CHARACTERIZATION OF TEMPERATURE PROFILES IN A THERMODENUDER

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Abstract
Thermodenuder (TD) systems are commonly used in aerosol research to induce particle evaporation and simulate evaporation that results from dilution and mixing in the atmosphere. TD experiments in both laboratory studies and field campaigns are commonly used to infer the volatility of organic aerosols. The TD developed in this experiment is slightly modified from that of the standard system used by Huffman et al. (2008), and it is characterized here in terms of the internal temperature profile. This altered TD design still produces the three regions of warming, heated, and cooling in a longitudinal temperature profile comparable to those from previous designs. Data from TD experiments are necessary in order to provide accurate interpretations of laboratory and field aerosol volatility measurements.

1. Introduction
Atmospheric aerosols are small particles suspended in the atmosphere and are of microscopic ($10^{-6}$ meters) or submicroscopic sizes ($<10^{-6}$ meters). Aerosols are commonly referred to as particulate matter (PM). For regulatory purposes, they are classified as PM$_{10}$ and PM$_{2.5}$, where the subscripts refer to the particle diameter ($D_p < 10$ µm and $D_p < 2.5$ µm, respectively). PM poses three main concerns: negative effects on human health, decrease of visibility and impacts on climate change.

Particulate matter is one of the six criteria pollutants regulated by the United States Environmental Protection Agency (EPA) per the National Ambient Air Quality Standards (NAAQS) as originally established by the 1970 Clean Air Act. PM is regulated in order to mitigate effects on human health. High levels of PM contribute to major smog events, which reduce visibility and have adverse health effects. Particles that have diameters less than 10 µm have the potential to be inhaled and trapped in the head airways and the lungs. Particles with $D_p<0.1$ µm are thought to have the largest adverse health effects because they are able to penetrate deep into the lungs and deposit in the alveolar region. In the mid-20th century, significant smog events in London, England and Donora, Pennsylvania resulted in a substantial increase of mortality rates, which consequently brought concerns about air pollution to the forefront of the public consciousness. Later, the Harvard Six Cities Study provided evidence from a long term cohort study to establish a clear correlation between high concentrations of PM and increased mortality rates in six different cities across the United States (Dockery et al., 1993).

In addition to health effects, PM can scatter solar radiation. One consequence of this is that haze and smog lead to visibility reduction. Long-term monitoring efforts of air quality in pristine wilderness areas, such as our National Parks, have focused on improving visibility. Furthermore, atmospheric aerosols affect global climate by scattering and absorbing solar radiation. The Intergovernmental Panel on Climate Change reports that climate forcing due to PM is highly uncertain (IPCC 2007), but overall PM is thought to have a cooling effect due to the scattering of light by the particles. Even more uncertain is the indirect effect of PM
on the modification of cloud properties and subsequent changes in light interactions.

In the mid-latitude region of the continental U.S., organic aerosols (OA) contribute 20-50% of the submicron PM mass (Saxena & Hildeman, 1996). OA can be either primary or secondary in origin. Primary organic aerosols (POA) are directly emitted from the surface, such as soot from a power plant. Secondary organic aerosols (SOA) are produced by condensation of products of gas-phase reactions in the atmosphere (Kanakidou et. al., 2005). SOA precursors are volatile organic compounds (VOCs) that can have either biogenic or anthropogenic origins. Biogenic VOCs are emitted from vegetation, whereas anthropogenic VOCs are the result of human activity.

The atmospheric lifetime of OA is dependent upon the particle composition, meteorological conditions, atmospheric oxidant concentrations and various other factors. Despite intensive research on aerosols, much remains unknown about the properties of OA in respect to their atmospheric behavior. In an effort to characterize evaporative behavior of OA, thermodenuders (TDs) have been used in both laboratory experiments (Cappa & Wilson, 2011) and field observations (Huffman et. al., 2008). TDs are typically very large, fragile and difficult to transport, but for the purpose of our experiment we needed an instrument that was more compact and had the ability to be taken apart and reassembled in a timely manner. Here, we characterize the temperature profile of a modified TD so that we can interpret the accuracy of volatility measurements. Having accurate knowledge of OA volatility is a key step towards understanding the evolution of OA in the atmosphere.

