identified (Table 2). Empore C18, 47mm diameter filters were chosen as the SPE filter. The Empore SPE filters are comprised of 90% SPE membrane, 10% PTFE, and are designed for extracting semi-volatile and non-volatile compounds (Sigma-Aldrich).

Table 2: SPE literature review to determine flow rates necessary for ample aerosol collection. (NR= not reported)

<i>Solid Phase Extraction Literature Review</i>			
Author	Q (L/min)	Conc.	Compounds
Bergh et al	1	47 ng/m ³	organophosphates and phthalates
Denola et al	36	NR	NR
van der Veen et al.	3	47 µg/m ³	phosphorous flame retardants
Staaf et al	3	1 µg/m ³	chlorinated organophosphate triesters
Takeuchi	10	20.8 µg/m ³	39 compounds
Tollbeck	15	NR	NR
van Pixteren	500	NR	NR

Because the mass collected during the Reed chamber experiments was low, calculations were performed to ensure enough mass was collected on the SPE filters. A mass concentration of 0.1ng/µL was assumed to be the minimum concentration of compound necessary for detection by MS. Sampling time necessary for desired mass loadings was calculated in Tables 3 and 4 using the following equation:

$$t = \frac{m}{cQ} \quad (\text{hours})$$

Where m is mass (µg), C is sample concentration (µg/m³) and Q is flow rate (L/min). Sample concentrations considered were 20, 500, and 1725 µg/m³. These concentrations were chosen to represent ambient atmospheric levels, high concentration laboratory levels, and tobacco smoke, respectively.

Table 3: Sampling time necessary for mass loading of 50 micrograms of aerosol on a SPE filter.

<i>Sampling Time for Mass Loading = 50 micrograms</i>		
Flow rate (L/min)	Concentration ($\mu\text{g}/\text{m}^3$)	Sampling time (hours)
1	20	41.67
1	500	1.67
1	1725	0.48
3	20	13.89
3	500	0.56
3	1725	0.16
10	20	4.17
10	500	0.17
10	1725	0.05

Table 4: Sampling time necessary for mass loading of 100 micrograms of aerosol on a SPE filter.

<i>Sampling Time for Mass Loading = 100 micrograms</i>		
Flow rate (L/min)	Concentration ($\mu\text{g}/\text{m}^3$)	Sampling time (hours)
1	20	83.33
1	500	3.33
1	1725	0.97
3	20	27.78
3	500	1.11
3	1725	0.32
10	20	8.33
10	500	0.33
10	1725	0.10

PSU Aerosol Samples – SPE Filters

The purpose of the second sampling experiment was to capture a greater amount of mass for analysis and to test the collection capabilities of the Empore C18 SPE filters. Sampling was performed in April, 2015 at Portland State University using tobacco smoke as the source of aerosol. A tobacco smoking apparatus was provided by the James Pankow Research group and was operated by Dr. Wentai Luo. The smoking apparatus simulated the inhalation of tobacco smoke by providing suction from a pump once per minute. The apparatus was designed to pull approximately 10mg of aerosol per “puff” per minute. Aerosol was drawn from two cigarettes

simultaneously, resulting in two puffs per minute (Figure 13). American Spirit brand cigarettes made with organic tobacco were used in the experiment. Flow rate from the pump was approximately 1L/min during the draw.

Figure 13: Smoking apparatus in the James Pankow research laboratory at Portland State University. Aerosol sample was drawn from two cigarettes simultaneously, and through two Empore C18 SPE filters set up in series.

Mass collected in the first trial was 6mg on the front filter and 2 mg on the back filter. Mass collected on the second trial was 2mg on the front filter and 0.9 mg on the back filter. SPE filters, including a blank, were shipped to EMSL for analysis using GC-MS with derivatization.

EMSL Analysis – SPE Filters

Sample analysis was performed by Young-Mo at EMSL in Richland, WA. Aerosol mass was extracted from the PTFE filters and derivatized using the methods described for the EMSL filter experiment. Figure 14 shows chromatographs from one blank filter and four filter samples: filters #1 and #5 correspond to the first trial, while filters #7 and #8 correspond to the second trial. Filters #5 and #8 were used as back filters in order to observe trapping of compounds that passed through the

first filter. Based on this experiment, a second SPE filter provides minimal characterization benefits: a small amount of breakthrough occurred and trace peaks of backup filters were similar to primary filters, suggesting no new compounds were trapped. Filter #1 trapped the greatest amount of aerosols and as a result was used for compound identification.

Chromatographic Comparison

Figure 14: GC-MS chromatogram for the PSU filter samples. SPE filter samples were extracted with a derivatizing agent. Sample #1 trapped the greatest mass of compounds. Analysis performed by Young-Mo Kim, DOE EMSL, 2014.

34 compounds were identified from filter #1 (Figure 15). Chemical formula, molecular weight, and boiling point values for compounds trapped are in the Appendix (Table A3). Preliminary identification shows several polar compounds of interest were trapped, including aldehydes, alcohols, phenols, and sterols. Many of these compounds spanned the C₆ to C₂₀ range with oxygenated functional groups, suggesting SPE filters are a successful filter media for trapping SVOCs. While volatility is a relative classification depending on many factors, SVOCs were identified using the EPA's classification range (boiling point between 240-400°C,

Figure 1). SVOCs trapped include 3-hydroxy-6-methylpyridine, benzoic acid, glycerol, catechol, 3-methylcatechol, hydroquinone, 1,6-anhydro- β -d-glucose, coniferol, hexadecanoic acid, and cholesterol.

Figure 15: GC-MS chromatogram for sample#1 from the PSU filter samples. Identifiable compounds were assigned numbers above their respective peaks. Analysis performed by Young-Mo Kim, DOE EMSL, 2014.

8 Next Steps and Outlook

Objectives 1 and 3 suggest GC-MS with derivatization can improve characterization of atmospheric organic aerosols. Preliminary chromatographs and compound identification show several polar compounds of interest were eluted from the GC column and available for detection. Objective 3 also shows that SPE filters can be used to trap polar atmospheric SVOCs. Existing literature on SPE filters and trapping atmospheric aerosols is limited; this research suggests SPE filters are a viable collection media option for improving characterization.

Next steps include taking the complete apparatus (PTFE + O₃ + ATD + SPE) to the EMSL lab in Richland, WA for aerosol collection in June 2015. VOCs will be analyzed at PSU using GCxGC-TOFMS. For SVOC characterization, the SPE filter is to be split in half to test two different methods of analysis: 2D-GC-MS with derivatization and 2D-LC-MS. Splitting the SPE filter in half and using two different analytical methods on the same sample is hypothesized to provide more complete characterization.

In addition to improved characterization abilities, this collection apparatus is advantageous due to size, operational variability, and affordability. With a footprint that can be minimized to approximately 2 square feet (or 2 cubic feet in volume), the apparatus is small enough to be easily implemented into field sampling. Operational variability includes collecting samples at multiple flow rates and collecting on multiple medias. Pumps and media can also be interchanged for specific collection requirements. The offline collection apparatus also provides economic benefit: expensive online equipment currently hinders research in this area. By providing an affordable, offline alternative to effectively characterize atmospheric aerosols the amount of research performed can increase significantly. An increased quantity of reliable sample collection and subsequent analysis can further the current knowledge in atmospheric organic aerosol sources, behavior, and fate.

9 Citations

Art, H.W., 1993, Volatile organic compounds, *in* Art, H.W., ed., A dictionary of ecology and environmental science: New York, New York, Henry Holt and Company, p. 581.

Duarte, Regina M B O, Ana C. Barros, and Armando C. Duarte. "Resolving the Chemical Heterogeneity of Natural Organic Matter: New Insights from Comprehensive Two-Dimensional Liquid Chromatography." *Journal of Chromatography A* 1249 (2012): 138–146. Web.

EPA, 2015. "Semi-Volatile Organic Compounds | Mid Atlantic Brownfields | US EPA." Web, 5/11/15. <http://www.epa.gov/reg3hwmd/bf-lr/regional/analytical/semi-volatile.htm>

Intergovernmental Panel on Climate Change (IPCC), 2007. "Climate Change 2007: Working Group I: The Physical Science Basis," IPCC Fourth Assessment Report: Climate Change 2007. Web, 2015.

Isaacman, Gabriel et al. "On-Line Derivatization for Hourly Measurements of Gas- and Particle-Phase Semi-Volatile Oxygenated Organic Compounds by Thermal Desorption Aerosol Gas Chromatography (SV-TAG)." (2014): 1–28. Web.

Kroll, Jesse H., and John H. Seinfeld. "Chemistry of Secondary Organic Aerosol: Formation and Evolution of Low-Volatility Organics in the Atmosphere." *Atmospheric Environment* 42 (2008): 3593–3624. Web.

Ligocki, M P, and J F Pankow. "Assessment of Adsorption/solvent Extraction with Polyurethane Foam and Adsorption/thermal Desorption with Tenax-GC for the Collection and Analysis of Ambient Organic Vapors." *Analytical Chemistry* 57.17 (1985): 1138–1144. Print.

Masters, G.M., Ela, W.P. "Ch. 7 – Air Pollution," *Introduction to Environmental Engineering and Science, 3rd Edition*. Prentice Hall, Upper Saddle River, NJ. p. 371

NASA. "Clouds and the Energy Cycle." *Weather* August (1999): 6. Print.