2. Methods and Instrument Design
A thermodenuder (TD) is an instrument used in laboratory experiments and field campaigns to induce the evaporation of aerosols by heating. As particles are heated, the vapor pressure of the compounds that makes up the particles increases and evaporation proceeds at an increased rate. TDs are compact and provide a quick method for quantifying bulk volatility of aerosols. As evaporation is induced, the concentration of gas-phase species increases with increasing temperature. In order to reduce the re-condensation of evaporated compounds upon cooling, activated charcoal is used as an adsorption medium. In order to accurately characterize volatility measurements, a heating profile of the TD is necessary. Here, the longitudinal temperature profile along the centerline was measured as a function of the set-point temperature and air flow rate through the TD.

In a first experiment, the TD was heated to several temperatures representative of those used during experiments at a fixed flow rate of 0.5 liters per minute (lpm). A Proportional Integral Derivative (PID) controller was used to set the TD to temperatures of 50 °C, 100 °C, 150 °C, and 200 °C. In a second experiment, the temperature was held constant at 150 °C while the flow rate was varied between 0.2 lpm, 0.5 lpm, and 1.0 lpm.

2.1 Instrument design
The TD is comprised of two sections: an actively heated section (Figure 1) and a charcoal denuder section (Figures 1 and 2). The TD used in this laboratory experiment is constructed based on the design of Huffman et al. (2008) with three modifications: 1) there is only one temperature region whereas Huffman et al. have three, 2) the insulation layer and the cooling fans are omitted, and 3) the distance between the heated section and the charcoal denuder is reduced. The purpose of modification number 3 is to minimize the amount of re-condensation that occurs as the air stream is cooled as it is transferred from the heated section to the charcoal denuder.
In order to minimize the distance between the end of the heated section and the beginning activated charcoal, the heated tube is welded directly to the top of the charcoal denuder. The stainless steel inlet to the charcoal denuder (ID = 1.9 cm) nestles inside the wire mesh that separates the airstream from the activated charcoal inside the denuder. A needle-valve controlled vacuum is attached at the outlet of the charcoal denuder. The flow rate through the TD system is controlled by adjusting the needle valve setting.

2.2 Temperature Verification

A procedure was established to take temperature profiles of the TD. First, the PID controller is powered on and set to a temperature at or below room temperature\(^1\). Then the PID controller is gradually increased with steps of \(\Delta T \leq 50\ ^\circ\text{C}\).

\(^1\) After the measurements have been taken, the PID controller must be turned down and allowed to cool before powering off. Failure to lower the temperature back to room temperature before turning off the PID may result in overheating of the TD the next time it is turned on.
until the set-point temperature is reached. Higher temperatures require a longer heating time. Temperature measurements throughout the length of the TD are then taken with the temperature probe, which is a K-type thermocouple wrapped around a marked rod. In this experiment, a rod with markings in increments of centimeters was used. The temperature can then be taken at any location within the TD along the centerline.

3. Results and Discussion
The longitudinal temperature profile of the TD is important for the interpretation of field and laboratory studies. The temperature inside the TD cannot be measured during experiments, so it needs to be verified prior to use to determine the relationship between the PID controller reading and the actual air temperature along the centerline of the TD. Direct measurement of the temperature profile can also indicate the extent to which heating propagates into the charcoal denuder.

3.1 Longitudinal temperature profile of the TD at variable temperatures
The longitudinal temperature profile of the TD was measured at four different set-point temperatures: 50 °C, 100 °C, 150 °C, and 200 °C. As seen in Figure 3, the plot displays consistent increases and decreases of temperature along the length of the TD for all temperatures. The observed longitudinal heating profile of the TD consists of a warming region, a heated region and a cooling region, similar to the distinct regions characterized by Huffman et al. (2008).

![Figure 3: Longitudinal temperature profile of the thermodenuder at different set-point settings on the PID controller. The vertical dashed line is at a distance of 71 cm, which is where the heated section ends and the charcoal denuder begins.](image)

The heated section is operationally defined as the region in which the temperature varies from the set point by no more than 10%. As seen in Figure 3, the experimentally determined heated region is between 20 and 60 cm. The warming region extends from the inlet until the beginning of the heated region (about 20 cm into the TD) and the cooling region begins at 60 cm and extends into the charcoal denuder. The active heating section is 71 cm long, but the temperature inside the TD remains elevated.
above room temperature into the charcoal denuder.

3.2 Longitudinal temperature profile of the TD at variable flow rates

The modified TD has already been used in several laboratory experiments during the course of which the flow rate through the denuder is often varied to accommodate experimental variability. It is important to determine how the different flow rates might change the longitudinal temperature profile and flow characteristics. The Reynolds number (Re), defined in Eq. 1, is a function of density (ρ), volume (V), diameter (d), viscosity (μ), and kinematic viscosity (ν) and is used to classify the flow rate as laminar or turbulent flow. A value of Re > 2300 indicates turbulent flow.

Equation 1

\[ Re = \frac{\rho V d}{\mu} = \frac{V d}{\nu} \]

For each flow rate, the Reynolds number (Re) has been calculated for the heated and charcoal denuder sections of the TD at room temperature in Table 1. In addition, the residence time in each section is determined. The residence time in the heated section of the TD determines the extent of particle evaporation for a given temperature. The residence time in the charcoal denuder is also calculated.

<table>
<thead>
<tr>
<th>Volumetric Flow Rate (lpm)</th>
<th>Thermal Denuder</th>
<th>Charcoal Denuder</th>
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<tbody>
<tr>
<td></td>
<td>Residence Time (s)</td>
<td>Re</td>
</tr>
<tr>
<td>0.20</td>
<td>81</td>
<td>12</td>
</tr>
<tr>
<td>0.50</td>
<td>32</td>
<td>29</td>
</tr>
<tr>
<td>1.00</td>
<td>16</td>
<td>58</td>
</tr>
</tbody>
</table>

All flow rates through the TD are laminar, i.e. the Reynolds number is less than 2300. Laminar flow means that particles are moving through the tubes smoothly without turbulence. In this experiment, laminar flow is preferable because it minimizes particle losses due to impaction with each other and to the walls of the TD.

As seen in Table 1, the residence time is inversely proportional to the volumetric flow rate. At an air flow rate of 0.50 lpm, the residence time of the particles in the thermal denuder is 32 seconds, while at twice the flow rate (1.00 lpm) the residence time is cut in half to 16 seconds. A longer residence time will expose the particles to a longer period of heating in the thermal denuder, which will increase the extent of evaporation of volatile compounds from the particles.

The temperature profile through the TD was characterized at the flow rates indicated in Table 1 with the PID set to a temperature of 150 °C to understand the extent to which varying the flow rate leads to changes in the temperature profile. Data were collected for flow rates of 0.2 lpm, 0.5 lpm and 1.0 lpm at 150 °C and the resulting temperature profile is displayed in Figure 4.
As shown in Figure 4, the temperature profile of the TD is relatively constant regardless of the mass flow rate through the set-up, displaying the same warming, heated, and cooling sections as Figure 3. The greatest variation in the temperature profile occurs near the inlet of the TD: the mass flow rates of 0.2 and 0.5 lpm have a slightly sharper increase in temperature at the inlet than the flow rate of 1.0 lpm. This is as expected because there is a finite amount of time required for heat transfer and the lower the flow the greater the residence time in the warming section.

3.3 PID Controller

During the course of the longitudinal temperature profile characterization, it was noted that the reading temperature of the PID controller did not match the temperature inside the TD exactly. The temperature set-point on the PID controller was therefore compared with the average temperature of the heated section as measured in the TD (Table 2).

<table>
<thead>
<tr>
<th>PID Temperature (°C)</th>
<th>TD Temperature (°C)</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.5</td>
<td>38.1</td>
<td>-3.54%</td>
</tr>
<tr>
<td>58.7</td>
<td>57.7</td>
<td>-1.70%</td>
</tr>
<tr>
<td>78.1</td>
<td>76.4</td>
<td>-2.18%</td>
</tr>
<tr>
<td>96.9</td>
<td>97.0</td>
<td>+0.10%</td>
</tr>
<tr>
<td>116.0</td>
<td>115.5</td>
<td>-0.43%</td>
</tr>
<tr>
<td>135.2</td>
<td>137.1</td>
<td>+1.41%</td>
</tr>
</tbody>
</table>
The oscillation of the percent difference between the set temperature of the PID and the actual temperature in the TD indicates an uneven heating in the TD by the PID. Although there is some difference between the set-point temperature and the temperature measured inside the TD, the difference is typically quite small. It is suggested that better thermal insulation of the heated section of the TD could help to rectify this difference.

4. Conclusions and atmospheric implications
The TD used in this experiment is slightly modified from that of Huffman et al. (2008), but it still produces the three regions of warming, heated, and cooling. This altered TD design produces a longitudinal temperature profile comparable to those from previous designs. The TD is currently being used to take volatility measurements of laboratory-generated SOA that is produced from the gas-phase reaction of α-pinene and ozone. The particle size and concentration of the SOA will be counted after undergoing evaporation in the heated TD and adsorption in the charcoal denuder to characterize its evaporative behavior.

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References