NASA, 2015. "Aerosols: Tiny Particles, Big Impact : Feature Articles." Web, 11 May 2015. <http://earthobservatory.nasa.gov/Features/Aerosols/page4.php>

Pachauri, R.K. et al. "IPCC Climate Change 2014: Synthesis Report." (2014): n. pag. Print.

Pankow, James F. "Organic Gas / Particle Partitioning." n. pag. Print.

Pietrogrande, Maria Chiara, and Dimitri Bacco. "GC / MS Analysis of Water-Soluble Organics in Atmospheric Aerosol : Optimization of a Solvent Extraction Procedure for Simultaneous Analysis of Carboxylic Acids and Sugars." (2013): 1095–1104. Web.

Pöschl, Ulrich. "Atmospheric Aerosols: Composition, Transformation, Climate and Health Effects." *Angewandte Chemie - International Edition* 44.46 (2005): 7520–7540. Web.

Ramaswamy, V., et al. (2001), Radiative forcing of climate change, in *Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. T. Houghton et al., chap. 6, pp. 349– 416, Cambridge Univ. Press, New York.

Stockholm Environment Institute, 2011. "Radiative Forcing." *Carbon Offset Research and Education*. Web. 8 Jun 2015. <http://www.co2offsetresearch.org/aviation/RF.html>

Watson, R T et al. "Greenhouse Gases and Aerosols." *Climate change: the IPCC scientific assessment* (1990): 1–40. Web.

10 Appendix

Flow meter calibration

Table A1: Flow meter calibration

Flow meter (35) calibration					
N₂ psi	Trial	Flowmeter (on center)	Agilent FM (ml/min)	FM Test	Agilent
15 psi	1	6	128	1.7	28
	2	5.5	109	2.8	43
	3	5	92	4.2	73
	4	4.5	76	5.3	102
	5	3.9	64	0.1	10.7
	6	3	45		
	7	2.5	36		
	8	1.5	25		
	9	0.7	16.7

Figure A1: Flowmeter calibration

Table A2: Flow meter calibration

Flow meter (63) calibration					
N₂ psi	Trial	Flowmeter (on center)	Agilent FM (ml/min)	FM Test	Agilent
15 psi	1	0.5	12.3	2.4	53
	2	2.2	47	1.2	24
	3	3	73	4.8	154
	4	3.5	92	4.2	123
	5	4.5	139	6.2	244
	6	5.5	197		
	7	6	227		
	8	6.5	266		
	9	4	112

Figure A2: Flowmeter calibration

Table A3: Chemical compounds found in tobacco smoke (using solid phase extraction filters (Young-Mo Kim, US DOE EMSL). Compounds were trapped using solid phase extraction filters.

PSU SPE filter samples						
#	ID	C	H	O	Molecular Weight (g/mol)	Boiling Point (1 atm)
1	pyruvic acid	3	4	3	88.06	165
2	Phenol	6	6	1	94.11	181.7
3	lactic acid	3	6	3	90.08	122
4	hexanoic acid	6	12	2	116.15	205
5	glycolic acid	2	4	3	76.05	-
6	2-furoic acid	5	4	3	112.08	231
7	3-hydroxypyridine	5	11	1	101.08	68
8	3-hydroxypropionic acid	3	6	2	74.08	141
9	m-cresol	7	8	1	108.14	202
10	3-hydroxy,6-methylpyridine	6	7	1	109.13	295.8
11	3-ethylphenol	8	10	1	122.16	218
12	benzoic acid	7	6	2	122.12	249
13	glyceraldehyde	3	6	3	90.08	228
14	glycerol	3	8	3	92.04	335
15	succinic acid	4	6	4	118.09	235
16	catechol	6	6	2	110.11	245
17	nicotine (huge)	10	14	-	162.23	247
18	3-methylcatechol	7	8	2	124.14	241
19	hydroquinone	6	6	2	110.11	285
20	malic acid	4	6	5	134.09	150
21	1,6-Anhydro-β-d-glucose	6	10	5	162.14	384
22	quinic acid	7	12	6	192.17	438
23	fructose	6	12	6	180.16	440
24	glucose	6	12	6	180.16	-
25	coniferyl alcohol	10	12	3	180.2	384
26	hexadecanoic acid	6	32	2	256.42	390
27	scopoletin	10	8	4	192.07	-
28	myo-inositol	6	12	6	180.16	-
29	linoleic acid	18	32	2	280.45	408
30	alpha-linoleic acid	18	32	2	280.45	-
31	alpha-tocopherol	29	50	2	430.71	579
32	cholesterol	27	46	1	386.65	360
33	campesterol	28	48	1	400.68	-